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Preface

We would like to present, with great pleasure, the inaugural volume-6, Issue-5, May 2020, of a scholarly journal, *International Journal of Environmental & Agriculture Research*. This journal is part of the AD Publications series *in the field of Environmental & Agriculture Research Development*, and is devoted to the gamut of Environmental & Agriculture issues, from theoretical aspects to application-dependent studies and the validation of emerging technologies.

This journal was envisioned and founded to represent the growing needs of Environmental & Agriculture as an emerging and increasingly vital field, now widely recognized as an integral part of scientific and technical investigations. Its mission is to become a voice of the Environmental & Agriculture community, addressing researchers and practitioners in below areas

Environmental Research:

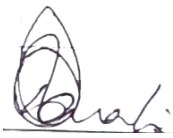
Environmental science and regulation, Ecotoxicology, Environmental health issues, Atmosphere and climate, Terrestric ecosystems, Aquatic ecosystems, Energy and environment, Marine research, Biodiversity, Pharmaceuticals in the environment, Genetically modified organisms, Biotechnology, Risk assessment, Environment society, Agricultural engineering, Animal science, Agronomy, including plant science, theoretical production ecology, horticulture, plant, breeding, plant fertilization, soil science and all field related to Environmental Research.

Agriculture Research:

Agriculture, Biological engineering, including genetic engineering, microbiology, Environmental impacts of agriculture, forestry, Food science, Husbandry, Irrigation and water management, Land use, Waste management and all fields related to Agriculture.

Each article in this issue provides an example of a concrete industrial application or a case study of the presented methodology to amplify the impact of the contribution. We are very thankful to everybody within that community who supported the idea of creating a new Research with *IJOEAR*. We are certain that this issue will be followed by many others, reporting new developments in the Environment and Agriculture Research Science field. This issue would not have been possible without the great support of the Reviewer, Editorial Board members and also with our Advisory Board Members, and we would like to express our sincere thanks to all of them. We would also like to express our gratitude to the editorial staff of AD Publications, who supported us at every stage of the project. It is our hope that this fine collection of articles will be a valuable resource for *IJOEAR* readers and will stimulate further research into the vibrant area of Environmental & Agriculture Research.

Mukesh Arora
(Managing Editor)



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Agricultural Sciences	
Soil Science	Plant Science
Animal Science	Agricultural Economics
Agricultural Chemistry	Basic biology concepts
Sustainable Natural Resource Utilisation	Management of the Environment
Agricultural Management Practices	Agricultural Technology
Natural Resources	Basic Horticulture
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Cereals or Basic Grains: Oats, Wheat, Barley, Rye, Triticale, Corn, Sorghum, Millet, Quinoa and Amaranth	Oilseeds: Canola, Rapeseed, Flax, Sunflowers, Corn and Hempseed
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Vegetable crops or Olericulture: Crops utilized fresh or whole (wholefood crop, no or limited processing, i.e., fresh cut salad); (Lettuce, Cabbage, Carrots, Potatoes, Tomatoes, Herbs, etc.)	Tree Fruit crops: apples, oranges, stone fruit (i.e., peaches, plums, cherries)
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Dairy Sheep	Water Buffalo
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Maple syrup	Forestry Growth
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Farmers' Perceptions of Agricultural Extension Agents' Performance in Sub-Saharan African Communities

Sennuga, Samson Olayemi[1], Oyewole, Samuel Olusola[2] and Emeana, Ezinne Merianchris[3]

[1]School of Agriculture Food and Environment, Royal Agricultural University, Stroud Road, Cirencester, Gloucestershire, GL7 6JS, United Kingdom,
[2]Forestry Research Institute of Nigeria, Federal Ministry of Environment, Forest Hill, Jericho, Ibadan, Nigeria
[3]Centre for Agroecology, Water and Resilience, Coventry University, Coventry, CV8 3LG, United Kingdom

Abstract— *Considering the important role extension agents perform in the rural community, potential exists to measure the performance of extension workers from the smallholder perspective. The study investigated farmers' perceptions of agricultural extension agents' performance in Kaduna State, Nigeria. Data were collected with structured questionnaires distributed to 200 rural smallholder farmers and 20 agricultural extension agents using a multiple stage sampling technique. The main aim of the study was to evaluate the performance of extension agents on agricultural production. Data were analyzed using descriptive statistics and Chi-square analysis was used to test significant relationship between farmers' perception regarding the role of extension services and increase in crop production. The result of the socio and demographic characteristics of the farmers showed that more than half (59%) are within the active age and are married and had one form of education or the other. The estimated chi-square value of 12.84 revealed that there is no statistical significant relationship between extension services and increase in crop production among farmers in the study area. In addition, majority (89%) of the respondents perceived lack of regular contacts with extension agents as a great challenge in the area, while a large proportion (82%) of the respondents reported that extension services was not effective in the area. However, since contact with extension agents was ineffective, the results obtained showed that smallholder farmers preferred traditional ICT, mainly radio (63%) as their main source of accessing agricultural information. The study however recommends that government should employ and train more agricultural graduates. More extension workers need to be hired in order to significantly reduce the problem of the extension workers to farm families' ratio which is currently 1:3000 in Kaduna State, Nigeria*.

Keywords— Extension agents, smallholder farmers, perception, extension ratio, village.

I. INTRODUCTION

Agriculture extension primarily deals with human resource development and the transfer of technology and knowledge from agricultural research centers to rural farmers. Extension agents are professionals in the extension system responsible for developing individuals in the community (Oladele 2015). However, a key failure point of traditional extension models is the number of farmers per extension officer – they cannot visit all the smallholder farmers effectively and in a timely manner. The ratio in Nigeria is currently one extension worker: 3000 farmers (Fawole and Olajide, 2012; Ogbe, 2016; Sennuga, 2019). This ratio is grossly inadequate and highly disturbing considering the World Bank's standard which is 1:500 (World Bank, 2010). Where extension workers act as bridges between researchers and farmers, for example, in traditional Training & Visit extension the ratio should be 1:200 farmers within a cluster so that they can have a meaningful impact by effectively teaching and monitoring the farmers' progress (Ogundele, 2016; Sennuga, *et al*. 2020). Furthermore, by focusing on lead farmers backed up by farmer to farmer extension, then a ratio of 1: 500 advocated by the World Bank could be effective.

Key challenges facing extension workers in Nigeria include extremely low extension agent to-farmers ratios; a lack of essential technical and communication skills for efficient functioning; a lack of a definite plan of work; too few qualified and trained extension staff using outdated information; under resourced transport and logistics; poor, weak and deteriorated infrastructure; extension organization and management problems; unclear extension mandates; lack of job descriptions for staff; poor remuneration of the personnel; and a high rate of absenteeism among staff (see Naswem *et al.* 2008; Baig and Aldosari 2013; Sennuga, *et al*. 2020). Consequently, in a reaction to the worrisome performance in the agricultural sector, the Nigerian Government embarked on several agricultural interventions and reforms, with policies and programs explicitly designed at reinvigorating the sector to its enviable position in the Nigerian economy between 1959 and 2003. The use of ICT potentially allows extension workers to contact more farmers with appropriate and up-to-date information in a timely manner. Asenso-Okyere and Ayalew-Mekonnen (2012) stressed that traditional ICT, particularly radio, can enable extension

worker to reach out to half a million smallholder farmers simultaneously in their local language with knowledge and information which enables farmers, strengthens them, assists smallholders in problem solving and allows farmers to make informed decisions.

1.1 Evolution of Agricultural Extension in Africa

Africa is the only continent in the world where agricultural productivity is largely stagnant whilst populations grow rapidly, resulting in food insecurity and malnutrition among the populace (Madhusudan, 2005; FAO 2015). Agricultural production has been limited by various constraints, such as lack of adequate research in science and technology, inadequate dissemination of research, ineffective utilization of soil resources, low commodity prices and unstable markets for agricultural products, as well as storage issues (Awoyinka, 2009; Saingbe, 2010; Awerije, 2014; Sennuga, *et al.* 2020).

All these constraints are frequently emphasized by the lack of capital which is fundamental for agricultural development (Kennedy, 2005). According to Simpson and Owen (2012) there are six key challenges facing agricultural extension in Africa:

1. Relevance and responsiveness of research to local concerns.
2. Systems learning and the generation of new knowledge.
3. Information flow and farmer-to-farmer communication.
4. Institutionalization and Local Organizational Development.
5. Changes in relationships.
6. The integration of the Farmer Field School into the existing program.

Experience from other parts of the world, particularly in the developing countries of Asia and Latin America, shows that agriculture has been rapidly transformed in recent years into a progressive commercial industry and treated as a full business (Thirtle and Piesse, 2013). Investment in the agricultural sector with adequate agricultural information technology has enabled farmers to intensify production and lead to sustainable development which enhances their standard of living as well as contributing significantly to national and rural prosperity within environmental constraints (Ali, 2011). This could also happen in Africa if smallholder farmers could be assisted with the necessary resources to intensify their farming activities through increased use/effectiveness of agricultural extension services delivery and information technology. There is a general consensus that extension services, if successfully applied, could result in outcomes which include observable changes in attitudes and adoption of Good Agricultural Practice technologies and improve the quality of lives of farming households (Yegbemey, *et al.* 2014, Sennuga, 2019). Similarly, it has been recognized that effective agricultural extension services could accelerate development in the presence of other important factors such as markets, agricultural improved technology, availability of supplies, production incentives (quality seeds, fertilizers and herbicides) and transport. Over the years, a number of extension models have been adopted in developing countries to enhance the effectiveness of agricultural extension services and service delivery. According to Anandajayasekeram *et al.* (2008) a model may be defined as a schematic description of a system, or phenomenon that accounts for its known or inferred properties and may be utilized for the further study of its characteristics.

Top-down extension approach is a system whereby agricultural information from the Universities or Ministry of Agriculture is disseminated to farmers through extension agents and is directly related to the diffusion of innovation theory. This extension structure is known as Transfer of Technology (TOT) through extension workers who are also passive recipients of technology from the researchers to farmers. Top-down methods characterized the United States extension model, which was also instituted by many colonial governments in Africa (Anandajayasekeram, *et al.* 2008). In Africa, the system helps to promote agricultural messages that have been designed and developed by research scientists, with limited input by the ultimate users (farmers) of the technologies. Technologies are spread vertically in the top-down approach (Anandajayasekeram, *et al.* 2008).

In developing countries, agricultural extension services have been the exclusive domain of the public sector and government responsibility, while in most developed countries, extension services are mainly privatized (Swanson and Samy, 2012) as agriculture becomes more commercial. Public extension deals with diverse policy issues, including responsiveness; relevance; cost-effectiveness and accountability (Swanson and Samy, 2012). The overall objective has constantly been to contribute to the increase of agricultural production and productivity of the rural population (Shinn *et al.* 2009), utilizing

mainly a top-down approach, through the Transfer of Technology (TOT). As mentioned previously, this model is strongly linked to the diffusion of innovation theory proposed by Rogers. This theory is known for the linear technology transfer which tends to work better only in the developed nations. Rogers himself moves away from linear technology process with the convergent model in the latest version of his theory (Rogers, 2003, Anandajayasekeram, *et al.* 2008). In this model, technologies are generated at research stations and diffused to extension agents who in turn disseminate them to the farmers (Davis and Place, 2003), in other words a one-way transfer of information.

The information flow from the Ministry of Agriculture is absolutely supply-driven and not area-specific (Raabe, 2008), meaning that in most cases the technical knowledge transferred into the field is distorted, outdated and often wrong for the specific situation. Thus, farmers see the quality of the information provided by the public extension staff as a major shortcoming (Oladele, 2015), where a top-down approach continues to hinder the full potential of the extension service delivery system (Raabe, 2008). Under the Ministry-based extension model, smallholder farmers' access to extension is also an issue, because of the low level of outreach by public extension services. The public extension model often has little to offer in terms of messages to a large section of the rural population. In fact, there is no specific answer to farmers' problems because it has not been a research concern to reach the farming community (Eicher, 2007). The top-down approach to information dissemination to farmers in Nigeria has indeed received various criticisms, while calls for participatory approach in both agricultural policy formulation and information dissemination that incorporates farmers' contribution persists (Emeana, *et al.* 2019).

As a result, public extension came under attack in the 1980s because of the cost of financing it coupled with condemnations of insignificance, inefficiency, ineptness and lack of equity (Rivera 2001). In addition, the current ratio of extension agents to farm families is extremely low in most developing countries and this has been a continual threat to efforts in achieving food sufficiency. This case is not different in Nigeria even with the current ratio of 1:3000 farm families; some states such as Lagos, Nigeria reported 1:10,000 (Ogundele 2016; Sennuga, 2019). Ideally, the ratio should be 1:200 farmers within a cluster so that they can make a meaningful impact by effectively training and monitoring the farmers' progress. Since the mid-1980s, agricultural extension has become a "pluralistic" method (Birner and Anderson, 2007). Public extension leaders have recognized the interdependent economic and social roles of NGO and private sector extension models in agricultural and rural development projects. The new ideas include decentralization, cost-recovery, outsourcing and involvement of other key stakeholders (Ferroni and Zhou, 2012). According to Swanson and Samy (2002), collaboration among the three key stakeholders is important to effectively work together in partnership for the development of the agricultural sector and rural community (Figure 1).

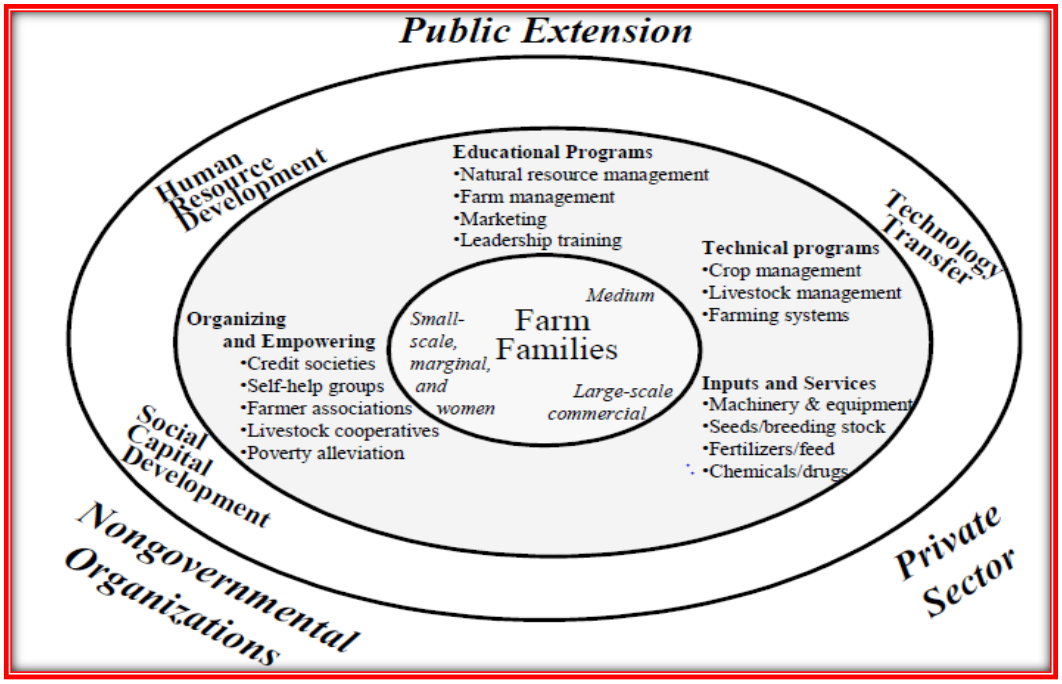


FIGURE 1: Conceptual framework depicting a Public, Private and NGO Partnership Adapted from Swanson and Samy 2012

This model also describes the partnership between the key players in agricultural extension and advisory services for sustainable agricultural development. The major responsibility of public extension is typically human resource development, technology transfer and educational programs in order to complement the social capital development of NGOs and the role of private sector extension model (Swanson and Samy 2012; Figure 1). In developing countries, there is a lot of collaboration between private sector, government, non-governmental organization and international donors to address food security issues and sustainable development (Sennuga and Fadiji, 2020).

According to World Bank (2010), public extension is incapable of serving resource-poor farmers due to inadequate linkages between research and extension; inadequate finance support; and poor human resource and facilities. In addition, the system's designer stressed the following characteristics: 1) a single line of command, with several tiers of management between the field and supervisor; 2) in-house technical expertise, whereby subject matter specialists are to provide training; 3) exclusive dedication to information dissemination; and, 4) a seasonal workshop with research personnel among others (Anderson and Feder, 2003). Farmers' perceptions regarding agricultural extension agents' performance in Northern Nigeria is yet to be established and this is why this study was conducted. Therefore, the main objective of this study is to investigate farmers' perceptions regarding agricultural extension agents' performance in Kaduna State, Nigeria.

The specific objectives of this study are to:

i. Examine the socio-economic characteristics of the farmers and extension agents;

ii. Investigate farmers' perceptions regarding extension agents' performance;

iii. Examine the relationship between farmers' perceptions regarding extension agents' role in helping smallholders to increase crop production;

iv. Explore the preferred sources of agricultural information among smallholder farmers;

v. Highlight the current problems affecting extension services in the study area.

II. METHODOLOGY

2.1 Kaduna State of Nigeria as the study area

This study was conducted in two randomly selected Local Government Areas of Kaduna State, Northern Guinea Savannah ecological zone of Nigeria, West Africa. Kaduna State is located between latitudes 9^0 03^1 and 11^0 32^1 North of the equator and longitude 6^0 05^1 and 8^0 38^1 East of the Greenwich Meridian (Kaduna State Ministry of Agriculture, 2014). However, two rural communities (Bassawa and Shika) were purposefully due to active engagement of the rural farmers in agricultural production in the district and for its proximity to Ahmadu Bello University, Zaria to facilitate access for the researchers. The major economic activity conducted by the rural dwellers in the two communities is farming. Very few people engage in hunting and smallscale business. The major food crops grown are yam, maize, millet, groundnut, rice, beans, melon, sweet potato, cassava, guinea corn and vegetables such as pepper, tomato and carrot.

2.2 Population of the study and research design

The study involved rural farmers in the two communities including those who had access to agricultural extension workers and those who do not. The study employed case study research design in order to explore and obtain in-depth information related to farmers' perceptions regarding agricultural extension agents' performance in Northern Nigeria and extension workers in their real-life settings.

2.3 Sample Size and Sampling Techniques

Purposively sampling techniques was employed to select the sample size for the study. Two rural communities (Bassawa and Shika) were purposely selected out of 22 villages primarily because of their age-long agricultural practice and presence of adoption practices noted there. Moreover, Bassawa community benefited in the Adopted Village Concept project initiated by National Agricultural Extension and Research Liaison Services (NAERLS), Zaria in 2012, while Shika community did not (Sennuga, 2019). Conversely, the two communities are the same in every respect except that one (Bassawa) is an adopted village from NAERLS. The two communities are similar in agro-climatic, ethnic group, religion and cultural settings.

However, Shika community gets only public extension services with about 3000 smallholder farmers per extension agent while Bassawa community receives extension services plus the research education establishment from Adopted Village Program with estimated ratio 1:85 farm families (Sennuga, *et al.* 2020).

2.4 Sample size

The sample size for the study was 200 smallholder farmers. It consists of 100 farmers from each community. Also, agricultural extension agents were purposively selected – 5 agents each from four (4) institutions that provide extension and advisory services in the country namely; the government (ADPs), Non-Governmental Organization (NGO), Academia (NAERLS) and the Private sector. A total number of 20 agricultural extension agents participated in the study.

2.5 Data collection

Primary data were collected using structured questionnaires, focus group discussion and in-depth interview from both rural dwellers and extension workers. Secondary data which relate to the objectives of the study were collected from the office Kaduna State Agricultural Development Project (ADP) and National Agricultural Extension and Research Liaison Services (NAERLS), ABU, Zaria.

2.6 Data analysis

The data collected were analyzed using descriptive statistics such as frequency count and percentages. Chi-square technique was used to test the significant relationship between extension services performance and crop production among farmers.

III. FINDINGS AND DISCUSSION

3.1 Socio-economic characteristics of the rural dwellers in the study area

The results of socio-economic characteristics of the respondents were presented in Table 1. The variables investigated in the study included: age, sex, marital status, household size, level of education, major crops cultivated, household assets and income level. The age of the farmers in the households ranged from 20 to 70 years. 59.2% of them fell within the middle age of 31-50years in both communities. This suggests that the majority of the respondents were within their economic active age and this enhances their productivity in order to be food secure (Table 1). The old age group (51-70) had the lowest impact in farm work with 24.2% contributing to active farming among the sampled population. However, it is generally assumed that younger people tend to be more productive than their older counterparts (Sennuga, 2019). In the same vein, the results in Table 1 below showed that all the respondents were males; this is because the cultural traditions of the study area do not allow females to be actively involved in farming activities (Sennuga, *et al*. 2020).

In term of the marital status of the respondents, overwhelming majorities (96.7%) of the respondents were married with half of these households having 10 or more members; the remainder had larger families of 21 plus members reflecting polygamy within the communities. The result is not surprising because large family sizes are the norm in the Northern Nigeria and large families provide accessible workforces. Furthermore, the cultural tradition and religion allows the men to marry at most four wives. The use of household labour for several activities was very common in the study area with activities such as ploughing, harrowing, planting, weeding, chasing away straying domestic animals, irrigation activities and harvesting. In the same vein, large household may also help to access more agricultural information.

Educationally, 44% of the respondents had acquired primary education, while 17% had secondary education. Only 7.5% of the respondents possessed higher education (Table 1). This suggests that the respondents in the study area obtained the basic education required for better understanding and ability to embrace new technologies especially the adoption of GAPs modern farming technology. In addition, it is generally thought that the level of education enhances the ability to comprehend and adopt relevant agricultural information. Indeed, according to Kalungu and Filho (2016), and Sennuga (2019) highly educated farmers tend to adopt relevant agricultural technologies better than illiterate ones. In term of household asset, 58% of the household keep poultry, a greater proportion (61.7%) keep sheep and goats. A sizeable proportion of the respondents (42%) also indicated that they rear cattle and only 6.5% specified that they keep other livestock such as camel, duck, turkey etc. The baseline livelihood survey shows that no single household keeps pigs in the study area. This was attributed to the religion (Muslims) of the respondents. It was revealed during the focus group discussion that the Muslim faithful do not rear pigs.

TABLE 1
DEMOGRAPHIC REPRESENTATION OF THE SOCIO-ECONOMIC CHARACTERISTICS OF THE SMALLHOLDER FARMERS (n= 200)

Variables	Percentage
Age (years)	
20-30	15.8
31-40	31.7
41-50	27.5
51-60	17.5
61-70	6.7
>70	.8
Gender (Sex)	
Male	100
Female	0
Marital Status	
Single	100
Married	0
Household size	
≤10	50.8
11-20	36.4
21-30	12.1
>31	0.7
Level of education	
No education	30.8
Primary	44.3
Secondary	17.0
Tertiary	7.5
Family education	
No education	3.3
Primary	55.0
Secondary	35.8
Tertiary	2.5
No Children yet	3.3
Household Asset	
Poultry	58.0
Sheep and goats	61.7
Cattle	42.8
Other livestock	6.5
Pig	0

3.2 Demographic Characteristics of the Extension Agents

The demographic characteristics of the extension agents who participated in the focus groups are reported here (Table 2). The 20 extensionists were selected and the foremost rationale was based on those who volunteered from academia - National Agricultural Extension and Research Liaison Services (*NAERLS*); government - Agricultural Development Programme (ADP); Non-Governmental Organizations (NGOs) and the private sector. A breakdown of the sample and where they are working is provided in Table 2 below.

TABLE 2
DISTRIBUTION OF EXTENSION WORKERS ACCORDING TO THE ORGANIZATION

Organizations	Working with Bassawa	Working with Shika	Total	The type of focus group discussion
Academia (NAERLS)	5	0	5	Extension in Nigeria.
Government (ADP)	3	2	5	How to improve it.
NGOs	2	3	5	Motivating extension workers.
Private sector	2	3	5	Summary of discussion
			20	

Source: Field survey 2016

The majority (16) of them were between 30-49 years old. Most (17) of the participants were males, while 3 were females. The study results show that 18 extension workers were married and 13 were from the household size of 10 or fewer members. Most (11) of the participants had Higher National Diploma Certificate (HND), followed by those (4) who had Ordinary National Diploma (OND) and (3) of them who had B.Sc. certificates, all in agriculture related subjects and signifying that they are literate (Table 3).

On secondary occupation, 14 of the extension workers were involved in farming as outside income-generating activities to complement their extension work, while 4 were involved in trading as a secondary occupation. The study results suggest that the majority of extension specialists have outside work to support their families. During the focus group discussion, extension workers reported that *there is a considerable economic pressure on agricultural extensionists as on other government employees in Nigeria, this situation forces them to diversify and supplement their incomes with other activities*. However, it seems that such pressure, or the opportunity for outside employment, is greater for the extension workers in Kaduna state as 18 out of 20 extension workers are involved in alternative/secondary occupations. Also, four in-depth interviews were conducted with senior extension managers from the four extension sectors. Three of the senior extension managers had more than 25-years' experience, while one had 33 years of experience and he reiterated that "*I am currently preparing for my retirement" (Extension manager no.3 - in-depth interview).* All the four participants were male.

TABLE 3
DEMOGRAPHIC REPRESENTATION OF THE SOCIO-ECONOMIC CHARACTERISTICS OF THE EXTENSION AGENTS (n= 20)

Variables	Frequency
Age (years)	
20-30	01
31-40	11
41-50	04
51-60	04
Gender (Sex)	
Male	17
Female	03
Marital Status	
Single	18
Married	02
Divorced	-
Level of education	
HND	11
OND	04
B.Sc degree	03
Secondary Occupation	
Farming	14
Trading	04
No Secondary occupation	02

3.3 Farmers' Perceptions Regarding Agricultural Extension Agents' Performance

As part of the evaluation survey, five point-Likert scales were used to elicit information on farmers' perceptions regarding extension agents' effectiveness in the study area. The scale was: *strongly agree = 5, agree = 4, indifferent = 3, disagree = 2 and strongly disagree= 1*. Figure 1 revealed that 89% of the farmers in Bassawa perceived lack of regular contacts with extension officers a challenge, while 82% in Shika reported likewise (Figure 2).

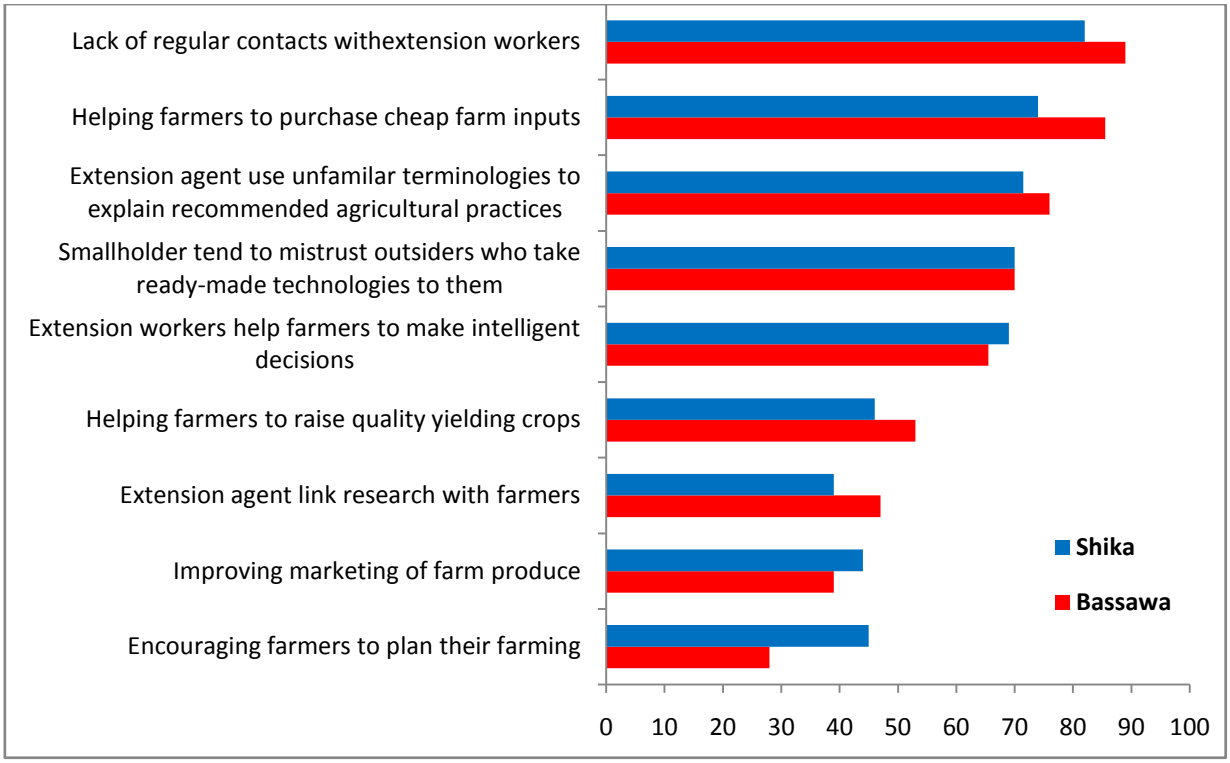


FIGURE 2: Perceptions of Shika and Bassawa communities regarding agricultural extension agents' performance before the intervention

Source: Survey 2016; Shika n=100; Bassawa n= 100 ***Scale: %***

Results in Table 4 revealed that the majority (86%) of farmers from Shika community reported that extension services were not effective, while 75% of the farmers from Bassawa reported likewise. The results also show that 67% and 73% of the smallholders surveyed disagreed with the statement 'extension workers play a role in helping rural farmers to increase crop production', whereas 25.5% and 24% from Shika and Bassawa respectively agreed with the statement and the remaining 7.5% and 3% responded that they didn't know. Further investigation reveals that the majority of those who disagreed with the statement explained that extension workers did not visit them and most of the time they source advice from their fellow farmers in the village or telephone the NEARLS staff. As depicted in Table 4, Chi-square analysis was used to test significant relationship between farmers' perception regarding the role of extension services and increase in crop production. The results revealed that there is no statistical significant relationship between extension services and increase in crop production. This may be because of the ineffectiveness of the extension services in the study area.

TABLE 4

CHI-SQUARE ANALYSIS OF RELATIONSHIP BETWEEN FARMERS' PERCEPTIONS REGARDING EXTENSION AGENTS' ROLE IN HELPING RURAL FARMERS TO INCREASE CROP PRODUCTION

Do you believe that extension workers play a role in helping rural farmers to increase crop production	Shika n=100	Bassawa n=100	Chi-Square	df	p-value
Yes	25.5	24	12.84	1	0.14**
No	67	73			
I don't know	7.5	3			
Do you think extension services is effective your area?					
Effective	9	23	22.29	1	0.16**
Not effective	86	75			
I don't know	5	2			

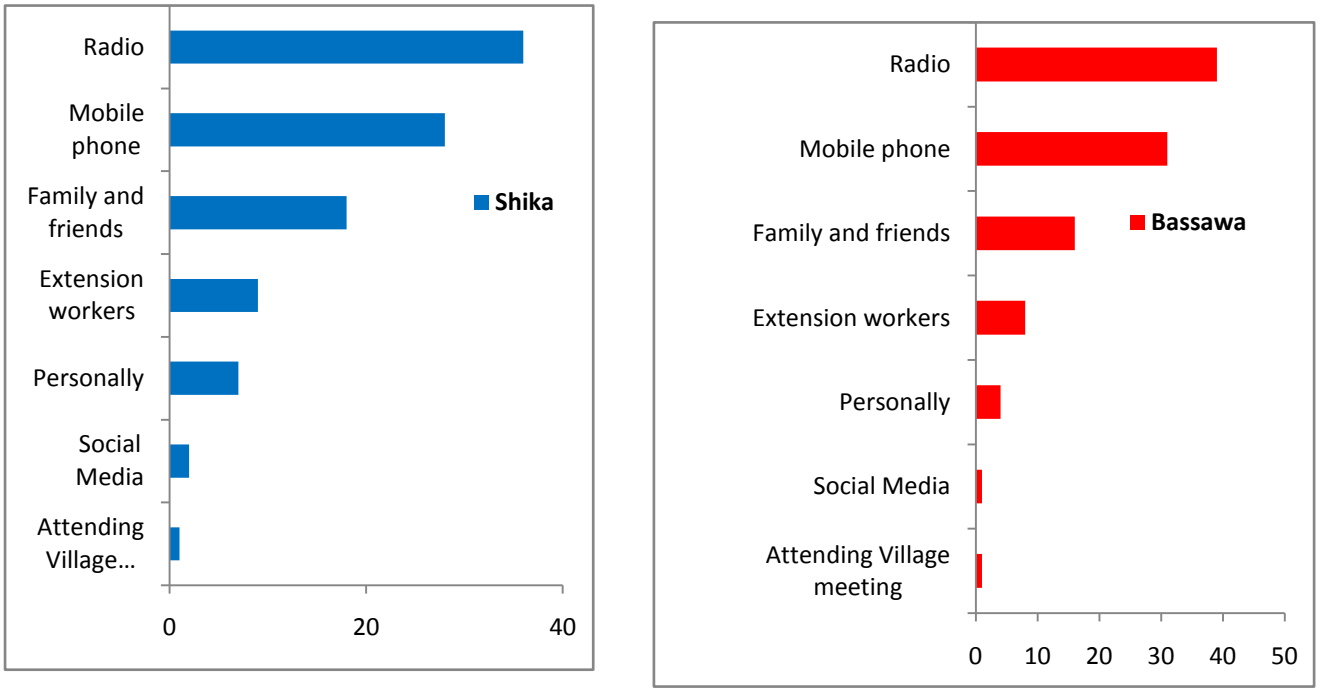
X^2 = Chi-square; ** = P< 0.001

Source: Survey; Shika n=100, Bassawa n=100

3.4 Preferred Sources of Agricultural Information among Smallholder Farmers

Information has become a critical factor to increase smallholders' production and productivity. As a result, the most preferred sources of information by smallholder farmers were investigated and respondents were requested to rank the sources of agricultural information used. As presented in figure 3a-b, the findings revealed that smallholder farmers preferred traditional ICT, mainly radio (36%) as their main source of accessing agricultural information followed by mobile phones (28%) for Shika community, while 39% and 31% of smallholder farmers from Bassawa community indicated that they prefer radio and mobile phone respectively.

The study results further indicate that agricultural extension agents, personal sources and social media were not considered as significance in obtaining agricultural information by the respondents. The findings of the study show that radio and mobile phones were relevant agricultural information which helps farmers to make informed decisions about what crops to plant and where to purchase affordable farm inputs and which market to sell their produce. In this regard, the need and choice of the sources of information on improved agricultural technology, and how the timely and relevant information is disseminated to the targeted smallholder farmers should be of paramount concern to both agricultural development practitioners and agricultural extension workers. However, the chi-square test shows that there were no statistically significant differences between the farmer's present sources of agricultural information.



(a) **(b)**

FIGURE: 3 a-b Present sources of agricultural information among smallholder farmers
Source: Survey; Shika n=100% ***Bassawa n=100 Scale: %***

3.5 Current Problems Affecting Agricultural Extension Services in the Study Area

During the focus group discussions, extension workers were asked to highlight and rank the current problems affecting extension organizations in the study area. As shown in Figure 4, of the ten problems mentioned, all of them seem to be affecting agricultural extension services in the area. However, the most significant of these problems ranked by the extension workers was the exceptionally low number of extension workers in the area, while poor funding of Agricultural Development Programme by the Government, lack of regular training for agents, inadequate ICT amenities and lack of incentives for field personnel were among the least important problems identified (Figure 4). Of course, this study acknowledges that ICT are not a panacea to social and economic development problem of the rural communities in Nigeria. Nevertheless, they have potential to help the smallholder farmers to leap some of the traditional obstacles to development by improving access to appropriate and timely information. Therefore, ICT can be used to support traditional extension models.

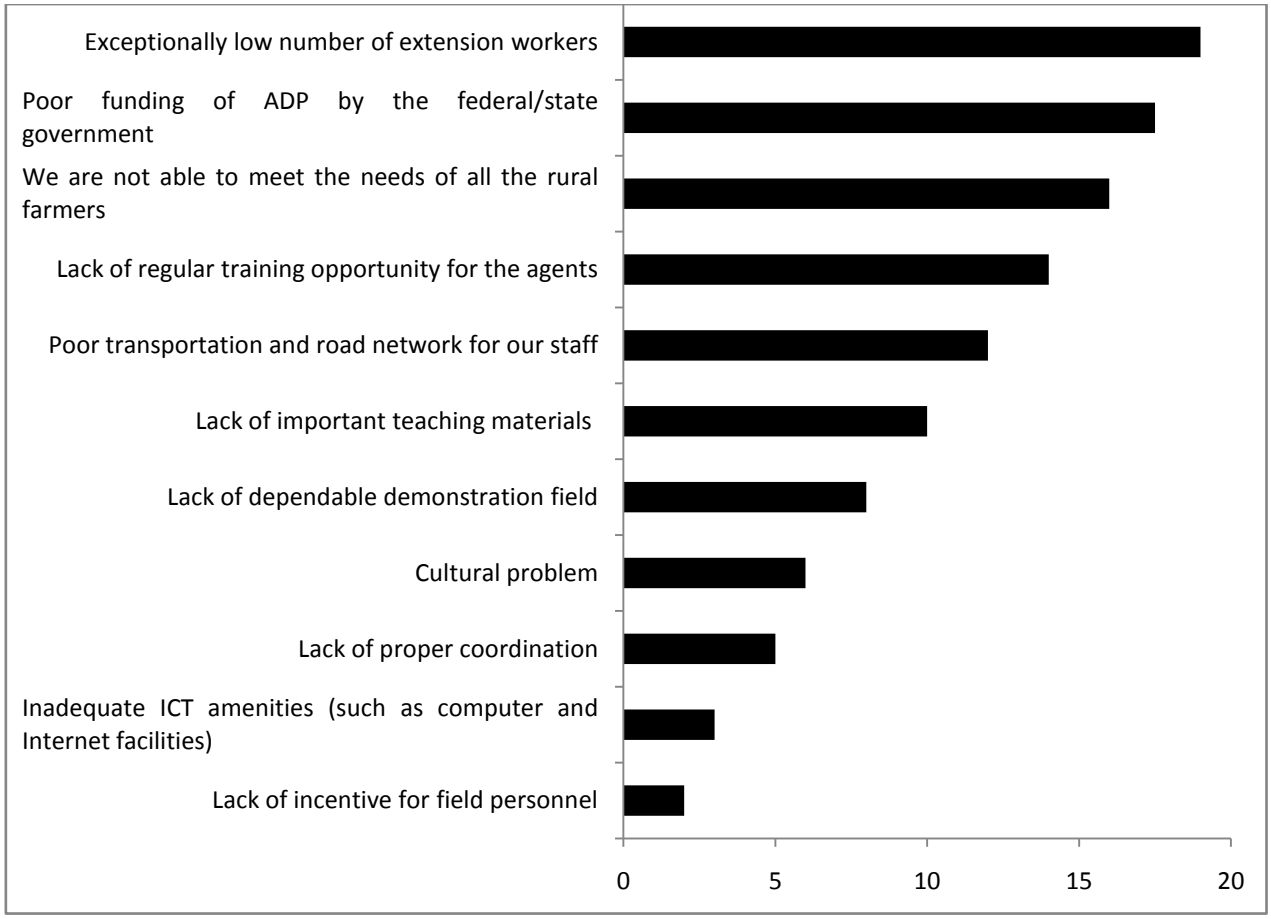


FIGURE 4: Problem affecting agricultural extension services in the study area Source: Survey; Extension workers n=20; Scale: 20 Extension workers

IV. CONCLUSION

The result of the study revealed that smallholder farmers do not have favorable perception regarding the effectiveness of agricultural extension agent in the area. A great proportion (89%) of the farmers perceived lack of regular contact with extension agents as a major challenge. Similarly, the majority of smallholders reported that extension services were not effective. The results of the chi-square analysis also showed that there was no statistical significant relationship between agricultural extension services and increase in crop production of the smallholder farmers. On the other hand, our results also revealed that radio is the most preferred source of agricultural information among the smallholder farmers in the area since extension services and delivery were not effective to meet their needs. On the contrary, extension agents suppose to be the best source of agricultural information and training for smallholders' participatory development, hence their credibility is very important for effective extension services. When smallholders have more regular contact with extension agents then they can get more timely and accurate information. However, the most significant of these problems ranked by the extension workers was the exceptionally low number of extension workers in the area, while inadequate ICT amenities and lack of incentives for field personnel were among the least important problems.

RECOMMENDATIONS

In view of the findings, the paper recommends that Government should employ more agricultural graduates' youths and train them. More extension workers need to be hired in order to significantly reduce the problem of the extension workers to farm families' ratio which is currently 1:3000 in the Kaduna State. Similarly, Federal Ministry of Agriculture should make an effort to provide additional funding support to Agricultural Development Programme for effectual extension services delivery to the rural farmers. Moreover, State Ministry of Agriculture can also improve the quality of extension services by conducting need assessment programme. Finally, Federal Government should support the development of other development partners that are involved in extension service delivery to rural farmers such as NGOs, private sectors, academia and farmer cooperative societies.

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Institutional Factors and Crop Farmer's Participation in Agricultural Insurance Scheme: Evidence from South Western Nigeria

Kolapo Adetomiwa[1*], Oladejo Olayinka.O[2], Muhammed Opeyemi.A.[3], Kolapo Adeyera.J[4]

[1,2]Department of Agricultural Economics, Faculty of Agriculture, Obafemi Awolowo University, Ile Ife, Osun State, Nigeria.
[3]Department of Agricultural Economics& Extension, Faculty of Agricultural Sciences, Ekiti State University, Ado-Ekiti, Ekiti State, Nigeria.
[4]Department of Agricultural Economics and Farm Management, Faculty of Agriculture, University of Ilorin, Ilorin, Kwara State, Nigeria.
***Correspondence authors**

Abstract*—The paper investigated the effect of institutional factors on crop farmer's participation in agricultural insurance schemes in South Western, Nigeria. Specifically, the study described the socio-economic characteristics of crop farmers in the study area, examined the level of awareness of the crop farmers, analyzed the factors influencing the participation of crop farmers and intensity of use of the agricultural insurance policy and compare the income between the participating and non-participating crop farmers in the study area. Multistage sampling techniques were used to select 240 respondents in the study area. Primary data were used for the study, which was sourced from a cross-sectional survey of crop farmers in the study area with the aid of a well-structured questionnaire. The data were analyzed using descriptive, Cragg's (double-hurdle) model, and t-test. The result of the descriptive analysis showed that the mean age of participant and non-participant was 49.47 (±16.36) and 48.19(±15.41) respectively, where the mean years of formal education for participants and non-participant were 10.23(±5.46) and 10.54(±5.72) respectively. The result of Cragg's model in the first hurdle (Probit model) showed that variables such as education, access to credit, farm size, membership of association, and awareness significantly influence the decision of crop farmers to participate in agricultural insurance scheme. In the second hurdle (truncated regression), access to credit, income, risk assessment, and contact with extension was significant to intensity of participation in agricultural insurance scheme in the study area. The result of the t-test showed that there is a significant difference in the income of participants and those that do not participate in agricultural insurances scheme in the study area. Even though a considerable proportion of respondents sampled were aware of agricultural insurance, there is still a need to increase awareness among the farmers so that more farmers can participate in the scheme in other to stabilize their income.*

Keywords*— *Agricultural Insurance, Participation, Crop farmers, Double- hurdle, South Western.

I. INTRODUCTION

Prior to the discovery of petroleum in Nigeria, Agricultural was the mainstay of the country's economy. Agriculture alone contributes about 57% to the GDP during this period (Oluyole and Sanusi, 2009). Crops like cocoa, groundnut, cotton, oil palm and livestock including cattle and goats were the major crops and livestock being produce during this period. However, Nigeria agriculture has witnessed many phases of policies till date even though those policies are yet to revive the stumbling situation of the agricultural sector in present day Nigeria. In Nigeria today, Agriculture provides employment for nothing less than 70% of the total work force (Obatolu, Fashina and Olaiya, 2003). Although majority of them being produce on a small scale. The agricultural sector is an important sector to Nigeria economy as it contributes substantially to the economy after the oil sector.

However, agriculture in Nigeria faces myriads of problems including pest and disease infestation, drought, flooding etc.(Obatolu, Fashina and Olaiya, 2003; Oluyole and Sanusi, 2009; Villalobos, 1989; Wood, 1985; Wright, 1993). Agriculture as an enterprise is faced with risk and uncertainties which has affected the productivity of farmers over time (Oluyole and Sanusi, 2009). Although, farmers have developed different strategies to cope with this unforeseen circumstances and events that might affect their production and output from their respective farms. One of the important strategies to cope with risk and uncertainties experienced on farm is agricultural insurance.

Agricultural insurance, in its widest sense may be defined as the stabilization of income, employment, price and supplies of agricultural products by means of regular and deliberate savings and accumulation of funds in small installments by many in favorable time periods to defend some or few of the participants in bad time periods (Arene, 2005).The term "insurance" is simply "a risk management strategy". The primary motive of any agricultural insurance policy is to serve as a security for losses resulting from natural disasters. Agricultural insurance is therefore the most important available device for minimizing the adverse effects of natural hazards. Nigerian farmers suffered various losses on their investment and had no means of going back to production. The frustration made them to move into cities in droves in search of easy means of livelihood. This situation led to depletion of farming populace, which was a serious threat to food security. The Federal Government was disturbed by the ugly trend, hence the establishment of Nigerian Agricultural Insurance Corporation (NAIC) to address the need of farmers. The need for a specialized Agricultural Insurance Company to provide insurance cover to farmers was informed by Government's concern over the vacuum created due to the unwillingness of conventional Insurers to accept Agricultural risks, which they considered too risky. This led to the establishment of the Nigerian Agricultural Insurance Scheme on 15th of November, 1987.The implementation of the Scheme was initially vested on the Nigerian Agricultural Insurance Company Limited, which was later incorporated in June, 1988 but later turned into a Corporation in 1993 by the enabling Act 37 of 1993. Nigerian Agricultural Insurance Corporation is therefore a wholly-owned Federal Government of Nigeria insurance company set up specifically to provide Agricultural risks insurance cover to Nigerian farmers, the name which later changed to Nigerian Agricultural Insurance Scheme (NAIS). The Nigerian Agricultural Insurance Scheme (NAIS) is to protect the Nigerian farmer from the effects of natural hazards by introducing measures which shall ensure a prompt payment of appropriate indemnity (compensation) sufficient to keep the farmer in business after suffering a loss

Many studies (Akinola, 2014; Falola *et al*., 2013; Ajiboye *et al*, 2018; Oluwatusin *et al*., 2018 and Akintunde, 2015)have been conducted to assess the situation of agricultural insurance policy use, acceptance and adoption by farmers in Nigeria. According to Akinola (2014), farmers' adoption of agricultural insurance will increase if there is increase in formal and extension education, higher level of awareness of insurance policy, more perception and concern for past experience with risk and less indifference resulting from too much confidence in their years of experience and alternative risk management strategies. According to Ajiboye *et al*. (2018), most of the farmers were influenced by the financial institutions (Bank of Agriculture (BoA)) compelling them to acquire insurance policy as a precondition for obtaining loans or as a practical response to some risks which they were faced with in the immediate preceding season. Akintude (2015) ascertained that Stock size, rearing system, access to extension services and poultry rearing experience were significant variables that influenced the participation of the poultry farmers in livestock insurance policy.

However, majority of these studies used logit regression model to analyzed the determinants of the use and adoption of agricultural insurance policy among the farmers in Nigeria. None of the studies on use of insurance policy in Nigeria had address the situation at hand using double- hurdle regression (Cragg's model) in other to further ascertain the intensity of the use of insurance policy among the participating farmers in Nigeria taking into consideration the effect of institutional factors. In this study, the institutional factors considered includes, access to credit, contact with extension agent and membership of association. Specifically, the study described the socio-economic characteristics of crop farmers in the study area, examined the level of awareness of the crop farmers, analyzed the factors influencing the participation of crop farmers and intensity of use of the agricultural insurance policy and compare the income between the participating and non-participating crop farmers in the study area.

II. METHODOLOGY

2.1 Area of Study

The study was carried out in South-Western region of Nigeria. The South-Western region represents a geographical area covering between latitude 6^0 North and 4^0 South. It comprises six states which include: Ekiti, Oyo, Osun, Ondo, Ogun and Lagos State. The region is bounded in the north by Kogi and Kwara States, in the South by Atlantic Ocean, in the West by Republic of Benin and in the East by Edo and Delta State. The tropical climate of the region is broadly of two seasons: rainy season (April-October) and dry season (November-March). Temperature throughout the year ranges between 21^0C to 29^0C and humidity is relatively high. The annual rainfall varies from 2,000mm in the southern areas to 1,150mm in the northern areas. Agriculture is the mainstay of the region and 65% of the region labour force is in agricultural sub-sector (Folayan, Oguntade and Ogundare, 2007). The South western region of Nigeria can boast of different varieties of arable and tree crops as the climatic conditions support the production of various arable and tree crops including cassava, maize, groundnut, cotton etc. Farmers in this region are often faced with myriads of climatic problem with posed threat to agricultural production in

this region. Agricultural insurance policy had been identified as an important strategy to combat risk and uncertainties to agriculture in this region, hence the choice of the study area for the study.

2.2 Sampling procedures and sample size

Multistage sampling procedures were employed for the study. The first stage involved purposive selection of three States including Ogun, Osun and Oyo States due to their high participation in agricultural insurance based on reconnaissance survey conducted during the 2017 agricultural season. The second stage involved the random selection of two Local Government Areas from each State. The third stage involved random selection of 20 participating and 20 non-participating crop farmers in each of the selected Local Government based on a list of farmers obtained from ADP and NAIC offices in each State. Thus, a total of 240 respondents were used for the study. Primary data were sourced from cross-sectional survey of crop farmers in the study area with the aid of well-structured questionnaire to cover information about the socio-economic characteristics of respondents, awareness, output and income of the farmers and reasons for participation in agricultural insurance scheme. Data were collected during the period of March, 2018- August, 2018.

2.3 Analytical techniques

The data were analysed using descriptive, Cragg's (double-hurdle) model and t-test

2.4 Descriptive statistics

Descriptive statistics were used to describe the socio-economic characteristics, awareness and reason for participatingin agricultural insurance scheme in the study area.

The Cragg's model two-step estimation procedure

The Cragg's model was chosen for this study because it relaxes the restrictive assumption of the Tobit model that the factors influencing the discrete decision (participation decision) and the continuous decision (intensity of participation) as well as their effects are the same. Hence, in the Cragg's model, the coefficients of the dependent variables of the first and second hurdle are different.

The first step analyses the factors influencing the decision of the crop farmers to participate in agricultural insurance scheme, while the second step deals with the intensity of participation in the agricultural insurance scheme.

Step 1: Probit model for the discrete participation decision

For the probit model, we assume that the decision of the 'i'th farmer to participate in agricultural insurance scheme or not depends on an unobservable utility index Y_i^*, that is determined by the explanatory variables, and that the higher the value of this utility index the higher the probability that the farmer will participate in agricultural insurance scheme. The decision probability (dependent variable) Y_i is limited between the values of 1 and 0.

$$Y_i = \begin{cases} Y_i^* \text{ if } Y_i^* > 0 \\ 0 \text{ if } Y_i^* \leq 0 \end{cases}$$

The probit model is expressed as:

$$\text{Prob}(Y^* > 0) = F(X'\beta) = \Phi(X'\beta) = \int_{-\infty}^{X'\beta} \emptyset(Z)dZ$$

Where; $F(X'\beta)$ = cumulative degree of freedom of the standard normal distribution.

$$Y_i^* = X'\beta + e_i$$

$$X'\beta = \beta_0 + \beta_1 AGE + \beta_2 GENDER + \beta_3 EXPER + \beta_4 EDUYRS + \beta_5 ACCRDT + \beta_6 FINCOME + \beta_7 FARMSIZE + \beta_8 LNDWNSHP + \beta_9 ASSN + \beta_{10} PERCEPTN + \beta_{11} RISK + \beta_{12} AWARE + \beta_{13} ACCMKT + \beta_{14} EXTN$$

Where; Y = decision to Participate (1= Participate, 0= not participate)

AGE is Age (years)

GENDER is Gender (1=male; 0=female)

EXPER is Experience (years)

EDUYRS is Years of Education (years)

ACCRDT is Access to credit (1=yes fertile; 0=yes)

FINCOME is Income (₦)

FARMSIZE is Farm size (ha)

LNDWNSHP is Land ownership (3=purchased; 2=leased; 1=borrowed; 0=inherited)

ASSN is Association membership (1=member; 0=non-member)

PERCEPTN is Perception (1=positive; 0=negative)

RISK is Risk affinity (#)

AWARE is Awareness (1=aware; 0=not aware)

ACCMKT is Access to market (1=yes; 0=no)

EXTN is Extension contacts (#)

Step 2: Model for the continuous decision (intensity of participation using uncensored observations)

The second hurdle model uses the truncated regression model to determine intensity of participation in agricultural insurance scheme.

$$E(Y|Y^* > 0) = X'\gamma + \sigma\lambda\left(\frac{X'\gamma}{\sigma}\right)$$

Here the Cragg's model makes use of uncensored observations i.e. the observations with zero participation level were not cut out of the observation, thus giving a better representation of the population.

$$X'\gamma = \gamma_0 + \gamma_1 AGE + \gamma_2 GENDER + \gamma_3 EXP + \gamma_4 EDUYRS + \gamma_5 ACCRDT + \gamma_6 FINCOME + \gamma_7 FARMSIZE + \gamma_8 LNDWNSHP + \gamma_9 ASSN + \gamma_{10} PERCEPTN + \gamma_{11} RISK + \gamma_{12} AWARE + \gamma_{13} ACCMKT + \gamma_{14} EXTN$$

Where; Y = Intensity of participations

AGE is Age (years)

GENDER is Gender (1=male; 0=female)

EXP is Experience (years)

EDUYRS is Years of Education (years)

ACCRDT is Access to credit (1=yes fertile; 0=yes)

FINCOME is Income (₦)

FARMSIZE is Farm size (ha)

LNDWNSHP is Land ownership (3=purchased; 2=leased; 1=borrowed; 0=inherited)

ASSN is Association membership (1=member; 0=non-member)

PERCEPTN is Perception (1=positive; 0=negative)

RISK is Risk affinity (#)

AWARE is Awareness (1=aware; 0=not aware)

ACCMKT is Access to market (1=yes; 0=no)

EXTN is Extension contacts (#)

T-test

This was used to achieve the impact of participation in agricultural insurance scheme on farmers" income. It was specified as

$$t = \frac{(\bar{X}_1 - \bar{X}_2)}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

Where:

X_1 = Mean income of participating farmers

X_2 = Mean income of non-participating farmers

S_1= Standard deviation of participating farmers

S_2= Standard deviation of non-participating farmers

n_1 = Sample size of participating farmers

n_2 = Sample size of non-participating farmers

III. RESULTS AND DISCUSSION

3.1 Socio-economic characteristics of respondents

The results of the socio-economic characteristics of the respondents were presented on Table 1. The mean age of participant and non-participant was 49.47 (±16.36) and 48.19(±15.41) respectively. This shows that there are no major differences in the ages of both the participant and non-participant as the two categories were in their active and productive age. This result agreed with Falola *et al*., 2013 who established that farmers in Nigeria were in mid and active age. As regarding gender, 53% of participants were male while 62% of the non-participant were male. This suggest that both male and female participant and non-participants respectively were actively involved in crop production in the study area. This result agrees with Oluwatusin *et al*., 2018. The mean years of formal education for participants and non-participant were 10.23(±5.46) and 10.54(±5.72) respectively. This suggests that crop farmers in the study area were literate as they possess considerable years of formal education. This result agreed with Ajiboye *et al*. (2018). The mean years of farming experience for participants and non-participants was 19.14(±11.19) and 19.32(±11.73) respectively. These implies that crop farmers in the study area had been into the business for many years and thus have the necessary experience to increase their production. From Table 1, 73% and 53% of the participants and non-participants respectively belong to one association or the other. This shows that the participant was more involved in society association than the non-participant. This might have influence the participant to take up agricultural insurance policy as they might have been influenced by group dynamism. This agree with Oluwatusin *et al*. (2018). About 86% of the participants had access to credit while 43% of the none participant had access to credit. This implies that the participant had more access to credit than the non-participant which might be largely due to their involvement in agricultural insurance. Furthermore, 76% of the participants had contact with extension agents while 51% of the non-participant had contact with extension agents. This implies that users of agricultural insurance in the study area had more contact than the non-users hence might have influence their decision to adopt agricultural insurance policy in the study area. The mean annual farm income of the participant and non-participant was 623543(±395839) and 482624(±294538) respectively. This result shows that there is a difference in their annual income. This difference might have been influence by the indemnity received by the participant at the end of production season.

TABLE 1
SOCIO-ECONOMIC CHARACTERISTICS OF RESPONDENTS BY GENDER

Variables	Participant	Non-participant	Pooled
Age	49.47 (±16.36)	48.19(±15.41)	48.79(±145.25)
Male (%)	53.00	62.00	64.00
Years of formal education	10.23(±5.46)	10.54(±5.72)	10.38(±5.41)
Years of farming experience	19.14(±11.19)	19.32(±11.73)	19.12(±11.31)
Association membership (%)	73.00	52.00	68.00
Access to credit (%)	86.00	43.00	76.00
Extension contact (%)	76.00	51.00	61.00
Farm income	623543(±395839)	482624(±294538)	549302(±293746)

Figures in parenthesis are standard deviation
Source: Data Analysis, 2018

3.2 Respondents level of Awareness of Agricultural insurance scheme

The level of awareness of the crop farmers as regarding agricultural insurance scheme were presented on Table 2. The result shows that 73.3% of the crop farmers were aware while 26.7% were not aware. This implies that majority of the farmers sampled have knowledge of the agricultural insurance scheme in the study area although some of the crop farmers despite their knowledge of agricultural insurance scheme, they still do not participate.

TABLE 2
DISTRIBUTION OF RESPONDENTS BY AWARENESS

Awareness	Frequency	Percentage (%)
Yes	176	73.3
No	64	26.7
Total	240	100.00

Source: Data Analysis, 2018

3.3 Reasons for participating in agricultural insurance

The various reasons why crop farmers participated in agricultural insurance scheme in the study area were presented in Table 3. About 15.9% of the participants take up agricultural insurance policy due to uncertainty of climatic conditions. Crop farmers have been faced with problem of climate change in recent years and this had affected their farm output in recent times. So, in other to brace up with the inputs invested in their respective crop production, they take up agricultural insurance policy as a cover up against risk and uncertainties of weather condition in the study area. About 13.7% of the participants partook in agricultural insurance due to availability of optional policies. Thus, NAIC have different insurance policy cover for crop farmers and the crop farmers in the study area have the opportunity to choose and decide which policy best suits their needs. About 18.2% of the respondents used agricultural insurance because of government subsidization on premium since the government including federal and state government in which the enterprise is established is responsible for 50% of premium payable by the crop farmers. Also, 20.7% of the respondents utilized agricultural insurance because of easy access to credit facilities. Most of the financial lending institutions in Nigeria requires agricultural insurance policy for granting loans and farmers have thus sees agricultural insurance policy as an easy gateway for obtaining credit facilities. This agrees with Ajiboye *et al*. (2018) who ascertained that most of the farmers were influenced by the financial institutions (Bank of Agriculture (BoA)) compelling them to acquire insurance policy as a precondition for obtaining loans. About 14.7% of the respondents participated in agricultural insurance policy due to prompt and early settlement of claims by NAIC. In time past majority of the farmers normally find it difficult to claim their indemnity. However, with the reform in NAIC in recent years, farmers have been experiencing early and prompt payment of indemnity and have thus encouraged them in taking up agricultural insurance policy in the study area. Furthermore, about 16.8% of the respondents participated in agricultural insurance because of provision of effective technical assistance to farmers. NAIC had over the years granted expertise assistance to farmers who took up agricultural insurance with them educating the farmers on best agricultural practices to be adopted. This has helped improved farmers productivity over the years and also, the capital that the farmers would have literarily paid for expertise consultation were been saved in the process.

TABLE 3
REASONS FOR PARTICIPATING IN AGRICULTURAL INSURANCE

Reasons	Frequency Percentage (%)	
Uncertain climatic condition	91	15.9
Availability of optional policies	78	13.7
Government subsidization on premium	104	18.2
Easy access to credit	118	20.7
Prompt and early settlement of claims by NAIC	84	14.7
Provision of effective technical assistance to farmers by NAIC	96	16.8
Total	571**	100.00

Source: Data Analysis, 2018
****Multiple responses***

3.4 Effect of Institutional Factors on Decision to Participate and Intensity of Participation in Agricultural Insurance

The result of the first hurdle (Probit model) was presented on Table 4. The study revealed that the generalized likelihood function was -83.583. The likelihood function implies that there is adequacy in the choice of explanatory variable set. The Prob > chi^2 statistic of 0.0893 ($p < 0.10$) obtained shows that the model gave a good fit for the analysis. From Table 4, variables such as education, access to credit, farm size, membership of association and awareness significant influence the decision of crop farmers to participate in agricultural insurance scheme. Education was positive and significant at 1%. This implies that the higher the level of education attained by the crop farmers, the tendency to participate and use in agricultural insurance policy. This is possible because farmers tend to get enlightened based on their educational exposure. This result agreed with Olubiyo *et al*. (2009); Masoumi *et al* (2013) and Farayola *et al* (2013). Access to credit was positive and significant at 1%. Farmer's access to credit facilities can encourage them to participate in agricultural insurance as they tend to ensure that they insured the risk they might experience so that should they experience issues on their farm, they will be able to repay the loan through indemnity received from the insurance company. Farm size was positive and significant at 1% level of probability. It is logical that as farm size increases, the farmers tend to ensure that they practice a risk management strategy and their participation and use of agricultural insurance policy might be possible. This result is consistent with that of Fallah *et al*. (2012). Membership of association was positive and significant at 5% probability level. This implies that group dynamic can influence the decision of crop farmers to use agricultural insurance policy in the study area. Farmers tend to be briefed about the necessity of agricultural insurance through their regular involvement in cooperative societies. Furthermore, Awareness was positive and significant at 10% level of probability. This shows that increased awareness on the importance of agricultural insurance to farmers might increase the chances of crop farmers participating in agricultural insurance scheme in the study area. This agreed with Ajiboye *et al*. (2018).

TABLE 4
FIRST HURDLE (DECISION TO PARTICIPATE)

Variables	Coefficients	Std. Error	T-value
Constant	0.110***	0.007	15.74
Age	0.020	0.020	1.01
Gender	0.001	0.005	0.28
Experience	0.197	0.139	1.42
Education	0.042***	0.007	5.63
Access to Credit	0.174***	0.049	3.56
Income	189.135	273.029	0.69
Farm Size	5618.24***	1183.819	4.75
Land Ownership	-0.045	0.029	-1.52
Association	0.610**	0.273	2.24
Perception	0.013	0.021	0.63
Risk Assessment	0.197	0.139	1.42
Awareness	12.686*	7.054	1.80
Access to Market	6.158	112.629	0.05
Extn. Contact	0.044	0.054	0.82
LRchi^2	14.74		
Log likelihood	-83.583		
Prob > chi^2	0.08930		

****, **, *** Significant at 10, 5 and 1% respectively***
Source: Data Analysis, 2018

From Table 5, the second hurdle shows that access to credit, income, risk assessment and contact with extension was significant to intensity (continuous) participation in agricultural insurance scheme in the study area. Access to credit was positive and significant at 5% probability level. This implies that farmers continue to use and participate in agricultural insurance scheme as long as they continue to access credit facilities in the study area. This is true because lending institution will continue to ask for agricultural insurance policy of the farmers before new credit facilities were given to them. Income was positive and significant at 1% level of probability. When farmers take up agricultural insurance policy, their income is expected to be stabilized and their income increases they tend to continue the use of agricultural insurance policy. Risk assessment was positive and significant at 5% probability level. As crop farmers assessed the risk they encountered before

and after their involvement in agricultural insurance scheme, they tends to continue the use of agricultural insurance policy and they likely found out that the risk they encountered after their involvement in agricultural insurance weigh less than before. Contact with extension agent was positive and significant at 10% level of probability. This implies that as long as the farmers continue to have contact with extension agents, they tend to be encouraged continuously to participate in agricultural insurance scheme in the study area.

TABLE5
SECOND HURDLE (INTENSITY OF PARTICIPATION)

Variables	Coefficients	Std. Error	T-value
Constant	0.400	0.375	1.06
Age	4.353	4.518	0.96
Gender	1.822	6.050	0.30
Experience	1.061	4.488	0.23
Education	0.005	0.021	0.23
Access to Credit	0.318**	0.141	2.25
Income	2.260***	0.744	3.03
Farm Size	0.947	0.903	1.04
Land Ownership	0.005	0.335	0.01
Association	1.219	1.711	0.71
Perception	0.004	0.157	0.02
Risk Assessment	0.445**	0.066	6.74
Awareness	0.027	0.052	0.51
Access to Market	0.033	0.026	1.50
Extn. Contact	0.021*	0.012	1.75
$LRchi^2$	19.47		
Log likelihood	-95.628		
Prob > chi^2	0.09247		

****, **, *** Significant at 10, 5 and 1% respectivelySource: Data Analysis, 2018***

T-test result showing the differences between the net income of the crop farmers participating and those not participating in agricultural insurance

T-test (Table 6) result shows that there is significant difference between the net income of the crop farmers participating and those not participating in agricultural insurance. This confirmed that the users of agricultural insurance policy had more net income than the non-participant at the end of the production season. This might be possible due to indemnity received by the participant after assessing their loss by the insurance company at the end of the production season.

TABLE 6
T-TEST RESULT SHOWING THE DIFFERENCES BETWEEN THE NET INCOME OF THE CROP FARMERS PARTICIPATING AND THOSE NOT PARTICIPATING IN AGRICULTURAL INSURANCE SCHEME

Variable	Mean difference	Standard error difference	T-test
Net income	34739.467***	148296.531	4.729

Source: Data Analysis, 2018.
******significant at 1 percent***

IV. CONCLUSION AND RECOMMENDATIONS

The study concluded that crop farmers in the study area were in their active age, literate and had the necessary experience in carry out their farming activities. In addition, the study concluded that farmers who participated in agricultural insurance scheme had access to credit and had more contact with extension agents. Considerable proportions of crop farmers were aware of agricultural insurance scheme in the study area. Furthermore, in the first hurdle (Probit model), variables such as education, access to credit, farm size, membership of association and awareness significant influence the decision of crop farmers to participate in agricultural insurance scheme. In the second hurdle (truncated regression), access to credit, income, risk assessment and contact with extension was significant to intensity (continuous) participation in agricultural insurance scheme in the study area. The result of the t-test showed that there is a significant difference in the income of participants and those that does not participate in agricultural insurances scheme in the study area.

Therefore, based on the findings of the study, the following recommendations were made in other to encourage farmers to participate in agricultural insurance scheme;

i. Farmers should be encouraged to get more education inform of training which will increase their chances of participating in agricultural insurance scheme in other for their income to be stabilized.

ii. Credit facilities should be made available to the farmers so as to increase their level of production which will instigate them to participate in agricultural insurance scheme.

iii. Farmers should be encouraged to join more association which will benefit them in many ways such as assessing loans which eventually instigate them to participate in agricultural insurance scheme.

iv. Despite the fact that considerable proportions of respondents sampled were aware of agricultural insurance scheme, there is still a need to increase awareness among the farmers so that more farmers can participate in the scheme in other to stabilize their income.

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Assessment of Yield of Tomato (*Lycopersicon esculentum* Mill.) and Soil CO_2 Emissions as Influenced by Compost Doses and Irrigation Regimes

Koffi-Kouma A. ALATE[1], Gbenonchi MAWUSSI[2*], Komla SANDA[3]

Department of Soil Sciences, Laboratory of Research on Agroresources and Environmental Health, Higher Agronomy School, University of Lome, Lome, Togo

Abstract— *Tomato (Lycopersicon esculentum Mill.) is one of the most important vegetables cultivated in Togo. Water stress constitutes one of limiting factors of production in dry season. Compost use improves soil properties and crop production but may lead to soil CO_2 emission into atmosphere. This study assessed the influence of compost doses and irrigation regimes on tomato yield and soil CO_2 emission. Trial agronomics were conducted in dry season in year 2018 and 2019 in a randomized complete block design with three repetitions. Treatments included control plots, compost plots and chemical fertilizer plots. Water was supplied according to three irrigation regimes of 1, 2 and 4 days interval. Tomato fruits were harvested when color was yellowish red. Soil CO_2 emission measurement was conducted in four months (120 days) during field experiment from January to April in 2019. Soil samples were collected from plots and incubated in laboratory. Soil CO_2 emission was measured every day during 28 day's incubation using 0.1 N HCl after precipitating the carbonate with a BaCl2 solution by alkali back-titrating. The results shown that highest tomato yield and highest soil CO_2 emission were recorded on plots treated with compost and submitted to two days interval irrigation while the lowest values of these parameters were obtained from control plots and treated plots submitted to daily and four days interval irrigation.This was noted that CO_2 emission from soil samples collected in third and fourth months of field experiment were more than those of first and second months.*

Keywords— Togo, household waste compost, irrigation interval day, tomato yield, soil CO_2 emission.

I. INTRODUCTION

In West Africa, cultural methods in many cases still remain ancestral characterized by the use of rudimentary tools and low use inputs (improved seeds, mineral and organic fertilizers etc.), thus contributing to the continuous soil degradation. Farmers traditionally relied on long fallow periods to restore land fertility. However, population increasing has shortened the fallow periods and decreased the available agricultural land. Furthermore, farmers remove crop residues from the field and use them for feeding their livestock or as fuel to cook their food. Crops are grown continuously on poor soils. Especially with continuous cultivation, physical properties and productivity of many soils commonly decline due to decrease in organic matter content (Lal, 1986). The red soil called "Terre de Barre" in coastal region of Togo does not escape this reality. These soils are overused and do not have the necessary time to replenish their organic matter stock. Demographic pressure and excess land use have led to a total depletion of these soils, resulting in a decrease in the stock of organic carbon and a destructuring of the surface horizons, reducing mainly food crop production (maize, cassava, cow pea, tomato etc.).

Researchers have shown that application of waste composts at reasonable rates improves soil physical properties, increases available soil nutrient levels and plant growth (Hossain et al. 2017; Coulibaly et al. 2019). According to Edwards and Araya (2009), compost increases soil fertility by holding and gradually releasing nutrients and building up organic matter levels in the soil, improves also the water holding capacity of the soil and makes crops better able to survive droughts.

On another side, the vegetable fields are small sizes about 0.25 – 0.50 ha in Togo where tomato (*Lycopersicon esculentum* Mill.) is one of the most important vegetables and cultivated in almost all parts of the country. Water stress constitutes one of the most important factor limiting plant growth and yield in dry season when the incidence of pests and diseases is minimal. Field water management practices is the most influential factors affecting crop yield particularly in irrigated agriculture (Al-Omran et al., 2005). Irrigation regime improves water use efficiency and has significant effect on the growth and yield of crops (Gudugi et al. 2012).Compost use in cropping systems may lead to soil CO_2 emission into atmosphere although the processes involved are not fully understood. Barton et al. (2016) reported that incorporating organic matter alters soil greenhouse gas emissions and increases grain yield in a semi-arid climate. Compost is known for its efficacy on agricultural productivity increase, but little is known about its effectiveness on tomato productivity in Southern Togo.The objective of this study was to assess the influence of household waste compost doses and irrigation regimes on the yield of tomato and the soil CO_2 emissions in coastal region of Togo.

II. MATERIALS AND METHODS

2.1 Field experiments

Field experiments were carried out at the University of Lome in the Teaching Research and Demonstration Farm of Agronomic School during two dry seasons in 2018 and 2019. The land had been cropped previously for many years. The soil type was a ferrallisol locally called "Terre de Barre" that developed from a continental deposit (Saragoni et al., 1991). This soil is red, deep and suitable for almost all crops. The particle size distribution analysis revealed that soil surface layer (0 - 15 cm) of experimental site was loamy sand. For this study, the land was manually ploughed and divided into plots with plot area of 3.84 m^2 (2.4 m x 1.6 m). Each plot was separated from the adjacent by 1 m interval while the replicates were separated by 1.5 m interval. Tomato (*Lycopersicon esculentum* Mill.) mongal F1 variety, a high-yielding hybrid cultivar, was used. The tomato seedlings were raised in the nursery for three weeks before transported on plots and planted at a spacing of 0.5 m. The treatments were arranged in a randomized complete block design. Each treatment was replicated three times. There were five treatments per block where T0 refers to control plots without any compost use while T20, T30 and T40 refer to plots treated with compost at 20 t ha^{-1}, 30 t ha^{-1} and 40 t ha^{-1} doses respectively and T_{MF} refers to mineral fertilizers NPK 15-15-15 and Urea (46% N) applied at 0.2 t ha^{-1} and 0.1 t ha^{-1}doses respectively. These treatments were in combination with three irrigation regimes (interval of 1, 2 and 4 days). The compost used was produced with 70% of household solid urban wastes collected from Agbalepedogan district in Lome mixed with 30% poultry manure (Alate et al., 2019). It was applied at the beginning of tomato cultivation before transplanting the young tomato plants. It was spread on the soil surface after ploughing and mixed with the topsoil at about 15 cm depth. Preventive phytosanitary treatments were performed against potential pests and diseases of tomato.

2.2 Irrigation regimes

Irrigation scheduling, including 1, 2 and 4 days interval irrigation, was applied during all experimental period. At each irrigation event, an amount of water corresponding to field capacity water content in 15 cm soil depth was applied. Irrigation was applied manually using a watering can with capacity known in order to make sure that all the experimental plots received the same amount of water. The combined effect of compost doses and irrigation regimes on yield of tomato and soil CO_2 emission was evaluated.

2.3 Soil sampling, incubation and CO_2 emission measurement

The soil samples collected in topsoil at about 15 cm depth on each experimental plot were dried, sieved at 2 mm and homogenized before the beginning of incubation in laboratory. The study was conducted in four months (120 days) during field experiment from January to April in year 2019. The protocol was adapted to those of Rahman (2013). Twenty five grams of each dry soil sample was incubated at 30°C in hermetically sealed glass vial of 1000 ml volume. The soil water content has been adjusted to 25% (i.e. 12.5 g of demineralized water for the 50 g of soil). The sodium hydroxide (NaOH, 1N) solution (20 ml 1.0 N NaOH + 25 ml distilled water) was prepared for trapping CO_2. The trap solution in plastic pill box was placed in the vial of 1000 ml volume containing soil sample. The CO_2 released during the incubation is trapped in 15 ml of sodium hydroxide (NaOH, 1N) contained in plastic pill boxes put with the soil in the glass vials. For each treatment, three repetitions are performed. The measurements were carried out every day during 28 days of incubation. At each measurement, the pillboxes are sacrificed for evaluation of the amount of CO_2 released inside the glass vials and soda solution (NaOH, 1N) is renewed. After each measurement, the NaOH vials are changed and the jars aerated. The humidity of the soil samples is checked and adjusted on the eighth, sixteenth and twenty-fourth day. The CO_2emission was measured from the soil using 0.1 N HCl after precipitating the carbonate with a $BaCl_2$ solution by back-titrating the alkali. The alkali solution pillboxes were removed and titrated with 0.1 N HCl solution using phenolphthalein indicator and $BaCl_2$ solutions. Controls for this experiment consist of glass vial without soil sample but with the alkali of same strength was used. The alkali solutions from the control were titrated to determine the quantity of alkali that has not reacted with CO_2 excess $BaCl_2$. The determination of the CO_2 emitted is done on 10 ml of trap solution (NaOH) taken after his homogenization in the pillbox. A few drops of phenolphthalein were added as indicator, and titrated with 0.1 N HCl directly in the beaker. The volume of acid needed to titrate the alkali was noted. The amount of CO_2emittedwas calculated using the following formula:

$$\text{Milligram of } CO_2 = [(B - V).N.E]/M$$

where ***B*** is the volume of HCl used to titrate the control (mL), ***V*** the volume of HCl used to titrate the sample (mL), ***N*** the normality of HCl, ***E*** (= 22) the molar mass of CO_2 divided by 2 (because 2 mol of OH^- is consumed by 1 mol of CO_2), *M* = soil weight.

2.4 Tomato fruit harvest

When the fruits turned yellowish red, they were harvested at a regular interval from each plot. Fruits were picked by hand at 3 days interval during three weeks. The tomato fruits were sorted into categories marketable and unmarketable (cracked fruits, unripe fruits, tiny fruits, fruits having blossom - end rot, diseased, malformed and damaged by insect pests). The first harvest in all treatments was considered as early ripening. The fruits of all pickings were added up and total yield was expressed in ton per hectare.

2.5 Statistical analysis

Tomato total yield data were grabbed into the Excel spreadsheet and analysis of variance (ANOVA) was carried out with the CropStat software. Means comparisons between treatments were performed with Newman & Keuls test at the threshold of 5%.

III. RESULTS AND DISCUSSION

3.1 Influence of compost doses and irrigation regimes on tomato total yield

Total yields of tomato which included early ripening yield, marketable yield and unmarketable yield were presented in Table 1. The highest values of tomato yield (14.20 t ha^{-1} - 30.59 t ha^{-1}) were recorded on plots treated with compost and mineral fertilizers and submitted to two days interval irrigation, while the lowest values (3.58 t ha^{-1} - 11.63 t ha^{-1}) were recorded on control plots and plots treated with compost and mineral fertilizers but submitted to daily and four days interval irrigation. It was noted that the yields of tomato were proportional to compost doses. This explained that tomato yield was influenced by compost doses applied and irrigation regimes. The tendency these results may be attributed to the fact that adequate watering conditions led to the development of an abundant ovules per floret consequently higher yield fruit under irrigation regime of two days interval. Our results were in line with the findings of Gudugi et al. (2012) who suggested that number of tomato fruits had been related with irrigation intervals.

TABLE1
EFFECT OF COMPOST DOSES AND IRRIGATION REGIMES ON TOTAL YIELD OF TOMATO

Treatments	Irrigation interval days	Total yield (t ha^{-1}) Year 2018	Total yield (t ha^{-1}) Year 2019
T0	daily	4.05±0.02g	3.62±0.01g
	2 days	4.19±0.02g	3.65±0.01g
	4 days	3.92±0.03g	3.58±0.02g
T20	daily	7.45±0.02f	8.49±0.01f
	2 days	14.20±0.04d	17.79±0.02c
	4 days	7.42±0.03f	8.53±0.01f
T30	daily	10.37±0.04e	11.57±0.01d
	2 days	20.12±0.04b	25.56±0.03b
	4 days	7.40±0.03f	10.25±0.02e
T40	daily	10.39±0.03e	11.63±0.01d
	2 days	24.84±0.02a	30.59±0.03a
	4 days	7.48±0.03f	10.26±0.02e
T_{MF}	daily	10.35±0.03e	11.70±0.03d
	2 days	18.54±0.02c	25.41±0.02b
	4 days	7.41±0.03f	10.24±0.03e

In Table 1, T0 refers to control plot without any compost use while T20, T30 and T40 refer to compost applied at 20 t ha^{-1}, 30 t ha^{-1} and 40 tha^{-1} doses respectively. T_{MF} refers to mineral fertilizers NPK 15-15-15 and Urea (46%) applied at 0.2 t ha^{-1} and 0.1 t ha^{-1} respectively. In a column, treatment mean values followed by same letter are not significantly different at the threshold of 5%.

Decreasing yield recorded on plots irrigated every day may be explained by the excess irrigation which would lead to water draining past the root zone, leaching nutrients and reducing water and nutrient use efficiency. This explains that water use efficiency rides with increase of water supply up to a certain point. According to Prihar et al. (1985), water supply has been observed to increase fertilizer use efficiency by increasing the availability of applied nutrients. Too much water in the root zone would reduce also the amount of oxygen available and leading to plant stress (Morard et al, 2000; Boru et al., 2003; Iwasaki, 2008; Rajanna et al., 2018). In conditions of too frequent irrigation, the roots were without air after each irrigation until the free water has drained from the soil profile. During this time, plant growth and development nearly would stop.

In other hand, the reduction in yield of plants irrigated at four days interval indicated that these plants were subjected to water deficit stress and yield decreasing may be explained by effect of water deficit stress (Bouazzama et al., 2012; Dhakar et al., 2018). Decreasing yield recorded from these plants may be explained by the high percent abortion observed on these severe stressed plants due to the fact that as the water stress increased, the number of ovules per floret decreased. Lower soil moisture may lead to the flower abortion and fewer fruits. Adams et al. (2001) reported that poor fruits set were observed at high temperatures. In this study, temperature in the air was higher during the experiment because conducted in dry and hot season. Birhanu and Tilahun (2010) reported a decreased number and sizes of tomato fruits from plants subjected to moisture stress. The same observation of water stress on tomato yield parameters was also reported by Zotarelli et al. (2009).

3.2 Influence of compost doses and irrigation regimes on soil CO_2 emissions

Although soil CO_2 emissions were measured every day during 28 days of incubation, because of general tendency of results obtained, only the results of twenty four hours of incubation, those of fourth, eighth, sixteenth and twenty eighth days incubation have been recorded in Tables 2 to 6.

TABLE 2
RESULTS OF SOIL CO_2 EMISSION (mg) IN TWENTY-FOUR HOURS OF INCUBATION

Treatments	Irrigation interval days	First month Year 2019	Second month Year 2019	Third month Year 2019	Fourth month Year 2019
T0	daily	0.60±0.02	0.78±0.02	0.96±0.02	1.10±0.01
	2 days	0.88±0.02	1.41±0.02	1.76±0.02	2.10±0.01
	4 days	0.40±0.03	0.44±0.03	0.52±0.03	0.60±0.02
T20	daily	0.77±0.02	0.99±0.02	1.20±0.02	1.38±0.01
	2 days	1.06±0.04	1.70±0.04	2.13±0.04	2.56±0.02
	4 days	0.35±0.03	0.39±0.03	0.46±0.03	0.53±0.01
T30	daily	0.78±0.04	1.02±0.04	1.25±0.04	1.41±0.01
	2 days	1.47±0.04	2.35±0.04	2.94±0.04	3.52±0.03
	4 days	0.72±0.03	0.79±0.03	0.94±0.03	1.08±0.02
T40	daily	0.88±0.03	1.14±0.03	1.41±0.03	1.58±0.01
	2 days	1.73±0.02	2.77±0.02	3.47±0.02	4.16±0.03
	4 days	0.75±0.03	0.83±0.03	0.98±0.03	1.13±0.02
T_{FM}	daily	0.69±0.03	0.89±0.03	1.10±0.03	1.20±0.03
	2 days	0.80±0.02	1.28±0.02	1.60±0.02	1.92±0.02
	4 days	0.37±0.03	0.41±0.03	0.48±0.03	0.55±0.03

In Table 2, T0 refers to control plot without any compost use while T20, T30 and T40 refer to compost applied at 20 t ha^{-1}, 30 t ha^{-1} and 40 tha^{-1} doses respectively. T_{MF} refers to mineral fertilizers NPK 15-15-15 and Urea (46%) applied at 0.2 t ha^{-1} and 0.1 t ha^{-1} respectively.

TABLE 3
RESULTS OF SOIL CO_2 EMISSION (mg) AT FOUR DAYS INCUBATION

Treatments	Irrigation interval days	First month Year 2019	Second month Year 2019	Third month Year 2019	Fourth month Year 2019
T0	daily	0.56±0.02	0.73±0.02	0.90±0.02	1.01±0.01
	2 days	0.75±0.02	1.20±0.02	1.50±0.02	1.80±0.01
	4 days	0.35±0.03	0.39±0.03	0.46±0.03	0.53±0.02
T20	daily	0.56±0.02	0.73±0.02	0.90±0.02	1.00±0.01
	2 days	0.73±0.04	1.17±0.04	1.47±0.04	1.75±0.02
	4 days	0.29±0.03	0.32±0.03	0.38±0.03	0.44±0.01
T30	daily	0.75±0.04	0.97±0.04	1.20±0.04	1.35±0.01
	2 days	1.17±0.04	1.87±0.04	2.34±0.04	2.81±0.03
	4 days	0.44±0.03	0.48±0.03	0.57±0.03	0.66±0.02
T40	daily	0.85±0.03	1.10±0.03	1.35±0.03	1.52±0.01
	2 days	1.55±0.02	2.48±0.02	3.10±0.02	3.72±0.03
	4 days	0.54±0.03	0.59±0.03	0.70±0.03	0.81±0.02
T_{FM}	daily	0.69±0.03	0.89±0.03	1.10±0.03	1.24±0.03
	2 days	0.73±0.02	1.17±0.02	1.46±0.02	1.73±0.02
	4 days	0.33±0.03	0.37±0.03	0.43±0.03	0.50±0.03

In Table 3, T0 refers to control plot without any compost use while T20, T30 and T40 refer to compost applied at 20 t ha^{-1}, 30 t ha^{-1} and 40 tha^{-1} doses respectively. T_{MF} refers to mineral fertilizers NPK 15-15-15 and Urea (46%) applied at 0.2 t ha^{-1} and 0.1 t ha^{-1} respectively.

TABLE 4
RESULTS OF SOIL CO_2 EMISSION (mg) AT EIGHT DAYS INCUBATION

Treatments	Irrigation interval days	First month Year 2019	Second month Year 2019	Third month Year 2019	Fourth month Year 2019
T0	daily	0.50±0.02	0.65±0.02	0.80±0.02	0.90±0.01
	2 days	0.60±0.02	0.96±0.02	1.20±0.02	1.44±0.01
	4 days	0.32±0.03	0.35±0.03	0.42±0.03	0.48±0.02
T20	daily	0.37±0.02	0.48±0.02	0.79±0.02	0.67±0.01
	2 days	0.52±0.04	0.83±0.04	1.04±0.04	1.25±0.02
	4 days	0.20±0.03	0.22±0.03	0.26±0.03	0.30±0.01
T30	daily	0.40±0.04	0.51±0.04	0.63±0.04	0.71±0.01
	2 days	0.90±0.04	1.45±0.04	1.81±0.04	2.17±0.03
	4 days	0.41±0.03	0.45±0.03	0.54±0.03	0.62±0.02
T40	daily	0.49±0.03	0.64±0.03	0.79±0.03	0.91±0.01
	2 days	1.31±0.02	2.10±0.02	2.62±0.02	3.15±0.03
	4 days	0.36±0.03	0.40±0.03	0.47±0.03	0.54±0.02
T_{FM}	daily	0.49±0.03	0.64±0.03	0.79±0.03	0.89±0.03
	2 days	0.70±0.02	1.12±0.02	1.40±0.02	1.68±0.02
	4 days	0.31±0.03	0.34±0.03	0.40±0.03	0.46±0.03

In Table 4, T0 refers to control plot without any compost use while T20, T30 and T40 refer to compost applied at 20 t ha^{-1}, 30 t ha^{-1} and 40 tha^{-1} doses respectively. T_{MF} refers to mineral fertilizers NPK 15-15-15 and Urea (46%) applied at 0.2 t ha^{-1} and 0.1 t ha^{-1} respectively.

TABLE 5
RESULTS OF SOIL CO_2 EMISSION (mg) AT SIXTEEN DAYS INCUBATION

Treatments	Irrigation interval days	First month Year 2019	Second month Year 2019	Third month Year 2019	Fourth month Year 2019
T0	daily	0.33±0.02	0.43±0.02	0.53±0.02	0.59±0.01
	2 days	0.55±0.02	0.88±0.02	1.10±0.02	1.32±0.01
	4 days	0.22±0.03	0.24±0.03	0.29±0.03	0.33±0.02
T20	daily	0.32±0.02	0.42±0.02	0.51±0.02	0.58±0.01
	2 days	0.43±0.04	0.70±0.04	0.86±0.04	1.03±0.02
	4 days	0.16±0.03	0.18±0.03	0.21±0.03	0.24±0.01
T30	daily	0.27±0.04	0.36±0.04	0.44±0.04	0.49±0.01
	2 days	0.44±0.04	0.71±0.04	0.88±0.04	1.06±0.03
	4 days	0.40±0.03	0.44±0.03	0.51±0.03	0.59±0.02
T40	daily	0.40±0.03	0.51±0.03	0.63±0.03	0.71±0.01
	2 days	1.17±0.02	1.87±0.02	2.34±0.02	2.81±0.03
	4 days	0.31±0.03	0.34±0.03	0.41±0.03	0.47±0.02
T_{FM}	daily	0.34±0.03	0.44±0.03	0.54±0.03	0.60±0.03
	2 days	0.60±0.02	0.96±0.02	1.20±0.02	1.44±0.02
	4 days	0.26±0.03	0.29±0.03	0.34±0.03	0.40±0.03

In Table 5, T0 refers to control plot without any compost use while T20, T30 and T40 refer to compost applied at 20 t ha^{-1}, 30 t ha^{-1} and 40 tha^{-1} doses respectively. T_{MF} refers to mineral fertilizers NPK 15-15-15 and Urea (46%) applied at 0.2 t ha^{-1} and 0.1 t ha^{-1} respectively.

The results presented in Tables 2 to 6 revealed the variation of soil CO_2 emissions. It was noted that soil CO_2 emission values depended on the irrigation regime, the nature of fertilizer (compost or mineral fertilizer), the dose of compost, number of days incubation (date of measurement of soil CO_2 emission) and the period of soil sampling. The highest soil CO_2 emission values were recorded on the plots irrigated at two days interval regardless fertilizer nature and compost dose, while the lowest values were obtained both on the control plots and on the plots receiving compost or mineral fertilizer and submitted to daily and four days interval irrigation. These results suggested that soil moisture and organic matter level affects microbial activities and soil respiration, which indirectly affected CO_2 emission. Irrigation at two days interval could enhance soil wetting-drying cycles, and thus increased the CO_2 fluxes by promoting microbial activities and respiration (Guo et al. 2017). The higher soil CO_2 emissions were potentially resulted from the effect of increased oxygen and soil microbial (Guadie et al. 2014).

TABLE 6
RESULTS OF SOIL CO_2 EMISSION (mg) AT TWENTY EIGHT DAYS INCUBATION

Treatments	Irrigation interval days	First month Year 2019	Second month Year 2019	Third month Year 2019	Fourth month Year 2019
T0	daily	0.07±0.02	0.13±0.02	0.16±0.02	0.19±0.01
	2 days	0.18±0.02	0.22±0.02	0.28±0.02	0.34±0.01
	4 days	0.09±0.03	0.15±0.03	0.19±0.03	0.24±0.02
T20	daily	0.15±0.02	0.17±0.02	0.21±0.02	0.23±0.01
	2 days	0.19±0.04	0.22±0.04	0.29±0.04	0.36±0.02
	4 days	0.17±0.03	0.20±0.03	0.24±0.03	0.25±0.01
T30	daily	0.20±0.04	0.22±0.04	0.23±0.04	0.29±0.01
	2 days	0.32±0.04	0.36±0.04	0.39±0.04	0.42±0.03
	4 days	0.24±0.03	0.25±0.03	0.26±0.03	0.30±0.02
T40	daily	0.21±0.03	0.28±0.03	0.34±0.03	0.38±0.01
	2 days	0.40±0.02	0.64±0.02	0.80±0.02	0.96±0.03
	4 days	0.28±0.03	0.36±0.03	0.38±0.03	0.42±0.02
T_{FM}	daily	0.10±0.03	0.13±0.03	0.16±0.03	0.18±0.03
	2 days	0.16±0.02	0.25±0.02	0.33±0.02	0.35±0.02
	4 days	0.14±0.03	0.17±0.03	0.19±0.03	0.22±0.03

In Table 6, T0 refers to control plot without any compost use while T20, T30 and T40 refer to compost applied at 20 t ha^{-1}, 30 t ha^{-1} and 40 tha^{-1} doses respectively. T_{MF} refers to mineral fertilizers NPK 15-15-15 and Urea (46%) applied at 0.2 t ha^{-1} and 0.1 t ha^{-1} respectively.

Irrigating too frequently could have negative impact on microbial population. In this case of daily irrigation, the microorganisms could have insufficient air. This explained the low values of soil CO_2 emission noted on plots submitted to daily irrigation. The low CO_2 emission from plots irrigated at four days interval indicated that these plots were subjected to high water deficit stress. Decreasing CO_2 emission recorded from these plots may be explained by the low microbial activities and respiration due to the water deficit stress increases. Our results were in line with the findings of Hou et al. (2019) who concluded that deficit irrigation effectively reduced CO_2 emissions from winter wheat field soils in northwest China.

It was noted that the soil CO_2 emission increased throughout the field experiment. Soil CO_2 emissions of third and fourth months were more than those of first and second months (Tables 2 to 6). These observations were in accordance with the study of Russell (1973) which stated that the presence of crops on the field affected (increased) CO_2 emissions from the soil. Soil CO_2 emission increasing in the two last months of field experiment was also in line with the finding of Han et al. (2012) who reported that the presence of vegetation or crop affected CO_2 fluxes primarily by photosynthesizing and by increasing the total ecosystem respiration.

However, CO_2 emission decreased gradually during day's incubation. Results of soil CO_2 emission in twenty-four hours of incubation were more than those recorded at four, eight, and sixteen and twenty eight day's incubation (Tables 2 to 6).All these variations in soil CO_2 emissions may be explained by the abundance or rarity of microorganisms in the soils sampled and incubated. From this view point, monitoring the soil CO_2 emission during incubation mean to measure the respiration of microbial populations in the soil. Our results suggested that the application of household solid urban waste compost increased soil microbial populations and soil CO_2 emissions. The levels of soil CO_2 emission observed in this study were in line with the findings of several authors. Previous studies had found that crop root and soil microbial respiration were the main sources of soil CO_2 emissions. Researchers performed a long-term fertilization study on wheat and maize growing season and observed that the highest soil CO_2 flux was found from organic fertilizer treatment (Galic et al. 2019). Compost application may be associated with increased amount of carbon available that increased the microbial activity and thus stimulated respiration of autotrophic and heterotrophic microorganisms in the soil (De Urzedo et al. 2013; Carmo et al. 2014).

IV. CONCLUSION

The influence of compost doses and irrigation regimes on tomato yield and soil CO_2 emissions was assessed. Tomato yield and soil CO_2 emission values were proportional to compost doses applied. These results indicated that the application of household solid urban waste compost increased soil microbial populations and consequently soil CO_2 emissions. The highest tomato yield and the highest soil CO_2 emission values were recorded on the plots irrigated at two days interval regardless

fertilizer nature and compost doses. As our experiments were relatively short, to better assess the CO_2 emissions from compost applied to soil, long-term experiments are needed for a more reliable conclusion on the effect of applying household urban solid waste compost on soil carbon dynamics.

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Formation of Dioxins during Energy Cogeneration by Burning Bagasse and Sugarcane Straw Fertilized with Chlorinated Compounds: State of the Art and Presentation of Alternatives

Felipe V. Duarte[1], Maria Clara V. M. Starling[2], Débora S. Moreira[3], Isabela S.S. de Oliveira[4]

[1,2]Federal University of Minas Gerais, Sanitary and Environmental Engineering Department, Av. Antônio Carlos, 6627, Campus Pampulha, Belo Horizonte, MG, Brazil, CEP: 31270-901
[3,4]Federal University of Minas Gerais, Institute of Geosciences, Av. Antônio Carlos, 6627, Campus Pampulha, Belo Horizonte, MG, Brazil, CEP: 31270-901

***Abstract*—** *Polychlorinated dibenzodioxins (PCDDs), also known as dioxins, are part of a group of organochlorine chemical compounds, highly persistent in the environment, with similar chemical structures. High levels of this compound are found in the burning ashes of the sugarcane and are attributed to the high concentration of chlorine present in bagasse and in the sugarcane straw that are used as a substrate for obtaining energy in the bioethanol production plants. This occurred due to the application of chlorine-containing fertilizers, such as potassium chloride, during the cultivation of sugarcane. Considering the high degree of toxicity of dioxins, the objective of this study was to conduct a literature review on the subject and research alternatives that can control the generation and emission of dioxins in bioethanol production plants, either through the application of appropriate technologies to control emission of dioxins generated during burning, or by substituting the chlorinated fertilizer used in the cultivation of sugarcane. From the analysis of different studies that researched the presence of dioxins in the ash of the bagasse burning boiler, there is a concentration that varies from 2, 2 to 190 picograms of dioxin equivalent toxicity (TEQ) per gram of ash. For the removal of these dioxins, the control systems commonly used in sugarcane plants have not proved to be efficient. In this context, the main alternatives would be the application of technologies for optimizing the combustion process combined with the treatment of end of pipe by means of a scrubber and bag filter or selective catalytic oxidation using NH3-SCR catalysts. Another option is the substitution of the potassium source, which presents itself as the most viable alternative, with the use of non-chlorine sources, such as Glauconitic Siltstone, Potassium Nitrate, Potassium Sulfate or vinasse instead of using chlorinated fertilizers such as Potassium Chloride.*

***Keywords*— Polychlorinated dibenzodioxins, cogeneration, control systems, Glauconitic Siltstone, bioethanol production.**

I. INTRODUCTION

Polychlorinated Dibenzodioxins (PCDDs), also known as Dioxins, comprise a group of organochlorine chemical compounds highly persistent in the environment, with similar chemical structures. The toxicity of these compounds varies according to the number and position of Chlorine atoms in these compounds (Ronald, 2011).

The 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), shown in Figure 1, is the most toxic molecule, of all dioxins, having four chlorine atoms. Such substance is considered as the most toxic, low molecular weight substance ever found by humans, proving to be only less toxic than some protein toxins, such as nicotine and sodium cyanide (Grossi, 1993).

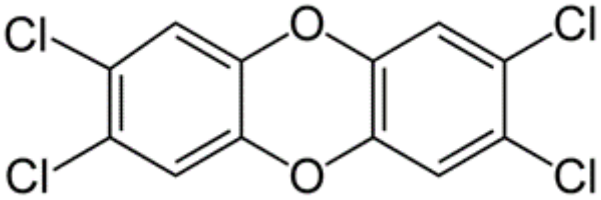

FIGURE 1: Chemical structure of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin molecule

Dioxins are extremely stable and tend to accumulate within the food chain, with a half-life of 7 to 9 years in humans (ATSDR, 1998; Xu et al., 2016). In natural sediments, on the other hand, it is estimated that the half-life of dioxins is longer than 100 years (Sinkkonen & Paasiverta, 2000). In addition to being stable, they are practically insoluble in water and

lipophilic (ATSDR, 1998; Ronald, 2011). Because they are highly resistant to chemical and microbiological degradation, in addition to accumulating within the environment, dioxins have been classified by the Stockholm Convention (2002) within the group comprised of 21 molecules known as "Persistent Organic Pollutants" (POPs) (Perlatti, 2012).

Brazil is among one of the 170 countries that, at the Stockholm Convention (2002), adhered to the treaty to eliminate the sources of production of these POPs, being one of the regional leaders in Latin America for the control of POPs through the Company of Environmental Sanitation Technology (CETESB) (Perlatti, 2012).

The cultivation of sugarcane in Brazil is of paramount relevance for Brazilian agribusiness, considering that the country is considered the largest producer of sugarcane and the largest exporter of ethanol and sugar in the world. In the 2018/2019 harvest, the estimated production of sugarcane was 615.84 million tons and the harvested area was around 8.63 million hectares (CONAB, 2018).

Brazil has a consolidated trajectory in national and global ethanol production due to the fact that Brazilian ethanol has been produced since the 1970s, as a result of the National Alcohol Program, also known as "Próalcool." The internal production of bioethanol has been increasingly growing, with an estimated production in the 2018/19 harvest equivalent to 32.31 billion liters of ethanol, which represents an increase of 18.6% compared to the previous harvest (CONAB, 2018).

Brazilian ethanol is mostly produced through First Generation Ethanol (E1G), in which the production process occurs from the juice resulting from the sugarcane milling process and the energy cogeneration comes from the burning of sugarcane bagasse (Ansanelli et al., 2016).

In addition to E1G, another manner that tends to grow in the country in the coming years, due to the replacement of burnt straw by mechanized harvesting, is the process known as Second Generation Ethanol (E2G). This process differs from E1G in the type of substrate used during the energy cogeneration process, since in E2G both bagasse and straw are used to obtain electrical energy (Ansanelli et al., 2016).

Although ethanol production is already well consolidated in Brazil, the formation of dioxins during the process of burning sugarcane containing a high concentration of chlorine for power generation is a latent problem in ethanol production that occurs due to the use of fertilizers containing chlorine during the planting of this crop (Guevara et al., 2016). Therefore, the present study aims to analyze the state of the art on dioxin emissions in ethanol production plants and the intervening factors for the formation of these compounds, as well as to propose some measures that can be adopted to control the emission of these substances in order to make the process more sustainable.

II. FORMATION OF DIOXINS IN COGENERATION PLANTS

Initially, it was believed that dioxins were formed exclusively due to anthropogenic activities, however it was observed that they can also be formed naturally, due to volcanic eruptions and forest fires. This is due to the presence of chlorine as a natural constituent of soil and plants (Green, 2004; Pereira, 2004; Perlatti, 2012).

In anthropogenic activities, the generation of dioxins as undesirable by-products of industrial processes has as main sources the combustion processes, especially incinerators (Kulkarni, 2008). The presence of dioxins in incinerators was verified at the end of the 1970s (Olie et al., 1977) and, later, it expanded to all incomplete combustion processes that occur the burning of substrates containing chlorine in their composition, whether from natural or industrial sources (Bumb et al., 1980; Perlatti, 2012). Laboratory analysis showed that burning straw as a stage prior to the harvest of sugarcane contributes to the emission and occurrence of dioxins within the environment, with an estimate of a generation of up to 253 nanograms of toxic equivalents of 2,3,7,8-TCDD per kilogram of carbon burned (Gullett, 2006; Perlatti, 2012).

The main mechanisms of formation of dioxins are homogeneous and heterogeneous reactions. The homogeneous reaction is the most likely source of generation of these pollutants within a combustion chamber. This way, the formation of dioxins occurs through the gaseous reaction of organochlorine precursors at high temperatures (between 400 °C and 800 °C) (Lopes et al., 2015; Stanmore, 2002; Tuppurairien et al., 2003).

Despite the consensus that dioxin formation occurs during combustion, it was believed that the high temperatures inside these chambers would destroy them. However, it was found that dioxins can be reconstituted after the gas leaves the combustion chamber and during its passage through a gas treatment system that operates at a lower temperature (between 200 °C and 490 °C) (Düwel et al., 1990; Reis, 2009). Therefore, while the homogeneous reaction is responsible for the

formation of dioxins inside the combustion chamber, it is the heterogeneous reaction that occurs as the preferred way for the formation of dioxins in the post-combustion area (Lopes et al., 2015; Stanmore, 2002).

The heterogeneous reaction can occur within a temperature window between 200 °C and 400 °C in two different ways: (i) De Novo synthesis, which involves oxidation and chlorination of the unburned carbon source present in the particles (Lopes et al., 2015; Stanmore, 2002); (ii) assisted catalytic coupling of the precursors, in which the incomplete combustion of organic residues in the incinerators leads to the appearance of organic fragments that may be precursors of the dioxin molecules on the surface of the ashes generated inside the incinerator (Mckay, 2002).

Considering that the cultivation of 120 tons of cane per hectare absorbs 66 kg of potassium from the soil, the replacement of this nutrient is essential for maintaining the cultivation area (Barnes, 1964). The source of potassium generally used for this purpose is Potassium Chloride (KCl), a fertilizer composed of a minimum of 39% chlorine and 50% potassium in the form of potassium oxide (K_2O) (Manning, 2010). Therefore, the application of potassium chloride to the soil introduces a high amount of chlorine into the environment. Once in the soil and in high concentrations, chlorine is absorbed by the plant, accumulating in different parts of the sugarcane tree (Hassuani et al., 2005; Jacome, 2014). As a consequence, the burning of sugarcane bagasse during the energy cogeneration process leads to the formation of dioxins as a by-product.

Due to the use of chlorinated fertilizers during the cultivation of sugarcane and the tendency to adopt the E2G process with simultaneous burning of straw and sugarcane bagasse in the energy cogeneration process, the formation of dioxins related to this activity tends to increase. This is because straw has a higher concentration of chlorine when compared to bagasse (Bizzo et al., 2014; Hassuani et al., 2005; Jacome, 2014). According to elementary analysis using titration, Bizzo et al., 2014, have observed that the chlorine concentration in straw reaches 440% higher than that found in sugarcane bagasse. Thus, it is important that alternatives are proposed to the use of fertilizer what about the process of air pollution control applied in bioethanol production plants in order to reduce the emission of dioxins by them.

2.1 Potassium-Based Fertilizers Used In the Cultivation of Sugarcane

Potassium is essential to ensure crop productivity and quality of agricultural cultivation (Tandon and Kemmler, 1986). Therefore, it is necessary to replace this nutrient in the soil, which is usually done by applying Potassium Chloride and other fertilizers such as Potassium Sulfate (K_2SO_4), Potassium Nitrate (KNO_3) and Glauconitic Siltstone (Violatti et al., 2019).

Glauconitic Siltstone is a potash fertilizer containing 10% K_2O. In addition, it is composed of 25% Silicon (Si) and 3% Magnesium Oxide (MgO) and 70 more trace elements. It is a promising fertilizer for supplying K and other micronutrients via soil for crops (Violatti et al., 2019). The process of obtaining the Glauconitic Siltstone relies on mechanical activation technology (Singla et al., 2019). Mechanical activation provides a physical improvement of the glauconite, which is performed by mineral processing operations such as size reduction, screening and separation.

Regarding the equivalent K_2O content, Potassium Chloride has 50%, being the largest among the four sources. Glauconitic Siltstone has 10% content, the lowest among the alternatives considered in this work. Regarding the chlorine content (Cl), KCl is the only one that has chlorine in its composition, having a minimum content of 39% of this substance (Table 1) (Brazil, 2018).

TABLE 1
CHARACTERISTICS OF POTASSIUM-BASED FERTILIZERS USED IN THE CULTIVATION OF SUGARCANE

Fertilizer	K_2O Content[1]	Cl Content[2]
Potassium Chloride (KCl)	60%	Minimum of 39%
Potassium Sulfate (K_2SO_4)	48%	0%
Potassium Nitrate (KNO_3)	44%	0%
Glauconitic Siltstone	10%	0%

2.2 Presence of Dioxins in the Ashes from the Combustion of Sugarcane Bagasse

The burning of sugarcane biomass in boilers during the energy cogeneration process leads to the production of ashes as waste. Bearing in mind that for each ton of sugarcane bagasse burned there is a generation of approximately 6 kg of ashes, it

is estimated that the 2018/2019 national crop generated about 3,700 tons of ashes in the burning of sugarcane in boilers (Bertoncini, 2008; Teixeira et al., 2011; Perlatti, 2012).

The ash from this burning is a material composed mainly of inorganic matter, with Silicon Dioxide (SiO_2) as its main chemical compound. In addition to this substance, the compound known as Loss on Ignition (LOI) is also present in ash, which refers to the loss of mass of a combustion residue whenever heated in an atmosphere of air or oxygen at high temperatures (Sales and Lima, 2010; Perlatti, 2012;).

The analysis of the ash from burning of bagasse during the energy cogeneration process at the Deep River Beau Champ plant, located in Mauritius, verified the presence of dioxins in both samples collected before the gas passed through the electrostatic precipitators used as control equipment for the particulate material, as well as in the samples collected after passing through the control system. Ten samples were collected, four before the electrostatic precipitator, four after this system, and two in the storage silo. The presence of dioxins was verified in all samples collected, in concentrations that ranged from 8 to 190 picograms of dioxin equivalent toxicity (EQT) per gram of ash. Among the samples analyzed, those with the highest concentrations of dioxins were those collected after the treatment, with an average concentration 12 times higher than those collected before the electrostatic precipitator. In the case of the samples collected in the storage silo, considering that the ashes present in this location were related to the parts before and after the treatment, the concentration of dioxins measured was lower than that of the samples collected after the precipitator and higher than the of the samples collected before the treatment process (Table 2) (Yive and Tiroumalechetty, 2008).

TABLE 2
COMPARISON BETWEEN THE CONCENTRATION AND THE LEVEL OF DIOXIN EQUIVALENT TOXICITY IN THE ASH COLLECTED BEFORE AND AFTER THE CONTROL SYSTEM AND IN THE STORAGE SILO.

Place of collection	Number of samples	Variation of concentration	Average
		pg OMS-TEQ/g[1]	pg OMS-TEQ/g[1]
Pre-treatment	4	2.2-19	10.9
Post-treatment	4	60-190	145
Storage silo	2	43-47	45

[1]pg OMS EQT/g = picogram of equivalent toxicity according to the World Health Organization per ash gram; YiveeTiroumalechetty, 2008

In another study conducted at São José da Estiva plant, located in Novo Horizonte, state of Sao Paulo, the presence of dioxins was analyzed in the ash and soot from the boiler where the bagasse was burned, in the filter cake and in the organic compost from windrow composting (Perlatti, 2012). The result found in this study corroborates the data obtained in the analysis made at the Deep River Beau Champ plant, since in both the EQT level found was higher in the samples from the box of ashes from the boilers. In the study conducted at São José da Estiva plant, a value of 38.1 nanograms of EQT per kg of ashes was found, a value that is within the range obtained in the study conducted at the Mauritius plant (Perlatti, 2012; Yive and Tiroumalechetty, 2008) .

Furthermore, the study conducted at the Novo Horizonte plant, state of Sao Paulo, identified the absence of dioxins in the samples collected in the filter cake and a great reduction in the concentration found in the samples from windrow composting. This result indicates that the main source of contamination is actually ashes from the burning of sugarcane bagasse during the energy cogeneration process (Perlatti, 2012).

The reduction in the amount of dioxins present in windrow composting is achieved by diluting the ash mixture from the pre and post treatment, which is a major factor in reducing the level of toxicity in the final product. However, this dilution is not sufficient for the dioxin emissions to meet the maximum levels of contamination defined by international parameters (Perlatti, 2012).

Considering the 3,700 tons of ashes generated during the burning of sugarcane in the boilers for the national harvest of 2018-19 and a rate that varies between 8 and 190 picograms of EQT per gram of ashes, it is estimated between 2.96 to 70.3 grams of EQT as the total ashes generated for that crop (Table 3).

TABLE 3
ESTIMATE OF DIOXIN EQUIVALENT TOXICITY (EQT) FOR TOTAL ASHES GENERATED IN THE 2018/2019 NATIONAL HARVEST

Harvest[1]	Amount of ashes in boiler[2]	EQT[3]	Total EQT
hectares	tons	picograms of EQT per gram	grams of EQT
8,630,000	3,700	8 - 190	2.96-70.3

[1] CONAB, 2018; [2] Teixeira et al., 2011; [3]Yive; Tiroumalechetty, 2008

III. DIOXINS WITHIN THE ENVIRONMENT: PERSISTENCE AND EFFECTS

3.1 Dispersion and Accumulation of Dioxins in the Environment

After the formation and emission of dioxins into the atmosphere, they associate with small particles in the air, such as ashes. From there, larger particles tend to settle near the source of emission and smaller particles are usually transported over long distances. Most of the dioxins formed are deposited on land or water, while a small portion will be decomposed by sunlight and chemicals present in the atmosphere (ATSDR, 1998; Rovira et al., 2010).

Considering the insolubility of dioxins in water, most of these substances are strongly bound to small particles of soil or organic matter, later depositing on the bottom of water bodies (ATSDR, 1998; Rovira et al., 2010). Thus, sediments from rivers, lakes and oceans can be considered reservoirs of dioxins. In a study conducted on the sediments of the Kymijoki River, located in Finland, for example, contamination by dioxins of up to 290 micrograms per gram of dry weight was identified in the analyzed sediments (Kuokka et al., 2014) .

Also in aquatic environments, dioxins can accumulate in the tissues of organisms, reaching higher concentrations in consumers and, especially, in tissues that contain a high concentration of lipids. This is due to the lipophilicity of dioxins. Considering that dioxins dissolve more easily or are more attracted to oily or fatty compounds than water, they are more persistent in animals with body fat than in water, a phenomenon called "Bioaccumulation," which can occur through absorption, ingestion or inhalation (ATSDR, 1998; Rovira et al., 2010).

Considering the persistence and bioaccumulation of dioxins within the environment, and the fact that the human being is a consumer in both aquatic and terrestrial food chains, the main source of exposure to dioxins by humans is through food, as detailed below.

3.2 Human Exposure to Dioxins: Main Sources

Dioxins can contaminate humans both directly (respiratory system and skin contact) and indirectly (soil and food). Among all these sources, the main way of contamination is through the ingestion of food contaminated with dioxins, corresponding to approximately 90% of all sources of contamination. The contamination of food by dioxins is mainly caused by the dry or wet deposition of particles emitted into the atmosphere and then deposited onto agricultural land and water bodies followed by bioaccumulation into both the aquatic and terrestrial food chains (ATSDR, 1998; Rovira et al., 2010).

Through a study conducted in the city of Montgomery, in the USA, it was identified that contamination by dioxins occurs mainly through the consumption of beef, dairy products and fish, followed by the consumption of vegetables (Table 4). If we disregard food, the main sources of contamination are ultimately dust ingestion and inhalation (Rolaf et al., 2000)

TABLE 4
MAIN SOURCES OF HUMAN CONTAMINATION BY DIOXINS

Source	Percentage of total amount from sources of contamination
	%
Consumption of beef and dairy products	87.1
Consumption of vegetables	5.1
Ingestion of dust	4.6
Inhalation	2.8
Other sources	< 1

[1] Jones, K., 1994.

Studies conducted in France and Denmark on the daily rate of contamination by dioxins (picrograms/person/day) from the ingestion of different foods have detected that the foods with the highest concentrations of dioxins are those with a high fat content, in particular those of animal origin, such as milk and dairy products, beef, pork and fish (Table 5). These results corroborate with the study conducted in Montgomery. Both results were expected, given that dioxins are lipophilic and bioaccumulate in adipose tissues (Rolaf et al., 2000).

TABLE 5
DAILY INTAKE OF DIOXINS FROM DIFFERENT FOODS IN FRANCE AND DENMARK

Food	France[1]	Denmark[2]
Milk and dairy products	25.8	46
Beef and pork	4.7	59
Fish	9.3	19.2
Eggs	4	3
Crustaceans	0.8	-
Shellfish	7.1	-
Total	51.7	127.2

[1]French Agency for Food Safety, 1999; [2] European Commission DG Environment, 1999

3.3 Toxicity of Dioxins to Human Health

Dioxins are extremely toxic substances that can cause several health problems, depending on the concentration and time of exposure to these compounds. An exposure to high concentrations of dioxins for a short period can cause the body – which absorbs these harmful congeners – to trigger symptoms quickly, such as skin lesions, including chloracne (Figure 2). Chloracne is a severe skin disease, characterized by lesions similar to acne and it usually appears on the face and upper body. Unlike common acne, chloracne is more difficult to cure and can be more deforming. A long-term exposure to dioxins, on the other hand, can lead to diabetes, weakness of the immune, nervous and reproductive systems; can cause endocrine disruption in humans and animals, and cause cancer (ATSDR, 1998; Schecter et al., 2006; Bila, 2007).

FIGURE. 2 - a) Viktor Yushchenko, former President of Ukraine, before and after 2,3,7,8-TCDD poisoning; b) Chloracne on the face of a Japanese worker who worked at an incineration plant [Schecter et al., 2006].

The endocrine system is comprised of a set of glands that have the function of producing hormones that will act on target organs. If there is a deregulation of the endocrine system, problems can occur in the reproductive system of fish, reptiles, birds and mammals (such as feminization of males) and changes in the immune system of marine mammals. In humans, this deregulation can cause a decrease in the amount of sperm produced, and an increase in some types of cancer, such as breast, testicular and prostate cancer (Bila, 2007).

According to the International Agency for Research on Cancer (IARC), dioxins are classified as a "known human carcinogen" (IARC, 1997; IARC, 2012). In an analysis conducted in subgroups related to mortality from exposure to dioxins, significant results were found for esophageal, laryngeal, kidney, lung cancer and non-Hodgkin's lymphoma (WHO, 1998; Xu et al., 2016). Considering the adverse effects caused by the exposure to dioxins, the World Health Organization (WHO)

established a tolerable daily intake of 1 to 4 picograms of equivalent toxicity (EQT) per kilogram of body weight as a safe dose to prevent the above mentioned effects from occurring (Rolaf et al., 2000).

IV. MONITORING OF DIOXINS WITHIN THE ENVIRONMENT

Considering the risks associated with the occurrence of dioxins within the environment, the periodic monitoring of these substances within the environmental compartments is extremely important, especially in areas close to bioethanol production plants, incinerators and industries in general. In Brazil, the only legislation in force even with regard to the issue of dioxins is Resolution No. 313 by CONAMA of October 29, 2012, which limits the presence of dioxins in gaseous effluents to 0.50 nanograms per cubic meter. In addition to this established emission standard, there is a limit for the presence of dioxins in products intended for animal feed ranging from 0.35 to 20.0 nanograms of EQT per kilogram of food, depending on the type and origin of the food (Brazil, 2016) . However, with regard to the presence of these substances in other sources, there are no established regulations (Perlatti, 2012).

The environmental monitoring of dioxins is usually performed by collecting sediment and air samples. For the determination of the amount of dioxins present in the sediment samples, high-performance gas chromatography coupled with high-resolution mass spectrometry is used, together with the isotopic dilution method (Rovira et al., 2010). For the analysis of air samples and analysis of dioxin concentration due to bioaccumulation, high resolution mass spectrometry is used (Pussente, 2016). Such equipment is the only one that has sufficient precision to satisfactorily determine the concentration of dioxins. However, such analyzes require long periods of time and a high degree of technical skillfulness so that the results obtained are reliable (Belin, 2016).

Regarding the concentration of dioxins due to bioaccumulation, in a study with the migratory bird known as "northern wheatear" (Oenanthe oenanthe), by using gas chromatography coupled with high resolution mass spectrometry, the presence of dioxins was found in the eggs of this bird (13.08 picograms of EQT per gram of product), in insects and larvae (7.08 picograms of EQT per gram of product) and in the soil around the nests (2.21 EQT picograms per gram of product). From the results found it was suggested that contamination of some insects and larvae by dioxins occurred when in contact with the soil. The contamination of the eggs, on the other hand, was due to the female, when feeding on the insects, then transferring the acquired contamination to the egg (Pussente, 2016).

The monitoring of dioxins is still poorly studied in Brazil. However, some studies have analyzed the presence of dioxins in the air and soil in some Brazilian cities in order to verify the concentration of dioxins within these environmental compartments. The investigation about the presence of dioxins in the air was conducted in the cities of Cubatao, Sao Paulo and Araraquara, in the state of Sao Paulo, and the cities of Cantagalo, Santa Cruz, Barra Mansa and Volta Redonda, in the state of Rio de Janeiro (Table 6). The observed concentrations ranged from 3 to 994 phentograms of EQT per cubic meter, with higher concentrations being observed in cities such as Santa Cruz and Barra Mansa, both in the state of Rio de Janeiro. These higher concentrations are apparently due to the fact that the samples were collected close to the industrial areas of these cities (Centeno et al., 2007).

TABLE 6
COMPILATION OF CONCENTRATIONS OF DIOXINS DETECTED IN THE ATMOSPHERE IN A STUDY CONDUCTED IN A SOME BRAZILIAN CITIES

City	Lower concentration	Higher concentration	Average
	fg I-EQT/m³	fg I-EQT/m³	fg I-EQT/m³
Araraquara/SP	16	267	141.5
Barra Mansa/RJ	18	839	428.5
Cantagalo/RJ	28		28
Cubatao/SP	38	48	43
Santa Cruz/RJ	994		994
Sao Paulo/SP	86	169	127.5
Volta Redonda/RJ	3		3

Centeno et al., 2007; fg I-EQT/m³ = phentogram of international equivalent toxicity per m³ of air sample collected

The soil analyzes were conducted in the cities of Araraquara and Cubatao, in the state of Sao Paulo; Rio de Janeiro, Cantagalo and Duque de Caxias, in the state of Rio de Janeiro; Manaus, in the state of Amazonas; and Belo Horizonte, in the state of Minas Gerais (Pussente, 2016), as shown in Table 7. Comparing the concentrations found in the soil and in the air in the cities where the monitoring was performed in both compartments, it is concluded that in the soil the values found show a higher contamination by dioxins, since, as for the values detected in the atmosphere, none of them were outside the standard established by Resolution No. 313 by CONAMA, which is 0.50 nanograms per cubic meter. In the case of the values measured for the soil, it was found that they are well above the international standards, such as those of Germany, the United States and Canada, which respectively stipulate an allowed limit of up to 10, 10 and 4 nanograms of EQT per kilogram of dry matter (Pussente, 2016).

TABLE 7
COMPILATION OF CONCENTRATIONS OF DIOXINS DETECTED IN THE SOIL IN A STUDY CONDUCTED IN A SOME BRAZILIAN CITIES

City[1]	Lower concentration	Higher concentration	Average
	ng EQT/kg	ng EQT/kg	ng EQT/kg
Araraquara/SP	0.1	1.2	0.65
Belo Horizonte/MG	0.38	4.44	2.41
Cantagalo/RJ	0.6	2.5	1.55
Cubatao/SP	11	341	176
Duque de Caxias	13	900	456.5
Formiga/MG	1.4	654	327.7
Manaus/AM	0.05	0.4	0.225
Rio de Janeiro/RJ - IA	1.1	654	327.55
Rio de Janeiro/RJ -UA	0.03	1.8	0.915

[1]Pussente, 2016; Nanogram of equivalent toxicity per kg of dry matter; IA = industrial area; UA = urban area

A questionnaire was sent to 100 sugarcane processing plants during this study, in order to conduct a survey on the current scenario of monitoring dioxins in these plants in Brazil. However, only 5 plants were willing to respond (Usina Sonora, Ituiutaba Unit of Usina BP, Usina Agropeu, Usina Itamarati, Usina Viralcool), but reported that no dioxin monitoring is performed at their respective premises.

V. CONTROL OF DIOXIN EMISSIONS IN BIOETHANOL PRODUCTION PLANTS

Wet gas scrubbers (for example, of the Venturi type), are often used to remove pollutants and gases generated during the energy cogeneration process in sugarcane processing plants. In addition to the gas scrubbers, bag filters and electrostatic precipitators are also used. However, none of these treatment systems is efficient at removing dioxins (see Table 8) (Kim et al., 2001; Lee et al., 2004).

TABLE 8
COMPILATION OF THE CHARACTERISTICS OF CONTROL SYSTEMS COMMONLY USED IN BIOETHANOL PRODUCTION PLANTS

Technology	Principle	Dioxin removal efficiency [1]	Limitation
		%	
Venturi-type gas scrubber[1]	Absorption	45	Low solubility of dioxins in water [1]
Bag filter	Filtration	8.2	Operating temperature [2]
Electrostatic precipitator	Particle ionization and electric field capture	Negative efficiency	Unknown

[1]Lee et al., 2004; [2] Sales and Lima, 2010.

The removal of dioxins verified when using Venturi gas scrubbers is around 45% (Lee et al., 2004). This low efficiency is related to the reduced solubility of dioxins in water, which is only 1.18 x 10^{-4} (Mackay et al., 1991). As a result, as this type of gas scrubber operates in a wet way, this system cannot remove these substances effectively (Kim et al., 2001). In addition, some studies point to an increase in the concentration of dioxins after passing through the gas scrubber (Barbosa, 2004; Vogg et al., 1994).

In the case of bag filters, the low efficiency is due to the operating temperature of this system, generally maintained between 110 °C and 140 °C, depending on the type of filter material, which makes it unsuitable for removing semi-volatile pollutants, such as it is the case of dioxins (Barbosa, 2004). However, it was found that the efficiency of dioxin removal in bag filters increases proportionally to the concentration of chlorine present in the system. The study suggests that dioxins with lower vapor pressure are more easily adsorbed onto the particles, which facilitates removal through bag filters. However, in the case of dioxin 2,3,7,8-TCDD, which is considered the most toxic and has only four chlorine atoms, the removal efficiency was minimal, reaching only 8.2% (Lee et al., 2004).

The electrostatic precipitator proved to be ineffective in removing dioxins, since there was an increase in the concentration of dioxins after passing through this system. Nevertheless, the 2,3,7,8-TCDD had its concentration increased (Sales & Lima, 2010).

VI. ALTERNATIVES FOR GREATER EFFICIENCY IN THE CONTROL OF DIOXINS IN COGENERATION PLANTS

The increase in efficiency in the control of dioxin emission can be obtained through the following solutions: (1) optimization of the combustion process combined with end-of-pipe treatment by using a gas scrubber and bag filter; (2) selective catalytic oxidation by using NH3-SCR catalysts (Mukherieea et al, 2016); (3) replacement of the KCl-based fertilizer with a compound having a low chlorine content.

6.1 Optimization of the Combustion Process Combined With End-Of-Pipe Treatment by Using a Gas Scrubber and Bag Filter

The improvement of the combustion process combined with end-of-pipe treatment requires some changes in the operational parameters related to the combustion of organic matter. Such modifications occur in the sense that, first, favor the complete combustion of this substrate and thus reduce the formation of dioxins and, later, adopt an end-of-pipe treatment that guarantees the significant reduction of these substances (Mckay, 2002; Mukherieea et al, 2016).

Bearing in mind that the combustion temperature plays a significant role in the formation of dioxins, since these compounds originate due to an incomplete combustion, it is suggested that the temperature during this process be kept between 850 °C and 1,000 °C in order to guarantee a complete combustion, with full destruction of the carbonaceous particles inside the boiler, associated with an average residence time of the residue in the appropriate furnace and adequate turbulence (Mukherieea et al., 2016).

One of the suggested end-of-pipe treatments is the use of a bag filter. In the case of the bag filter, it is suggested that the addition of carbon be made at a concentration of 50 milligrams per cubic meter at a temperature between 120 °C and 150 °C, so that the carbon is burned in the incinerators, in order to inhibit the formation of dioxins (Mckay, 2002; Mukherieea et al., 2016).

The improvement of the combustion process combined with end-of-pipe treatment by using a gas scrubber and bag filter has a satisfactory efficiency, reaching 96% removal (0.01 nanograms of EQT per cubic meter) (Table 9). In addition, it is an alternative that offers a favorable benefit-cost ratio and operational simplicity. However, if the organic matter contains a large amount of chlorine, this alternative will not be able to control the emission of dioxins (Mckay, 2002; Mukherieea et al., 2016).

TABLE 9
OPERATION CONDITIONS OF THE STUDY IN WHICH IT WAS ASSESSED THE OPTIMIZATION OF THE COMBUSTION PROCESS ASSOCIATED WITH A CONTROL TECHNOLOGY AIMED AT REDUCING THE EMISSION OF DIOXINS

Furnace	Post-combustion zone	Scrubber	BF	
◦C	◦C	◦C	◦C	
850-1000	Abrupt cooling from 450 to 200	NA	120-150*	
Time inside furnace	Addition of AC	Concentration of dioxins		Removal
		Pre-treatment	Post-treatment	
s	mg/N³	ng EQT/m³	EQT/m³	%
120-150*	50	0.24	0.01	95.8

McKay, G., 1984; BF = Bag filter; AC = Activated charcoal; *200 ◦C maximum

In addition, due to the memory effect, an increase in the concentration of dioxins in the flue gas may occur even with the adoption of this treatment alternative (Mckay, 2002; Mukherieea, 2016). The memory effect can appear when the concentration of dioxin in the flue gas decreases and with that dioxins can form and desorb from the residual carbon in the duct walls (Wevers & De Fré, 1998).

6.2 Selective Catalytic Oxidation by Using NH3-SCR Catalysts

The mechanism involved in this alternative involves the reheating of the flue gas that is later added to the catalytic reactor, in which the high temperature favors the oxidation of dioxins on the catalyst. For this process to be effective, a set of operational conditions must be met (Boos et al., 1992; Chang et al., 2009; DvoĜák et al., 2010; Lu et al., 2013; Mukherieea, 2016). First, the flue gas must be reheated after leaving the main combustion chamber from 125 °C to 130 °C, to 220 °C to 230° C by using a heat exchanger (gas-gas). After this step, the reheated flue gas enters the catalytic reactor where the decomposition takes place at 300 °C, which is the most efficient temperature for the decomposition of dioxins by using V2O5-WO3/TiO2 catalysts (Boos et al., 1992; Chang et al., 2009; DvoĜák et al., 2010; Lu et al., 2013; Mukherieea et al., 2016).

The main mechanism of inhibition of dioxins by this technology is the transformation of these into inorganic and non-toxic substances such as H2O, CO2 and HCl through V2O5-WO3/TiO2 catalysts. Such transformation occurs inside the catalytic reactor at a temperature of 300 °C (Boos et al., 1992; Chang et al., 2009; DvoĜák et al., 2010; Lu et al., 2013; Mukherieea, 2016).

The use of selective catalytic oxidation by means of NH3-SCR catalysts as an alternative to reduce dioxins is efficient, and when accompanied by the complete combustion of the raw material it can present results above 90% efficiency for the removal of dioxins (Mukherieea et al., 2016).

However, the proper functioning of this system requires a periodic monitoring of the catalyst feed in order to avoid its overload, which can reduce the efficiency of the treatment. In addition, this alternative involves high operating and investment costs, which limits its use in large-scale plants (Mukherieea et al., 2016).

All of the treatment systems presented above are good alternatives for the removal of dioxins. However, for these technologies to present a good efficiency, in fact, some conditions must be met, among them a low concentration of chlorine in the raw material. This condition is not currently met, given the high concentration of chlorine found in sugarcane due to the use of KCl as a source of potassium. Thus, a third alternative for reducing the emission of dioxins in the bioethanol production process is the replacement of the fertilizer used in planting sugarcane with others that contain reduced chlorine content. Such an alternative also benefits the control technologies mentioned here.

6.3 Replacement of the Fertilizer used for Planting

The use of KCl as a source of potassium in the cultivation of sugarcane is inadequate, in view of the high concentration of chlorine in this fertilizer, which favors the formation of dioxins. As a result, it is necessary to replace this potassium source with another that has low chlorine content. Comparing KCl with potassium fertilizers K_2SO_4, KNO_3 and Glauconitic

Siltstone, there is a great variation in the concentration of K_2O in each of these options, with KCl being the alternative that has the highest concentration of K_2O in its composition.

Therefore, the definition of the most viable alternative must consider the environmental and economic factors, and it is necessary to analyze the cost of acquiring each of these alternatives. Considering the price per ton of each fertilizer already included, the cost, insurance and freight, that is, the price in the CIF modality for the region of the state of Sao Paulo (the state that concentrates most of the sugarcane cultivation in the country), the Glauconitic Siltstone is the option that presents the lowest value among the 4 options, having a cost of BRL 220.00. This value is lower when compared to the prices per ton for KCl (BRL 1,368), K_2SO_4 (BRL 2,886.28) and KNO_3 (BRL 3,681.02) (Table 9).

Thus, the price per kilogram of K_2O for Glauconitic Siltstone is also the lowest of the four alternatives. The total cost to supply the demand for 150 kg of K_2O is estimated at around BRL 330.00 per hectare for this alternative. This cost is ultimately the lowest when compared to the other three options (Table 10). Therefore, considering both the financial and the environmental aspects, the option that offers the best benefit-cost ratio among the four commonly used fertilizers is Glauconitic Siltstone.

TABLE 10
ECONOMIC ANALYSIS OF THE APPLICATION OF POTASSIUM-BASED FERTILIZERS USED IN THE CULTIVATION OF SUGARCANE

Fertilizer	CIF price[1]	Price per kg of applied K_2O	Total cost for application (150 kg of K_2O)
	BRL/ton	BRL	BRL/ha
Potassium Chloride (KCl)	1,368.00	2.28	342
Potassium Sulfate (K_2SO_4)	2,886.00	6.01	901.9
Potassium Nitrate (KNO_3)	3,681.00	8.37	1,254.90
Glauconitic Siltstone	220	2.2	330

[1] ***CIF price for the region of Sao Paulo state in February 2020***

In addition to these four potassium fertilizers used, other alternatives that are also used in the cultivation of sugarcane are: sludge from Sewage Treatment Plants (STPs) and vinasse. The use of sludge from STPs in agricultural soils as a fertilizer is one of the most rational ways of using this material. Among the agricultural crops in which the application of sludge from STPs can be performed is sugarcane for the production of bioethanol. The cultivation and harvesting of sugarcane leads to the loss of nitrogen (N) from the soil, thus requiring the replacement of this nutrient, which can be obtained from the use of sludge from STPs through fertigation. The same is true for micronutrients, such as Cu and Zn (Chiba et al., 2008).

Despite the attractiveness of the use of sludge from STPs as an interesting and sustainable, alternative source of potassium in the cultivation of sugarcane, one should consider the potassium concentration found in this material, which is approximately 8 grams of potassium per kilogram of sewage sludge. Bearing in mind that on average there is a need to apply 150 kg of K2O per hectare, there would be a need to apply 18,750 kg of sewage sludge on average to supply this demand (Chiba et al., 2008). Given this value, the alternative is ultimately unfeasible, since the costs of transporting and applying sludge from STPs in the soil would be high.

A second alternative as a source of potassium is vinasse, the main by-product of the sugar and alcohol industry. Vinasse is an acidic liquid effluent (pH: 3.5-5), which has a high organic content (with a chemical oxygen demand between 50 to 150 grams per liter) and an unpleasant odor (España et al., 2011). The chemical composition of vinasse varies, depending on the plant used in the production of ethanol and the distillation process. This effluent is usually composed of 93% water and 7% organic and mineral solids (Laime et al., 2011). The production of vinasse in the sugar and alcohol sector is considerable, with an average of 10 to 15 liters of this by-product being generated for each liter of ethanol, depending on the distillery equipment used (Cortez et al., 1992). Due to the large volume of vinasse generated, several uses have already been proposed for this residue, mainly due to its physical-chemical characteristics, since the disposal of this residue in water bodies can cause contamination of the environment (Demattê et al., 2004).

One of the uses adopted for vinasse is fertigation, which consists of the infiltration of crude vinasse into the soil through the irrigation of sugarcane crops (Camargo et al., 2009). This use proved to be beneficial for the cultivation of sugarcane, with an increase in productivity (Barbosa, 2010; Júnior et. Al., 2007).

Vinasse is composed on average of 2.056 kg of potassium per cubic meter (Christofeletti et al., 2013). In view of the need to apply 150 kg of K_2O per hectare, there would be a need to apply 72 cubic meters of vinasse to supply this demand.

Regarding the unique costs for the transportation and application of vinasse, the cost per cubic meter applied is between BRL 1.20 and BRL 4.56, considering a distance between 2 to 40 kilometers. Thus, the application of 72 cubic meters of vinasse would have an estimated total cost between BRL 86.4 and BRL 328.32 (Cruz, 2011) (Table 11)

TABLE 11
COST FOR TRANSPORTATION AND APPLICATION OF VINASSE

Distance	Transportation[1] + Application[2]	Transportation[1] + Application[2]
Km	BRL/m³	BRL/72m³
2	1.2	86.4
4	1.38	99.36
6	1.56	112.32
8	1.73	124.56
10	1.91	137.52
12	2.09	150.48
14	2.26	162.72
16	2.44	175.68
18	2.62	188.64
20	2.79	200.88
22	2.97	213.84
24	3.14	226.08
26	3.32	239.04
28	3.5	252
30	3.67	264.24
32	3.85	277.2
34	4.03	290.16
36	4.2	302.4
38	4.38	315.36
40	4.56	328.32

Adapted from Cruz, L.F.L.S., 2011; [1]Transportation considering trucks of 25 + 30 m³; [2]Application by using Hydro Roll

Although the use of vinasse in the cultivation of sugarcane is an apparently sustainable option, since it involves the valuation of a waste from its use as a by-product, preventing its dumping into the water body, one must be parsimonious in relation to the direct application of this material into the soil. After all, its excessive application can cause salinization, leaching of metals present in the soil, changes in soil quality due to the imbalance of nutrients, mainly manganese, and losses in the harvest (Christofeletti et al., 2013).

In addition to the problems mentioned above, vinasse has a high concentration of chlorine in its composition. Because of this, its application in the soil in order to supply the demand for potassium can introduce a high amount of chlorine in it, which, in a similar way to KCl, can cause this chlorine to be absorbed by the sugarcane tree, thus accumulating in different parts of it. Consequently, the burning of sugarcane bagasse during the energy cogeneration process can lead to the formation of dioxins as a by-product (Christofeletti et al., 2013; Piacente, 2005)

Finally, considering the four alternatives proposed to replace KCl as a source of potassium in the cultivation of sugarcane, the options that offer the best cost-benefit ratios are Glauconitic Siltstone and vinasse. However, when analyzing the composition of these two alternatives, vinasse is not a recommended option as a substitute for the use of fertilizers containing chlorinated compounds, considering the high concentration of chlorine found in this potassium source.

VII. CONCLUSION

This study shows that, among the intervening factors for the formation of dioxins, the presence of chlorine in sugarcane appears as one of the main precursors for the formation of these compounds. In addition to this, it has been found that the treatment systems used in sugarcane processing plants have low efficiency in the removal of dioxins, leading to the emission of these toxic substances that represent a risk to human health and environmental integrity.

The ineffectiveness of Venturi gas scrubbers, bag filters and electrostatic precipitators as methods of controlling the emission of dioxins to the environment requires modifications in the process of control or production, so that the emission of dioxins is effectively controlled. However, as shown in this study, the alternatives that can be adopted to increase the efficiency of emission control are expensive, as is the case with the adoption of selective catalytic oxidation, or are inefficient when sugarcane has a high content of chlorine, in the case of optimization of the combustion process combined with end-of-pipe treatment.

In this context, and considering that one of the main factors for the formation of dioxins in bioethanol production plants is the presence of chlorine in sugarcane, the most viable alternative, both environmentally and financially, is the replacement of the source of potassium used.

For this purpose, fertilizers containing a high chlorine content, such as Potassium Chloride (KCl), must be replaced with a non-chlorinated potassium source, as is the case with Potassium Nitrate, Potassium Sulfate and Glauconitic Siltstone. An economic analysis of these alternatives has pointed to Glauconitic Siltstone as the option with the best cost-benefit ratio, considering that this alternative has more competitive prices than Potassium Chloride, Potassium Nitrate and Potassium Sulfate.

Once Brazil has committed itself to eliminate sources of POPs production at the Stockholm Convention of 2002, it is necessary to establish a limit for the occurrence of dioxins for sources other than gas and products intended for animal feed, in addition to a continuous monitoring of boiler ashes, since the presence of dioxins in this residue has already been proven, as well as the replacement of potassium sources used in crops.

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Ultrasonic Radiation Influence on the Bioadsorbent Characteristics of Citrus *(Citrus x Lemon) & (Citrus x sinensis)*

García Raurich, Josep[1], Martínez Roldán, Tania[2], Monagas Asensio, Pedro[3], Soler López, Carles[4], Torres Domínguez, Nadia[5]

CRESCA (Centre de Recerca en Seguretat i Control Alimentari de la UPC). ESEIAAT Colom 1, 08222-Terrassa (Barcelona)

Abstract— *Of all the materials used as adsorbents, activated charcoal is the most popular as it is excellent for reducing/eliminating a wide variety of contaminants. This capacity is mainly due to its structural characteristics that give it a large surface area. However, it has several disadvantages. The most important are that the adsorbent material is quite expensive as is its regeneration. For this reason, more economical absorbents have been sought, highlighting the study of adsorption phenomena in some types of biomass as adsorbents.*

Bioadsorption is considered a viable alternative to the physical-chemical methods currently used for the recovery or removal of heavy metals dissolved in liquid effluents. Its main attraction, from an industrial point of view, is its low cost due to the great abundance, easy to obtain and low price of the bioadsorbent material. Bioadsorption is very effective in treating metal concentrations below 100 mg/L, where the application of physical-chemical methods is neither technically nor economically feasible.

One of these materials of interest is citrus peels, because, due to their abundance as a waste product of the food industries, they are hardly reused and currently have little economic value. However, these residues have a low adsorption capacity, so both physical and chemical modifications are required to increase their adsorption properties.

This study compares the characteristics of orange and lemon peels undergoing a physical-chemical treatment with ultrasonic radiation assistance and the optimization of experimental conditions to obtain useful bioadsorbents in discontinuous processes (batch).

Keywords— bioadsorption, orange peel, lemon peel, ultrasonic radiation, heavy metal removal.

I. INTRODUCTION

Conventional methods for the treatment of wastewater with low concentrations of heavy metals in the ion state are extremely costly. For this reason, adsorption techniques have gained acceptance due to their effectiveness in removing pollutants that are too stable for conventional methods, resulting in high-quality effluents (Basso et al, 2002). Beyond research with living plants (Seki et al, 1988), the use of plant waste material for the recovery of heavy metals has been addressed. An adsorbent can be considered inexpensive if it requires little processing, is abundant in nature, or is a by-product or waste from another industry. (Bailey et al, 1999).

Generally, the bioadsorbents studied come from waste that has problems for reuse and which do not represent any economic value, a clear example of this is waste from industry and agricultural area (Crini, 2006). They have adequate adsorption capacity: pine bark (Al-Asheh et al, 2000), conifers (Aoyoma et al, 2000), rice husk (Feng et al, 2004), etc. In this sense, the easiest and most accessible bioproduct is plant biomass (Mani & Kumar, 2014).

The cell walls of bioadsorbent materials contain polysaccharides, proteins and lipids. Therefore, they contain numerous functional groups capable of linking heavy metals on the surface of these (Wei et al, 2010). Among the functional groups present are the amino, carboxylic, hydroxyl, phosphate and thiol groups that differ in their affinity and specificity with respect to susceptibility to bind to the different metal ions (Ghimire et al, 2003). However, it should be noted that the content in functional groups in the bioadsorbent material may be different depending on the species, the season, the geographical area, etc. The most commonly consumed fruit peels are apple (Mallampati & Valiyaveettil 2013), banana (Memon et al, 2009) orange (Feng et al, 2011), lemon (Tejada et al, 2015), and mango (Iqbal et al,2009). All of them should be included among widely used bioadsorbents.

Citrus fruits are a diverse group of species native to tropical and subtropical regions of Asia that are cultivated in the world. The fruits of these species, in particular oranges, mandarins, lemons, limes and grapefruits, play an important role in the feeding of millions of people, whether as fresh fruit, concentrate, drink or in culinary preparations. The two largest producers are Brazil and the United States, with 21.4% and 14.5% of world production respectively. China, Mexico, Spain and India follow in importance, representing together 27.6% of the global total (FAO,2017).

Citrus essential oils are obtained from fruit bark (flavedo) (Tranchida et al., 2011). Different extraction techniques are employed, including direct methods such as shell compression and indirect methods such as steam stripping distillation and microwave radiation-assisted water (HDMO) distillation. The best method to extract them is steam distillation due to the variety of volatile molecules extracted, such as terpenes and terpenoids, phenol-derived aromatic components and aliphatic components (Palazzolo et al., 2013). However, this process requires several hours, high energy consumption, conventional heating and hot water agitation (Durán & Villa, 2014). HDMO is a very fast and relatively inexpensive process and the essential oils obtained are free of thermal decomposition products and contaminants. Recently, the extraction of microwaves without the addition of solvent has been introduced and using only water that is removed in situ from the tissues (Ferhat et al., 2006) obtaining higher yields and better quality of the oil in a shorter time.

Citrus pectin, a thickener commonly used in the food industry, is obtained from the extraction of albedo (white layer between the shell and pulp). However, in most processes, the production of pectins is linked with the obtaining of essential oil (Cerón-Salazar & Cardona-Alzate, 2011). Alternatively, high methoxyl pectins have been obtained from orange peels by performing an acid extraction to the orange albedo by a low-pressure steam injection (15 psi) (Fishman et al, 2003).

The industrial production of citrus pectin has the following stages: in the first, the peel must be washed to remove the greatest amount of soluble solids and impurities, as these components hinder the purification process. The peels are then subjected to a drying process, which inactivates the pectinaesterase enzyme and decreases the moisture content, increasing the stabilization of the peel for storage and reducing the cost of transport (Martí et al, 2014). Subsequently, the dry matter suspended in hot water with the necessary amount of a strong acid, starting the hydrolysis process.

During this process, starting from the macromolecular structure formed by cellulose, hemicellulose and pectins, hemicellulose begins its degradation to glucose, galactose and fructose; cellulose to glucose and pectin to pectin monomer through a depolymerization process (Chen et al, 2015). After a while, by filtration, the liquid phase is separated from the solid phase. Then the liquid phase is mixed with alcohol. As a consequence, the polymer that precipitates rapidly in the form of pectin is recovered. The precipitate is extracted and purified by washing it with more alcohol. Finally, it is dried and ground (Claus, 2002).

Depending on the source, pectins may vary in molecular size, degrees of acetylation and methylation, galacturonic acid content and neutral sugar residues. Therefore, pectins exhibit versatile gelling properties and are able to form complexes with other natural compounds and, as a result, are useful for designing food products (Gawkowska et al., 2018).

The resulting material from the extraction of pectin is a poor dietary supplement for animals due to its low protein content and high in sugars (Siles et al, 2016). However, it presents the optimal conditions for further treatment as a bioadsorbent (Masmoudi et al, 2008).

Acid-soluble pectin extraction is necessary for its ability to absorb large amounts of water and the formation of colloids. If not extracted, the final product would not have a sufficient degree of consistency to be used as a bioadsorbent. Along with pectin, acidic hydrolysis involves the solubilization and degradation of carbohydrates, especially xylan and hemicellulose, since glucomanane is relatively stable in acid medium (Van Buren, 1991).

Accepted the acid attack as the first phase to increase the adsorption capacity of the citrus shell, the second phase consists of an attack in alkaline medium, intended for the saponification of ester groups that have not been extracted during the acid attack and subsequent crosslinking with Ca(II) (Cardona Gutiérrez et al, 2013). Usually this process is carried out with NaOH, which is followed by crosslinking with $CaCl_2$ to increase the activation sites. However, it is proven (Arjona et al., 2018) that both processes can be carried out in a single stage with the use of a $Ca(OH)_2$ 0.2 M solution.

Process intensification is currently one of the areas with the greatest development potential in the food industry. Through more sustainable technologies, the aim is to increase the productive performance, quality and safety of the processed product,

as well as reduce the size of equipment, waste and energy needs (Benali & Kudra, 2010). Among the different techniques that can be used for the intensification of processes (microwave, infrared, electrical pulses) it is worth highlighting the application of acoustic energy (Knorr et al, 2004). One of the main characteristics of power ultrasound is its ability to improve matter transfer processes (Cárcel et al., 2011).

In recent years there has been increased interest in the use of ultrasound to intensify the pectin extraction process as they not only increase the performance of the operation, but also reduce the extraction time compared to the conventional process (Bagherian et al., 2011; Minjares-Fuentes et al., 2014; Maran & Priya, 2015; Wang et al., 2015; Sundararaman et al., 2016; Freitas de Oliveira et al, 2016; Grassino et al., 2016).

II. MATERIAL AND METHOD

The transformation of citrus peels as cationic exchangers requires a physical-chemical treatment.

2.1 Treatment of citrus peels

This process begins with the collection and cleaning of the peels. It is important to select peels in good condition, i.e. without fungi, worms or decomposing parts. The edible part (endocarp) is then separated so that the peel (flavedo and albedo) is free from the pulp residues and is cleaned with detergent. In this way, waxes are extracted that, superficially, are incorporated to improve the appearance of these fruits in the commercial circuit. Next, the citrus peels are dried with forced air to constant weight and they are ground and sieved.

Physical modifications involve proper sizing of the peels by cutting or crushing, complemented by heat treatments such as reflux, microwave or ultrasonic irradiation. Chemical modifications include treatment with different types of chemical agents, which are used to increase binding groups in the final bioadsorbent, eliminate inhibitory groups and increase their surface area (Patel, 2012).

The chemical treatment begins with a process of acidification of the peels by hydrochloric acid, aimed at the extraction of pectin. Although the obtaining of pectin from orange peels has been extensively studied (Msebahi et al.,2005; Liu et al., 2006; Yeoh et al.,2008), from previous experiences (Arjona et al., 2018) the chemical attack is performed with ultrasonic radiation assistance (US), using a US Elmasonic bath model LC 30 H with a fixed frequency of 37.5kHz and time and temperature regulation, for a period of 45 minutes.

The acid treatment is repeated until obtaining a solid free of sugars and of the pectin and hemicellulose fractions soluble in these experimental conditions. One repeat is usually sufficient for the reducing sugar test (Fehling method) to be negative.

Once the pectin, hemicellulose and reducing sugars soluble in acid medium have been extracted, a treatment is carried out with distilled water to remove the excess hydrochloric acid used initially.

The resulting solid is then treated in an alkaline medium. In this way, saponification of non-soluble pectin in an acid medium is achieved, as well as solubilization of the soluble fraction of hemicellulose in an alkaline medium (Grace et al., 1996). The saponification and crosslinking process is carried out in a single stage with the use of a $Ca(OH)_2$ solution in the US Elmasonic bath model LC 30 H over a period of 45 minutes. After this treatment, excess Ca (II) is removed by washing with distilled water. The bioadsorbent obtained is dried at 110ºC and ground until the final product is obtained, which is kept in a hermetically closed container.

2.2 Behavior of citrus peels before chemical treatment

Orange peels and lemon peels have a different water absorption capacity, before undergoing chemical treatment. The experimental check was carried out as follows: 5g samples of orange and lemon peel were placed in a beaker, distilled water was added, drop by drop, with the help of a burette and the mixture was homogenized by means of a magnetic stirrer at a set speed of 400 rpm.

Progressively, a compact mass formed, to the point of reaching saturation. To perform its verification, the beaker was gently flipped. When a drop of liquid was released, the volume of water that had been poured into the glass from the burette was recorded (Figure 1).

FIGURE 1: Detachment of a drop of liquid from the water-saturated solid

Table 1 shows the mean values (3 repetitions) of the behavior of both types of citrus peel as a function of grain size. It was found that:

- Lemon peel presented a double adsorption to the adsorption of orange peel in all cases
- Adsorption decreased as particle size decreased

This second behavior was attributed to the possibility of caking increases when there is more contact between the particles.

In general, the smaller and less uniform they are, the greater the probability of caking (Pietsch 2002). The powdery particles become wet, sticky and compact, finally reaching the liquefaction phase (figure 2). In view of this behavior, it was decided to discard the particle size of less than 250 µm.

TABLE 1
WATER ADSORPTION ON SAMPLES OF 5 GRAM CITRUS PEELS OF DIFFERENT PARTICLE SIZES AT ROOM TEMPERATURE

Orange	Particle size	mL H_20 Average	mL/g
	1mm>X>500 µm	37,8 ± 0,35	7,6
	500 µm>X> 250 µm	28,2 ± 0,5	5,6
	X<250 µm	23,1 ± 0,8	4,6
Lemon	1mm>X>500 µm	71,5 ± 0,85	14,3
	500 µm>X> 250 µm	59,5 ± 1,25	11,9
	X<250 µm	52,6 ± 0,45	10,5

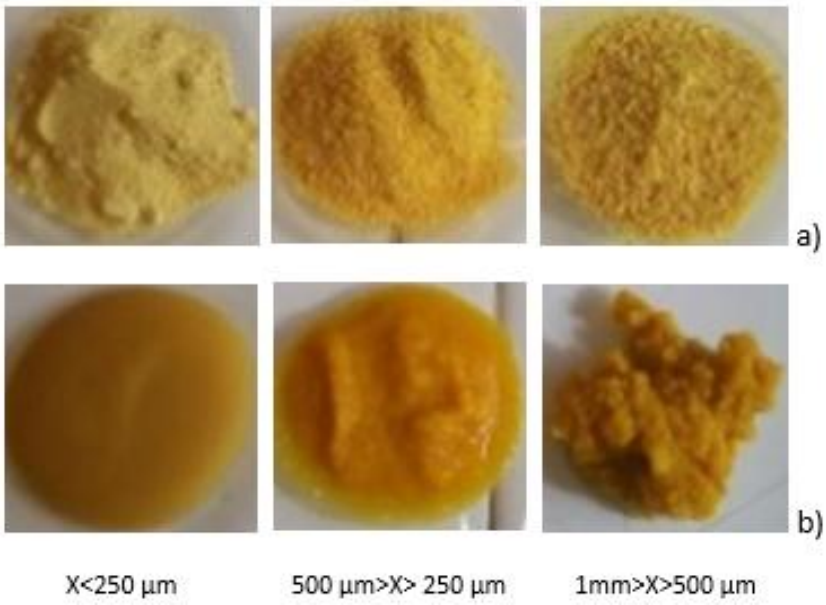

FIGURE 2: Appearance of orange peel vs particle size a) dry b) saturated with water

2.3 Influence of chemical treatment

The effectiveness of the various stages of chemical treatment was tested through the extracted organic matter content. To this end, the organic matter eliminated in acidic treatments and alkaline treatment was determined by the action of KMnO4 in sulphuric medium (permanganimetry) and expressed as mg O2/L. Table 2 compares the results obtained when citrus peels with a particle size between 1000 µm - 500 µm were used, showing the mean values of 3 repetitions.

TABLE 2
ORGANIC MATTER EXTRACTED IN EACH ATTACK (mg/L O_2)

Particle size 1000µm>X>500 µm	First acid attack	Second acid attack	Alkaline attack
Orange	103,7 ± 1,4	68,8 ± 2,1	34,4 ± 4,0
Lemon	155,5 ± 4,5	128,6 ± 5,8	53,6 ± 5,6

As expected, in both orange and lemon peel, the first acid attack was more effective than the second, with significantly higher extraction of organic matter observed in the lemon peel in both attacks. This behavior was associated with the higher lignin content in orange peel, whose three-dimensional structure with amorphous ordering, acts as a protective agent of cellulose conferring resistance and impermeability to the biomass in which it is located and, simultaneously, to the higher cellulose content in lemon peel (Ververis et al, 2007). The alkaline attack, responsible for the saponification and crosslinking of the pectin not soluble in acid medium, presented the same behavior, although the absolute value of the extracted organic matter was significantly lower.

On the other hand, in acid hydrolysis, polysaccharides experience hydrolysis (Sánchez-Orozco & Vázquez-Velázquez 2017). Through the Fehling test detected the presence of monosaccharides in the resulting liquid, after the attack of the citrus peel in hydrochloric medium with ultrasonic radiation (US) assistance. Figure 3 shows the evolution of the reducing sugar content at the various stages of chemical treatment on an orange peel until it is transformed into the final bioadsorbent.

FIGURE 3. Fehling trial in the different liquid fractions of the chemical treatment of an orange peel: a) first acid attack; b) second acid attack; c) rinse with distilled water; d) alkaline attack; e) rinse with distilled water; f) final bioadsorbent

The effectiveness of the chemical treatment was checked by determining the infrared (IR) spectrum of the shells (initial bioadsorbents) and the products obtained through chemical treatment (final bioadsorbents).

Figure 4 shows the IR spectra before and after the chemical treatment of an orange peel, analogous to those obtained with lemon peel, performed with a Perkin Elmer model Paragoni 500 spectrophotometer. In both spectra the presence of the functional groups is confirmed: OH, C=O, C-O-C and C-O, as well as CH and CH_2 before and after chemical treatment.

The peaks that appear centered at 1741cm^{-1} and 1633cm^{-1}, which appear in the orange peel spectrum before chemical treatment, are attributable to the carbonyl group (C=O) as indicators of free and esterified carboxylic groups. In fact, the disappearance of the peak at 1741cm^{-1} in the spectrum of the orange peel once subjected to chemical treatment indicates the disappearance of high methoxyl pectins (García Raurich et al, 2019).

On the other hand, the signal in the form of a broadband between (3600-3200 cm^{-1}) centered at 3369 cm^{-1} before the chemical treatment and centered at 3420 cm^{-1} after the chemical treatment, is attributable to the hydroxyl group. This group is found in cellulose, pectin, absorbed water, hemicellulose and lignin, components present in the citrus peel. The presence of

cellulose as the main component of citrus peels means that the removal of hemicellulose is not, for practical purposes, observable.

Finally, the peaks centered around 1430 cm^{-1} justify the presence of aliphatic and aromatic bonds (C-H), and the peaks centered around 1060 cm^{-1} correspond to the group C-O, present in alcohols, carboxylic acids, esters and ethers. A study in which the IR spectra of pectin, cellulose, hemicellulose and lignin appear is found in (Arroyo Salas et al, 2008).

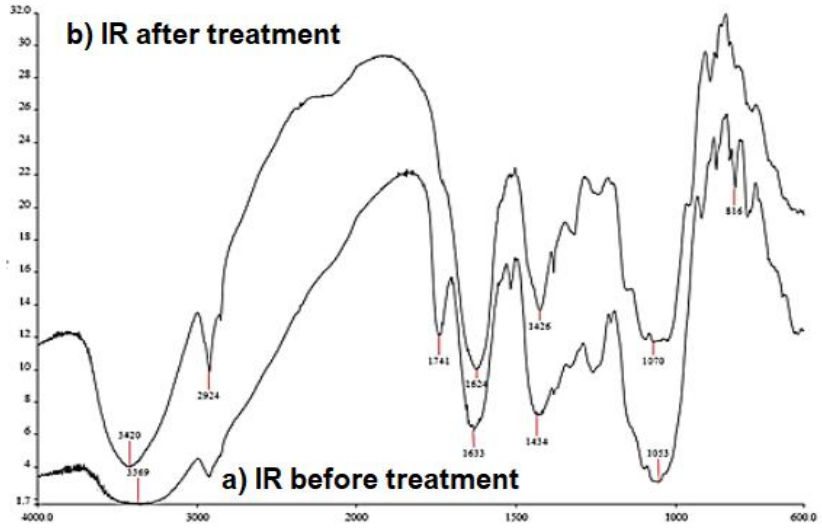

FIGURE 4. a) IR spectrum of orange peel before chemical treatment, b) IR spectrum of the final bioadsorbent

2.4 Increase in Ca(II) in final bioadsorbent

Ca(II) present in samples of orange and lemon peels that had only undergone physical treatment was determined and compared with the Ca(II) content in the final bioadsorbents. The particle size was set at 500-1000 μm and the samples were subjected to a calcination process at 525ºC inside a Hobersal JB 20 muffle for 4 hours.

Different proportions were used in the alkaline attack to check the influence of $Ca(OH)_2$ concentration: 1; 2,5 y 5 g de $Ca(OH)_2$.

The determination of Ca(II) and Mg(II) was made volumetrically, after solubilizing the corresponding ashes. EDTA 0.01M (Ethylenediaminetetraacetic acid) was used as a valuing agent and NET (Eriochrome Black T) was used as an indicator.

First, the total amount of Ca(II) and Mg (II) was determined. In another aliquot, Ca(II) with 0.05M oxalic acid was precipitated and then the complexometric titration was repeated, determining only the Mg(II) content, so that the amount of Ca(II) was quantified as the difference between the total and the amount of Mg(II).

After the alkaline attack, the content of Mg (II) disappeared into the final mass of the resulting bioadsorbents. In contrast, the content of Ca (II) experienced a significant increase. Table 4 shows the increment of Ca (II) as a percentage. These results are consistent with the four-stage adsorption mechanism: migration of metal ions from the solution to the surface of the adsorbent; diffusion through the surface layer of biomass, fixation in the active group and diffusion into the biomass (Horsfall & Abia, 2003).

TABLE 4
PERCENTAGE INCREASE IN Ca(II) IN FINAL BIOADSORBENT

Orange	g $Ca(OH)_2$	Δ Ca(II)
	1	150 %
	2,5	178 %
	5	248 %
Lemon	1	153 %
	2,5	294 %
	5	402 %

2.5 Determining the efficiency of final bioadsorbents

The characteristics of the bioadsorbents obtained were checked with a series of synthetic Cu (II) solutions prepared from CuSO4·5H2O, supplied by the company Panreac (Barcelona).

First, a qualitative trial was conducted to visually determine the degree of bioadsorption of Cu(II). To do this, 0,5 were added; 1 or 2g of the final bioadsorbents obtained with different chemical treatments, at 100mL of synthetic solutions of 500 mg/L of Cu(II) contained in containers that closed tightly.

Bioadsorbents differed in particle size (250-500µm or 500-1000µm), the amount of calcium hydroxide added in the alkaline attack (2,5 or 5g) and the hydration time of the final bioadsorbent (1 or 3 days) before adding the copper solution.

The containers were stirred for 15 minutes in a roller mixer, supplied by the company Selecta (Barcelona). After this time, the bioadsorbents turned green. Then, from each container, a 5 mL aliquot was removed to which 5 mL of a 5% (w/v) solution of KI was added and then 5 mL of dichloromethane. The emergence of a pink coloration of the organic phase confirmed the formation of iodine in the experiences in which the exchange capacity of the bioadsorbent had been exceeded.

In all cases, it was observed that the best results were obtained when the highest amount of bioadsorbent, 2g, was added in the 100mL of synthetic Cu (II) solution and that one day of hydration was sufficient. Visually, neither the particle size of the bioadsorbent nor the amount of $Ca(OH)_2$ added in the alkaline attack did not significantly influence the amount of copper exchanged.

Quantitative determination of copper removal from synthetic Cu(II) solutions was performed using an AA-6300 Shimadzu atomic absorption spectrophotometer. The initial and final particle size of the bioadsorbents was taken into account, using both the 250-500µm and the 500-1000µm.

The final bioadsorbent from the orange peel (OB) was used with a 30 mg/L Cu(II) solution. 25 mL of this solution and 0,5 g of the different versions of (OB) were introduced into test tubes with screw caps. The copper removal results showed an average adsorption of 97.04%±3.83, regardless of the particle size used, both initial and final.

The particle size was set at 500-1000µm and the behavior of (OB) was determined in a wide range of concentrations. For this, it was decided to establish two groups: Cu(II) concentrations up to 250 mg/L and concentrations greater than 250 mg/L. A working concentration of 1.5 g of bioadsorbent/100 mL of Cu(II) solution was established. This amount of bioadsorbent, previously hydrated for 24 hours, was in contact with the corresponding Cu(II) solution inside a hermetically sealed container with stirring for 15 minutes.

In the group of experiences of Cu(II) concentrations less than 250 mg/L, the residual Cu(II) concentration by atomic absorption was determined. In the group of Cu(II) concentrations greater than 250 mg/L, the concentration of non-bioadsorbed Cu(II) was determined by a redox titration, using as a titrating agent a dissolution of sodium thiosulphate 0.1M prepared from $Na_2S_2O_3$-$5H_2O$ supplied by the company Panreac (Barcelona).

The results obtained by atomic absorption are shown in Table 5. It can be seen that, with the exception of the concentration of 5 mg / L, the percentage of bioadsorbed Cu (II) exceeds 90%.

On the other hand, the relationship -γ- between the initial concentration of Cu (II) with respect to the mg/L of Cu (II) bioadsorbed/gram of bioadsorbent, confirms that this cation exchange takes place through an equilibrium process.

TABLE 5
BEHAVIOR OF SOLUTIONS WITH A CONCENTRATION OF Cu(II) < 250 mg/L

$[Cu(II)]_o$ (mg/L) -α-	mg/L Cu(II) bioadsorbeds	% Cu(II) bioadsorbed	mg Cu(II) absolutes	mg Cu(II)/ g bioadsorbent -β-	γ=α/β
5	3,27	65,4	0.5	0.22	22.73
10	9,02	90,2	1	0.60	16.67
25	22,74	91,0	2.5	1.52	16.45
50	47,21	94,4	5	3.15	15.87
100	95,64	95,6	10	6.38	15.67
250	241,86	96,7	25	16.12	15.51

The results obtained volumetrically are shown in Table 6. It can be seen how the percentage of Cu(II) bioadsorbed decreases as the initial concentration of Cu(II) increases, showing a tendency to saturation of the orange bioadsorbent (OB).

TABLE 6
BEHAVIOR OF SOLUTIONS WITH A CONCENTRATION OF Cu(II) >250 mg/L

$[Cu(II)]_o$ (mg/L) -α-	mg/L Cu(II) bioadsorbeds	% Cu(II) bioadsorbed	mg Cu(II) absolutes	mg Cu(II)/ g bioadsorbent -β-	γ=α/β
500	475.0	95.00	50	31.70	15,77
750	562.5	75.00	75	37.50	20,00
1000	657.9	65.79	100	43,86	22,80
1500	810.0	54.00	150	54,00	27,78
2000	1027.8	51.39	200	68,52	29,19
2500	1175.0	47.00	250	78,30	31,93
3000	1200.0	40.00	300	80,00	37,50
4000	1437.9	35.95	400	95,86	41,72

When the final bioadsorbent from the lemon peel (LB) was used, 1.0 g of LB, previously hydrated for 24 hours, was established as a working concentration, which was contacted with 100 mL of the different Cu(II) solutions inside a set of hermetically closed containers. These containers were subjected, during a period of 15 minutes, to a stirring process on the same roller mixer.

From the results of table 4, it was decided to determine the influence of the concentration of Ca(II) on the LB, as well as the particle size. For this, the particle sizes of 250-500 µm and 500-1000 µm were used.

In an analogous way to the procedure with (OB), in experiences with concentrations greater than 250 mg/L, the content of Cu(II) was determined by redox titration, using as a titrating agent a 0.1M sodium thiosulphate solution prepared from $Na_2S_2O_3 \cdot 5H_2O$ and, in the experiences of concentrations below 250 mg/L, the concentration of non-adsorbed Cu(II) was determined by an atomic absorption spectrophotometer AA-6300 Shimadzu. Table 7 details the percentages of bioadsorbed Cu (II), in the series of experiences with concentrations greater than 250 mg/L Cu (II), by the final lemon bioadsorbent (LB). The initial particle size of the bioadsorbent before chemical treatment (LBo), the amount of $Ca(OH)_2$ used in the alkaline attack and the particle size of the final bioadsorbent (LB) were taken into account.

TABLE 7
INFLUENCE OF EXPERIMENTAL CONDITIONS IN OBTAINING (LB) ON THE BIOADSORPTION

[Cu(II)] mg/L	[%] Cu(II) bioadsorbed							
	LB_o 500-1000 µm		LB_o 250-500 µm		LB_o 500-1000 µm		LB_o 250-500 µm	
	Alkaline attack: 1g $Ca(OH)_2$				Alkaline attack: 5g $Ca(OH)_2$			
	µm LB 500-1000	µm LB 250-500	µm LB 500-1000	µm LB 250-500	µm LB 500-1000	µm LB 250-500	µm LB 500-1000	µm LB 250-500
500	30.77	46.15	30.77	46.15	61.54	76.92	61.54	84.62
750	23.53	29.41	23.53	35.29	41.17	52.94	47.06	58.82
1000	17.86	25.00	21.43	28.57	39.28	50.00	46.42	57.14
1500	13.89	16.67	13.89	16.67	33.33	38.89	36.11	41.67
2000	10.42	14.58	12.50	14.58	31.25	37.50	33.33	37.50
3000	5.63	7.04	7.04	9.86	19.72	23.94	23.94	23.94

Percentages of Cu(II) at concentrations greater than 250 mg/L

The influence of $Ca(OH)_2$ concentration and particle size of the initial bioadsorbent (LB_0) and the final bioadsorbent (BL) were revealed. The highest percentages of bioadsorption were determined at high concentrations of $Ca(OH)_2$ and particle size of 250-500 µm of both the initial bioadsorbent (BL_0) and the final bioadsorbent (BL).

Table 8 is analogous to Table 7. It details the results obtained in the experiences carried out with Cu(II) solutions with concentrations below 250 mg/L. Comparison of Cu (II) bioadsorption percentages from both tables shows a significant

increase in values at concentrations below 250 mg/L compared to concentrations above 250 mg/L. In fact, the values in Table 7 show a trend towards bioadsorbent saturation.

TABLE 8
INFLUENCE OF EXPERIMENTAL CONDITIONS IN OBTAINING LB ON THE BIOADSORPTION PERCENTAGES OF Cu(II) AT CONCENTRATIONS BELOW 250 mg/L

[Cu(II)] mg/L	[%] Cu(II) bioadsorbed							
	LB_0 500-1000 µm		LB_0 250-500 µm		LB_0 500-1000 µm		LB_0 250-500 µm	
	Alkaline attack: 1g $Ca(OH)_2$				Alkaline attack : 5g $Ca(OH)_2$			
	µm LB 500-1000	µm LB 250-500	µm LB 500-1000	µm LB 250-500	µm LB 500-1000	µm LB 250-500	µm LB 500-1000	µm LB 250-500
5	83.60	85.40	78.00 *	85.40	86.40	89.40	87.60	90.60
10	86.80	90.40	85.20	91.50	92.30	93.40	92.20	93.90
25	78.48*	91.56	85.32	89.88	94.20	95.96	94.80	96.24
50	80.56	90.96	77.86*	85.92	92.44	95.76	95.28	95.94
100	84.24	88.19	83.14	87.79	92.87	95.43	95.61	96.26
250	93.23	93.39	93.23	93.60	93.80	95.45	93.96	96.40

outliers values

With the results of the experience carried out with a particle size of 250-500 µm with both (LB_0) and (LB), having used 5 grams of Ca (OH) 2 in the alkaline attack, table 9 was obtained.

TABLE 9
BEHAVIOR OF SOLUTIONS WITH A CONCENTRATION OF Cu(II) >250 mg/L

$[Cu(II)]_0$ (mg/L) -α-	mg/L Cu(II) bioadsorbeds	% Cu(II) bioadsorbed	mg Cu(II) absolutes	mg Cu(II)/ g bioadsorbent -β-	γ=α/β
5	4.53	90.60	0.5	0.45	11.11
10	9.39	93.90	1	0.94	10.64
25	24.06	96.24	2.5	2.41	10.37
50	47.97	95.94	5	4.80	10.42
100	96.26	96.26	10	9.63	10.38
250	241.01	96.40	25	24.10	10.37

Analogously to what was observed in the behavior of (OB), this time the relationship -γ- between the initial concentration of Cu (II) with respect to the mg of Cu (II) bioadsorbed/gram of bioadsorbent, also confirms that this exchange Cationic passes through a process of equilibrium.

Figure 5 shows, jointly, the values of mg of bioadsorbed Cu(II)/gram of bioadsorbent as a function of the initial concentration of Cu (II) in mg/L obtained both for concentrations below and above 250 mg/L.

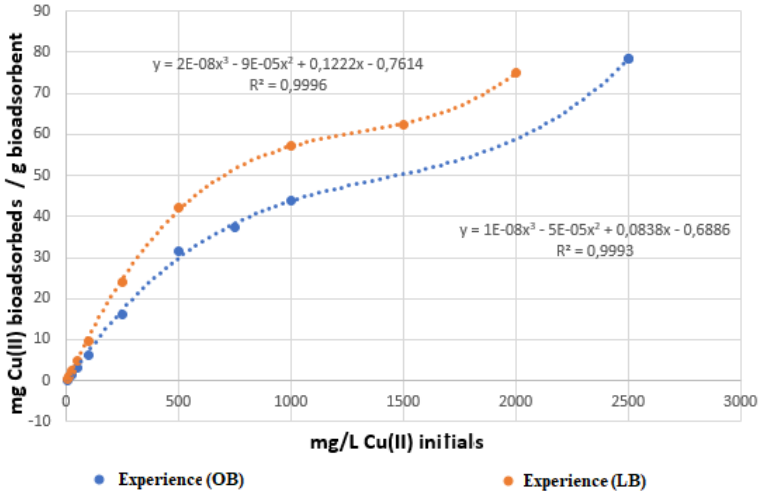

FIGURE 5. mg Cu(II) bioadsorbeds/ gram bioadsorbent vs [Cu(II)] initial (mg/L)

In the case of the lemon bioadsorbent, the values corresponding to the set of experiences carried out with a particle size between 250-500 µm for (LB_0), (LB) and 5 grams of $Ca(OH)_2$ in the alkaline attack have been represented.

In both cases, a polynomial trend line of order 3 is observed that can be adjusted to the BET equation (Brunauer et al, 1938). As a result, it can be admitted that adsorbate covers the adsorbent until a monolayer is formed and the process continues with adsorption in multilayers. However, if only values for concentrations below 250 mg/L of Cu(II) are considered, they conform to the Langmuir equation (Langmuir, 1916). Consequently, it is apparent that for high concentrations of Cu(II) the process of diffusion into the biomass is predominant, while at low concentrations surface fixation predominates (Horsfall & Abia, 2003).

Another parameter considered was the contact time, i.e., the time required to reach the equilibrium point, especially in discontinuous processes (batch). When this value is reached, no further bioadsorption occurs, even if the two phases (adsorbate and bioadsorbent) remain in contact.

In general, bioadsorption processes are rapid, between 15 and 30 minutes a considerable percentage of the cation present in the dissolution has already been eliminated. This fact seems to suggest that the bonding of metal ions with the active sites of the bioadsorbent probably takes place preferably on the surface of the bioadsorbent. (Yus&Mashitah, 2014).

It was confirmed that the period of time initially established, 15 minutes, both for the bioadsorbent obtained from the orange peel (OB) and that obtained from the lemon peel (LB) was sufficient in batch experiences. Using (LB), the bioadsorption percentage of three Cu(II) solutions of 10, 50 and 250 mg/L was compared at 15 and 120 minutes of contact. The results obtained shown in Table 10 correspond to a particle sizeof 250-500µm of both the initial bioadsorbent (LB_o) and the final bioadsorbent (LB).

TABLE 10
INFLUENCE OF STIRRING TIME

	% Cu(II) bioadsorbed	
$[Cu(II)]_0$ mg/L	15’	120’
10	93,90	94,60
50	95,94	96,48
250	96,40	96,50

Obtaining virtually identical results confirmed that a period of contact between adsorbate and 15-minute bioadsorbent is sufficient to establish the corresponding balance in discontinuous processes (batch).

III. DISCUSSION

Conventional adsorbents are those natural or synthetic materials that must be treated to activate, such as charcoal or clays, and that, after use, can be regenerated. Non-conventional adsorbents are alternative materials (biopolymers, plant parts, etc.) that do not necessarily need to be pretreated to activate. However, its activation improves its adsorption capacity (Valladares-Cisneros et al, 2018).

Bioadsorption is a particular type of adsorption process. It consists of the adsorption of chemical species by a biomass (living or dead). In wastewater treatment it is defined as “the ability of biological materials to accumulate heavy metals in wastewater through metabolic mediation or chemical capture means” (Volesky, 2003).

Lignocellulosic biomass obtained from fruit and vegetable waste is considered one of the cheapest sources for bioadsorbent production that plays an important role in the removal of traces of contaminating metals from wastewater (Basso et al, 2002). Citrus waste is one of the most important sources because it is rich in carbohydrates and has a low lignin content (Ververis et al, 2007).

Citrus waste includes shells, pulp and membrane residues, and seeds, which make up approximately 40-60% of the whole fruit. This amount exceeds 110-120 million tonnes per year worldwide (Mahato et al, 2020).

Among the fundamental characteristics that distinguish a good bioadsorbent are taken into account: its high porosity, its large contact surface and the specific adsorption sites (Valladares-Cisneros et al, 2018).

The biomaterials used in these bioadsorption processes act in short contact times and generate high quality effluents by different mechanisms (Sharma et al., 2007). In the presence of heavy metals, the mostly accepted mechanism is ion exchange, especially in divalent metal ions that are exchanged with polysaccharides' own ions present in biomass. Most sorbents contain Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} salts in their structures. These cations can be exchanged for the metal ions being attached to the material. (Li et al., 2008). However, bioadsorption mechanisms depend on the metal and sorbent material in each case. However, due to the complex structure of the different bioadsorbents, it is considered that more than one mechanism may appear simultaneously in the bioadsorption of heavy metals (Villaescusa et al., 2004).

The set of physical and/or chemical processes that lead to the selective separation of the polymers that make up biomass are fractionation processes. Polysaccharides, cellulose and hemicellulose are hydrolyzable in acidic media obtaining sugary solutions. Hemicellulose is the most easily attackable polymer, while lignin is little affected by acids and remains as solid residue. Alkaline treatments or hot water treatments under moderate conditions dissolve only hemicellulose. Polysaccharides are difficult to oxidize, while lignin is easily degraded by oxidative methods. (Feng &Guo, 2012).

Citrus peel is mainly composed of cellulose, pectin (galacturonic acid), hemicellulose, lignin, chlorophyll pigments and other low molecular weight compounds, including limonene. These components contain several functional groups, such as carboxyl and hydroxyl, which make citrus peel a potential adsorbent material to remove metal ions from aqueous solutions (Titi& Bello 2015).

The use of citrus peel has been carried out under different conditions, such as:

a) Simply washing it with distilled water to remove the dirt attached, dried in acirculating air furnaceat 100-105ºC for 24 h and, after drying, grinding and sieving through a mesh size of 150-mesh and used as such (Ajmal et al, 2000).
b) Washing with deionized water, dried at 70ºC, ground, sifted and treated with NaOH (0.1M) for 24 hours. After decanting and filtration, the treated biomass was washed with deionized water until the solution reached a pH value of 7.0 (Khormaei et al, 2007).
c) Washing it with deionized water, dried in a convection furnace at 50 ° C for 72 h. It is then ground and sieved to a size of approximately 0.1 to 0.2 mm. The influence of different treatments was compared: washing with isopropyl alcohol, alkaline saponification, attack with citric acid and attack with citric acid followed by alkaline saponification (Li et al, 2007).

Traditional techniques used for solvent extraction of natural products are associated with longer extraction times and lower yields. The effects of ultrasound applied to liquid media are associated with the phenomenon of cavitation, which consists in the formation, growth and implosion of nano/microbubbles of gas within the liquid as a result of pressure fluctuations generated by the passage of ultrasonic waves (Adewuyi , 2005; Virot et al., 2010; Shirsath et al., 2012).

The use of ultrasound can be a very useful process for the cleaning treatment of impurities in citrus peels, since ultrasound waves can destroy bonds that hold compounds such as sugars, oils or low molecular weight polymers (Romero de Ávila et al., 2006).

Its use helps to achieve a final product with a degree of consistency useful to be used in both batch and continuous applications. In the latter case, the particle size must be taken into account, resulting in the 500-1000 μm being more effective than the between 250-500 μm (García Raurich et al, 2020).

IV. CONCLUSION

The incorporation of ultrasonic radiation into the chemical treatment allows pectins to be extracted more quickly than by conventional heat treatment.

The inherent physicochemical properties of bioadsorbents significantly influence their adsorption capacity before being chemically treated.

After chemical treatment, the behavior of the bioadsorbent obtained from the lemon peel (LB) is determined by the particle size and by the concentration of $Ca(OH)_2$ used in the alkaline attack, contrary to what was observed in the bioadsorbent obtained of the orange peel (OB).

In batch applications, both the 250-500 μm and 500-1000 μm particle sizes can be used. The choice of particle size is affected by the nature of the adsorbate (metal ion, organic molecule).

In continuous applications, the particle size 500-1000 μm has a better response, since it presents a degree of compaction that allows the homogeneous advance of the eluent at atmospheric pressure.

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Nanotechnology and its Application in Water Treatment: A Review

Porkodi, G[1] and G. Anand[2]

[1]Assistant Professor (Soil Science & Agricultural Chemistry), ICAR-KVK, Cuddalore
[2]Assistant Professor (Agricultural Extension), ICAR-KVK, Vellore

Abstract— *Environmental pollution, mainly caused by toxic chemicals, includes air, water, and soil pollution. This pollution results not only in the destruction of biodiversity, but also the degradation of human health. Pollution levels that are increasing day by day need better developments or technological discoveries immediately. In this sense, Nanotechnology, is the production and art of operating matter at the nanoscale (1–100 nm), offers the potential of novel nanomaterials for treatment of surface water, groundwater, and wastewater contaminated by toxic metal ions, organic and inorganic solutes, and microorganisms. Nanotechnology has three main capabilities that can be applied in the fields of environment, including the cleanup (remediation) and purification, the detection of contaminants (sensing and detection), and the pollution prevention. Different nanomaterials and their application in water treatment, purification and disinfection is reviewed in this article.*

Keywords— Nanotechnology, Nanoparticles, Water Purification, Water Remediation, Wastewater treatment.

I. INTRODUCTION

In this day and age where enterprises have been modernized and propelled, our condition is filled with different kinds of toxins transmitted from human exercises or mechanical procedures. Instances of these toxins are carbon monoxide (CO), chlorofluorocarbons (CFCs), substantial metals (arsenic, chromium, lead, cadmium, mercury and zinc), hydrocarbons, nitrogen oxides, natural mixes (unpredictable natural mixes and dioxins), sulfur dioxide and particulates. Human exercises, for example, oil, coal and gas burning, can possibly change outflows from regular sources. Notwithstanding air contamination, there is additionally water contamination brought about by different elements, including waste removal, oil slicks, spillage of manures, herbicides and pesticides, results of modern procedures and burning and extraction of petroleum products.

Contaminants are for the most part discovered blended noticeable all around, water and soil. Along these lines, we need an innovation that can screen, recognize and, if conceivable, clean the contaminants from the air, water and soil. Right now, offers a wide scope of capacities and innovations to improve the nature of existing condition.

Nanotechnology is additionally used to forestall the arrangement of toxins or contaminants by applying the material innovation, mechanical procedures and others. Consequently, three significant utilizations of nanotechnology in the fields of condition can be classified, to be specific

1) Restoration (remediation) and purification of contaminated material,
2) Pollution detection (sensing and detection) and
3) Pollution prevention.

With rapid increment of pollutant species and concentration, the development of instruments that able to treat and prevent it is necessary.

II. NANOTECHNOLOGY FOR CLEAN WATER

About 30% of all water on the Earth is not surrounded in the ice or glaciers and only 0.08% of it is clean water (Krantzberg *et al.,* 2010), a similarity of 1 teaspoon of water versus a 5 litre container of water. As of late, water has become a vital

issue, and it is very difficult to tackle the related issues. The advancement of nanotechnology can be utilized to improve water quality. A few strategies that can utilize nanotechnology use responsive media for separation and filtration, bioremediation and disinfection.

Remediation is the method to evacuate, minimize or neutralize the water contaminants that can harm human wellbeing or environments. Remediation technologies can be divided into three classifications, in particular

1) Thermal method

2) Physicochemical method and

3) Biological method

Most customary strategies, for example, extraction, adsorption and oxidation are less effective, costly and tedious, whereas the more environmentally friendly biological degradation is inexpensive, but very time-consuming. A propelled technique that can be utilized is nanomaterials, with improved affinity, capacity and selectivity for heavy metals and other contaminants. The benefits of utilizing nanomaterials are their higher reactivity, larger surface contact and better removal ability. There are a few instances of nanoparticles and nanomaterials that can be utilized for remediation of water, for example zeolites, carbon nanotubes (CNTs), self-amassed monolayers on mesoporous bolsters, biopolymers, single-enzyme nanoparticles, nanoparticles of zero valent iron (ZVI), among others.

III. NANOTECHNOLOGIES FOR WATER REMEDIATION

The use of metals and chemicals in process industries has resulted in the generation of large quantities of effluent that contain high levels of toxic heavy metals, whereas mining and mineral processing operations also generate toxic liquid wastes (Coetser *et al.,* 2007). Moreover, groundwater is often contaminated by spills, agricultural practices, past waste disposal practices and leaking underground storage tanks (Kemper 2004; Foley *et al.,* 2005). The presence of different organic and heavy metal contaminants in these, as well as other environmental water sources has a large environmental, public health and economic impact. In addition to highly toxic metallic cations such as arsenic (As), lead (Pb), chromium (Cr), cadmium (Cd), and mercury (Hg) (Jarup 2003; Lee *et al.,* 2005), inorganic anions such as nitrate (NO_3^-) and perchlorate (ClO_4^-) are also of concern. Whereas high levels of nitrates in drinking water may be harmful to newborn babies and contribute to cancer (Yang and Lee 2005), perchlorate, which has emerged as a high profile contaminant and has consequently received considerable regulatory attention (Cheng *et al.,* 2007), has been reported to lead to hypothyroidism in adults (Blount et al. 2006). Moreover, almost all of the chlorinated aromatic compounds exhibit high toxicity and several of these compounds are carcinogenic (Xu *et al.,* 2005b). Notably, trichloroethene (TCE) is considered to be one of the most common hazardous organic contaminants found in groundwater and has been linked to liver damage and impaired pregnancies in humans (Nutt *et al.,* 2006). In addition, halogenated aromatic compounds have become a serious environment contamination problem because they have a long life, are chemically stable and are non-biodegradable (Keum and Li 2004).

Most of the traditional technologies such as solvent extraction, activated carbon adsorption, and common chemical oxidation, whilst effective, very often are costly and time consuming (Schwarzenbach *et al.,* 2006). Biological degradation is environmentally friendly and cost-effective; but it is usually time-consuming (Ahluwalia and Goyal 2007). Thus, the ability to remove toxic contaminants from these environments to a safe level and doing so rapidly, efficiently, and within reasonable costs is important (Savage and Diallo 2005). Nanotechnology could play an important role in this regard. An active emerging area of research is the development of novel nanomaterials with increased affinity, capacity, and selectivity for heavy metals and other contaminants. The benefits from use of nanomaterials may derive from their enhanced reactivity, surface area and sequestration characteristics (Zhang 2003; Li *et al.,* 2006). A variety of nanomaterials are in various stages of research and development, each possessing unique functionalities that is potentially applicable to the remediation of industrial effluents, groundwater, surface water and drinking water (Table 1).

TABLE 1
EXAMPLES OF NANOSTRUCTURED AND NANO-REACTIVE MEMBRANES FOR USE IN WATER FILTRATION

Membrane	Pollutant	Reference
Nanostructured membranes		
Carbon nanotubes	Carbon nanotubes	Srivastava *et al.* (2004)
Nanoreactive membranes		
Alumina membrane formed from A-alumoxane	Synthetic dyes	DeFriend *et al.* (2003)
Alumina membranes functionalized with poly(styrene sulfonate) or poly(allylamine hydrochloride)	Divalent cations	Stanton *et al.* (2003)
Silica and cellulose-based membranes functionalized with amino acid homopolymers	Metal ions	Bhattacharyya *et al.* (1998)
Polycarbonate track-etched membranes functionalized with amino acid homopolymers	Metal ions	Hollman and Bhattacharayya (2004)
Pt/Fe laden cellulose acetate film	Trichloroethylene (TCE)	Meyer *et al.* (2004)
Zero-valent Fe laden cellulose acetate membrane	TCE	Wu *et al.* (2005)
Ni/Fe or Pd/Fe laden polyacrylic acid/polyether sulfone composite membranes	TCE	Xu *et al.* (2005a)
Ni/Fe laden cellulose acetate membrane	TCE	Wu and Ritchie (2006)
Alumina or polymeric membranes with gold nanoparticles	4-nitrophenol	Dotzauer *et al.* (2006)
Polymer-impregnated ceramic TiO2 filters	Polycyclic aromatic hydrocarbons (PAHs)	Arkas *et al.* (2006)
Polymer-impregnated ceramic alumina & silicon-carbon filters	Trihalogen methanes, PAHs, pesticide	Allabashi *et al.* (2007)

3.1 Water remediation with iron nanomaterial

A typical framework that has been created throughout the years to remediate water is known as a 'pump and treat' system (Tratnyek and Johnson, 2006). The system is intended to pump water from the soil to the surface, to deal with it and afterward to infuse it once more into the ground (Fig 1). Until 1998, the pump and treat system was as yet utilized as an approach to remediate water. Another approach to remediate water is by utilizing permeable reactive barrier (PRB). PRB cleans subsurface groundwater and remediate without the need to carry the water to the surface (Fig. 2). This treatment can be utilized to tidy up contaminations, for example, chlorinated hydrocarbons, aromatic nitro compounds, polychlorinated biphenyls (PCBs), pesticides and chromate compounds (Yunus *et al.,* 2012).

The PRB technique (Fig.2), which is expected to replace the pump and treat method, has some disadvantages, such as its cost (it is very expensive) and there is no definite time of replacement. Once in a while the reactivity of iron is reduced due to the presence of impurities in the form of metal hydroxide and metal carbonate compounds. Several alternative methods have been done to overcome these shortcomings. In the early 1990s, it was found that some zero-valent metals such as iron (ZVI), proposed as a filter material of PBR, can handle or diminish perilous contaminants in the water in large quantities (Uyttebroek, *et al.,* 2010). The small particle size makes nano-iron capable of multifunctional use for remediation purposes. In general, ZVI is classified into two types:

1) Nnanoscale ZVI (nZVI) and

2) Reactive nanoscale iron product (RNIP).

They are made using the fundamental techniques of nanotechnology. nZVI particles have a diameter of 100–200 nm composed of iron (Fe) with a valence of zero, though RNIP particles comprise of 50/50 wt% Fe and Fe_3O_4 . Although real application data is not yet produced, the potential use of ZVI is good. Miehr et al. (2004) have identified that ZVI has high reactivity to a enormous number of contaminants, including Cu^{2+}, chlorinated hydrocarbons, CrO^{2-} and NO^{3-}.

Notwithstanding the utilization in PRB, nano-iron can also be used by means of direct injection into the soil, sediment or solid waste. Try to blend the nanoparticles with water to form slurry. Once injected, the particles will remain in the form of a suspension and a treatment zone will be formed. Another way is to attach the nanoparticles to a solid matrix such as activated carbon which has proven very effective.

Nano-iron could be subbed with different metals. Metals, for example zinc and tin have the ability to reduce contaminants such as iron. Two metal alloys such as iron and iron–nickel–copper have been utilized to degrade trichloroethene and trichloroethane (Carroll *et al.*, 2012). The commonly used metals are palladium, silver, platinum, cobalt, copper and gold, while aluminum is used as an inert.

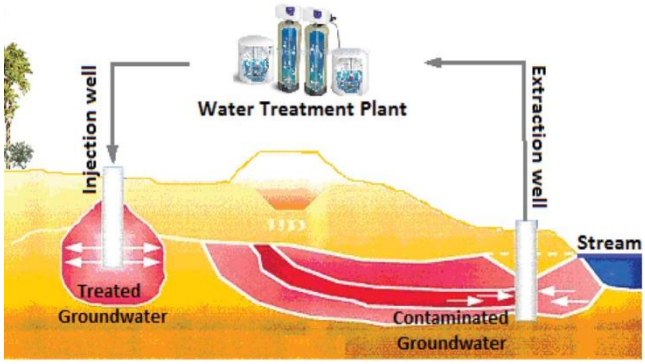

FIGURE 1: Pump and treat system

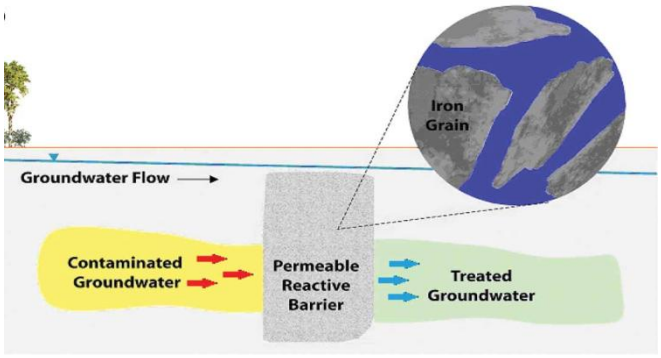

FIGURE 2: Permeable Reactive Barrier

3.2 Water remediation with ferritin

Ferritin is an iron-containing protein that is able of controlling the formation of mineralized structures. Ferritin can be found in animals and plants and its capacity is to store iron. Ferritin is formed when 24 polypeptides that are structurally similar to each other form a cage-like protein structure (Theil, 1987). Once the cage is formed, the iron molecules can enter the cavity through the protein shell, where the mineralization process transforms iron molecules into ferrihydrite nanoparticles.

Researchers have discovered the ability of ferritin to remediate toxic metals and chlorocarbon under visible light or solar radiation (Moretz, 2004). The advantages of ferritin over ordinary iron catalyst are:

1) Ferritin does not react under photoreduction; and

2) It is also more stable.

One obvious application of ferritin which has been proven in the laboratory is to change chromium Cr(VI) into Cr(III). Cr(VI) is carcinogenic pollutant that is generally contained in the industrial waste, while Cr(III) is formed naturally as a Cr compound, which is less poisonous and insoluble in water.

3.3 Water remediation with polymer nanoparticles

Polymer nanoparticles have different utilization, including water treatment and sunscreen. Using a similar principle as surfactant micelles, polymeric nanoparticles have amphiphilic properties, where every particle has hydrophobic and hydrophilic parts. When water is available, the polymer will form a polymer cell with a diameter of several nanometres inside the hydrophobic part, while the hydrophilic part is outside. On polymer nanoparticles, crosslink occurs prior to the aggregation of particles so that their stability is maintained. Amphiphilic polyurethane (APU) nanoparticles have good prospects as a remediation agent. Tungittiplakorn *et al.* (2004) used a poly urethane acrylate anionomer (UAA) and poly (ethylene glycol) modified urethane acrylate (PMUA) as the reactant/precursor chains.

In the application, polymeric nanoparticles offer a solution for commonly used conventional surfactants to improve remediation of hydrophobic organic contaminants using a pump and treat system. These contaminants are generally classified into nonaqueous-phase liquid which adheres firmly to the ground so that it is difficult to cleanse, leading the remediation process to be less and less effective. In this manner, a surfactant is needed to tidy up these contaminants.

3.4 Water remediation with zeolites

Zeolites are inorganic crystalline porous materials that have a highly ordered structure and are generally comprised of silicon (Si), aluminium (Al), and oxygen (Camblor *et al.*, 1998). Their physicochemical characteristics such as high mechanical and chemical resistance in addition to their high surface area have formed the basis for their widespread use in catalysis, separation, and ion-exchange (Tavolaro *et al.*, 2007). Although conventional synthesis methods produce zeolites on the scale of 1 to 10 µm, nanoscale zeolites, which comprise discrete, uniform crystals with dimensions ranging from 5 to 100 nm, have been synthesized successfully (Ding and Zeng 2007). Compared to micron-scale zeolites, the nanocrystalline

zeolites exhibit greater external surface areas, smaller diffusion path lengths and a greater aversion to coke formation. The Si/Al ratio of zeolites can be varied either during synthesis or post-synthetically and, in general, zeolites have a low Si/Al ratio and therefore a high ion-exchange capacity. Conversely, if the Al content and thus the ion-exchange capacity of a zeolite is reduced, it becomes more hydrophobic or organophilic in its adsorptive characteristics (Tavolaro *et al.*, 2007).

In contrast to nanocrystalline zeolites, micron-scale zeolytes have been tested for a variety of environmental applications. NaP1 zeolites, which can be synthesized inexpensively by alkaline hydrothermal activation of coal fly ash in 1–2 M NaOH solutions, have been used successfully to remove heavy metals from acid mine wastewaters (Moreno *et al.*, 2001) and to remove Cr(III), Ni(II), Zn(II), Cu(II), and Cd(II) from metal electroplating wastewaters (Alvarez-Ayuso *et al.*, 2003). Moreover, surfactant-modified zeolites (SMZ) have also been used to not only remediate water containing the radioactive species ^{137}Cs and ^{90}Sr found in nuclear plant wastewater, but also to adsorb both tetrachloroethene and chromate (CrO_2^-) from groundwater, and to remove petroleum hydrocarbons such as benzene, toluene, ethylbenzene, and xylene from oilfield wastewater (Bowman 2002). In contrast, nanocrystalline zeolites appear to be in the research phase and no specific water remediation processes have been proposed. The synthesis of nanocrystalline NaY zeolites capable of absorbing Ca. 10% more toluene and Ca. 30% more nitrogen dioxide relative to commercial NaY zeolites have, however, been described (Song et al. 2005). In addition, nanocrystalline ZSM-5 zeolites, with a particle size of 15 nm, have been reported to adsorb Ca. 50% more toluene than ZSM-5 samples with larger particle sizes (Song *et al.*, 2004), furthermore suggesting that such nanoscale zeolites may be potentially superior to traditional micron-scale zeolite sorbents

3.5 Water remediation with carbon nanotubes

Carbon nanotubes (CNTs) are cylinder-shaped macro- molecules of which the walls of the tubes are made up of a hexagonal lattice of carbon atoms and they are capped at their ends by one half of a fullerene-like molecule (Iijima 1991). CNTs can be divided essentially into single-walled carbon nan- otubes (SWCNTs) and multi-walled carbon nanotubes (MWC-NTs) based on the principle of hybridized carbon atom layers in the walls of CNTs. Whereas SWCNTs have diameters ranging from 0.3 to 3 nm, the MWCNTs are composed of a concentric arrangement of many cylinders and can reach diameters of up to 100 nm (Iijima and Ichihashi 1993). Since their discovery, carbon nanotubes have attracted considerable attention which stems from their out- standing structural, mechanical, and chemical properties (Popov 2004; Miyagawa et al. 2005). In addition to their potential application in electronics, chemical and biological sensing, catalysis, and reinforced composite materials (Polizu *et al.*, 2006), their large surface area and tubular structure also make CNTs a promising adsorbent material.

Carbon nanotubes (CNTs) have been evaluated for the sorption of 1, 2-dichlorobenzene (DCB) and it was reported that they can be used in a wide pH range of 3 to 10 and that sorption of DCB onto the CNTs took 40 min to reach equilibrium with a maximum sorption capacity of 30.8 mg/g. More recently, novel sorbents with high surface areas (in excess of 189 m^2 /g) have been developed that consists of cerium ox- ide supported on either carbon nanotubes (CeO2 -CNT) (Peng *et al.*, 2005) or on aligned carbon nanotubes (CeO_2 -ACNTs) (Di *et al.*, 2006). Although the CeO_2 -CNTs were effective sorbents for As(V), addition of the divalent cations Ca(II) and Mg(II) at concentrations ranging between 1 and 10 mg/l was reported to increase the amount of sorbed As(V) (from 10 to 82 mg/g) (Peng *et al.*, 2005). The CeO_2 -ACNTs exhibited high Cr (VI) adsorption efficiency from drinking water at a pH range of 3 to 7.4. The largest Cr(VI) adsorption capacity reached was 30.2 mg/g at pH 7.0, which was ca. two times higher than that of activated carbon and Al_2O_3 (Di *et al.*, 2006).

Nanoporous activated carbon fibers (ACFs), prepared by electrospinning of CNTs, with surface areas ranging from 171 to 483 m^2 /g, have been synthesized. Their organic sorption capability was compared to granular activated carbon and in all cases, the ACFs had much higher organic sorption equilibrium constants for benzene, toluene, xylene, and ethylbenzene than granular activated carbon (Mangun *et al.*, 2001)

Multiwalled carbon nanotubes (MWCNTs), pre-treated with nitric acid, have been used successfully for the sorption of different heavy metal ions, including Pb(II) (97.08 mg/g), Cu(II) (24.49 mg/g), and Cd(II) (10.86 mg/g) from an aqueous solution. These sorption capacities were three and four times higher than those of powder and granular activated carbon, respectively (Li *et al.*, 2003).

Salipira *et al.*, (2007) reported that copolymerization of cross-linked nanoporous polymers with functionalized CNTs resulted in novel polymers capable of efficient removal of organic pollutants from water. These novel polymers removed p-nitrophenol by 99% from a 10 mg/l spiked water sample, whereas granular activated carbon removed only 47%. Moreover, these polymers removed trichloroethylene (10 mg/l spiked sample) to non-detectable levels (detection limit <0.01 parts per billion (ppb)) compared to 55% for granular activated carbon.

In addition to their ability to sorb heavy metals and organic compounds, CNTs may also be useful as adsorbents for toxins and herbicides in environmental water. Based on a report by Long and Yang (2001), indicating that significantly higher dioxin removal efficiency is found with CNTs than with activated carbon, MWCNTs have subsequently been used successfully as the sorbent for the preconcentration and separation of chlorophenols and different herbicides, including triazine herbicides, DDT and its metabolites, as well as sulfonylurea herbicides, from river, tap and lake water samples. The ability of CNTs to adsorb MC-RR and LR, the most prevalent microcystin (MC) toxins produced by cyanobacterial bloom, has also been evaluated. Cyanobacteria blooms in natural waters have become a growing environmental problem worldwide due to the increased discharge of nitrogen- and phosphorus-containing wastewater into rivers and lakes, and MC-RR and LR have been found in fresh water bodies as well as in oceans (Haider *et al.,* 2003). Generally, MCs are very stable in the water body and resistant to removal from drinking water by traditional water treatment technology. Compared to wood-based activated carbon and clays (sepiolite, kaolinite and talc), the adsorption amounts of MCs in lake water by CNTs, of which the outer diameters ranged from 2 to 10 nm, were four times higher (Yan *et al.,* 2006), suggesting that CNTs may be a potentially promising nanomaterial for the removal of MCs from drinking water.

Whilst the above studies indicate that CNTs are potentially efficient adsorbents for a variety of pollutants in both drinking and environmental waters, their practical application may be hampered by their high cost, as well as their poor solubility and the difficulty in collecting them from their dispersing medium. It is therefore interesting to note that in a recent study, Lu *et al.,* (2007) performed statistical analyses on the replacement cost of NaClO-oxidized SWCNTs and MWCNTs, both of which had been reported to be effective Zn(II) sorbents and could be reused through 10 cycles of water treatment and regeneration. The results of their analyses revealed the use of such reusable carbonaceous sorbents can indeed be cost-effective in spite of their high unit cost at the present time. Moreover, Jin *et al.,* (2007) reported a simple method for fabricating magnetic Fe nanoparticle functionalized MWCNTs, which not only displayed improved water solubility, but could also be recovered easily from the water by magnetic separation. The functionalized water-soluble MWC- NTs (Fe-MWCNT-CH2COONa) were also tested as a sorbent using four model aromatic compounds. The results indicated that addition of 10 mg of Fe-MWCNT-CH_2COONa to aqueous solutions containing 8.6 ppb of the corresponding model compound, adsorbed benzene (79%), toluene (81%), dimethylbenzene (83%), and styrene (88%) very effectively. Notably, after being washed several times with methanol and dried in vacuum, the Fe-MWCNT-CH_2COONa could be reused.

IV. CONCLUSION

Water plays a role in day to day of human activity, it is becoming an increasingly scarce resource in many parts of the world. Besides utilization of non-traditional sources for production of high-quality freshwater and the conservation and protection of water bodies from pollution, equally important is the development of innovative new technologies and materials whereby challenges associated with the provision of safe potable water can be addressed. It is widely recognized that nanotechnology and its applications play an important role in resolving issues relating to water shortage and water quality. Due to large surface areas of nano particles, size and shape dependent catalytic properties, significant efforts are started to explore uses of nanomaterials in applications such as membrane separations, catalysis and adsorption. In addition, nanomaterials can be functionalized with different chemical groups to increase their attraction toward a given compound, thus resulting in ligands that are not only recyclable but also have a high capacity and selectivity for organic and inorganic solutes, just as lethal metal ions and inorganic anions in aqueous solutions.

While much consideration has been focused on the development and potential benefits of nanomaterials in water treatment processes, concerns have also been raised regarding their potential human and environmental toxicity. Undoubtedly, contemplates have demonstrated that the similar properties of nanomaterials that make them alluring (e.g., size, shape, structure, reactivity) may likewise make them be lethal. It is difficult, however, to assess the effect of nanomaterials on health and the environment because the methods and tools for such a task have not been well developed yet. In addition, common frameworks for risk research, risk assessment, and risk management are lacking at present. It is vital that these processes be developed and investigated to ensure that nanomaterials are as safe as possible, while reaching their full potential. Despite these information gaps, it is sure that new nanomaterials, particularly in water and wastewater treatment, will play key roles in guaranteeing adequate and good quality water to satisfy the ever-increasing need for consumable water.

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Assessment of Nutriseed Pack Technology on Maize in Cuddalore District

Porkodi, G

Assistant Professor (Soil Science & Agricultural Chemistry), ICAR-Krishi Vigyan Kendra, Vridhachalam, Cuddalore District, India

Abstract— *On Farm Trail was conducted in five locations of Mangalore and Nallore Block of Cuddalore District to assess the 'Nutriseed pack' technique on maize. Nutriseed pack is a small tubular form that is 20 mm diameter, 10 cm height. Nutriseed pack contains seed at top, manure in the middle and fertilizer at bottom. The experiment consisted of three treatments viz., Farmer practice (TO1), recommended dose of fertilizer (TO2) and Nutriseed Pack (TO3) The results revealed that, the grain yield recorded with different treatment ranged between 65.44 to 74.00 q ha^{-1}. Among the technologies, Nutriseed pack (TO3) was recorded more yield of 74.00 q ha^{-1} (13.08% increased yield over control) than that of 71.92 q ha^{-1} recommended dose of fertilizer applied in the field followed by farmers practice (65.44 q ha^{-1}). Similar trend of results were also observed in yield parameters. Enrichment of manure pellet and fertilizer that is Nutriseed pack was effective when compared to other technologies.*

Keywords— Nutriseed Pack, Hybrid Maize, Yield, Yield Attributes.

I. INTRODUCTION

After rice and wheat, maize is the third most important field crop in India. It accounts for ~9 per cent of total food grain production in the country. Maize has three growing seasons in India, *viz., Kharif, Rabi and Spring*. Fertilizers play an important role in increasing the maize yield to the tune of 40-45 per cent over unfertilized crop. Normally fertilizers are broadcasted. Many times, straight fertilizers are used as the source of nutrients. Application of straight fertilizer leads to loss of nutrient through leaching and volatilization. In order to manage these losses split application is recommended for soluble fertilizers especially for urea and muriate of potash. Now a days, newly emerging technology namely "Nutriseed Pack Technique" is developed in the Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University (TNAU), Coimbatore. This technology reduces the nutrient losses in the soil. Hence, Nutriseed pack technique helps in improving the nutrient use efficiency and yield. The present study was carried out to assess Nutriseed pack technology on maize in Cuddalore District.

II. MATERIALS AND METHODS

The experiment was conducted in the farmer's field of Nallur and Mangalore Block of Cuddalore District, Tamil Nadu, India. The texture of the experimental soil was sandy loam and pH 8.15. The nutrient status of the experimental soil was low organic carbon (0.47 %), low in available nitrogen, medium in available phosphorus and high in available potassium. The hybrid maize COH(M) 6 was grown as test crop. The technologies *viz.*, TO1 - Farmers practice, TO2 - Recommended doses of fertilizers (250:75:75 kg N, P_2O_5 and K_2O ha^{-1}) and TO3- Nutriseed pack technology were taken for this study.

Nutriseed pack is a small tubular assembly (20 mm diameter, 10 cm height), which contains seed at top, manure in the middle and fertilizer at bottom. For maize crop, 100 % recommended dose of NPK fertilizers was calculated and mixed up thoroughly and fertilizer pellet was prepared by using the fertilizer pellet making machine. Then each fertilizer pellet was encapsulated in polyester coated paper pouch having micropores and sealed by sealing machine. Manure pellet was prepared by enriching vermicompost with micronutrients. During enrichment, 60% of moisture was maintained. To achieve complete enrichment frequent mixing of manure was done. After 10 days of incubation, the enriched manure was pelletized by using manure pellet making machine. Nutriseed pack was composed by placing encapsulated fertilizer pellet at bottom, manure pellet in the middle and seed (hybrid maize COH(M) 6 with bioinoculant mixture (*Azosprillum*, phosphobacteria and

Trichoderma) on the top and then wrapping them together by newspaper as a tubular roll. Instead of sowing seeds, 'Nutriseed packs' were placed in soil at 5 cm depth.

The 'Nutriseed packs' was placed on the sides of the ridges horizontally at a spacing of 60 × 30 cm so as to accommodate the recommended plant population. For surface application, 100% P and K were applied basally and 50% N was applied at basal. The remaining 50% of N was applied as 25% at 25th day after sowing and 25% on 45th day after sowing. First irrigation was given immediately after sowing. Subsequent irrigations were scheduled once in three days. Growth parameters and dry matter production were observed at growth stages. Yield and yield attributes were recorded.

III. RESULT AND DISCUSSION

3.1 Plant height

The plant height was recorded at vegetative stage, tasseling stage, milking stage and harvest stage. Plant height ranged between 48.6 to 75.1 cm at vegetative stage, 119.4 to 151.9 cm at tasseling, 151.7 to 181.0 cm at milking and 169.1 to 208.1 cm at harvest stage of maize (Table 1). The results revealed that at all growth stages of maize, 'Nutriseed pack' registered higher plant height when compared to farmers practice. This obvious effect of 'nutriseed pack' could be attributed to placement of N, P and K fertilizers in the root zone, which would have synergistically induced crop growth (Kalaiselvi and Arulmozhiselvan, 2013). The lowest height of maize hybrid registered in recommended dose of fertilizer followed by farmers practice plots irrespective of the growth stages

TABLE 1
PLANT HEIGHT OF HYBRID MAIZE AT DIFFERENT STAGES

Treatment	Vegetative stage (cm)	Tasseling stage (cm)	Milking stage (cm)	Harvesting stage (cm)
TO 1 - Farmer Practice	48.6	119.4	151.7	169.1
TO 2 - RDF Dose of Fertilizer	70.2	138.3	170.4	191.5
TO 3 - Nutriseed pack	75.1	151.9	181.0	208.1

3.2 Dry matter production

Dry matter production of maize crop recorded at vegetative stage, tasseling stage, milking stage and harvest stage ranged from 2350 to 5006, 5946 to 7821, 6471 to 9588 and 7890 to 11469 kg ha^{-1} respectively (Table 2). The highest dry matter production of 5600 kg ha^{-1} at vegetative stage, 7821 kg ha^{-1} at tasseling stage, 9588 kg ha^{-1} at milking stages and 11456 kg ha^{-1} at harvesting stage were recorded in treatments that received continuous application of nutrients through 'nutriseed packs'. This might be due to deep placement of NPK fertilizers and enriched manure in the root zone. Similar findings were observed by Muhammad *et al.* (2002).

TABLE 2
DRY MATTER PRODUCTION OF HYBRID MAIZE (kg ha^{-1})

Treatment	Vegetative stage	Tasseling stage	Milking stage	Harvesting stage
TO 1 - Farmer Practice	2350	5946	6471	7890
TO 2 - RDF Dose of Fertilizer	3642	4675	8311	10156
TO 3 - Nutriseed pack	5006	7821	9588	11469

3.3 Yield attributes and yield of maize

The yield and yield attributing parameters *viz.*, number of grains per cob, 100 grain weight cob length was recorded (Table 3). Number of grains per cob, 100 grain weight and cob length ranged between 469.22 to 547.2, 30.5 to 35.6 g and 18.84 to 20.26 cm respectively. Yield attributes were high in 'nutriseed pack' over other treatments. This might be the indication of

adequate supply of nutrients at all critical stages of the plant growth. Similar results were observed by Singh and Singh (2006).

The grain yield ranged between 65.44 to 74.00 q ha^{-1}. Among the technologies, Nutriseed pack technology was recorded more yield of 74.00 q ha^{-1} (13.08% increased yield over control) than that of 71.92 q ha^{-1} recommended dose of fertilizers applied in the field followed by farmers practice (65.44 q ha^{-1}). The results revealed that enriched manure pellet was more effective on increasing yield of maize over surface application of fertilizer. Radhika (2010) reported that Nutriseed Pack with Furadan resulted in the highest grain yield of 5290 kg ha^{-1} under surface irrigation, which was 832 kg higher than surface broadcast; and of 4489 kg ha^{-1} under drip irrigation, which was 525 kg higher than surface broadcast. Placement of Nutriseed Pack with 125% NPK was comparable to 100% NPK Nutriseed Pack with Neem, Furadan, manure + fertilizer mixture indicating a saving of 25% N, both under surface and drip irrigation.

Similar findings were observed by Asha and Arulmozhiselvan, (2006), Kalaiselvi and Arulmozhiselvan (2013), Muthukrishnan and Arulmozhiselvan (2013) and Hota *et al.*, (2017).

TABLE 3
YIELD AND YIELD PARAMETER OF HYBRID MAIZE

Treatment	Grain yield (q ha^{-1})	No. of grains / cob	100 grain weight (g)	Cob length (cm)
TO 1 - Farmer Practice	65.44	469.22	30.5	18.84
TO 2 - RDF Dose of Fertilizer	71.92	499.54	32.7	19.72
TO 3 - Nutriseed pack	74.00	547.2	35.6	20.26

3.4 Economics

The economics of the trial showed that the highest net return (Rs. 59500) with the Cost Benefit ratio of 2.01 were obtained in Nutriseed pack technology when compared to farmers practice (B:C ratio 1.50).

IV. CONCLUSION

In conclusion, we can say that nutrient support is provided by Nutriseed pack to the highest extent to the plant in the root zone. Weeds have less chance to tap the nutrients from Nutriseed Pack. Slow release of nutrients support the crop throughout the cropping period and results in higher yields. The Nutriseed pack technique has shown better result than any other fertilizer placement or application because of pelleted form as well as point placement and also has proven to reduce the fertilizer dose and increase the fertilizer use efficiency. Hence, Nutriseed pack technology was found to be a novel way of achieving high yield in hybrid maize.

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Relationship between California Mastitis Test Scores and Somatic Cell Counts in Different Crossbred Dairy Cattle Genotypes

Daniel. C.V. Tarbal[1], Joseph. O. Jung' a[2], Rawlynce. C. Bett[3]

Department of Animal Production, College of Agriculture and Veterinary Sciences, University of Nairobi, P.O. Box 29053 - 00625 Kangemi, Nairobi

***Abstract*—** *The objective of this study was to evaluate relationship between California Mastitis Test scores (CMT) and Somatic Cell Counts in different crossbred dairy cattle genotypes. A total of 152 milk samples were screened for mastitis using the California Mastitis Test (CMT) kit. Somatic Cell Count (SCC) in milk samples were analysed directly using microscopic method. Based on the analysis of CMT score, the study found out that 55.92 % of udder quarters were negative while 43.99 % were positive for subclinical mastitis. The Least Square Difference (LSD) for pairwise comparison between CMT scores and lactation stage were significantly different between First and second lactation at 0.25±0.11; second and third at 0.27±0.0118 at P≤ 0.05. The means of SCC among the breeds were significantly different at P≤0.05; Ayshires and Friesians (68,055±18.82 cells/ml); Ayshire and Guernsey (71,976±23.844 cells/ml); Friesians and Jerseys (64.863±21.429 cells/ml); and Guernsey and Jersey (68.78±25.952 cells/ml). In conclusion, this study provides baseline information in the area of selection for mastitis resistant breeds of dairy cattle. This study also strongly recommends the use of this technique in screening for somatic cell counts in udder quarters of crossbred dairy cattle*.

Keywords; Crossbred, Mastitis resistant, Somatic Cell Count, Somatic Cell Score.

I. INTRODUCTION

Good management practices especially on udder health are fundamental for quality and profitability of dairy production (Sadeghi & Amer, 2015; Gupta *et al*,. 2016). Somatic Cell Counts (SCC) are an important primary indicator of milk hygiene (Jingar *et al.,* 2017). They are also linked to the level of profitability of dairy enterprises (Hadrich *et al*,.2015; Holland *et al.,* 2015; Jadhav *et al.,* 2016). These cells include; macrophages, polymorphonuclear neutrophils, lymphocytes, and epithelial cells, which resulted from infections of udder quarters. The number of cells are usually reported in milk per millilitre (Division, 2018), and are used internationally to scrutinize/screen milk quality and udder health status in the dairy herds (Li *et al.,* 2014). The SCC above 310,000 cells/ml is the recommended value as a monitor of udder health status (Jadhav *et al.,* 2018). However, the threshold level for assessing and monitoring in dairy herds is often 2.0 x 10^5 cells/ml and below (Division, 2018). Somatic Cells play a critical role in the immune response of infected udder quarters of cows (Li *et al*., 2014; Azmi et al., 2017; Iraguha*et al.,* 2017). The increased somatic cell counts in the milk as a resultof udder tissues' inflammation, which subsequently affects the quality and quantity of milk produced (Division, 2018; Malik *et al*., 2018).

The presence of somatic cells in milk is attributed due to an infection of the mammary glands, which eventually results in mastitic condition of the udder quarters (Balaji *et al*., 2016). Subclinical mastitis does not show visible clinical symptoms, but can results in severe economic losses from discarded milk, the sudden death of cattle, cost of veterinary services, the decline in quality and milk produced (Sadeghi & Amer, 2015; Hadrich *et al*.,2018).

The low heritability of mastitis makes it unfavourable for selection of mastitis resistance breeds of dairy cattle in conventional breeding (Boas *et al.,* 2017). The heritability for milk production traits is usually moderate to high. Therefore, the low SCC could be employed in selection for mastitis resistance in crossbred dairy cattle in an attempt to reduce mastitis incidences the smallholder dairy farmers.

The clinical mastitis is genetically correlated to SCC. The correlation varies from 0.64 to 0.77. Udder health and SCC significantly affect the quality of milk produced by dairy cows (Bhutto *et al.,* 2012). The objective of the present study was to assess the relationship between California Mastitis Test scores (CMT) and Somatic Cell Counts in different crossbred dairy cattle genotypes.

II. MATERIALS AND METHODS

2.1 Study Area

The study was done in Kanyariri Veterinary Teaching Farm, which is a learning and research facility for the University of Nairobi. The farm sit on a 375acre piece of land in Lower Kabete located 2 kilometres West of the College of Agriculture and Veterinary Sciences and 15 kilometres from the Nairobi city centre. Kanyariri farm is on an elevation of 5,600 feet (1,700 meters) above sea level with an average temperature of 18.7˚C. It receives rainfall amount of about 869 mm per annual.

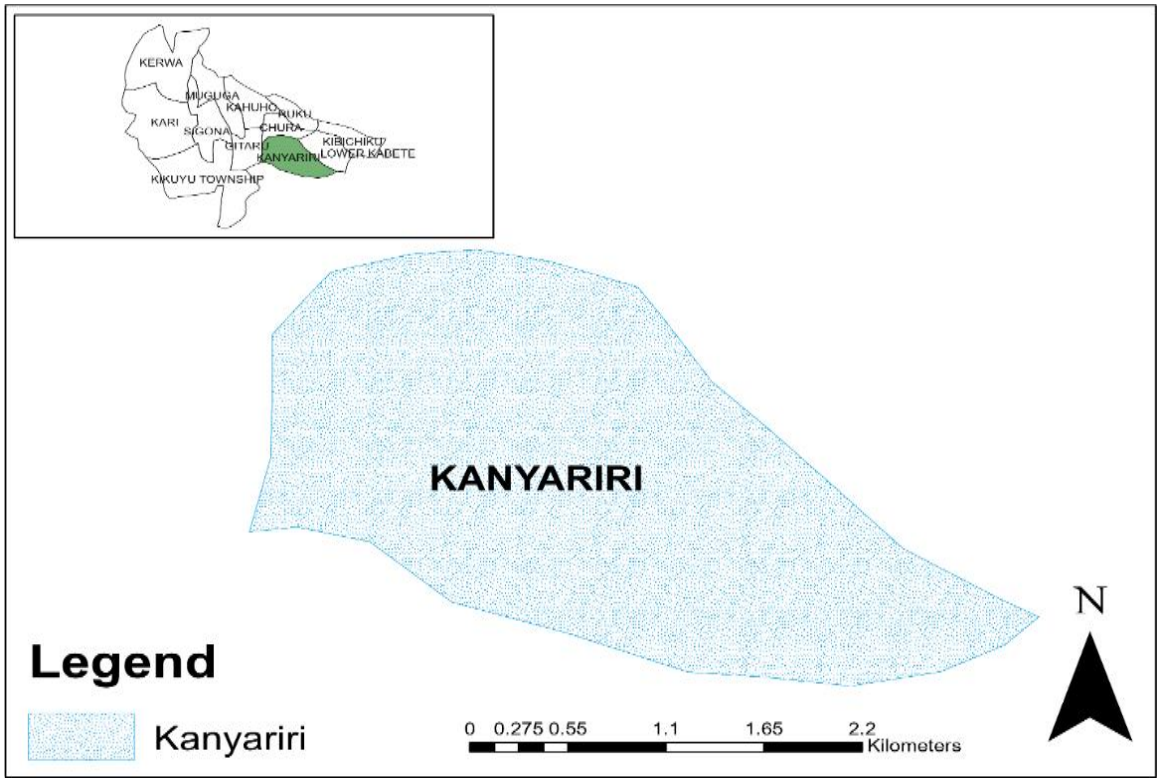

FIGURE 1: A Map of Kiambu showing Kanyariri Veterinary Farm – University of Nairobi

2.2 Sample collection

Thirty-eight crossbred cows were selected based on lactation. A total of 152 quarters from full udder quarters of the 38 cows were screened for mastitis using California Mastitis Test scores (Schalm, 1957). For SCC each of the udder quarters were cleaned using 75 percent ethanol before collecting 5ml of milk samples aseptically into 10ml screw cupped tubes. These were then transported at -20℃ to the Microbiology Laboratory in the Department of Food Science and Nutrition, Faculty of Agriculture, University of Nairobi. Milk samples were stored in a freezer at -21℃ before they could be analyzed for Somatic Cell Counts.

2.3 Microscopic procedure for SCC

The slides were labelled to match the sample container identification numbers. The slides were smeared with the milk samples, stained and allowed to dry (Prescott and Breed, 1910). They were later examined under Electric microscopy with the magnification of 100X (Ferronatto et al., 2018). Somatic Cell Counts were observed as dark-spots which were counted and recorded. To obtain Somatic Cell Scores, SCC were log transformed using the formula Log2 [SCC/100,000 +3] (Rupp *et al.*,1999; Yuan *et al.*, 2013).

2.4 Statistical analysis

The SCC data was analyzed using SPSS version 21.0. To calculate correlation coefficients, Tukey test, LSD and to test if there was a significant difference of breed effect on mastitis susceptibility traits; CMT Scores were analyzed using one-way ANOVA at $P \leq 0.05$ level of significance. The models below were used in testing the effect of breed on SCC.

1) $y_{ij} = \mu + G_i + e_{ij}$

Where y_{ij} is the effect of the SCS in the udder quarters**,** μ is the average for traits, G_i is the breed's effects, e_{ij} is the residual error. The analysis of the association among the breeds with SCC that reflects mastitis susceptibility traits was solved using the equation below;

2) $y_{ij} = \mu + G_i + p_t + e_{ij}$

Where y_{ij} is the observation of somatic cell count, μ is the overall mean of SCC, G_i and , p_t were the fixed effect of breed and the fixed effect of SCC respectively, and e_{ij} residual error

III. RESULTS

Figure 1. Presents the result of the 152 quarters examined for mastitis by California Mastitis Test (CMT) 55.92 % (N=85) were negative for mastitis with a somatic Cell Score range of 0 to 2.0 x 10^5 cells/ml. Those that tested positive for subclinical mastitis were trace (N = 65) and +1 score (N= 2) at 42.67 percent (2.10 x 10^5 cells/ml to 3.0 x 10^5 cells/ml) and 1.32 percent (3.10 x 10^5 cells/ml to 5.10 *x* 10^5cells/ml) respectively.

In Table 1; Tukey test was carried out to determine if there were significant differences between CMT scores and Somatic cell scores (SCS) using one-way ANOVA. Results revealed that there was a significant association between CMT and SCS at the P≤0.05. The analysis showed that all values were greater than High Significant Difference (HSD) values of 0.23, and the least significant difference (LSD) was greater than the mean of 0.17. Further, results indicated that both HSD and LSD were significantly different at P≤0.05. Generally, the result shows that there were significant association between CMT scores and SCS of crossbred dairy cattle genotypes.

TABLE 1
MULTIPLE COMPARISON OF THE EFFECT CMT AND SCS ACROSS UDDER'S QUARTERS OF THE CROSSBRED DAIRY CATTLE.

CMT SCORE	Normal	T	1^+ score
Normal (healthy)	—	0.863* ± 0.1	0.46* ± 0.0023
T	—	—	0.403* ± 0.101
1^+ score	—	—	—

Normal =Negative score for subclinical mastitis, T = Trace (subclinical mastitis), &1^+ score (subclinical mastitis)
**** The significant difference when P≤0.05 level of significance***
CMT Score = California Mastitis Test Scores, SCS = Somatic Cell Scores

Table 2; associations between the age of crossbred dairy cows and CMT scores were significantly different at P≤0.05. An increase of 2.1% in CMT results into an equal in the age. The linear associations between the age and CMT can be used in the prediction of subclinical mastitis.

TABLE 2
REGRESSION BETWEEN AGE (PREDICTOR) AND CMT SCORE OF MILK SAMPLE

ANOVA	SM	df	Mean Square	F	sign
Regression	1.125	1	1.125	4.16	0.043^b
Residual	40.553	150	0.27		
Total	41.678	151			

The independent variable is the Somatic cell count.
R = 0.164, R^2 = 0.027, Adjusted R^2 = 0.021, SE = 0.520, and Y = -0.036 + 1.701.

The table 3; presents that the mean of SCS and Lactation Stages for first and lactation stages (0.25±0.11) and second and third (0.27±0.0118) were significant at P≤0.05. Thus, there were significant association between SCS and lactation Stage, this can be used in predicting level of SCS in milk as per lactation stage. There was no association in somatic cell scores between first and second; and second and third lactation stages (Tables 3).

TABLE 3
MEAN DIFFERENCE BETWEEN SOMATIC CELL SCORE AND LACTATION STAGES OF THE CROSSBRED DAIRY CATTLE.

Lactation stage	First	Second	Third
	Mean ± SE	Mean ± SE	Mean ± SE
First	–	0.25* ± 0.11	0.021 ± 0.097
Second		–	0.27* ± 0.0118
Third			–

**** This indicated the result was significant at P≤0.05***

Figure 2. Four breeds of crossbred dairy cattle namely Ayshires, Friesian, Guernsey, and Jersey were used in this study. In figure 3 their mean distribution of Somatic Cell Counts and standard error mean were 246.64±15.177 cells/ml, 178.59±10.008 cells/ml, 174.67±13.212 cells/ml, and 243.45±21.997 cells/ml for each breed, respectively. The SCC varied from one breed to one another (Ayrshire = 1.06 x 10^5 to 4.0 x 10^5cells/ml; Friesian = 9.7 x $10^4$to 3.12 x 10^5cells/ml; Guernsey = 9.2 x $10^4$to 3.1 x 10^5 cells/ml; and Jersey = 9.2 x 10^4 to 3.94 x 10^5cells/ml).

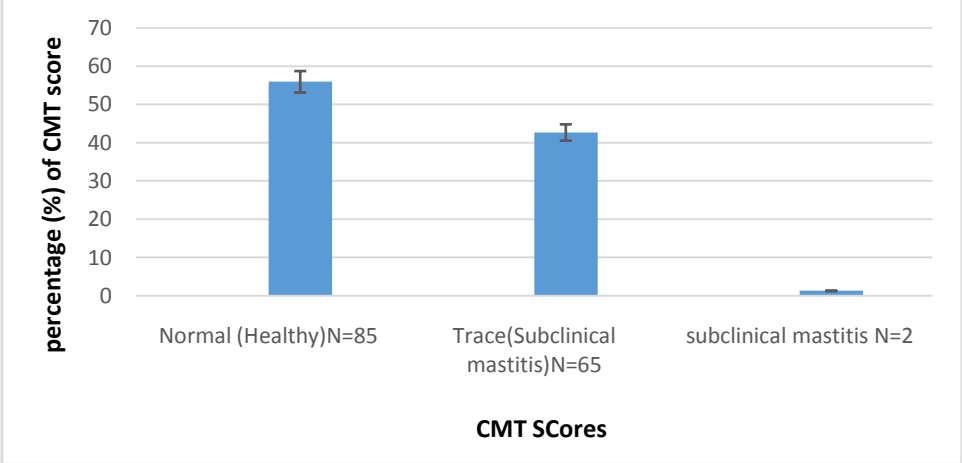

FIGURE 2: Infection status of lactating dairy cattle genotypes.

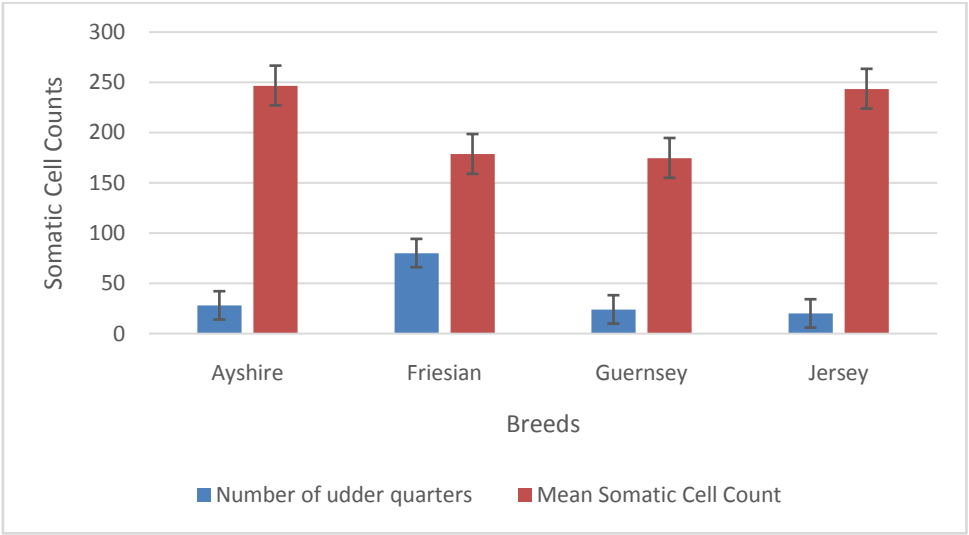

FIGURE 3: Number of udder quarters and Mean of Somatic Cell Counts of crossbred cows

Ayshire genotype of the crossbred dairy cattle had the highest numbers of Somatic Cell Counts (246.64±15.177 cells/ml), and Jersey genotype had the least amount of SCC (174.67±13.212 cells/ml). It implies that Ayshire genotype was highly susceptible to mastitis incidence and Jersey genotype was slightly resistant to mastitis.

Table 4; Means of SCC were significantly different between Ayshire and Friesian; Ayshire and Guernsey; Friesian and Jersey and Guernsey and Jersey at P≤0.05. Their means were found be to greater than 56.162 for the Tukey analysis. For the case of the Least Significant Differences (LSD) analysis, the means were elevated more than 23.69 for significant values at P≤0.05.

TABLE 4
PAIRWISE COMPARISON OF SOMATIC CELL COUNTS BETWEEN FOUR GENOTYPES OF CROSSBRED DAIRY COWS.

Breed	Friesian	Guernsey	Jersey
	Mean ± SE	Mean ± SE	Mean ± SE
Ayshire	68.055* ± 18.821	71.97*± 23.844	3.193 ± 25.095
Friesian	–	3.921 ± 19.949	64.863* ± 21.429
Guernsey		–	68.78* ± 25.952
Jersey			–

The mean is significant at P≤0.05, SEM; standard error mean

The result showed that there were significant differences in term of SCC between Ayshire and Friesian; Ayshire and Guernsey; Friesian and Jersey and Guernsey and Jersey. However, the differences between Ayshire and Jersey; and Friesian and Guernsey genotypes were small, and therefore, they were no significant.

The correlation between Somatic Cell Counts and udder quarters were significantly correlated at P≤0.01. The higher scored were in Left front and Right hind quarters while as Left hind and Right front quarters were moderate (Table 5).

TABLE 5
CORRELATION BETWEEN SOMATIC CELL SCORE AND THE UDDER QUARTERS OF CROSSBRED DAIRY CATTLE GENOTYPES.

somatic cell count (x1000 cells/ml)				
Quarter	**Left front**	**Left hind**	**Right front**	**Right hind**
Left front	0.831**	0.993**	0.742**	0.751**
Left hind	1.00**	0.848**	0.937**	0.904**
Right front	0.900**	0.763**	0.942**	1.00**
Right hind	0.902**	0.761**	0.938**	1.00**

Correlation is significant when P≤0.01 level of significance (2-tailed)

IV. DISCUSSION

4.1 California Mastitis Test scores

The California mastitis test scores for the udder quarters were tested 55.92% Negative for mastitis and 44.08% positive subclinical. Figure 2 results were in disagreement with the findings of Hoque and Das (2014), who stated that CMT results are 25% Negative and 75% positive for subclinical mastitis. The differences in results can be attributed to factors such as climatic variations, geographical, and sometimes breed differences. Hoque and Das, (2014) also reported that CMT results positive for subclinical mastitis are usually less than 25% as compared to the findings of this study, which were 44.08%. These are contrary to the findings of this study, as shown in Figure 2. Iraguha *et al*., 2017 also reported that 60% and above of the udder quarters were positive for subclinical mastitis. The aforementioned is contrary to the findings of this study (Figure 2).

CMT is a simple technique which is affordable, reliable, economically viable and which requires minimum expertise to apply (Holland *et al.*,2018). This factor makes CMT a tool which can be applied by most smallholder dairy farmers for early detection of mastitis. Early detection helps farmers to prevent mastitis incidence. Thus improving hygiene as well as the quality and quantity of the milk they produce, this is in agreement with Abebe et al., 2016; Kandeel *et al.*,2018.

The associations between California Mastitis Test (CMT) score and Somatic Cell Score (SCS) across the udder quarters were significantly associated. This is in agreement with Das et al. (2018) which stated CMT scores and Somatic cell scores varied significantly across udder quarters. The associations between CMT scores and SCS could be utilized as a marker-assisted in selective breeding for mastitis resistance. Meredith et al., 2012; Republic, 2017 reported that SCS can be applied as pseudo phenotypic trait for selection of mastitis resistance, because SCS has higher heritability as compared to both mastitis and SCC.

The Least Significant Differences (LSD) of mean differences between California Mastitis Test (CMT) scores and lactation stage were significantly different at $P \leq 0.05$. These results are in agreement with Jadhav *et al*. (2018)

The regression between age and CMT score revealed that they were significantly different at $P \leq 0.05$. Table 3 This could be utilized by dairy farmers as a tool to predict the level of somatic cell count through the application of the California mastitis test reaction at a particular corresponding age of a dairy cow. Optimal distributions of quarter CMT scores for the healthy cows were similar at $P \leq 0.01$ and $P \leq 0.05$, respectively, this is line with Morin *et al.(*2018).

4.2 Somatic Cell Counts

This study showed that number of Somatic Cells for healthy cows were between o to 200,000 cells/ml, this is not agreement with Hemati Doust *et al.* (2014) which that the number range between 250,000 cells/ml and 300,000 cells/ml on average.

In table 3; Tukey analysis of the amount of Somatic Cell Count (SCC) in the udders' quarters among the breeds, Ayshire and Friesian were 68.055*±18.821 cells/ml, Ayshire and Guernsey were 71.97*±23.844 cells/ml, and Friesian and Jersey were 64.863*±21.429 cells/ml, and there were no significant differences between Ayshire and Jersey had 3.193±25.095 cells/ml and Friesian and Guernsey were 3.921±19.949 cells/ml. The ability of a breed to produces significant amounts of somatic cells in milk is treated an indicator of robust immune responses to mastitis infections. This ability is used as a first line of response to infection and is used as an intervention before the disease worsens. Therefore, an increase in Somatic Cell Counts in milk can facilitate a rapid and effective response to an intramammary infection (IMI) in dairy herds (Hussein *et al.*, 2018).

Table 5; There was a strong correlation between somatic cell counts and udder quarters. The SCC varied progressively among udder quarters at $P \leq 0.01$, as previously reported by Das et al. (2018) that SCC increases across the udder quarters.

4.3 Somatic cell count as an indicator of udder health.

In dairy herds, somatic cell counts should be taken regularly in order to minimize mastitis incidences. This is vital in monitoring and evaluation of the udder health status and intramammary infection (IMI) incidence in dairy herds (Hussein et al., 2018). The direct microscopic examination is the most suitable and straightforward technique for evaluating the level of somatic cell counts in milk. The percentages of macrophages in milk can be reckoned for differential somatic cell counts (Jadhav *et al.,* 2016). In figure 2 the amount of somatic cell count for Ayrshires and Jersey were slightly above the threshold 246,640 cells/ml and 243,4500 cells/ml respectively, and the somatic cell count for Friesian and Guernsey were below the threshold level 178,590 and 174,670 cells/ml respectively.

However, the decline in milk production has also been attributed as results of other factors such as physiological aspects of lactation, Feeds, Climatic condition and geographical location of an area that influences the production of milk (Sharma *et al*.,2011). The occurrence of mastitis in mammary glands trigger inflammation of udder tissues which eventually interrupts release oxytocin hormone in udder during milking hence less milk produced. Therefore, somatic cell count in udder quarters is taken as an important trait that may be used in selective breeding for mastitis resistance in dairy herds. This is because of their higher heritability as compared to clinical mastitis. Somatic cell score in e udder quarters is also another strategy which can be explored in a selection of mastitis resistant breeds of dairy cows.

V. CONCLUSIONS

The study found out that CMT and SCS were significantly associated across all the udder quarters of these crossbred dairy cattle. Therefore, they can be used to predict amount of Somatic Cells presence in milk. It was also found out that an increase in age of crossbred cow results in a proportionate increase in California mastitis Test scores. The amount of somatic cell

counts varies from one breed to another, and they were significant associated among the four genotypes of crossbred dairy cattle.

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Functional and Sensory Characteristics of Sorghum-Cocoyam-Cassava (SCC) Composite Flour Bread

Udoudoh, P. J.[1*], Udofia, P. G.[2], Umokaso, M.[3]

[1,2]Department of Food Technology, Akwa Ibom State Polytechnic, Ikot Osurua, Akwa Ibom State, Nigeria
[3]Department of Science Technology, Akwa Ibom State Polytechnic, Ikot Osurua, Akwa Ibom State, Nigeria

***Abstract*—** *This study was carried out to evaluate the bread characteristics and sensory attributes of sorghum- cocoyam-cassava flour composite bread using simplex lattice of experimental design of response surface methodology (RSM). The sensory evaluation results from semi-trained panelists were generated into a 3D plot for color, taste, aroma, texture and overall acceptability. Wheat bread was used as control for comparison. The loaf weight of the bread samples ranged from 216.0g by sorghum-cocoyam-cassava bread to 177.5g of wheat bread(control); the loaf specific volume ranged from 251.9cm^3 of wheat to 187.2cm^3 of sorghum bread while loaf specific volume ranged from 1.42cm^3/g to 1.10cm^3/g. The linear mixture components of sorghum-cocoyam, sorghum-cassava, cocoyam-cassava and sorghum-cassava-cocoyam flours were not significant on the attributes. The mean hedonic score values for all tested attributes were different from the bread sample (control) at p<0.05. The overall acceptability of the samples showed p>0.05 indicating poor acceptance of the composite bread. Generally the samples under study showed dark brown external and internal colour with increased coarseness and firmness. However, a successful use of sorghum, cocoyam and/or cassava with improved processing methods leading to production of indigenous bread would save many less developed countries from importation of wheat.*

***Keywords*— Bread characteristics, sensory evaluation, composite flour, mixture experimental design, Response Surface Methodology (RSM).**

I. INTRODUCTION

Bread is the second most consumed non-indigenous food product after rice in Nigeria (Idowu, *et al.,* 1996). Wheat flour is a major component of bread with the proteins glutein and glutenin giving it unique baking properties. Glutein is responsible for the elasticity of the dough by causing it to rise and trap the carbon dioxide generated by yeast during fermentation (Mepba *et al;* 2007). Wheat production in tropical countries vis-à-vis Nigeria is inadequate, hence the heavy reliance on importation thus depleting the lean foreign reserve.

Efforts have been made to promote the use of composite flours using locally grown crops to replace wheat flour in bread making thereby decreasing demand for imported wheat and stimulating production and use of locally grown non-wheat products. Studies on the use of various oilseeds, legumes, and high protein seeds in bread making have been reported (Yue *et al.,* 1991 and Olaoye *et al;* 2006).

According to Mongi *et al;* (2011), 2-10% non-wheat flour can be used without undesirable changes in bread characteristics. Cocoyam, cassava, plantain and other tubers have been reported as alternative sources of major raw materials for bread making (Mepba, *et al* 2007; Udofia *et al;* 2013; Idowu *et al;* 1996). Casier *et al;* (1976) reported the production of good quality bread from pure millet and sorghum flour as well as mixtures of maize and cassava flour. Well structured bread from pure seed sorghum flour was obtained using 3% rye pentosan. The pentosan acted as a binding agent simulating the role of gluten from wheat. Certain bread improvers such as calcium stearate or relatively high percentage of fat and sugar are used to improve the bread characteristics of non-wheat flour (Idowu *et al;* 1996).

Sorghum flour is made from *Sorghum bicolor* and is rich in protein, B Vitamins, dietary fibre and antioxidant. (Tekle, 2009) Sorghum flour would be an excellent substitute for wheat flour in which some consumers are gluten-intolerant. Cocoyam are commonly consumed as energy giving foods. The mainly edible varieties are *Colocasia Esculenta* (taro) and *Xanthosoma Sagittifolium* (tannia). Cocoyam contains minute size starch which enhances digestibility and is ideal for people with digestive problems especially the elderly, invalids, and the diabetics (Idowu *et al.,* 1996). According to Idowu *et al.,* (1996) Cocoyam is nutritionally superior to other roots and tubers in terms of digestibility, crude proteins content, and minerals such as calcium, magnesium, and phosphorus. A major limiting factor in the utilization of cocoyam is the presence of oxalates which cause acridity and irritation when eaten (Bradbury and Holloway, 1988; Bencini, 1991). Proper processing methods however would diminish the acridity. Cassava is a tropical crop with high content of carbohydrate. Though some varieties

contain cyanide, improved processing methods are capable of alleviating the cyanide content. Physio-chemical properties of cassava starch are suitable for supplementation of wheat flour in bread making without compromising its sensory attributes (Eduardo *et al;* 2013).

The use of substitutes for wheat flour in bread making if feasible would lower the dependency of developing nations on imported wheat. The major objective of this study therefore was to examine the effect of selected experimental variables (levels of sorghum, Cocoyam, cassava flour) using response surface analysis (RSA) on the physical characteristics of bread (bread volume, loaf volume, organoleptic) of the composite flour bread.

The overall aim was to produce an acceptable indigenous bread like the Pita bread of Arabia and Syria, Roti Bread of Asia, (wheat, millet, cocoyam), Rye bread of Europe (Rye/Wheat); Ezekiel bread, Rye/Wheat. Krisa bread of Sudan (Sorghum), Chapatti bread of India (Sorghum), Tortilla bread of Central and South America (Sorghum). (Asiedu, 1989).

II. MATERIALS AND METHODS

American hard red winter wheat flour was obtained from Niger Mills, Calabar. Sorghum (*Sorghum bicolor*) was purchased from Ikot Ekpene main market. Samples of cocoyam (*Xanthosoma*) and cassava variety TMS (4) 1428 were collected from Root Crop Research Institute Umudike, baking ingredients, reagents and chemicals were sourced from reputable shops in Ikot Ekpene, Nigeria.

2.1 Preparation of sorghum flour

The cleaned sorghum seeds were ground in attrition mill. The ground sorghum was sifted using a sieve DIN 4188 (0.12M) aperture, then stored in plastic container for use.

2.2 Preparation of cocoyam flour

Fresh crowns of cocoyam were washed with water, peeled using stainless steel knife, rewashed and sliced into 0.5 cm thickness. The slices were washed to remove the mucilage, put into 0.5% potassium bisulphide solution for 5-10 minutes to check browning. The slices were drained and dried to a constant weight in a hot air oven at 105^0c for 24 hours before milling into flour using a grinder fitted with a 500µ mesh sieve. The flour obtained was packed in sealed plastic container to check moisture absorption.

2.3 Preparation of cassava flour

The preparation of cassava flour was carried out according to the method adopted by Udofia *et al;* (2013). The cassava tuber was peeled about, 10 hours post harvest, washed, sliced thinly with a shredder (Qlink, China) removing the fibre part. The shredded cassava was washed with ample water and allowed to drain. It was dried in hot air oven (Therm Gross Kucken, le Chef, Sweden) at about 60^oC until moisture content was reduced to about 13%. The cassava flakes were ground through a corn meal grinder to pass through a sieve of 500 cm mesh. The flour was packed in plastic container to deter water absorption.

2.4 Experimental design

The mixture experimental design was used to study the effect that the proportions of the different ingredients in the composite flour have on the food product properties of interest (Hu, 2000). A mixture experiment is one in which the food quality indices (responses) are assumed to depend only on the selective proportions of the ingredient. Response in a mixture experiment is a function of properties and not amounts of the mixture components. On a food formulation study, the mixture experimental design models the relationship between the component proportion (variables) and the food quality indices (responses) shown on the response surface. A full second degree polynomial equation was used to describe the relationship between the variables and responses after fitting the experimental data in the regression model. The experimental design assumes equation (1)

$$Y_i = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_3 X_1 X_J^2 \quad (1)$$

Where Y_i is any response, β represents coefficient to be fitted via regression analysis, X_1, X_1, X_2, X_1J^2 are the linear, interaction and quadratic effect of the components respectively. A simplex lattice design of the mixture experimental design was adopted.

TABLE 1
EXPERIMENTAL LAYOUT OF AUGMENTED SIMPLEX LATTICE DESIGN OF SORGHUM-COCOYAM-CASSAVA FLOUR COMPOSITE BREAD

Randomized runs	Sorghum flour (A)	Cocoyam flour (B)	Cassava flour (C)
1	0.33	0.33	0.33
2	0.00	0.50	0.55
3	0.00	0.00	1.00
4	0.17	0.17	0.67
5	1.00	0.00	0.00
6	0.50	0.50	0.00
7	0.00	1.00	0.00
8	0.00	0.00	1.00
9	0.00	1.00	0.00
10	1.00	0.00	0.00
11	0.00	0.50	0.00
12	0.17	0.67	0.17
13	0.50	0.00	0.50
14	0.67	0.17	0.17

Note: Each run produced a sample of the respective mixture

2.5 Preparation of composite flour

Component flour was prepared by intimate mixture of proportion of the three component flours-sorghum, cocoyam, cassava, according to Table 1 (Hugo, 2002). Blends of the mixture were the pure sorghum (A), cocoyam (B) and cassava (C) while the binary mixtures were sorghum and cocoyam (AB) sorghum and cassava (AC) Cocoyam and Cassava (BC); the overall centroid was ABC- sorghum, Cocoyam Cassava flour. One hundred (100%) wheat flour was used as a control. The flour were packed in plastic containers and stored until needed.

2.6 Preparation of dough and baking

The composite flour dough was prepared and baked according to the method specified by Eduardo *et al;* (2013) the whole wheat bread and the composite breads were made by mixing the flour with graded levels of ingredients as follows:

Four (4)g salt, 9g margarine, 5g sugar, 3g yeast in 500 ml water followed by stirring using a Kenwood mixer (Model A 907D) for 5 minutes to obtain a dough. The dough was allowed to ferment in a bowl covered with clean muslin cloth for 55min at room temperature (28^oC). Later the dough was punched and scaled to 40 g dough pieces. The dough pieces were proofed in a cabinet for 90 min at 35^oC 80% relative humidity and baked at 210^oC for 8 min in a hot air oven (Therma Gross Kuchen Le Chef, Sweden). The bread samples were allowed to attain room temperature ($28^oC \pm 10^oC$) before assessing for the bread characteristics (loaf weight, volume) and sensory attributes, crust and crumb color, taste, Texture and general acceptability.

III. EVALUATION OF BREAD CHARACTERISTICS

Bread characteristics were evaluated by measuring the loaf weight, loaf volume and specific loaf volume.

3.1 Loaf weight

Loaf weight was measured 30 minutes after the loaves were removed from the oven using a weighing balance (Iwe, 2002).

3.2 Loaf volume

Loaf volume was measured using the rapeseed displacement method as modified by Giami, *et al.,* (2004). A box of fixed dimensions (23.00x14.30x17.010cm) of internal volume 5660.37cm^3 was put in a tray, half filled with millet seeds, shaken vigorously four times, then slightly overfilled so that overspill fell into the tray. The box was shaken again twice, and then a straight edge was used to press across the top of the box once to give a level surface. The seeds were decanted from the box into a receptacle and weighed. The procedure was repeated three times and the mean value for seed weight was noted (Cg). A weighed loaf was placed in the box and weighed seeds (3500g) were used to fill the box and leveled off as before. The overspill was weighed and from the weight obtained the weight of seeds around the loaf and volume of seed displaced by the loaf were calculated using equation (2) (AACC, 2000).

Seed displaced by leaf (L) = Cg + overspill weight- 3500g

$$\text{Volume of bread} = \frac{\text{L x } 5660.37}{\text{C}} \text{ cm}^3 \quad (2)$$

Cg = Mean seed value

3.3 Specific loaf volume

Specific loaf volume was determined by dividing the load volume by its corresponding loaf weight (cm^{3}g) as described by Araki *et al*, (2009)

$$\text{Specific volume} = \frac{\text{Volume (cm}^3\text{)}}{\text{Weight (g)}} \quad (3)$$

3.4 Sensory evaluation

Sensory evaluation based on the sensory attributes were conducted using the 9 points hedonic scale method (where 1 = dislike extremely and 9= like extremely) as described by Larmond (1997). A total of 10 semi trained panelists' aged 20 years old and above were involved in the evaluation for crust and crumb colour, aroma, taste, texture and overall acceptability. Among these panelists 5 were males and 5 were females. The bread samples were sliced into pieces of uniform thickness (2 cm) and it was served to the panelists at about 11:15am with distilled water for rinsing the mouth after every sample taste in randomized order. The panelists were instructed to rate the attributes indicating their degree of liking or disliking by putting a number as provided in the hedonic scale according to the preference. The panelists were made to work under controlled condition to avoid biased results. The data after ratings were converted to numerical scores and analyzed using Analysis of Variance (ANOVA) at $p < 0.05$.

IV. RESULTS AND DISCUSSION

Bread samples were produced from composite flour of Sorghum-Cocoyam-Cassava. Table 2 shows characterization of the composite bread samples (i.e. loaf weight, loaf volume and load specific volume). The 3-dimensional plot of mean loaf weight, loaf volume and specific loaf volume with respect to the component flours are shown in Fig. 1, 2 and 3 respectively

TABLE 2
CHARACTERISTICS OF BREAD SAMPLES OF SORGHUM-COCOYAM-CASSAVA COMPOSITE FLOURS

Samples	Wt. of loaf (g)	Vol. of loaf (cm^3)	Specific vol. of loaf (cm^3/g)
100% wheat flower bread (control)	177.5	251.9	1.42
A	195.2	197.29	1.11
B	189.1	213.3	1.20
C	183.2	220.4	1.24
AB	191.0	201.2	1.10
AC	182.4	232.0	1.30
BC	182.4	232.0	1.30
ABC	216.0	231.0	1.16

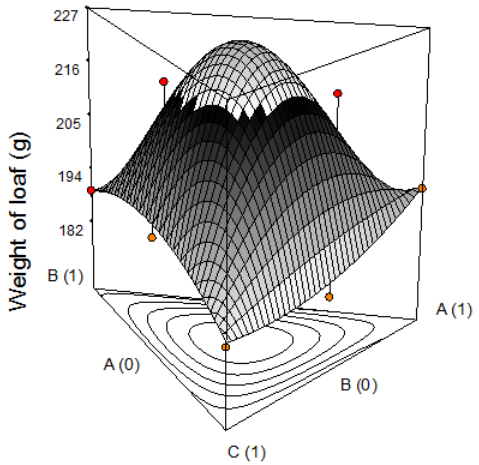

FIGURE 1: Response surface plot of mean weight of composite bread loaves against A, B and C component flours

MWL = 195.76A +189.54B +184.11C -17.01AB -18.41AC +27.48BC +1039.46ABC (4)

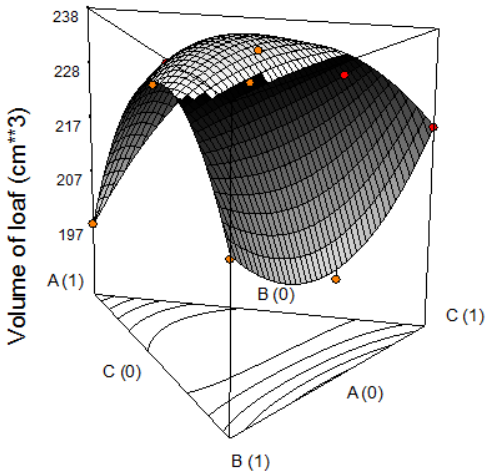

FIGURE 2: Response surface plot of mean vol. of composite bread loaves against A, B and C component flours

Mean volume of composite loaves = 197.24A +213.95B +220.68C+108.00AB +93.99AC -56.99BC + 257.70ABC ..(5)

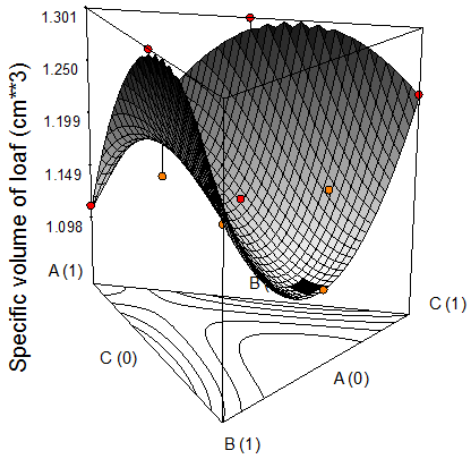

FIGURE 3: Response surface plot of mean specific volume of composite bread loaves against A, B and C component flours

Mean specific volume of composite loaves = 1.11A +1.20B +1.24C +0.57AB +0.47AC –0.48BC -2.91ABC (6)

The wheat bread had loaf weight of 177.5 g, loaf volume 251.9 cm3, and loaf specific volume of 1.42cm^3/g, sorghum bread had loaf weight of 195.2g, loaf volume 197.2cm^3 and specific loaf volume 1.11cm^3, cocoyam bread had loaf weight of 183.2g, loaf volume 220.4cm^3 and loaf specific volume 1.24cm3/g, cassava bread had loaf weight of 189.1g loaf volume 213.3cm3, and loaf specific volume 1.2cm3/g, while cassava cocoyam bread had loaf weight of 191.0g, loaf volume 0f 201.2cm3 and loaf specific volume of 1.10cm3/g, sorghum cassava bread had loaf weight of 182.4g, loaf volume 2.320cm3 and loaf specific volume 1.3cm3/g, sorghum cassava bread had load weight of 182.4g, loaf volume 2.32cm3 and loaf specific volume 1.30cm^3/g, sorghum cocoyam bread had loaf weight of 179.3g, loaf volume 241.8cm^3 and loaf specific volume 1.36cm^3/g, sorghum cocoyam, cassava bread had loaf weight of 216.0g, loaf volume of 231.0cm^3 and loaf specific volume of 1.16cm^3/g.

Table 3 shows the results of the mean consumer acceptance scores observed from bread sample produced from wheat flour which acted as the control, sorghum flour, cocoyam flour and cassava flour. The table reveals that sorghum cassava composite four bread sample of blend AC was the most acceptable in texture, taste, colour, aroma and overall acceptability.

TABLE 3
OVERALL ACCEPTABILITY OF SCC COMPOSITE BREAD SAMPLES

	LW	LV	SLV	Taste	Colour	Aroma	Texture	Acceptance	Preference
Model	0.989	0.856	0.414	0.038	0.221	0.069	0.127	0.104	0.079
A	196.12	205.18	1.42	6.77	4.15	2.14	4.69	4.56	2.10
B	178.31	213.98	1.24	5.77	4.50	2.05	3.44	4.02	3.40
C	184.00	205.89	1.20	2.78	2.24	6.18	1.74	3.02	2.54
AB	-11.43	65.97	-0.136	NA	-2.30	16.56	-2.54	-3.80	-3.80
AC	-22.42	78.18	-0.056	NA	8.78	-11.58	7.77	2.20	2.21
BC	28.36	-117.42	-0.496	NA	4.36	-1.53	-2.91	6.08	-5.59
ABC	ND	ND	0.0247	NA	-62.69	-58.86	-73.64	0.600	NA
R^2	0.102	0.308	0.961	0.377	0.613	0.884	0.683	0.973	0.655
Mean	185.81	209.98	1.22	5.25	3.31	3.04	2.91	3.91	3.20

Note: A= sorghum flour, B= cocoyam flour, C=cassava flour, NA = not application, LW (g) = weight of loaf, LV (cm**3) = loaf volume, SLV (cm**3)/g = specific loaf volume.

V. DISCUSSION

Bread samples were evaluated for their loaf weight, loaf volume and specific loaf volume. The sorghum-cocoyam-cassava (SCC) bread had the highest loaf weight of 216.0g followed by sorghum bread with loaf weight of 195.2g while the wheat bread had the lowest loaf weight of 177.5g. Wheat bread (control) had highest bread loaf volume of 251.9cm^3 followed by sorghum-cocoyam bread with 241.8cm^3 while sorghum bread had loaf volume of 187.2cm^3. Sorghum-cocoyam-cassava bread had highest loaf weight because of the dense starch content (sorghum 27%, cocoyam 24.5%, cassava 27.5% Asiedu, 1989) and quadratic effects of the components. Loaf volume is influenced by the entrapment of carbon dioxide gas in the dough during fermentation, hence the corresponding loaf volume increase.

Wheat glutein causes the dough to leaven whereas there was no rising in the others because of lack of gas entrapment. Some baked goods however rely on carbon dioxide emanating from baking powder added together with air whipped into the mixture for the purpose of leavening the dough (Sivasanker, 2010). Fermented material could produce carbon dioxide to increase dough volume and desirable texture development (Asiedu, 1989).

The models of the results of the variable effect on definite responses shown in a 3-dimensional plot depicted the linear, quadratic interactive effects of the mixture component on the response attributes. The linas shown in Figs. 4, 5, 6, 7 with respect to taste, colour, aroma and texture. The linear mixture component of AB, AC, BC, and ABC were not significant on the attributes. The mean hedonic score values for all tested attributes were different from the bread sample at $p<0.05$. The overall acceptability of the sample showed $p>0.05$ indicating poor acceptance of the composite bread.

Taste had mean hedonic score of 5.25 and F value of 3.33 and was not significant at $p < 0.05$ contributing 33.29% of variation. The goodness of fit (R^2) of 37.738% of the model was not significant ($p>0.05$). The response surface plot for taste showed a straight plane indicating significant effect of the variables. Taste is an important attribute to any food as it affects food acceptability and intake. Sensory attributes of color and texture were not significant ($p>0.05$) with goodness of fit (R^2) in each case was not sufficient description of the models except in case of aroma with goodness of fit of 59.46% and SCC bread samples significant at $p<0.05$. Inspite of the poor statistical characteristic of the model, the 3-D projection showed

some contribution to the parameter showing a linear relationship of all components while aroma and overall acceptability showed a curvilinear relationship of the components.

There were associations of the component flours in case of overall acceptability with some components producing similar values of response.

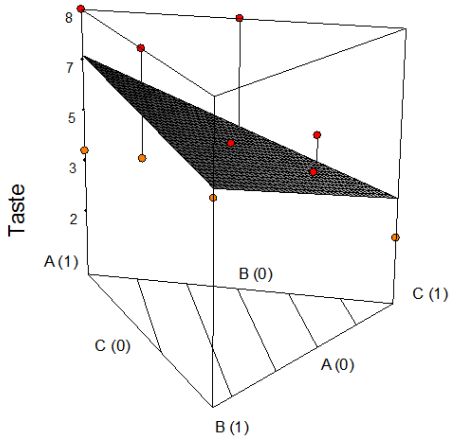

FIGURE 4: Response surface plot for Taste against SCC composite flour bread

Taste = 7.55A + 1.59B + 3.02C (7)

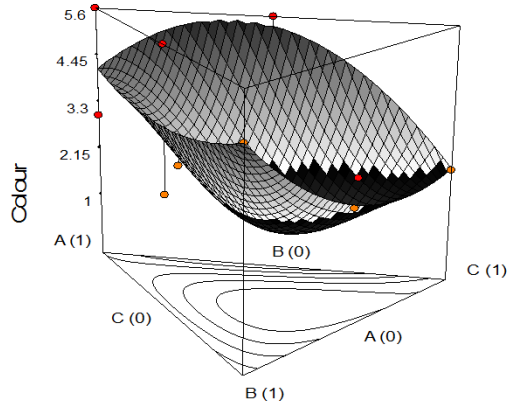

FIGURE 5: Response surface plot of crust colour of composite bread samples against A, B and C components

Colour = 4.15A + 4.50B + 2.24C – 2.30AB + 8.75AC – BC – 62.69 (8)

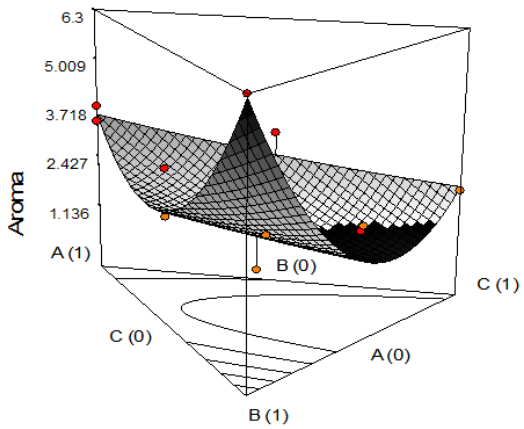

FIGURE 6: Response surface plot for aroma against SCC composite flour bread

Aroma = 2.14A + 2.05B + 6.18C – 16.56AB – 11.58AC – 1.53BC -58.86ABC (9)

Texture

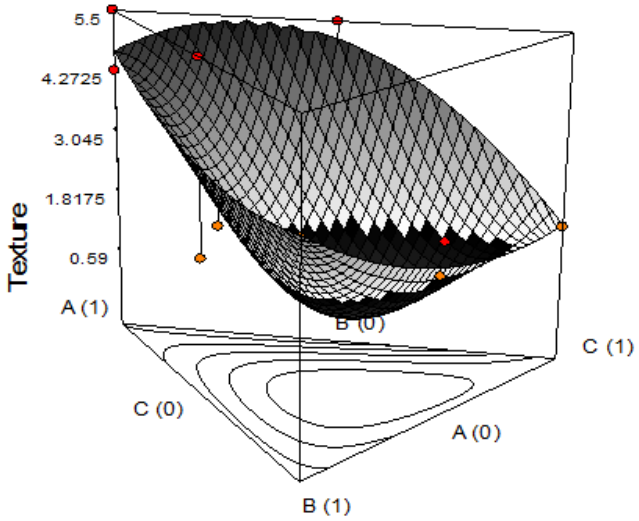

FIGURE 7: Response surface plot for texture against SCC composite flour bread

Texture = 4.69A+3.44B+1.74C–2.54AB–7.77AC-2.53BC-75.64ABC (10)

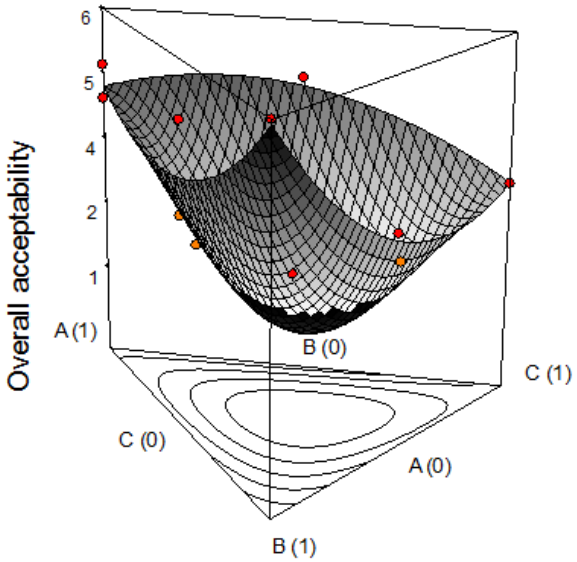

FIGURE 8: Response surface plot for Overall acceptability against SCC composite flour bread

Acceptability = 4.56A + 4.02B + 3.02C – 3.80AB – 2.20AC – 6.08BC – 78.56A²BC – 213.92AB²C – 196.48ABC² (11)

VI. OPTIMIZATION PROCESS

Optimization analysis of the process revealed that 0.12, 0.08, and 0.80 proportions of sourghum, cocoyam and cassava produced 1.855.14 g, 2.21 cm^3, 1.21 cm^3/g, 3.45, 3.09, 3.85 and 4.86 of loaf weight, loaf volume, loaf specific volume taste, colour, aroma, texture and overall acceptability respectively at 0.547 desirability level.

VII. CONCLUSION

It was observed that all parameters failed to meet the important attributes of pure wheat bread which hindered general acceptability of the bread sample. However sorghum–cassava bread showed much acceptability. Levels of brownness were shown by the weight increase which consumers are familiar with in all wheat flour bread which would easily be accepted. It is envisaged that regular supply, publicity, nutritional and health claims on the products may improve production and acceptability of sorghum- cocoyam- cassava flour bread as an indigenous food product.

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