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African Journal of Environmental Science and Technology

Table of Contents: Volume 12 Number 9 September 2018

ARTICLES

Analysis of spatial variability in rainfall trends in Baringo County, Kenya

Ednah Chemutai Koskei, Jackson John Kitetu and Charles Wambongo Recha

Healthcare waste management practices and risk perception of healthcare workers in private healthcare facilities in an urban community in Nigeria

Afolabi Olusegun Tope, Aluko Oludare Olufemi,
Afolabi Bolade Kehinde and Fehintola Funmito Omolola

Seasonal variation of heavy metal speciation in soil and stream sediments from hospital waste dumpsite in Ilesa, Southwestern Nigeria

Fakoya O. T., Oluyemi E. A., Olabanji I. O., Eludoyin A. O.,
Makinde O. W., and Oyinloye J. A.

The impacts of climate change and variability on crop farming systems in Semi-Arid Central Tanzania: The case of Manyoni District in Singida Region

Jackson Sawe, Claude G. Mung'ong'o and Godfrey F. Kimaro

Equilibrium, kinetic and thermodynamic studies of biosorption of zinc ions from industrial wastewater using derived composite biosorbents from walnut shell

Olafadehan, O. A., Akpo, O. Y., Enemu, O., Amoo, K. O. and Abatan, O. G.

Full Length Research Paper

Analysis of spatial variability in rainfall trends in Baringo County, Kenya

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This study assessed actual rainfall trends and variability in Baringo County. The objective of the study was to determine whether there were variations in rainfall trends by agro ecological zones. Meteorological rainfall data for the period 1981 to 2010 from three distinct agro-ecological zones covering highland (LH 2), low land (IL 6) and midland (LM 5) was used. The choice of rainfall stations was informed by agro-ecological zones and percentage of missing data. Data were analyzed on annual and monthly basis. Trend analysis and coefficient of variation was used to analyze actual trends and rainfall variability. Trend analysis showed year to year variability in rainfall. The trends were by agro-ecological zones. Annual rainfall in LM5 and IL6 showed decreasing trends while in LH2, it showed increasing trend. IL6 and LH2 exhibits a very high coefficient of variation for annual rainfall (CV > 30%), indicating high rainfall variability. Increasing awareness of climate variability and development of mitigation options will be necessary response strategies in Baringo County.

Key words: Rainfall trends, rainfall variability, trend analysis, Baringo County.

INTRODUCTION

Climate Change and Climate Variability are two important characteristics of climate. Climate change has emerged as one of the defining scientific, political and socioeconomic issues of the twenty-first century. IPCC (2014) describes climate change as a change in the state of the climate that can be identified by changes that persists for an extended period, usually decades or longer. Although an area's climate is always changing, the changes do not usually occur on a time scale that is immediately obvious to people. Weather changes can be

observed from day to day but slight climate changes are not as readily detectable. Climate takes the following elements into account, the most important of which are: Air temperature and humidity, type and amount of cloudiness and precipitation (e. g. rainfall), air pressure, and wind speed and direction. FAO (2007) describes climate variability refers to variations in the mean state and other climate statistics such as standard deviations, and the occurrence of extremes among others on all temporal and spatial scales beyond those of individual

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weather events. Variability may result from natural internal processes within the climate system (internal variability) or from variations in natural or anthropogenic external forces (external variability). Every year in a specific time period, the climate of a location is different. Some years have below average rainfall, some have average or above average rainfall.

Climate, with particular reference to rainfall, is known to be changing worldwide (Chaponniere and Smokhtin, 2006). Rainfall exhibits notable spatial and temporal variability in Africa (Hulme et al., 2005). Inter-annual rainfall variability is large for the most part of the continent and, for some regions; multi-decadal variability is also large. The water supply is highly variable in Africa and dry or wet spells can range from months to decades. Inter-annual rainfall variability in Africa is influenced by several factors: El Niño Southern Oscillation (ENSO), Inter-Tropical Convergence Zone (ITCZ), topography, urbanization and global warming (Matondo, 2010). The annual rainfall cycle in East Africa is influenced by the movement of the Inter-Tropical Convergence Zone (ITCZ), which migrates between 15°S and 15°N between January and July respectively, and by the monsoon circulation. The monsoonal winds of the ITCZ are the major source of moisture flux in countries like Kenya, for example Ogallo (1992). These rainy seasons occur during the transitions between the winter and summer monsoons, when air in both hemispheres converge near the equator (Hastenrath et al., 2004). Eastern Africa's diverse topography also contributes to the high spatial variance in seasonal distribution of rainfall. The "short rains" have shown more inter annual variability than the "long rains" despite the larger amounts of rainfall received in March, April and May (Black et al., 2002; Clark et al., 2003; Hastenrath et al., 1993). Projections in East Africa suggest that increasing temperatures due to climate change will increase rainfall by 5 to 20% from December to February, and decrease rainfall by 5 to 10% from June to August by 2050 (IPCC, 2007; Hulme et al., 2001). Rainfall in Kenya is variable and annual variations follow El Niño and La Niña episodes (Parry et al., 2012). Some regions experience frequent droughts during the long rainy season while others experience severe floods during the short rains (RoK, 2013).

Climate change affects rainfall distribution and weather patterns (Taylor et al., 2012). Long term fluctuations in rainfall distribution pattern around the world have been linked to the effects of climate change (Scott, 2004). Climate change has altered not only the overall magnitude of rainfall but also its seasonal distribution and inter-annual variability worldwide (Easterling, 2000; Trenberth et al., 2007; Zeng et al., 1999). Such changes in the rainfall regimes will be most intensely felt in arid and semiarid regions where water availability and timing are key factors controlling biogeochemical cycles (Zeng et al., 1999). Developing countries, Arid and Semi-Arid

Lands (ASALs) and the poor in society are the most vulnerable and likely to be hit hardest by climate change due to their low adaptive capacity (Boko et al., 2007; IPCC, 2007b). Poverty determines vulnerability through several mechanisms, principally in access to resources to allow coping with extreme weather events and through marginalization from decision making and social security (Kelly and Adger, 2000). The existing developmental challenges such as endemic poverty, complex governance and institutional dimensions; limited access to capital, including markets, infrastructure and technology; ecosystem degradation; and complex disasters and conflicts have contributed to Africa's weak adaptive capacity (Boko et al., 2007). Although arid and semi-arid regions are already climatically stressed with high temperatures, low rainfall and long dry seasons, they are often thought of as being particularly vulnerable to climate change (ACDI, 2016).

Approximately 80% of Kenya's land mass is arid and semi-Arid (ASAL) characterized by average annual rainfall of between, 200 to 500 mm per year, and is prone to harsh weather conditions according to Serigne (2006). Some areas in the northwest and east receive only 200 mm per year (NCEA, 2015). Kenya has a population estimated at 38.6 million (RoK, 2010). Over two thirds of the country is classed as ASALs (Orindi et al., 2007), and these areas are home to approximately 30% (~12 million) of Kenya's people, a third of Kenya's population (UNDP, 2016). The principal climatic hazard in the ASALs is drought. Most of the droughts exhibit such characteristics as false and late onset of the rains, pronounced breaks during the rainy season, and early cessation of the rains, leading to drastic alterations in the pattern of seasonal rainfall distribution (Jones and Thornton, 2003; Lobell and Burke, 2010; Nyoro et al., 2007). Baringo County in mid-west Kenya is predominantly arid and semi-arid lands.

While Kenya, like countries in other parts of the world, have considerable experience in dealing with climate variability, climate change is likely to present them with new and tougher challenges. Consequently, the country needs to adopt new strategies to cope with new situations. The current technologies and approach especially in water are unlikely to be adequate to meet projected demands, and increased climate variability will be an additional stress (IPCC, 2001). Consequently, the country needs to adopt new strategies to cope with new situations. The current technologies and approach especially in water are unlikely to be adequate to meet projected demands, and increased climate variability will be an additional stress (IPCC, 2001). The present study sought to analyze rainfall variability with specific focus on annual trends, rainfall amount and distribution of rainfall. The analysis aims at quantifying the magnitude of variation in Baringo County. This information shall be used to relate the implication of rainfall variability on water access at household level. Characterizing rainfall

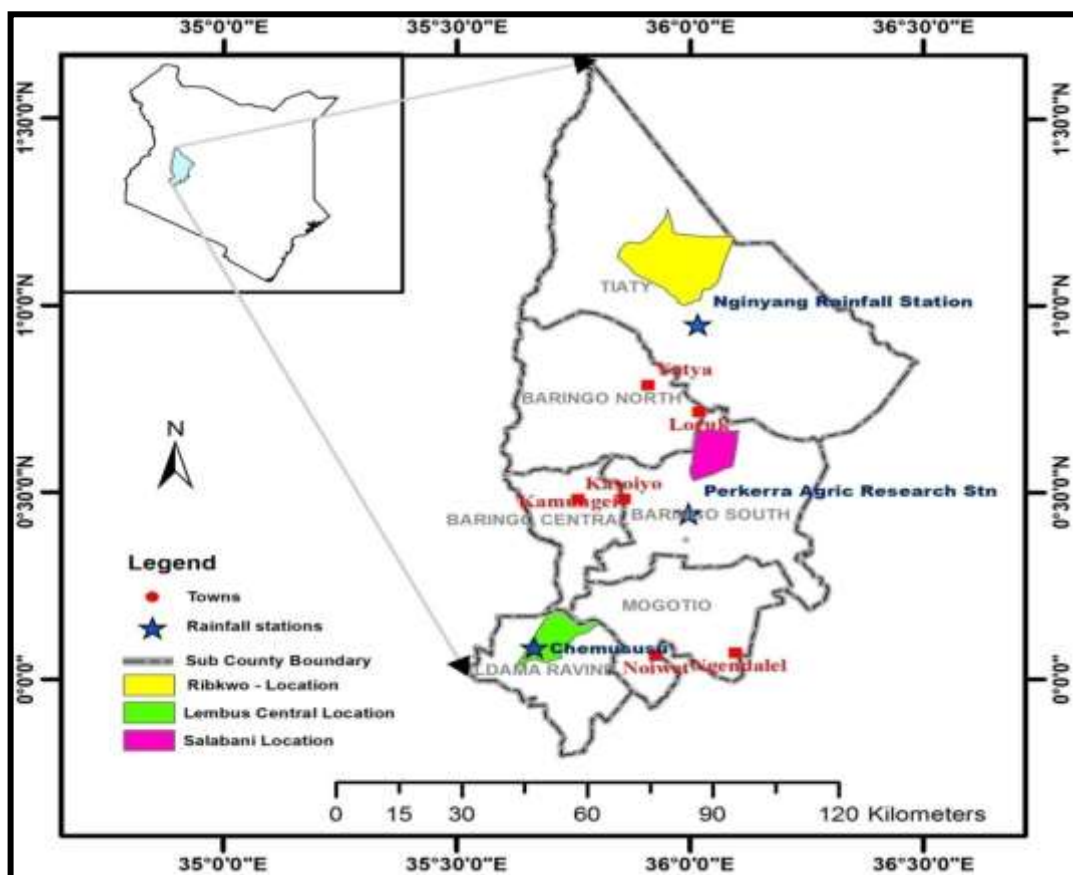


Figure 1. Geographical location of the study area in Kenya.

variability is of great importance to rural households not only in Baringo County but also in other parts of Kenya that have the same climatic conditions.

MATERIALS AND METHODS

Study area

This study was conducted using meteorological data records from Nginyang, Chemususu and Perkerra stations, located in Baringo County Northwestern part of Kenya. Geographically, Baringo is situated between Latitudes $00^{\circ} 13'$ South and $1^{\circ} 40'$ North and Longitudes: $35^{\circ} 36'$ and $36^{\circ} 30'$ East (Figure 1). The County is cut across by the Equator at the southern part. According to the 2009 Kenya population and Housing census results, Baringo's human population stood at 555,561 people (KNBS, 2010). This figure is projected to increase by about 5% in the next census. Baringo County covers a range of climatic zones, from semi-arid (zone iv), arid (zone v), and very arid (zone vi) through semi-humid (zone iii) and sub-humid (zone ii), to a small portion in the humid zone (zone 1). The mean annual rainfalls in these zones are 450 to 900 mm (semi-arid), 800 to 1,400 mm (semi-humid), 1,000 to 1,600 mm (sub-humid) and 1,100 to 2,700 mm (humid). The mean annual potential evaporation amounts for these areas are 1,650 to 2,300 mm (semi-arid), 1,450 to 2,200 mm (semi-humid), 1,300 to 2,100

mm (sub-humid), and 1,200 to 2,000 mm (humid) (Odada et al., 2006). Baringo County is divided into three major agro-ecological zones namely the highlands, midlands and lowlands and the following sub-zones: UH 1, UH 2, LH 2, LH 3, UM 3, UM 4, UM 5, LM 4, LM 5, LM 6 and IL 6 (RoK, 2013).

The choice of rainfall stations for this study was informed by agro-ecological zones (Jaetzold et al., 2007) and percentage of missing data (less than 10% for any given year as required by the World Meteorological Organization). Thus, the selected rainfall stations were Nginyang (IL6), Salabani (LM5) and Lembus Central (LH2) and each had a data set of over 20 years and it is fairly a representation of the entire Baringo homogenous climatological zone identified by RoK (2013). This study relied on secondary data sources. The data was obtained from Kenya Meteorological Department. Daily rainfall data was collected for three stations: Perkerra, Chemususu and Nginyang to represent agro-ecological zones LM5, LH2 and IL6 respectively. The data collected from LH2 and IL6 was for the period 1981 to 2010 while the data collected from LM5 was for the period 1981 to 2008 because there was no sufficient data. Nonetheless, the data was within the above 25-year threshold required for a climatological analysis (Atheru, 1999).

Data analysis

To show rainfall variability, this study carried out a trend analysis. The year-to-year variation of annual rainfall over the studied agro-

Table 1. Summary of rainfall variables for the study sites.

Agro-ecological zone	Rainfall (mm)	Annual
IL6	Minimum	99.6
	Maximum	1517.7
	Mean	792.81
	Coefficient of variation	0.45
LH2	Minimum	353.8
	Maximum	6471.4
	Mean	2209.13
	Coefficient of Variation	0.70
LM5	Minimum	237.6
	Maximum	926.8
	Mean	576.1
	Coefficient of Variation	0.33

ecological zones was analysed. Results of the values were cumulatively added to each other for the period of record and plotted to achieve long-term trends of annual rainfall. The mean annual rainfall for the three agro ecological zones LM 5, IL 6 and LH 2 was calculated. To show rainfall variability, a coefficient of variation (CV), defined as the ratio of standard deviation to the mean, was also calculated for rainfall amount for each station. The correlation coefficient is a measure that assesses the degree to which two variables' movements are associated (Abdi, 2009).

RESULTS AND DISCUSSION

The mean annual rainfall for agro ecological zones LM 5, IL 6 and LH 2 was 616.9, 792.81 and 2209.13, respectively. According to the performed analysis (Table 1), maximum annual rainfall (1517.7 mm) was observed in the year 2010 in Nginyang station while in Chemususu station, maximum annual rainfall (6471.4 mm) was observed in the year 2005. For Perkerra station, maximum annual rainfall (926.8 mm) was observed in the year 2007. The minimum annual rainfall (99.6 mm) was observed in the year 2000 in Nginyang station while in Chemususu station, minimum annual rainfall (353.8 mm) was observed in the year 1984. The lowest annual rainfall (237.6 mm) recorded in Perkerra station also was in 2002. The findings concur with those of Opiyo et al. (2014) who observed the lowest annual rainfall (54.2 mm) in 1984 in Lodwar, Turkana County. The lowest rainfalls recorded in the same year (1984) in the two agro ecological zones may be linked to the 1983 to 1985 droughts which afflicted Africa's dry lands. There was a failure of Kenya's 'long rains' in April to May of 1984 (ODI, 1987).

The coefficients of variation for annual rainfall amount for IL 6 (Nginyang station) is 0.45 while LM 5 (Perkerra station) stands at 0.33. LH 2 (Chemususu station) exhibits

a very high coefficient of variation for annual rainfall amount (0.70) (Table 1). According to Araya and Stroosnijder (2011), a coefficient of variation greater than 0.30 is an indicator of large rainfall variability. This variability in rainfall in Baringo may be linked to the 1982, 1994 and 2007 El Nino rains that characterized the average annual rainfall in Kenya (GoK, 2000). Amisshah et al. (2002) in Kenya also found that annual rainfall increased during El Nino events compared with neutral years and that highland sites had the highest rainfall variability between El Nino events than lowland sites. Shisanya et al. (2011) also reported above normal rainfall during short rains season than preceding long rains season rainfall in ASALs of Kenya during El Nino years. Links between El Nino and climate variability have also been suggested by other studies (Anyah Semazzi, 2007; Ngongondo, 2006).

According to the results of the trend analysis (Figure 2), rainfall in AEZ IL6 (Nginyang rainfall station) of Baringo County has been on the decrease over the period of study. The years 1982, 1994 and 1997 recorded highest amount of rainfall while the years 1996, 1999, 2000 and 2009 recorded the lowest amount. Rainfall in the years 1996, 1999, 2000 and 2009 decreased at the rates of -1.4, -1.2, -1.9 and -1.1 per annum respectively. The findings concur with those of Jenny and Svensson (2002) who observed a similar pattern in Baringo lowlands. Kansiime et al. (2013) also observed a decreasing trend of total annual rainfall for low lying areas in Uganda. However, according to Arthur et al. (2002), sites in the highland wet ecoregion of Kenya had the greatest decrease in annual rainfall than lowland and midland.

The results of the trend analysis (Figure 3) show that rainfall in AEZ LH 2 (Chemususu station) Baringo County depicted increasing trends over the period of study. The years 1983, 1984, 1991 and 1993 depicted highest

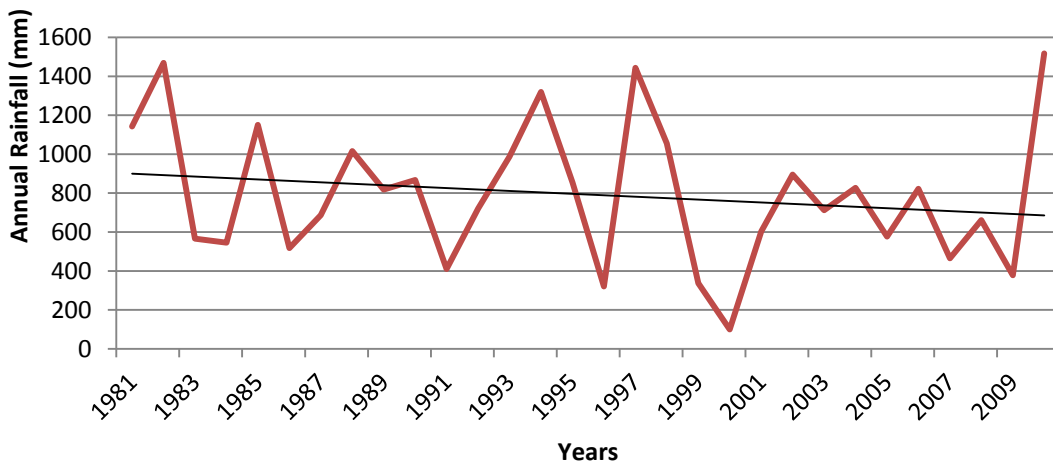


Figure 2. Trends in annual total rainfall for lowland.

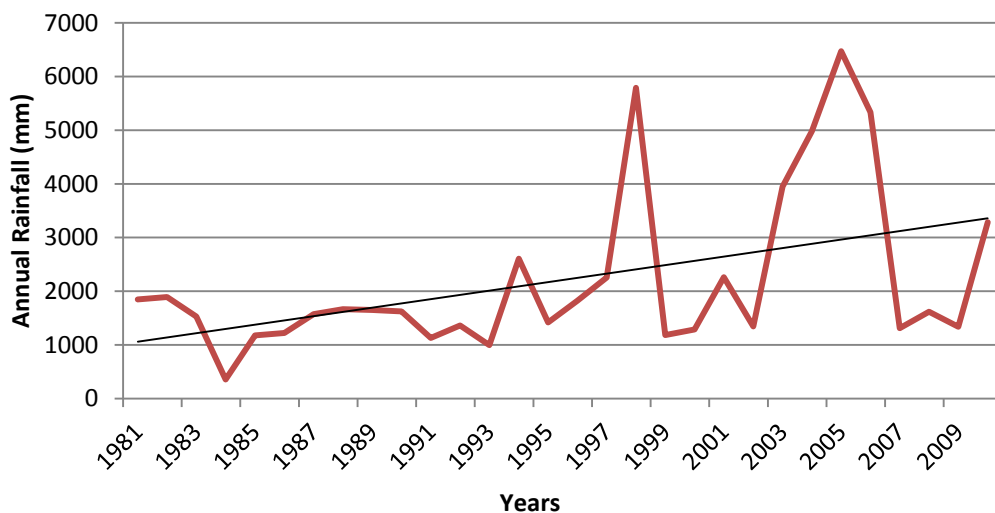


Figure 3. Trends in annual total rainfall for highland.

negative decreasing trends while the years 1998, 2003, 2004, 2005 and 2006 depicted highest positive increasing trends. The results are in line with those of Kansime et al. (2013) in Uganda who observed an increasing trend of total annual rainfall for highland areas. Basalirwa (1995) also predicted an increase of approximately 10 to 20% in rainfall for high ground areas, and more drying conditions for low lying areas of Uganda.

At AEZ LM5 (Perkerra rainfall station), the results of the trend analysis (Figure 4) show that there was a decrease in rainfall over the period of study. The year 2007 depicted highest increasing trend. A noticeable decrease of rainfall was observed in the years 1984, 2002, 2002 and 2004 while the other years showed a fluctuating decreasing and increasing scenarios which were not

noticeable. The findings concur with those of Jenny and Svensson (2002) who observed a similar pattern in the same station in Baringo. Arthur (2002) also observed a decrease in annual rainfall in midland sites of Kenya. However, Kansime et al. (2013) in Uganda observed an increasing trend of total annual rainfall for mid lying areas.

Trend analysis performed on annual scale to examine if there are patterns in the data at this scale showed varied results. Rainfall showed year to year variability in the amount and distribution. The data also revealed wide variation in rainfall trends by agro-ecological zones. This is a common finding from other studies on actual rainfall trends and variability such as in Lower Eastern Kenya (Omoyo et al., 2015), Eastern Uganda (Shisanya et al.,

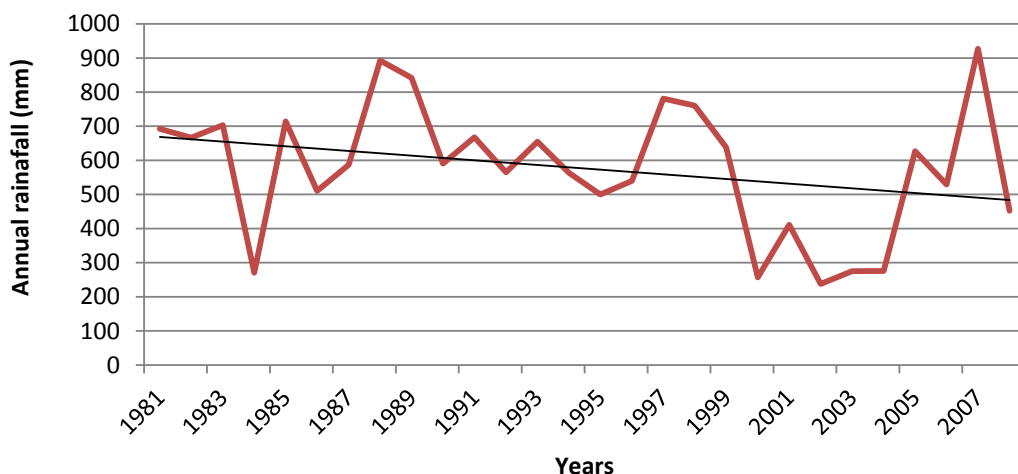


Figure 4. Trends in annual total rainfall for midland.

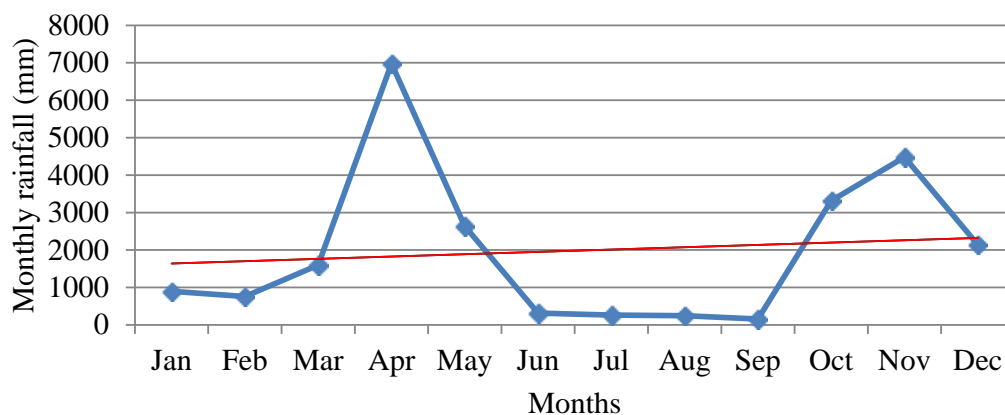


Figure 5. Monthly rainfall trend from 1981 to 2010 for Ngingyang.

2011), semi-arid central Tanzania (Slegers, 2008), Ethiopia (Tilahun, 2006) and Sudano-Sahelian regions (Sivakumar, 1991). Graphical visualization of annual rainfall data in the studied agro-ecological zones presented in Figures 2 to 4 shows that there is an observed increasing trend of total annual rainfall for Baringo highland and a decreasing trend for Baringo lowland. Baringo midland also showed a decreasing trend. This variation in rainfall amounts among the three agro-ecological zones may be attributed to variations in altitude and land use intensity in the specific locations.

Monthly rainfall trends

According to the performed analysis on monthly rainfall trend, the highest monthly rainfall was observed during the month of April in the three agro-ecological zones. The maximum monthly rainfall was 6,981, 9,861.7 and

2,572.6 mm for IL6 (Ngingyang), LM5 (Chemususu) and LH2 (Perkerra) stations respectively. The lowest rainfall monthly totals were recorded during the month of January in Chemususu (1508.7 mm) and Perkerra (575.2 mm) stations while in Ngingyang, it was recorded during the month of September and this was 156.5 mm. The monthly rainfall in the three agro-ecological zones had a mixture of increasing and decreasing trends. Figures 5 to 7 illustrate monthly total rainfall trend pattern for the three agro ecological zones of Baringo County. The highest monthly rainfall recorded in the month of April in Baringo may be attributed to long rains that occur in April to August.

Conclusion

The study examined rainfall variability in Baringo County by providing trends since the 1980's, coefficient of

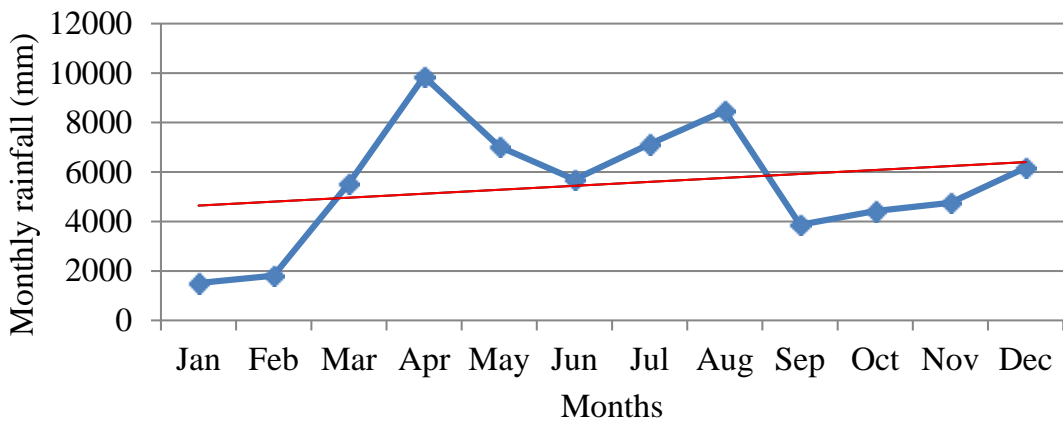


Figure 6. Monthly rainfall trend from 1981 to 2010 for Chemususu.

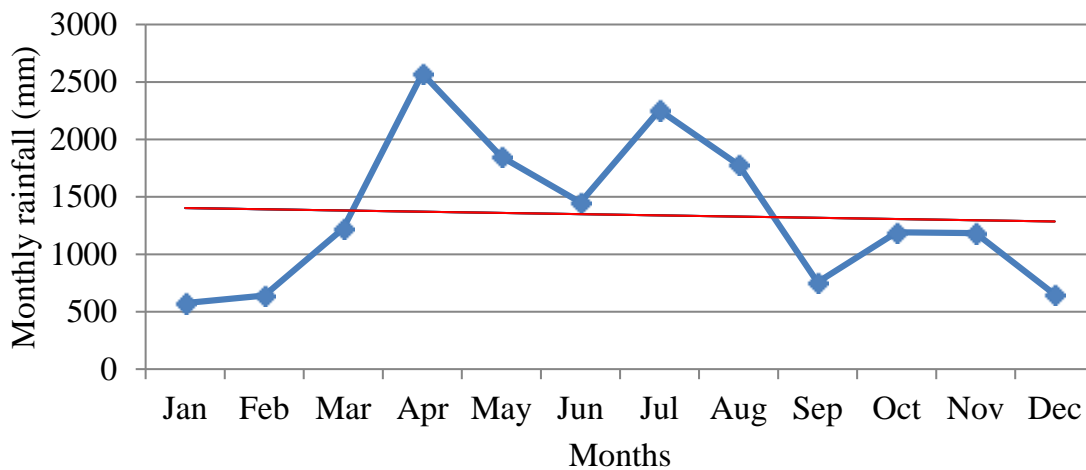


Figure 7. Monthly rainfall trend from 1981 to 2008 for Perkerra.

variation and mean rainfall amount. The findings of this study have established that rainfall is variable as demonstrated by inter-annual variability. Total annual rainfall also varied among the three Agro-ecological zones. Annual rainfall in LH2 (Lembus central) showed a positive trend whereas in LM5 (Salabani) and IL6 (Ribkwo), it showed negative trends. Nearly all the years in IL6 showed below normal mean rainfall. This is attributed to increase in extremes of rainfall on the annual scale such as high intensity rainfall and droughts thus affecting the variability. Variations in amount of rainfall by agro-ecological zones are attributed to variations in altitude and land use intensity in the specific locations. High land areas showed increasing amounts and higher variability in rainfall as opposed to low lying areas which showed decreasing amounts and less variability within and between the years. There is climate variability in Baringo which in the long term would constitute climate

change. This has huge implications on hydrological systems and water resources. The study has confirmed that the arid and semi arid lands (ASALs) suffer from significant climate variability which has huge implications on water resources. The constraints posed by climate variability on water resources range from pronounced seasonality of rainfall to severe and recurrent droughts. Generally, extreme climatic events and mean value of rainfall influence water resources that are mainly rain-fed. Thus, to counter the adverse effects of climate change, there is a need for increase in awareness of climate change and development of appropriate mitigation measures. Local and national governments need to be proactively involved in local, national and global efforts to adapt to and mitigate climate change impacts. This is particularly important in ASALs where the impact of climate change is more severe than in humid lands, yet adaptation and mitigation capabilities in these areas are

weak.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

ABBREVIATIONS

ACDI, African Climate and Development Initiative; **ASAL**, Arid and Semi-Arid Lands; **FAO**, Food and Agriculture Organization; **IL6**, Inner Lowland 6; **IPCC**, Intergovernmental Panel on Climate Change; **KNBS**, Kenya National Bureau of Statistics; **LH2**, Lower Highland 2; **LM5**, lower Midland 5; **ODI**, Overseas Development Institute; **RoK**, Republic of Kenya; **UNDP**, United Nations Development Programme.

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Full Length Research Paper

Healthcare waste management practices and risk perception of healthcare workers in private healthcare facilities in an urban community in Nigeria

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Medical waste, despite the relatively small amounts in which it is generated, is a major concern for healthcare professionals and the government mainly because it poses risks to humans and the environment. Previous studies have shown that there is poor management of medical waste in developing nations, and Nigeria is not an exception. Some have surveyed the associated risks but few have studied the risk perceptions among healthcare professionals, particularly in this environment. This study therefore aimed at assessing the waste management practices among healthcare professionals at privately owned health facilities in Ife Central LGA. The study was a cross sectional study that assessed 24 private health facilities in Ife Central Local Government Area of Osun state, Nigeria using self-administered questionnaires, observational checklist and weighing of wastes. Risk perception of respondents was graded on a scale of 1 – 10 as low risk (1-4), average risk (5-6) and high risk (7-10). The facilities assessed generated a median waste of 500 g/day. 62.5% of them separated the waste, while 25% colour coded; however, none correctly matched the colours with the appropriate category of waste. 79.2% stored their waste in dustbins, and 75% of them burned while 20.8% buried the waste as a means of disposal. 45.8% had sharps boxes, 29.2% disinfected sharps before disposal; disposal was mostly by burning (41.7%). Over 90% of respondents were aware of health risks associated with health care waste management, with HIV (71%) and HBV (67%) being the most reported. Over a third (38%) of the respondents considered themselves to be at average risk with regards to health care wastes. Generation of medical waste is low in Private health facilities. However, open burning remains the way of disposal for such wastes and the health care professionals do not consider themselves at high risk from these wastes.

Key words: Health care waste, management, private facilities, hospital, medical.

INTRODUCTION

Waste is an inextricable product of life that is generated from a variety of sources including homes, offices, industries, healthcare facilities amongst others. Medical waste is considered as waste which is generated in the

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diagnosis, treatment or immunization of human beings or animals, in research pertaining thereto, or in the production and/or testing of biological entities (WHO, 2015; USEPA, 2013). Medical waste can be categorized into two broad categories: general (non-hazardous) and hazardous (infectious and highly infectious) waste (Brichard, 2002). General waste generated in healthcare facilities is similar to household waste and do not pose any risk of injury or infections under conditions in which they are generated, if separated at source. Hazardous waste is one whose health outcome is related to undesired physical, chemical and biological health damages in the course of its handling, processing and management (Park, 2009; Johannessen et al., 2000).

Medical waste should be of major concern to healthcare workers and government at all levels because it can be both infectious and hazardous (Wahab and Adesanya, 2011). Doctors, nurses, midwives, technicians, sweepers, clients, hospital visitors and patients are at high risk of exposure if poorly managed (Bendjoudi et al., 2009; Alagoz and Kocasoy, 2008). It poses threats to the environment beyond where generated and thus, requires specific treatment and management prior to its final disposal (Johannessen et al., 2000; Klangsin and Harding, 1998). Although, medical waste represents a relatively small portion of the total waste generated in a community, its careful handling and treatment as well as sanitary management is prioritized worldwide (Cheng et al., 2009) since 10-25% of it is regarded as hazardous and creates a variety of health risks (Pruss et al., 1999). Notable among the health risks posed by medical mishandling are infections by Human Immunodeficiency Virus (HIV) and Hepatitis B and C viruses. Other potential consequences associated with HCWs include infections by antibiotic resistant bacteria, punctures, abrasions and cuts from sharps as well as exposure to chemical irritants (Wahab and Adesanya, 2011).

The World Health Organization estimates that each year there are about 8-16 million new cases of Hepatitis B virus (HBV), 2.3-4.7 million cases of Hepatitis C virus (HCV), and 80,000 to 160,000 cases of HIV due to unsafe injections and mostly due to very poor HCW management systems (WHO, 2015; Townend and Cheeseman, 2005). There should be safe handling of HCW from production to the point of disposal. Unlike domestic waste, medical waste cannot be disposed of through regular channels because of its infectious characteristics. There has to be a HCW management protocol and facilities to be used by its handlers to avoid infection and cross contaminations. The quantity of HCW is increasing which should be handled and managed sanitarily; it should therefore necessitates development, adoption and use of standard HCW management protocol to avoid wide and varied consequences on public health beyond where they are generated.

Medical waste is expected to be separated at source through colour coding of bins or bin-liners; this should be followed by treatment and disinfection highly infectious

waste, prior to sanitary disposal of the hazardous components by incineration while the general waste should be disposed with municipal waste management stream. However, there are concerns that medical waste is being disposed with domestic waste (Awodele et al., 2016; Al Emad, 2011). This can have grave consequences. There has been an initiative recently to increase knowledge on the hazardous nature of medical waste among healthcare workers, but there seems to be a dearth of knowledge on how generated medical waste can be disposed.

What happens beyond the storage of the waste? There seems to be poor implementation of the National Healthcare Waste Management Plan, poor documentation of the quantity of medical waste generated, and how the waste generated is disposed. Studies have shown that there is poor management of medical waste in developing nations (Hassan et al., 2008). Some have surveyed the associated risks but few have considered the risk perceptions among healthcare professionals (Ferreira and Teixeira, 2010). In Nigeria, several studies (Abah and Ohimain, 2011; Stanley et al., 2011; Fadipe et al., 2011) have looked at different dimensions of health care waste management in Nigeria, especially in public settings. This study therefore aim to assess the quantity and categories of waste generated by private facilities, their waste management practices, determine the level of implementation of waste management policies if they exist and assess the risk perception of health care personnel towards medical wastes.

MATERIALS AND METHODS

The study was conducted in the ancient town of Ile-Ife in Ife Central Local Government Area of Osun State, Nigeria. The population of the town was estimated to be 167,254 and majority of the residents are farmers, traders and civil servants. The town has 20 registered private hospitals/clinics and several public primary health centers, 2 secondary health facilities and 1 tertiary hospital. The study design was descriptive cross-sectional in nature and all the private healthcare facilities within the study area were assessed.

The study utilized mix-methods in data collection using quantitative and qualitative instruments. The study adapted and used the UNEP/WHO (2004) questionnaires for assessing health care waste, comprising of open and closed ended questions in three sections. The first section of the questionnaire assessed facility attributes, while the second section assessed their medical waste management practices. The third section assessed the level of risk perception of the respondent on a Likert scale from 1 to 10 and risk was graded as low risk (1-4), average risk (5-6) and high risk (7-10). A pre-test of the questionnaire was carried out in Modakeke, an adjoining community, using ten health facilities to assess the relevance of the questions asked and for content validity. Data was obtained using the pretested, self-administered semi-structured questionnaire which was administered to the in-charge/ owner of the facility after obtaining informed consent. Qualitative assessment was also carried out by direct observation using a facility assessment checklist regarding waste generation, storage, collection, recycling and disposal.

The HCFs were given waste disposal bags to store their waste from 8 am till 7.59 am the following day. Waste generated from

Table 1. Characteristics of facilities assessed.

Variable	Frequency (N=24)	Percentage
Type of facility		
Hospital	9	37.5
Clinic	11	45.8
Maternity Centre	2	8.3
Medical Laboratory	2	8.3
Services offered (multiple answers allowed)		
Medical	15	62.5
Obstetrics and Gynaecology	12	50.0
Surgical	13	54.2
Paediatric	13	54.2
Emergency	13	54.2
Radiology	3	12.5
Laboratory	3	12.5
Have existing waste management policy	15	62.5
Have waste management plan in facility	19	79.2
Have designated waste management officer	12	50.0
Health care waste manager trained	7	29.2

each health facility was weighed at 8am every day for 1 week, using a SECA® weighing scale and measured in gram. Univariate (tables and charts where appropriate) and Bivariate (Kruskal-Wallis) analyses were done using Statistical Product for Service Solution (IBM-SPSS) version 17. The level of significance was set at <0.05. Ethical clearance was sought and obtained from the ethics committee of the Institute of Public Health, Obafemi Awolowo University, Ile-Ife. Written informed consent was obtained from head of facilities before administration of questionnaires and collection/weighing of wastes.

RESULTS

Table 1 presented the characteristics of the private HCFs studied. Most of the facilities assessed (46%) operated as clinics while 38% operated as hospitals. Over 60% offered medical services while over half offered specialty services such as Obstetrics and Gynaecology, Surgery, and Paediatrics. Over 60% of the facilities had waste management policies with 80% having a waste management plan; while 50% had a designated waste management officer and only about 30% have had any training. The facilities assessed had a median weight of generated waste of 500 g/day ranging between 100-2000 g/day. Dressings were the type of waste most generated, accounting for 87.5% of facilities followed by sharps (83.3%) and domestic waste (79.2%). Majority of the facilities (62.5%) claimed they segregated waste at source with only 25.0% reporting that they colour coded sorted wastes. However, none were able to identify the colour codes for the different categories of waste generated. Dustbin was the most commonly used method of collecting waste (79.2%) followed by plastic bags

(42.0%). Enclosed open burning was the most frequent method of waste disposal (75%) followed by burying (20.8%), while 17.0% dump it alongside communal waste (Table 2).

In addition, Table 3 showed that less than half (45.8%) of the facilities assessed had sharps boxes and few (29.2%) disinfected sharps (majorly by boiling (42.9%) before disposal which most (41.7%) did by burning. Table 4 shows that 91.7% of individual respondents were aware of health risks associated with handling medical waste mostly of HIV (70.8%) and HBV (66.7%) infections. 87.5% of them felt they were at risk and most (75%) use personal protective equipment commonly gloves as means of protection from these risks. Over a third of the respondents (38.1%) felt they were at average risk while 28.6% felt they were at high risk and a third (33.3%) felt they were at low risk, as shown in Figure 1. Although there was no significant association between professions and perceive risk, over half of the doctors interviewed (55.6%) have low risk perception compared to none of the nurses and 50% of other health workers (Table 5).

DISCUSSION

This study assessed healthcare waste management practices of private hospitals and observed that only 62% had a copy of the waste management policy and 79% had a facility health care waste management (HCWM) plan which should serve as a roadmap for waste management. These figures are much higher than those reported in other studies (Ngwuluka et al., 2009; Joseph

Table 2. Characteristics of waste generated in the facilities.

Variable	Frequency (N=24)	Percentage
Median weight of waste generated daily (g)	500	
Range of waste generated daily (g)	100 – 2000	
Type of waste generated (multiple options chosen)		
Domestic waste	19	79.2
Sharps	20	83.3
Blood	15	62.5
Dressings	21	87.5
Others (injection bottle, intravenous fluids)	4	16.7
Waste segregation at source		
Yes	15	62.5
Waste colour coded		
Yes	6	25
Correctly matched waste with appropriate colour	0	0
Means of waste storage (multiple options chosen)		
Trash bins	19	79.2
Plastic containers	10	41.7
Nylon bags	8	33.3
Others	1	4.2
Method of waste disposal (multiple options chosen)		
Communal bin	4	16.7
Burning	18	75.0
Incineration	4	16.7
Burying	5	20.8
Landfill	2	8.3

and Krishnan, 2004). Despite the availability of HCWM plan, only half of the private facilities had a designated staff and only a quarter had received training on HCWM which is much higher than 7% as reported by Oli et al. (2016) in Nigeria, but lower than reports from other studies (Ferreira and Teixeira, 2010; Joseph and Krishnan, 2004). The amount of waste generated in this current study range from 0.1kg to 2.0 kg per health facility with the median waste generated been 0.5kg which is similar to that found by Fadipe et al. (2011) in Osun state that found the range to be 1.0kg to 2.8kg and 1.0kg as the average. This suggests that waste generation is low in private hospitals in this environment which might be indicative of low client load.

Waste segregation at source is a veritable step in proper waste management. Though, two-thirds (65%) reported segregating waste at source which is much higher than 12% reported by Oli et al. (2016). Also, a quarter (25%) of the facilities assessed reported colour coding wastes; although the veracity of this claim could not be ascertained as none could correctly identify the colour codes for different medical wastes. This is contrary to the findings from a study by Ngwuluka et al. (2009) in

Jos that reported that some health facilities correctly matched the colours and Awodele et al. (2016) in Lagos where more than half could correctly identify the colour codes.

Waste generated in health facilities need to be stored hygienically to prevent contamination and spread of nosocomial infections; however in this study, 80% store in regular trash bins which is similar to findings from other studies (Fadipe et al., 2011; Ngwulakwu et al., 2009) and buttresses the fact that colour coding of waste is poorly practiced. A sixth of facilities still dispose their waste along with communal wastes though far lower than reports from Fadipe et al. (2011) and this poses a significant threat to the community where scavenging is still very rife due to poverty. This might be a pathway for hospital infections to get into the community. Only half of the facilities assessed had safety boxes, which is a key component of waste segregation and a vital prevention mechanism for sharp associated accidents. This is much lower than 75% of facilities reported by Awodele et al. (2016).

Majority (60%) of the respondent felt they were at risk which is consistent with the findings of Ferreira and

Table 3. Disposal of sharps in the facilities.

Variable	Frequency (N=24)	Percentage
Presence of sharp boxes	11	45.8
Disinfect sharps before disposal	7	29.2
Method of disinfection (N=7) (multiple options chosen)		
Autoclave	1	14.3
Boiling	3	42.9
Chemical	2	28.6
Others	4	57.2
Method of sharp disposal (multiple options chosen)		
Burning	10	41.7
Burying	7	29.2
Incineration	3	12.5
Open dumping	1	4.2
Communal bin	3	12.5
Others	2	8.3

Table 4. Awareness of risks associated with handling health care wastes among respondents.

Variable	Frequency (N=24)	Percentage
Awareness of health risk associated with HCWM		
Yes	22	91.7
No	2	8.3
Health risks (multiple options chosen)		
Hepatitis B	16	66.7
Hepatitis C	11	45.8
HIV	17	70.8
Tetanus	13	54.2
Chemical irritation	14	58.3
Physical injury	13	54.2
Feel at risk from handling medical waste	21	87.5
Method of self-protection from risks		
Use Personal Protective Equipment	18	75
Use Disinfection or Proper Disposal Methods	1	4.2
Being careful	4	16.7

Teixeira (2010) in Portugal and nurses felt more at risk than doctors. However, despite the perceived risk, only a few took precautions to protect themselves which is consistent with the findings reported by Awodele et al. (2016) in Lagos. This disconnection between perceived risk and protection of self may be attributed to ignorance or lack of personal protective equipment. Most people felt they were at risk of acquiring Human Immunodeficiency syndrome, hepatitis B virus infection, and chemical irritation; while only a few felt they are at risk of hepatitis C virus infection, Tetanus and physical injury.

Conclusion

Waste generated in private health facilities is small compared to other health facilities, and despite the availability of HCWM plans, implementation is still poor. Most people are aware of the risks associated with handling medical waste; however, risk perception is still low. Health Care Workers should be trained on waste management to address waste segregation, colour coding, protection from hazards and increase their risk perception.

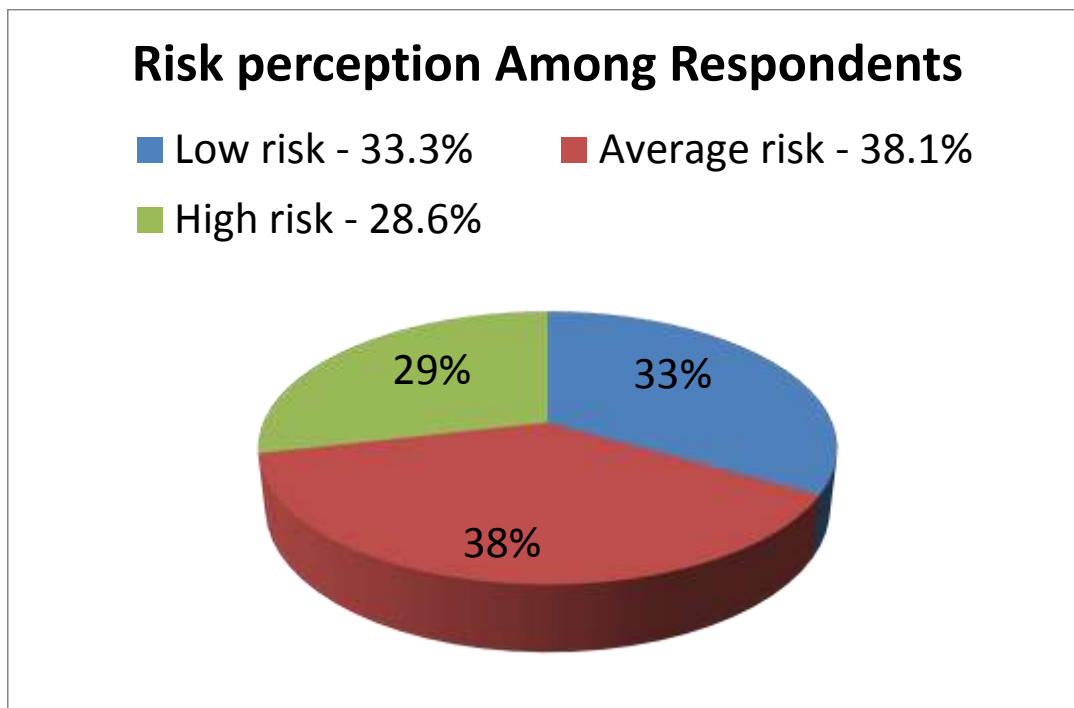


Figure 1. The risk perception among respondents.

Table 5. Association between profession and level of perceived risk.

Person Interviewed (N=18)	Level of perceived risk			
	Low risk (Percentage)	Average risk (Percentage)	High risk (Percentage)	
Doctor (N=9)	5 (55.6)	3 (33.3)	1 (11.1)	K-W = 5.76 p = 0.06
Nurse (N=7)	0 (0)	3 (42.9)	4 (57.1)	
Others (N=2)	1 (50)	0 (0)	1 (50)	
Total	6 (33.3)	6 (33.3)	6 (33.3)	

K-W: Kruskal-Wallis Statistic.

Limitations

The researcher was unable to characterize the waste generated after weighing because of the inherent risk inseparation of these wastes. They were also unable to undertake a proper risk assessment and had to rely on self-reported risk perception, which is subjective and may be prone to social desirability bias.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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Full Length Research Paper

Seasonal variation of heavy metal speciation in soil and stream sediments from hospital waste dumpsite in Ilesa, Southwestern Nigeria

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A speciation study of selected heavy metals in soil and stream sediments around a hospital waste dumpsite was investigated. Sequential extraction procedure was used to fractionate the metals into 4 fractions: Exchangeable and bound to carbonate, oxyhydroxide of Fe and Mn, organic matter and the residual fraction. Speciation analysis of Fe, Mn, Zn, Cu, Cd and Pb in soil revealed that a major portion of the metals were associated with the residual fraction. The exchangeable and carbonate fraction was the most important fraction for Mn_(Dry/Wet) and Zn_(Dry/Wet) with an average of (27%, 35.6%) Mn and (20.8%, 27.3%) Zn. Cd, Fe and Cu were associated with the oxyhydroxide of Fe and Mn fraction with an average of (61%, 44.2%) Cd_(Dry/Wet), (41%, 21%) Fe_(Dry/Wet) and (25.3%, 22.5%) Cu_(Dry/Wet). A significant amount of Pb_(Dry/Wet) (10.7%, 21.8%) was bound to organic fraction during dry and wet season respectively. In sediments, Mn_(Dry/Wet) occurred mainly in exchangeable and carbonate fraction (45.2%, 29.3%), Fe_(Dry/Wet) and Cd_(Dry/Wet) in the oxyhydroxide of Fe and Mn fraction were (41%, 31.2%) and (26.6%, 93.6%) respectively and the amount of Pb_(Dry/Wet) bound to the organic fraction was (86.9%, 27.3%). A significant amount of Cu_(Dry/Wet) (20.8%, 29.4%) was bound to the organic fraction and Zn_(Dry/Wet) (35.5%, 73%) was retained in the residual fraction. In soil and sediments, Mn was potentially more bioavailable. However, the level of lead in organic matter fraction of soil suggest that it may be remobilized under oxidizing condition, hence, bioavailable.

Keywords: Speciation, hospital waste, heavy metal, sediments, soil.

INTRODUCTION

Hospital wastes are waste generated within the hospital environment which comprises of pharmaceutical, radioactive, general, sharp, laboratory waste and radioactive materials capable of causing infectious diseases resulting from patient investigation, treatment

and diagnosis (Akter, 2000; Abor and Bower, 2008). Waste produced in the hospital and other health care facilities in developing countries have raised serious concerns due to the inappropriate treatment and final disposal practices accorded to them. In Nigeria, more

disposed in open land area (Vivan et al., 2011). Open dumping of hospital waste is an important cause of natural environmental degradation and constitute a health hazard due to the release of heavy metals, chemical solvents, preservatives and infectious substances into the underlying soil and possibility of leachate entering an aquifer or nearby surface water (Akter, 2000).

Heavy metals are metals and metalloids with atomic density of 4 g/cm^3 , greater than that of water (Hutton and Symon, 1986, Garbarino et al., 1995). Heavy metals are also called trace elements because of their presence in trace amount in various environmental matrices. The essential heavy metals such as Cu, Fe, Cr, Se, Zn, Mn and Ni exert biochemical and physiological functions in plants and animals. They are important constituents of several key enzymes and play important roles in various oxidation-reduction reactions (WHO, 1996). However, toxic heavy metals are arsenic, cadmium, chromium, lead and mercury. Because of their high degree of toxicity, these five elements rank among the priority metals that are of great public health significance. They are all systemic toxicants that are known to induce multiple organ damage, even at lower levels of exposure. According to United State Environmental Protection Agency (USEPA) (2002), these metals are also classified as either "known" or "probable" human carcinogens based on epidemiological and experimental studies showing an association between exposure and cancer incidence in humans and animals. The bioavailability of heavy metals may be influenced by physical factors such as temperature, phase association, adsorption and sequestration. It is also affected by chemical factors that influence speciation at thermodynamic equilibrium, complexation kinetics, lipid solubility and water partition coefficients. Biological factors such as species characteristics, trophic interactions and biochemical/physiological adaptation, also play an important role (Verkleji, 1993).

Over the years, heavy metals have been a threat to the environment as they can bioaccumulate to toxic level within an ecosystem and endanger its health. When agricultural lands are polluted with heavy metals, they are assimilated by plants (Trueby, 2003); animals feed on contaminated plants and accumulate the metals to toxic level which move quickly through the food chain, affecting the health of animals and humans (Peplow, 1999). Today, it is generally recognized that measurements of total metal concentration has the potential of grossly overestimating the risk (Ogunfowokan et al., 2009).

Despite high total concentration of metals in certain soil and sediments, the metals are not readily available for

incorporation in the biota, hence associated environmental effects may be low (Marco et al., 2005).

Therefore, to estimate the effects and potential risks associated with elevated elemental concentrations that result from natural weathering or anthropogenic activities, information on the physicochemical forms: the mobility, pathway and bioavailability is determined by selective chemical speciation in soil and sediments (Kot and Namiesnik, 2000; Davis et al., 1994). Chemical speciation can be broadly defined as the identification and quantification of the different defined species, forms or phases in which an element occurs (Ure et al., 1993; Hu et al., 2003). Investigating the distribution and speciation of heavy metals in soil will not only provide information on the degree of pollution but the actual environmental impact as regards metal bioavailability and their origin.

Previous work done in the study area by Olabanji et al. (2015) on total metal concentration of the soil showed that the hospital waste dumpsite greatly contribute to the increase in concentration of elements in the soil. The pH shows that characteristics of a slightly acidic soil may enhance metal dissolution for soil uptake. Therefore, surface runoff from the hospital dumpsite and erosion from surrounding land areas may eventually increase the level of metals and other pollutants in the stream water and sediments. Hence, this study aimed at quantifying the amount of metal ion that are bioavailable in soil and sediments for uptake. Agricultural practices around the dumpsite and the presence of a nearby stream where run-off from the dumpsite is emptied necessitate this study.

MATERIALS AND METHODS

General description of the study area

The area designed for this study was OAUTHC located in Ilesa East Local Government, Osun State. The sampling location is Lat $07^{\circ} 36' 819''$ N and Long $004^{\circ} 44' 968''$ E with elevation of 387 m.

Sample collection and pre-treatment

The land area around the hospital dumpsite as shown in Figure 1 was divided into five segments, soil samples were collected randomly from each sampling point with a pre-cleaned hand driven auger. Sediment samples were collected from a stream located at 110 m from the dumpsite with a stainless steel hand trowel. The samples were put in a polyethylene bags, brought back to the laboratory and air dried. The dry samples of soil and sediment were crushed with pre-cleaned porcelain mortar and pestle and passed through 2 mm mesh size sieve and then stored at room temperature prior to analysis (Sharma et al., 2009) (Figure 2).

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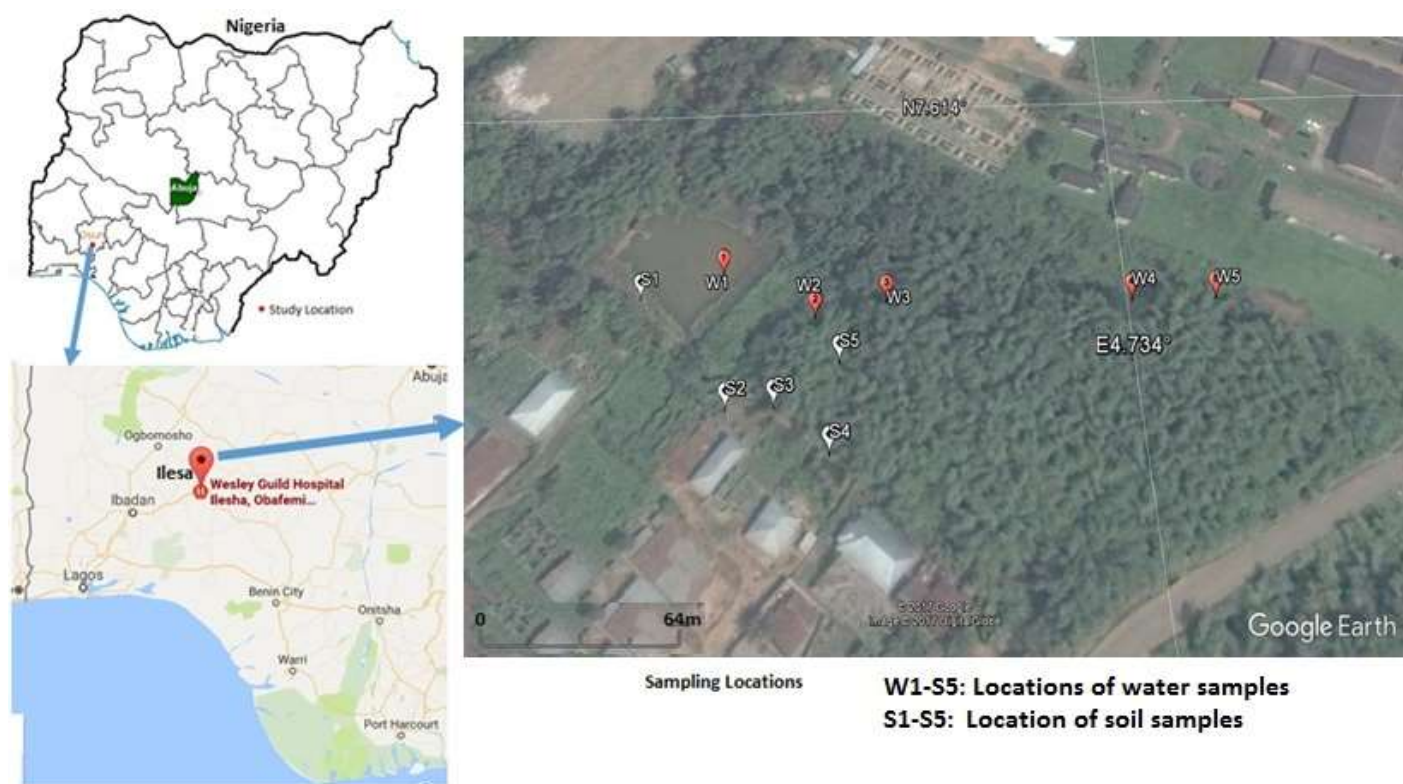


Figure 1. Map of the study area showing the sampling points.

Sterilization of apparatus

All glassware, polypropylene tubes were washed with liquid detergent, rinsed first with tap water and distilled water, and then soaked in 10% HNO_3 (v/v) for 48 h. Then, they were re-washed with liquid detergent and rinsed thoroughly with doubly distilled water. Thereafter, the apparatus were oven dried for 12 h at a temperature of 80°C. All the reagents used were of analytical grade.

Sequential extraction procedure

The selective sequential extraction method used was based on the procedure used by Baffi et al. (1998), with improvements made according to the European Community Bureau of Reference (BCR 701), which examined and finally eliminated irreproducibility sources. The BCR procedure is made up of three steps, which dissolve the following phases of metals, respectively: exchangeable and bound to carbonate, bound to Fe and Mn oxides and hydroxides, bound to organic matter and sulphides (Ure et al., 1993).

Exchangeable and bound to carbonate phase (phase 1) was extracted with 0.11 M acetic acid, while the fraction bound to Fe-Mn oxides (phase 2) with 0.5 M hydroxylamine hydrochloride, was adjusted to pH 2 with nitric acid (65%). The fraction bound to organic matter and sulphides (phase 3) was extracted with 8.8 M hydrogen peroxide. The metal content of the residual phase was obtained from the difference between the total content and the sum of phases 1, 2 and 3, according to Ianni et al. (2001) and Mester et al. (1998). After each extraction, the samples were centrifuged at

4000 rpm for 20 min by placing the samples in Teflon centrifuge tubes, followed by decantation and filtration. Deionized water was used to wash the residues after subsequent extractions in order to ensure selective dissolution and avoid possible interference from interphase mixing between the supernatants. All samples were run in triplicates.

Quality control measures

Blank determination

Together with each determination was a blank prepared to check for background levels of Fe, Mn, Cu, Zn, Cd and Pb in the reagents used for the various leaching procedure. Blank correction was carried out in the result of metal determination.

RESULTS AND DISCUSSION

Table 1a to f present the mean percent distribution of particular speciation forms of the metals in the stream sediments. Manganese in sediments was found mainly in the exchangeable and carbonate fraction, which is the bioavailable form (45.2 and 29.3%) and the residual fraction (27.9 and 54%) during dry and wet seasons, respectively. In a smaller amount, Mn was bound to the hydrated iron and manganese oxide fraction (16.8 and



Figure 2. (a) Dumpsite. (b) Representative of the sampling points W2 to W5. The locations are covered by vegetation in Figure 1. (c) Farming activities on hospital waste dumpsite.

14.3%); only 8.9 and 2.4% was found in the organic matter fraction during dry and wet seasons, respectively.

Iron in the sediments was mainly found in the hydrated iron and manganese oxide fractions (41 and 31.2%) and the residual fraction (24.4 and 40.9%) during the dry and wet seasons, respectively. The fraction of iron in the exchangeable and carbonate form was smaller (10.1 and 25.8%) and in the organic matter fraction, it was 20.6 and 2.1% during the dry and wet seasons, respectively.

Zinc in the sediments was mostly retained in the

residual fraction (35.5 and 73%), lesser amount of zinc was found in the organic matter fraction (39 and 9.8%), exchangeable and carbonate fraction (21 and 5.6%) was found in the hydrated iron and manganese oxide fraction (4.5 and 11.8%) during the dry and wet seasons, respectively. During the wet season, large amount of zinc is occluded in the residual fraction, which may be responsible for low amount found in the other mobile fractions.

A similar distribution of zinc in the chemical fraction

Table 1a. Selective extraction for manganese (mg/kg) in sediments.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
W2	113.25±0.05	39.93±0.23	37.50±0.0	14.55±0.00	21.27	101.3±0.17	33.60±0.01	21.78±0.01	3.88±0.00	42.04
W3	88.63±0.13	24.30±0.00	6.90±0.00	2.35±0.00	50.08	54.80±0.02	14.33±0.01	1.38±0.00	0.73±0.00	38.36
W4	122.55±0.07	68.23±0.01	3.58±0.00	15.75±0.00	34.99	69.72±0.01	25.13±0.00	11.00±0.00	1.23±0.00	32.36
W5	99.20±0.11	59.15±0.01	23.08±0.00	5.05±0.00	11.92	99.86±0.01	22.33±0.00	12.45±0.01	1.88±0.00	63.20
W1 (ctrl)	75.40±0.0.12	24.65±0.00	9.68±0.00	19.43±0.66	21.64	92.90±0.05	10.45±0.01	5.08±0.00	5.90±0.01	71.47
Mean	105.9	47.90	17.76	9.43	29.57	81.43±0.02	23.84	11.65	1.93	43.99

F1 = Exchangeable and specifically adsorbed fraction; F2 = bound to oxide and hydroxide of Fe/Mn; F3 = bound to organic matter fraction; RF = residual fraction; W = stream water sediment; S = soil; Ctrl = control.

Table 1b. Selective extraction for iron (mg/kg) in sediments.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
W2	1620.8±0.14	264.5±0.01	729.0±0.06	193.1±0.02	434.3	1276.3±0.03	323.50±0.01	413.75±0.06	79.15±0.01	459.90
W3	1431.6±0.07	29.1±0.01	619.5±0.07	265.8±0.02	517.2	1136.4±0.11	293.50±0.02	350.25±0.04	12.53±0.00	480.12
W4	1699.2±0.03	105.9±0.02	582.5±0.03	500.5±0.04	510.3	1322.8±0.02	331.5±0.04	377.50±0.02	9.00±0.05	604.80
W5	1701.5±0.12	254.5±0.21	712.3±0.04	372.8±0.04	361.9	1053.0±0.03	286.5±0.037	351.75±0.03	ND	414.75
W1(ctrl)	1310.1±0.05	192.8±0.03	698.5±0.02	0.05±0.00	418.75	897.5±0.14	70.50±0.04	299.0±0.02	ND	528.0
Mean	1613.3	163.5	660.8	333.05	393.4	1197.1±0.10	308.75	373.3	25.18	489.9

F1 = Exchangeable and specifically adsorbed fraction; F2 = bound to oxide and hydroxide of Fe/Mn; F3 = bound to organic matter fraction; RF = residual fraction; W = stream water sediment; S = soil; Ctrl = control.

Table 1c. Selective extraction for zinc (mg/kg) in sediments.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
W2	63.31±0.02	4.25±0.00	2.50±0.00	35.13±0.01	21.43	43.60±1.05	0.45±0.00	4.73±0.00	2.98±0.00	35.44
W3	59.85±0.01	14.68±0.00	5.90±0.00	2.40±0.00	36.87	48.96±0.02	2.25±0.00	4.38±0.00	9.00±0.00	33.33
W4	72.93±0.91	25.60±0.01	ND	21.18±0.01	26.15	44.52±0.00	1.03±0.00	8.63±0.00	3.93±0.00	30.93
W5	98.96±0.01	17.35±0.01	4.98±0.01	56.45±0.01	20.18	63.10±0.01	7.45±0.00	5.82±0.00	3.40±0.00	46.43
W1(ctrl)	32.60±0.11	2.43±0.00	2.48±0.00	2.66±0.08	25.03	30.87±0.00	0.58±0.00	4.58±0.00	2.78±0.00	22.93
Mean	73.78	15.47	3.35	28.79	26.16	50.05±0.02	2.80	5.89	4.83	36.53

F1 = Exchangeable and specifically adsorbed fraction; F2 = bound to oxide and hydroxide of Fe/Mn; F3 = bound to organic matter fraction; RF = residual fraction; W = stream water sediment; S = soil; Ctrl = control.

Table 1d. Selective extraction for copper (mg/kg) in sediments.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
W2	22.15±0.00	1.75±0.001	7.03±0.00	0.25±0.00	13.12	31.78±0.01	3.68±0.00	1.78±0.00	2.75±0.00	23.57
W3	23.23±0.00	0.70±0.002	1.98±0.00	2.20±0.001	18.35	16.62±0.00	1.40±0.00	1.70±0.00	6.90±0.00	6.62
W4	31.40±0.02	1.35±0.001	2.03±0.00	14.48±0.001	13.54	22.15±0.01	1.33±0.00	6.75±0.00	10.33±0.00	3.74
W5	26.86±0.00	5.50±0.059	9.68±0.002	4.65±0.001	7.03	10.38±0.01	0.68±0.00	2.65±0.00	3.78±0.00	3.27
W1(ctrl)	20.51±0.01	4.33±0.00	10.18±0.00	ND	6.00	45.60±0.00	12.7±0.00	11.25±0.00	4.58±0.00	17.07
Mean	23.91	2.33	5.18	5.40	13.13	20.23	1.77	3.22	5.94	9.3

F1 = Exchangeable and specifically adsorbed fraction; F2 = bound to oxide and hydroxide of Fe/Mn; F3 = bound to organic matter fraction; RF = residual fraction; W = stream water sediment; S = soil; Ctrl = control.

Table 1e. Selective extraction for lead (mg/kg) in sediments.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
W2	1.05±0.00	ND	0.98± 0.02	ND	0.07	22.02±0.01	1.03±0.01	17.00±0.02	3.83±0.00	0.16
W3	0.03±0.00	ND	ND	ND	0.03	27.81±0.00	2.20±0.01	19.25±0.03	5.90±0.00	0.46
W4	25.71±0.2	ND	ND	25.60±0.02	0.11	17.77±0.01	1.55±0.02	5.50±0.02	10.20±0.02	0.50
W5	2.68±0.00	ND	2.53± 0.01	ND	0.15	27.02±0.00	2.33±0.02	18.63±0.03	5.88±0.02	0.18
W1(ctrl)	0.42±0.01	ND	0.40±0.01	ND	0.02	23.71±0.02	1.45±0.01	18.08±0.01	4.15±0.02	0.03
Mean	7.37	0	0.87	6.40	0.09	23.67	1.78	15.10	6.45	0.33

F1 = Exchangeable and specifically adsorbed fraction; F2 = bound to oxide and hydroxide of Fe/Mn; F3 = bound to organic matter fraction; RF = residual fraction; W = stream water sediment; S = soil; Ctrl = control.

was found in copper, as it occurs in large amount in the residual fraction (50.6 and 46%), lesser amount were bound to the organic matter fraction (20.8 and 29.4%), hydrated iron and manganese oxide fraction (20 and 15.9%) in small amount, and copper was bound to the exchangeable and carbonate fraction (9 and 8.8%) during dry and wet seasons, respectively. Although, a large percentage of copper was retained in the residual fraction, a significant amount was found in z

fraction III, the oxidizable fraction. This may be because Cu has high affinity for organic matter, which indicates that Cu is associated with strong organic legends (Qiao et al., 2003).

Lead in the sediments was not found in the exchangeable and carbonate fraction, probably, due to minimal concentration of lead extracted in this fraction which is below the detection limit of the instrument. Large amount of Pb was found only in location 3 in the organic matter fraction

(86.9%) and in the form bound to hydrated iron and manganese oxide fraction (11.9%) during dry season. However, there is high percentage extraction in all the fractions during the wet season where lead was mainly found in the hydrated iron and manganese oxide fraction (63.8%), and a significant amount of Pb occurred in the organic matter fractions (27.3%) which may be mobilized and released to bulk water under oxidizable condition. Only 7.5% lead was found in

Table 1f. Selective extraction for cadmium (mg/kg) in sediments.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
W2	0.34±0.00	0.23± 0.00	0.10± 0.00	ND	0.01	0.02±0.00	ND	ND	ND	0.02
W3	0.26±0.00	0.23± 0.00	ND	ND	0.03	0.10±0.00	ND	ND	ND	0.10
W4	1.71±0.00	0.25± 0.00	1.40± 0.00	ND	0.06	2.53±0.01	ND	2.48±0.00	ND	0.05
W5	3.32±0.01	0.55± 0.00	ND	2.58±0.00	0.19	ND	ND	ND	ND	ND
W1(ctrl)	0.25±0.00	0.23± 0.00	0.10± 0.00	ND	0.02	0.11±0.00	ND	ND	0.10±0.00	0.01
Mean	1.41	0.32	0.38	0.65	0.07	0.66±0.00	0	0.62	0	0.04

F1 = Exchangeable and specifically adsorbed fraction; F2 = bound to oxide and hydroxide of Fe/Mn; F3 = bound to organic matter fraction; RF = residual fraction; W = stream water sediment; S = soil, Ctrl = control.

Table 2a. Selective extraction for Manganese (mg/kg) in soil.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
S2	145.5±0.01	48.50±0.01	92.33±0.00	4.03±0.01	4.64	111.15±0.02	40.38±0.00	1.58±0.00	0.65±0.00	68.54
S3	144.5±0.00	39.93±0.01	67.70±0.01	ND	36.87	118.20±0.01	21.28±0.00	20.55±0.00	0.80±0.01	75.57
S4	139.4±0.01	33.53±0.01	46.53±0.01	ND	59.34	70.52±0.01	31.30±0.00	29.60±0.00	0.50±0.00	9.12
S5	149.3±0.01	6.48±0.00	126.1±0.01	1.30±0.00	15.42	75.11±0.01	13.45±0.00	48.00±0.01	7.35±0.01	6.31
S6	121.4±0.01	60.65±0.14	6.58±0.00	4.58±0.00	49.59	66.00±0.02	50.75±0.00	3.23±0.00	1.20±0.01	10.82
S1(ctrl)	242.1±0.01	54.83±0.01	145.5±0.01	3.85±0.00	37.92	98.00±0.00	9.75±0.00	73.7±0.00	8.53±0.00	6.02

F1 = Exchangeable and specifically adsorbed fraction; F2 = bound to oxide and hydroxide of Fe/Mn; F3 = bound to organic matter fraction; RF = residual fraction; W = stream water sediment; S = soil, Ctrl = control.

the exchangeable and carbonate fraction. Lead in low amounts was determined in the residual fraction (1.22 and 1.4%) during dry and wet season, respectively.

Cadmium in the sediments during dry season occurred mainly in the organic matter fraction (45.8%). Smaller amount was found in the hydrated iron and manganese oxide fraction (26.6%) and in the exchangeable and carbonate fraction (22.4%). During the wet season, a major fraction of cadmium was found in the hydrated

iron and manganese oxide form (93.6%). It was below detection limit in the exchangeable and carbonate fractions, and in the organic matter fraction. Like lead, cadmium in low amounts was also found in the residual fraction (5.15 and 6.42%) during the dry and wet seasons, respectively. The low amount of Cd which is below the detection limit in the exchangeable and carbonate fractions and in the organic matter fraction suggests loss of labile metal fraction due to dissolution by acid rain.

The results of sequential extraction of metals in soil are shown in Table 2a to f. In the soil, manganese was sporadically distributed in the hydrated iron and manganese oxide fraction (48.5 and 23.4%), exchangeable and carbonate fraction (27 and 35.6%) and in the residual fraction (23 and 38.6%), and in small amount, manganese was bound to the organic matter fraction (1.4 and 2.4%) during the dry and wet seasons, respectively.

Iron in soil, was mainly found in the hydrated

Table 2b. Selective extraction for iron (mg/kg) in soil samples.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
S2	1,145.9±0.19	1.25± 0.00	499± 0.09	440.3±0.04	205.35	1,225.4±0.09	223.23±0.02	211.73±0.01	ND	790.44
S3	1362.2±0.07	5.78± 0.00	433.3±0.02	675.0±0.02	248	1,398.0±0.02	207.58±0.03	255.25±0.02	ND	935.17
S4	981.4±0.06	4.00± 0.00	387.5±0.06	404.8±0.02	185.1	1,003.2±0.10	80.25±0.01	227.88±0.03	ND	695.07
S5	1796.4±0.04	381.3±0.02	727.0±0.10	422.3±0.03	265.8	1,266.1±0.07	314.5±0.04	270.25±0.02	ND	681.35
S6	1240.1±0.07	12.98±0.01	608.5±0.02	491.3±0.03	127.62	1,310.2±0.12	338.5±0.06	304.75±0.03	ND	666.95
S1(ctrl)	1017.3±0.03	1.15± 0.00	495.8±0.07	402.8±0.03	117.55	998.7±0.15	272.78±0.10	240.13±0.02	ND	485.79

F1 = Exchangeable and specifically adsorbed fraction; F2 = bound to oxide and hydroxide of Fe/Mn; F3 = bound to organic matter fraction; RF = residual fraction; W = stream water sediment; S = soil, Ctrl = control.

Table 2c. Selective extraction for zinc (mg/kg) in soil samples.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
S2	487.4±0.04	120.9±1.77	4.55±0.01	38.70±0.01	323.25	127.2±0.01	48.95±0.00	14.45±0.00	0.40±0.01	63.40
S3	114.6±0.02	10.75±0.58	40.53±0.021	ND	63.32	129.1±1.03	31.68±0.01	21.23±0.00	4.90± 0.00	71.25
S4	98.7±0.91	5.88±0.01	6.28±0.001	0.60±0.00	85.94	98.3±0.1.15	32.55±0.00	20.60±0.00	0.85±0.00	54.0
S5	452.3±0.06	111.1±1.51	174.8±0.55	50.18±0.01	116.22	82.7±0.02	6.43±0.00	10.68±0.01	53.68±0.09	70.75
S6	96.3±0.04	14.1±0.00	3.13±0.00	6.73±0.01	72.34	26.5±0.01	6.60±0.00	16.35±0.01	ND	3.4
S1(ctrl)	104.6±0.01	5.10±0.00	28.15±0.00	2.80±0.00	68.55	22.3±0.03	3.05±0.00	5.55±0.00	2.78±-0.01	10.92

F1 = Exchangeable and specifically adsorbed fraction; F2 = bound to oxide and hydroxide of Fe/Mn; F3 = bound to organic matter fraction; RF = residual fraction; W = stream water sediment; S = soil; Ctrl = control.

Table 2d. Selective extraction for copper (mg/kg) in soil samples.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
S2	65.83±0.01	0.85±0.00	8.93±0.00	16.78±0.00	26.56	31.81±0.01	0.02±0.00	2.30±0.00	3.10±0.00	26.39
S3	57.73±0.00	6.43±0.10	13.70±0.00	2.51±0.00	35.09	28.20±0.01	0.43±0.00	14.63±0.00	6.25±0.00	6.89
S4	28.52±0.01	1.63±0.01	9.18±0.00	1.85±0.00	15.86	19.38±0.01	0.63± 0.01	10.23±0.00	3.3±0.00	5.22
S5	109.1±0.01	4.80±0.02	44.65±0.00	4.00±0.00	55.65	44.43±0.00	3.08 ±0.00	5.78±0.00	25.55±0.00	10.02
S6	58.68±0.01	4.10±0.00	4.63±0.00	2.63±0.00	47.32	31.78±0.00	0.45±0.002	2.15±0.00	2.28±0.00	26.90
Ctrl	65.75±0.01	0.55±0.00	38.55±0.00	13.25±0.00	13.4	16.60±0.02	0.55±0.00	4.53±0.00	1.23±0.00	10.29

F1 = Exchangeable and specifically adsorbed fraction; F2 = bound to oxide and hydroxide of Fe/Mn; F3 = bound to organic matter fraction; RF = residual fraction; W = stream water sediment; S = soil; Ctrl = control.

Table 2e. Selective extraction for lead (mg/kg) in soil samples.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	RF
S2	51.50±0.00	ND	41.0± 0.01	4.75± 0.01	4.00	24.65±0.01	1.65±0.02	2.73±0.02	5.83±0.02	14.44
S3	34.45±0.05	ND	9.55± 0.01	7.45± 0.01	17.45	17.78±0.01	2.25±0.00	5.48±0.03	3.90±0.02	11.63
S4	39.6±0.01	ND	17.45±0.02	4.18± 0.00	17.95	8.43±0.01	1.90±0.00	5.28±0.04	ND	1.25
S5	13.8±0.01	ND	3.95± 0.01	1.50± 0.01	8.35	29.50±0.01	1.80±0.03	18.2±0.02	5.90±0.01	3.60
S6	33.62±0.13	ND	16.15±0.01	0.60± 0.01	16.87	18.23±0.00	1.95±0.02	2.75±0.01	1.58±0.02	11.95
S1(ctrl)	49.45±0.01	ND	ND	1.43±0.01	48.0	27.50±0.00	1.08±0.04	17.43±0.01	5.58±0.02	3.41

F1 = Exchangeable and specifically.

Table 2f. Selective extraction for cadmium (mg/kg) in soil samples.

Location	Dry season (mg/kg)					Wet season (mg/kg)				
	Total	F1	F2	F3	RF	Total	F1	F2	F3	F4
S2	2.95±0.00	0.35± 0.00	1.13± 0.00	0.98± 0.00	0.49	4.74±0.01	ND	2.90±0.00	1.63±0.00	0.21
S3	1.21±0.00	0.10± 0.00	0.30± 0.00	ND	0.82	5.66±0.00	ND	2.73±0.00	1.88±0.00	1.05
S4	12.0±0.01	1.55± 0.00	9.50± 0.00	0.73± 0.00	0.22	5.09±0.00	ND	2.55±0.00	1.43±0.00	1.11
S5	2.46±0.00	1.65± 0.00	0.63± 0.00	0.15± 0.00	0.03	3.84±0.01	ND	2.35±0.00	1.40±0.04	0.09
S6	3.25±0.01	0.88± 0.03	2.18± 0.00	ND	0.19	4.75±0.00	ND	2.55±0.00	1.73 ±0.00	0.47
S1(ctrl)	1.01±0.00	0.05± 0.00	0.13± 0.00	0.45± 0.00	0.38	5.03±0.00	ND	2.43±0.00	1.93±0.03	0.67

F1 = Exchangeable and specifically adsorbed fraction; F2 = bound to oxide and hydroxide of Fe/Mn; F3 = bound to organic matter fraction; RF = residual fraction; W = stream water sediment; S = soil; Ctrl = control.

iron and manganese oxide fraction (41 and 20.5%) and in the residual fraction (15.8 and 60.8%) during the dry and wet seasons, respectively. Iron occurred in the organic matter fraction (37.3%) during the dry season only. In smaller amount, it was found in the exchangeable and carbonate fraction (6.2 and 18.8%) during the dry and wet seasons, respectively.

Zinc was mainly retained in the residual fraction (53 and 56.7%), and in smaller amount, it occurred in the exchangeable and carbonate

fraction (20.8 and 27%) and hydrated iron and manganese oxide fraction (18.4 and 18%). Only 7.9 and 12.9% of zinc was bound to the organic matter fraction during the dry and wet seasons, respectively.

Copper was mainly found in the residual fraction (54.6 and 48.6%) and in the form bound to hydrated iron and manganese oxide fractions (25.3 and 22.5%) during the dry and wet seasons, respectively. In small amount, copper was bound to organic matter fraction (8.8 and 26%) and in

exchangeable and carbonate fraction (5.6 and 2.9%) during the dry and wet seasons, respectively. The high amount of copper in the organic matter fraction may be attributed to the ease of complexation and peptisation products formed between the metal and natural organic matters like humic and fulvic acids. This suggests it high affinity for organic compounds.

Lead in the soil was mostly found in the hydrated iron and manganese oxide fraction (50.9 and 35%) and the residual fraction (37.3 and

43.7%), smaller amount of lead was bound to organic matter (10.7 and 11.7%) during the dry and wet seasons, respectively. 9.6% lead occurred in the exchangeable and carbonate fractions during the wet season, while Pb was below the detection limit during the dry season. As a result, Pb was immobilized in the sediment.

Cadmium in soil was found mostly in the hydrated iron and manganese oxide fraction (61%) and in exchangeable and carbonate fraction (20.5%), and small amount of it was determined in the organic matter fraction (9.4%) and residual fraction (9.1%) during the dry season. In the wet season, cadmium occurred in large amount in the hydrated iron and manganese oxide fraction (54.2%) and the organic matter fraction (33.3%); 12.5% Cd was bound to the residual fraction while it was below detection limit in the exchangeable and carbonate fraction.

The mobile and bioavailable form of metals for uptake in soil and sediments are the exchangeable- carbonate and the organic matter fractions, the release is largely influenced by the pH. Lead and cadmium among other metals determined in this study are toxic metals. The high levels found in the exchangeable carbonate and organic matter fractions which are the bioavailable form of the metals, suggest that the metals could be released and bioaccumulated overtime in the ecosystem. The health hazards of lead include renal failure, impairment of hearing ability, increased frequency of miscarriages and still births, interference with red blood cells and delayed or impaired neurobehavioral development in children (Goyer et al., 1991). Cadmium exposure may lead to chronic kidney stones, severe osteoporosis and osteomalacia with simultaneous severe renal dysfunction (ATSDR, 1999).

Generally, high percentage of metals in the residual and Fe-Mn oxide fractions of the soil and sediment was probably due to the high association or retention ability of the mineral crystal structure, such as with the dendritic silicates and resistant sulphides.

Conclusion

Speciation study of metals has been investigated in soil and sediments. The distribution of the studied metals in the various fractions confirms their differences in bioavailability. There are indications that manganese among other metals occurred mainly in the exchangeable and carbonate forms. Therefore, it can be released to bulk water as a result of changes in ionic composition or decrease in pH of the medium. Iron, cadmium and lead were mostly bound to the hydrated iron and manganese oxide form, organic matter fraction and the residual fraction. Copper in significant amount were found in the organic matter fraction, which indicate the high affinity of copper to form organic compounds. The significant

amount of lead and cadmium in the organic matter fraction suggest and that it may be released during decomposition or oxidation of organic matter under oxygen rich condition. Overtime, these metals may be released into the ecosystem, enter the food chain and bioaccumulate to toxic level in man. A similar distribution pattern of the metals in the chemical fraction in soil and sediments indicates that the dumpsite impact the environment negatively. Hence, continuous monitoring of the metals in this study area and similar site is important. Also, proper hospital waste disposal should be enforced for environmental safety.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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Full Length Research Paper

The impacts of climate change and variability on crop farming systems in Semi-Arid Central Tanzania: The case of Manyoni District in Singida Region

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This paper focuses on the impacts of climate change and variability on crop farming. The main objective of this paper is to assess the impacts of climate change and variability on crop farming systems in Manyoni district, Tanzania. This paper used mixed research design with both quantitative and qualitative research approaches. The research used different methods in collecting information concerning the impacts of climate change and variability on crop farming systems such as key informants interviews, focus group discussions and observations methods. Secondary data were collected through documentary review. Questionnaires were administered to 362 heads of households from four study villages namely Lusilile, Udimaa, Makanda and Magasai. Findings of the research revealed that majority of the farming households acknowledged occurrences of climate change and variability in their localities for the past 30 years. Heads of households perceived that rainfall has decreased while temperature has been increasing. This findings are in collaboration with that from the Tanzania meteorological data. Moreover, the findings revealed that climate change and variability have impacted crop farming system in different ways such as, damaging of crops and persistent low yields, reduction of crop varieties and species, decreasing soil fertility, increasing crop pests and diseases and drying of water sources. Therefore, this paper recommends that, collective efforts from government and other stakeholders should be harnessed and implemented in order to respond to these impacts so as to improve households' food security in the study area.

Key words: Climate change, climate variability, crop farming systems, Manyoni district.

INTRODUCTION

Climate change is one of the substantial global challenge in the twenty first century. As stipulated in the IPCC third

assessment report, changes in rainfall and temperature are anticipated to have an extensive impacts on crop

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Production (IPCC, 2007). The report also forecasts that mean annual global surface temperature will increase by 1 to 3.5°C by 2100 and the global mean sea level will rise by 15 to 95 cm (Apata et al., 2009). The projected increase in global average surface temperature is expected to bring or increase spatial and temporal variations in patterns of precipitation. Due to this report, farmers who depend on rainfed agriculture are considered as the most vulnerable group to climate change impacts because agriculture is highly sensitive to climate variability (Bates et al., 2008).

Crop farming is the main economic activity in Africa. It contributes 20 to 30% of Africa's gross domestic product (GDP) and 55% of the total value of African exports, with 70% of the continent's population depending on the sector for their livelihood (OECD, 2014). However, due to unpredictable rainfall and changes in temperature, crop production has been severely affected resulting in decrease in food security. Africa has thus become the most vulnerable continent to impacts of climate change. Furthermore, the vulnerability of the region is aggravated by the fact that the climate is predictably becoming hotter (Lyimo and Kangalawe, 2010). Authors like Nelson et al. (2009) as quoted by Cooper et al. (2016) projected that climate change and variability will reduce agricultural production by 10 to 20% by 2050 by changing rainfall patterns and increasing frequency of extreme weather events.

The projected reduction will mainly result from the changing rainfall patterns and the increase in the frequency of extreme weather events. This will also increase the prevalence of crop pests and diseases. The effects of these changes are expected to be particularly severe in SSA, where persistent poverty makes populations more vulnerable than in other parts of the world, and importantly the huge reliance on agriculture in this region. The sector contributes about 40% of gross domestic product of sub-Saharan Africa (SSA) countries and employs 62% of the population (Cooper et al., 2016)

The most vulnerable areas in the region have been rural SSA, especially for the arid and semi-arid lands in countries such as Sudan, Somalia, Ethiopia and Tanzania (Agrawala et al., 2003; IPCC, 2007; Molua, 2002). These areas have frequently been exposed to climate variation-induced food shortages and famine. These areas are considered among the most food insecure regions in the world (Devereux and Edward, 2004; Deressa et al., 2008). According to some observers, climate change and variability have also exacerbated extreme poverty in their rural communities (Hellmuth et al., 2007). For Tanzania, specifically, the National Adaptation Programme of Action (NAPA) projected that, the mean daily temperature will rise by 3 to 5°C throughout the country (URT 2007), with annual rainfall decrease of between 5 and 15% in areas of unimodal rainfall and between 5 and 45% in areas of

bimodal rainfall. Such rainfall decreases will not only pose intensive effects on crop farming but they will impact the whole agricultural sector in general.

However, it should also be noted that such climatic impacts will not affect the region uniformly due to East Africa's diverse climatic patterns, from equatorial to semi-arid and arid climates (WFP/ICPAC, 2014). Therefore, communities living in these different climatic regimes will be affected differently by climate change. Hence, they will be adapting their systems of production to match with the shortage of rainfall and other climate change factors. Thus, East Africa has and will continue to have some of the most multifaceted production systems in the world. They include systems such as the perennial farming systems, mixed crop farming systems, and the agro-pastoral and pastoral production systems.

Therefore, these systems have been impacted differently by climate change and variability (Majule, 2008). So far, the impacts of climate change and variability have been revealed through droughts, floods, erratic rains and extreme events. For instance, URT (2011) reported that famine as a result of food shortage have drastically increased since the mid-1990s thus affecting the livelihoods of the farming community, especially in semi-arid central Tanzania. Furthermore, a number of studies that have been done in Tanzania revealed that climate change and variability are real and are accompanied by significant impacts on a diversity of sectors including agriculture which is considered as the major source of peoples' livelihood (Wambugu and Muthamia, 2016). Following the impacts of climate change and variability, farmers in semi-arid and arid east Africa have developed and adopted various adaptation strategies as a mechanisms to respond to impacts of climate change and variability. Such adaptation mechanisms includes, adoption of mixed crop farming system, growing of drought tolerant crops, changing of farming calendar and operating non-farm activities (Lyimo and Kangalawe, 2010).

Generally, most of the literature has highlighted impacts of climate change and variability on agriculture at global level. Moreover, these impacts are based on agriculture in general which combine both crop farming and livestock keeping. Hence, this paper aimed at assessing in detail, the impacts of climate change and variability on crop farming systems at community level which are often not well documented. Specifically, the paper examines the perception of farmers on climate change and variability, establishes the trends and patterns of rainfall and temperature and assesses their impacts on crop production. It is anticipated that information gathered from the study will not only add knowledge to the existing literatures but it will also be used by various stakeholders such as the government, policy makers and non-government organizations to address issues related to impacts of climate change and

variability on crop farming in an effort to promote food production so as to enhance household food security.

MATERIALS AND METHODS

Description of the study area

Geographical location of Manyoni District

Manyoni District is one of the six districts of Singida Region in Tanzania. The district capital is the town of Manyoni. The district lies between Latitude 54°0'0"S and longitude 33°40'0"E covering an area of 28,620 km² that is about 58% of the entire area of Singida Region. The district is bordered to the north by the Ikungi and Kondoa Districts, to the east by Dodoma Rural District, to the south by Iringa District, to the southwest by Chunya District, and to the west by Sikonge District. According to the 2012 National Census Report, Manyoni District was administratively divided into 20 wards. Four villages, namely Lusilile, Udima, Makanda and Magasai were purposively selected from Kintinku Makanda wards for the study (Figure 1). The two wards are located in two distinct agro-ecological zones. Kintinku is located in the rift valley while Makanda is located in the plateau.

Climatic characteristics

The district experiences low and often erratic rainfall with fairly widespread droughts in one year out of four. The average annual rainfall ranges from 500 to 700 mm per annum with high geographical, seasonal and annual variations. There are two well defined seasons: the short rainy season during the months of December and March which fades away in May, followed by the long dry season to November (Benedict and Majule, 2015). The district forms part of the semi-arid central zone of Tanzania (Manyoni District Profile, 2014). The long-term mean annual rainfall is 624 mm with a standard deviation of 179 mm and a coefficient of variation of 28.7%. The long-term mean number of rainy days is 49 with a standard deviation of 15 days and a coefficient of variation of 30.6%. However, there is some variation in terms of rainfall distribution in the district over years. In some areas, rainfall amount is high while in other areas, it is low. Rainfall distribution for the district is presented in Figure 2.

Temperatures in the district range from about 20°C in July to 30°C during the month of October. Temperatures are almost constant throughout the year. August, September and October are the hottest months due to relatively small difference in elevation. There is also a well-defined difference in temperatures between day and night. Maximum temperatures during the day can go up to 32°C and decrease in nights; going down to 15°C (Manyoni District Profile, 2014).

Data collection and analysis

The study used both primary and secondary data in order to ensure the study objectives were addressed appropriately. Secondary sources used in this study includes various published research paper and reports, rainfall and temperature data collected from Tanzania Meteorological Agency, crop yield data (maize, millet and groundnuts) collected from National Bureau of Statistics, internet search and other relevant sources. Primary data sources includes focus group discussions (n=8 for each village), trend analysis (n=8

per village), interviews with key informants (n=10) consisting of village leaders, agricultural extension officers and village elders. Household survey (n=362) and direct field observation through transect walks were other sources of primary data. Field observation was deemed necessary in order to confirm some of the issues raised during in-depth interviews, focus group discussions and the household survey. The sample size of the household survey consisted of 10% of the total number of heads of households in each study village. Simple random sampling procedure was used in the selection of the sample whereby about 59.5% of males and 40.3% of females were interviewed.

Quantitative data collected from the questionnaire survey were coded and analyzed with the help of SPSS version 20. A spread sheet was used for the analysis. Descriptive statistics was run in order to get the frequencies and then cross tabulation was done so as to compare the study themes in the four study villages. Multiple response questions were analyzed so as to get frequencies and percentages. Rainfall, temperature and crop yield data were analyzed by using Microsoft Office Excel, 2007, to examine patterns and trends of the variables. Tables and figures were used to present the findings.

RESULTS AND DISCUSSION

Socio-economic profile of respondents in the study area

Educational level

Education is anticipated to be an important factor in accessing advanced information on new improved agricultural technologies and increased agricultural productivity (Norris and Batie, 1987; Elahi et al., 2015). The study revealed that, there were clear distinctions on levels of education amongst the interviewed heads of household. The results showed that majority of heads of household (68%) in the study area attained primary education, 8% attained secondary, while 24% admitted to have not attended school at all (Table 1).

Economic activities

The findings revealed that crop farming was the leading economic activity performed in the study area which accounted for 76.8% of the 362 interviewed heads of households (Table 2). Agro-pastoralism was the second economic activity conducted in the study area which accounted for 19.6% of the total heads of households. Small business and casual labour both accounted for 1.4% while formal employment accounted for 0.8% of the interviewed respondents and this was mostly practised in Lusilile village (2.8%) due to the presence of many public institutions like hospitals and schools (Table 2). According to Table 2, crop farming was practiced more in Makanda village (81.2%), while agro-pastoralism was practiced more in Magasai village. This difference was due to the presence of more Sukuma immigrants from

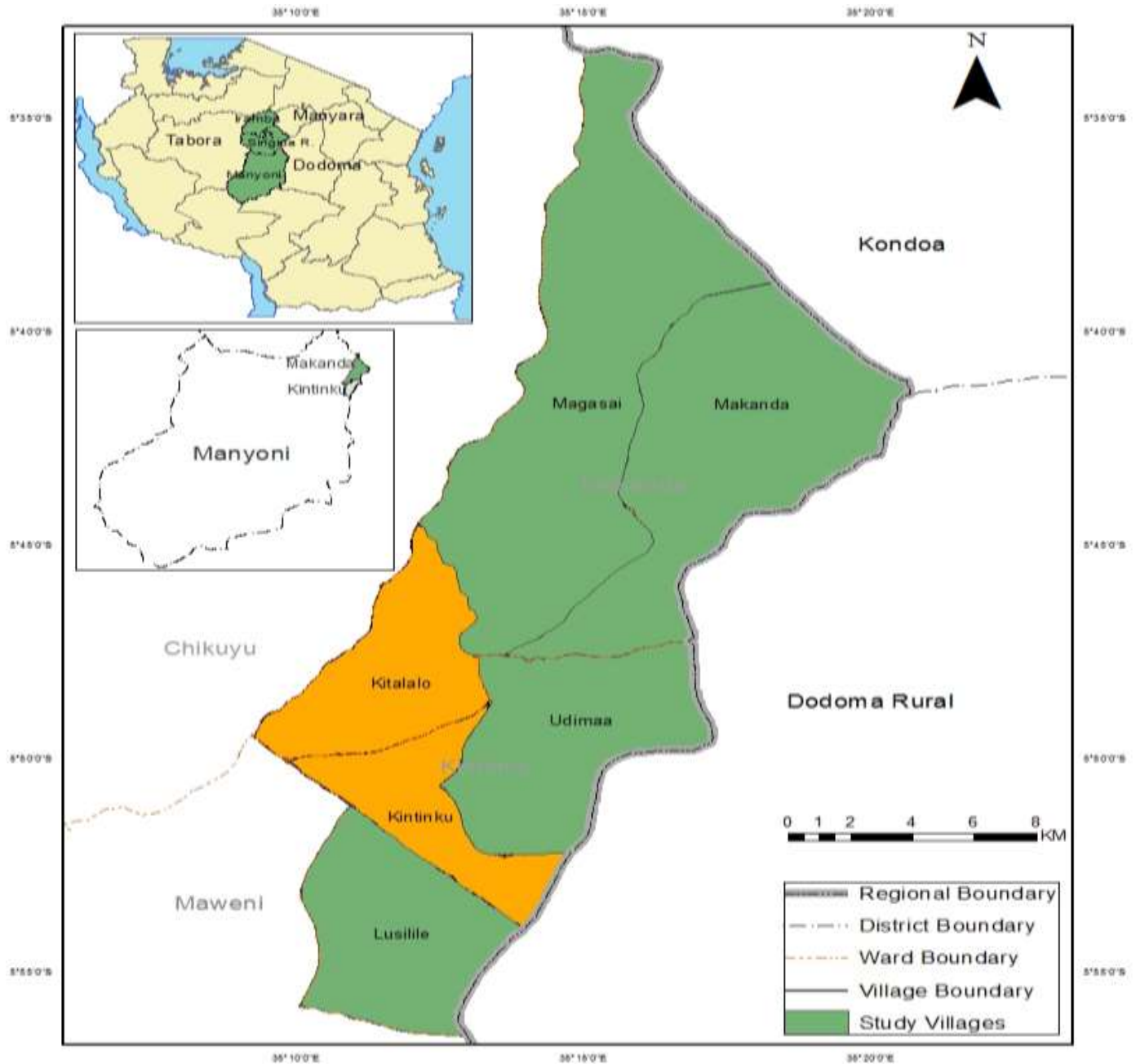


Figure 1. Map of Manyoni District showing the study villages.

Lake Zone regions who are traditionally agro-pastoralists. Small businesses and casual labour were conducted mostly in Udimaa village as the village is urbanized than the rest and is located near the tarmac road that connect Dodoma and Singida regions.

Farmers perceptions on climate change

The findings revealed that about 98% of the total

respondents perceived that climate has been changing, while only 2% perceived that climate had not changed. Majority of the farmers associated the concepts of climate change and variability with, changes in climatic elements. It was thus reported that 48.9% of the heads of households perceived climate change as long term changes in rainfall, while 33.6% perceived it with long term changes in temperature. About 10.5% perceived climate change through changes in wind intensity, while 2.1 and 1% of heads of households perceived it is through

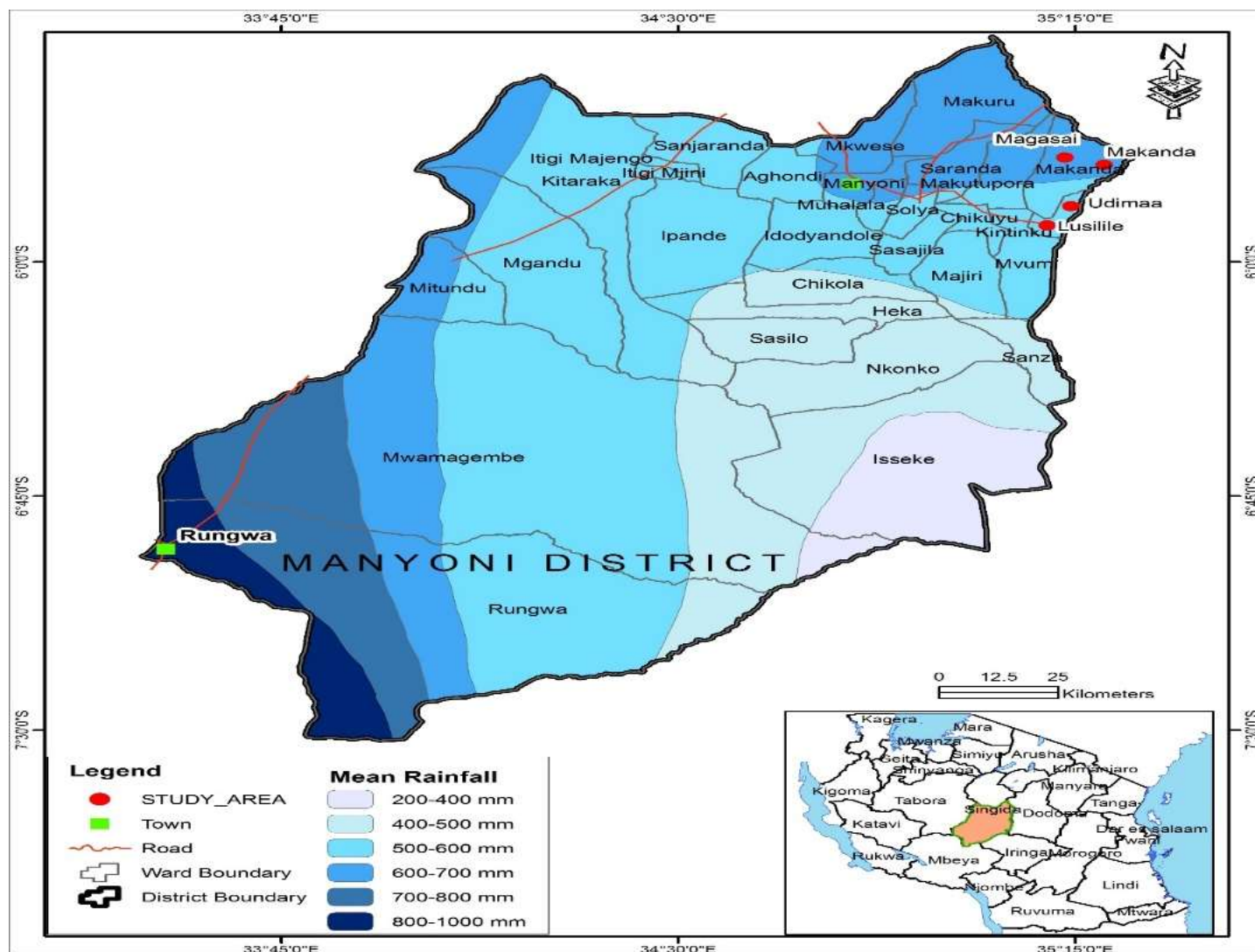


Figure 2. Mean rainfall distribution in the study area.

flood incidences and change in humidity, respectively (Figure 3)

Farmers’ perceptions on long-term changes in rainfall and temperature

Specifically, while the findings revealed that 81.0% of the farmers perceived that rainfall had been decreasing as compared to thirty years ago, 18.2% perceived rainfall had been fluctuating while about 0.8% affirmed to have not noted any changes at all in rainfall amounts and patterns. Similar results were reported by Lema and Majule (2009) who mentioned that there had been a decreasing trend in rainfall amounts and intensity in most parts of Tanzania and Africa generally. Moreover,

Nhemachena and Hassan (2007) observed that in the Southern Africa region, majority of smallholder farmers perceived that there were decreases in rainfall amounts from the year 1976 to 2006.

The findings of this study was also supported during interview with key informants in Makanda village as narrated:

“... In the past when I was young, about thirty years ago, rainfall was sufficient, regular and predictable. Although there were some fluctuations in terms of amount in some years but generally, the rainfall was sufficient for crop production. My father was able to produce in surplus food whereby some amount of harvests were sold in the market at Kintinku while some amount were given to our relatives who were living at Manyoni Town. My dear

Table 1. Education levels of the heads of households.

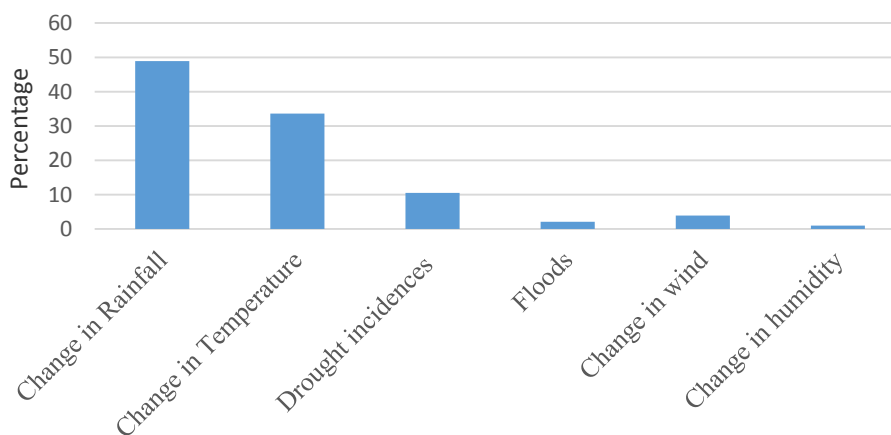
Education level	Study Villages								Sample Size (N=362)	Total
	Lusilile		Udimaa		Makanda		Magasai			
	N	%	N	%	N	%	N	%		
No education	15	13.8	24	33.8	16	15.8	32	39.5	87	24.0
Primary education	83	76.1	41	57.7	76	75.3	46	56.8	246	68.0
Secondary and above	11	10.1	6	8.5	9	8.9	3	3.7	29	8.0
Total	109	100.0	71	100	101	100	81	100	362	100.0

Source: Field data (2017).

Table 2. Main economic activities in the study area.

Occupation	Study Villages								Total	
	Lusilile		Udimaa		Makanda		Magasai		(N=362)	%
	N	%	N	%	N	%	N	%		
Crop farming	88	80.7	57	80.3	82	81.2	51	63	278	76.8
Formal employment	3	2.8	0.0	0.0	0.0	0.0	0.0	0.0	3	0.8
Agro-pastoralist	15	13.8	11	15.5	16	15.8	29	35.8	71	19.6
Small business	1	0.9	1	1.4	3	3	0.0	0.0	5	1.4
Casual labor	2	1.8	2	2.8	0.0	0.0	1	1.2	5	1.4
Total	109	100	71	100	101	100	81	100	362	100

Source: Field data (2017).

**Figure 3.** Farmers' perceptions on climate change and variability.
Source: Field data (2007).

researcher, currently, we are suffering a lot, rainfall has decreased and totally not sufficient. This season (2016/2017), the situation is more than worse because up to now (February, 2017), we have experienced rainfall only for three days" (Interview with village executive officer, Magasai village).

With regard to temperature, the findings revealed that about 88.7% of heads of households perceived temperature to have increased as compared to thirty years ago, 10.5% perceived temperature had been fluctuating and 0.8% perceived no changes. The same results were found by Shemdoe (2011) and Mongi et al.

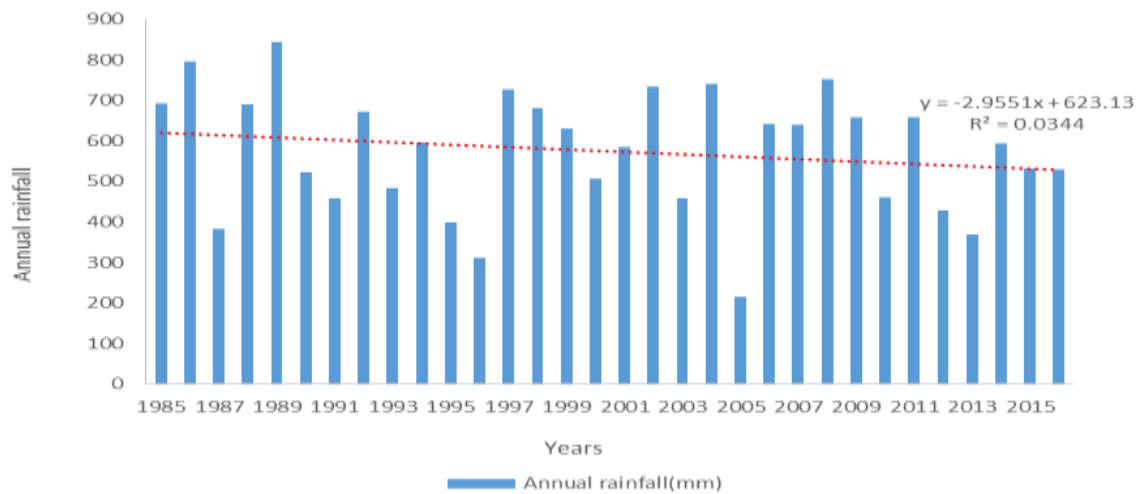


Figure 4. Average annual rainfall trends in the study area.

Source: Field data (2017)

(2010). Both authors reported that majority of the heads of households in semi arid Tanzania perceived temperature to have increased.

Moreover, during in-depth interviews with key informants and focus group discussions, it was stated that the amount of temperature has currently increased as compared to thirty years ago which is associated with recurrent droughts and frequent food shortages:

..... "There is no doubt that the amount of temperature in our village has increased dramatically in recent years as compared to thirty years ago. You know temperature used to be high mostly in November and early December both day and night. But now, day's temperature has become unpredictable because even those months which were used to have low temperature like January, April and May, the situation has changed, we are also experiencing high temperature in those months" (In-depth interview with Female, 67 years in Magasai village).

..... "I can say that when I was in primary school about 39 years ago, we were facing a minimum amount of temperature. When I compare with the current temperature, surely, the temperature has increased that's why we are getting poor harvests" (Male 42 years in Lusilile village).

..... "What my fellow speaker has said is true but he has forgotten to say that due to increase in temperature our natural water sources like river Bubu and other natural wells which depend on water from the river have dried up very early this year as compared to twenty years ago. Normally, we were able to access water from our sources

for almost four months once the rainfall end" (Female 52 years in Lusilile village).

....."Let me also say something concerning the topic, I remember my late father was a fisherman and he was getting a lot of money from such activity but nowadays because the ponds has dried up due to increase in temperature, we are no longer getting fish. Actually, the increase in temperature have further accelerated the increase in drought incidences in our village to the extent that agriculture has become unpredictable because even the rainfall amount has decreased to the maximum any way let us pray that God will hear us " (Female, 69 years in Lusilile Village).

Statistical analysis of rainfall and temperature trends in the study area

Analysis of scientific rainfall and temperature data obtained from Tanzania Meteorological Agency was done in order to determine if there was consistency between these data with the farmers' perceptions on changes in rainfall and temperature collected during the household survey.

Rainfall trends

The analysis of rainfall data was done by using simple regression model. The results are presented in Figure 4. In general, the findings indicated a slight decrease trends in the pattern of rainfall as shown by $y = -2.9551x + 623.13$ mm. Moreover, the decrease in trend is described

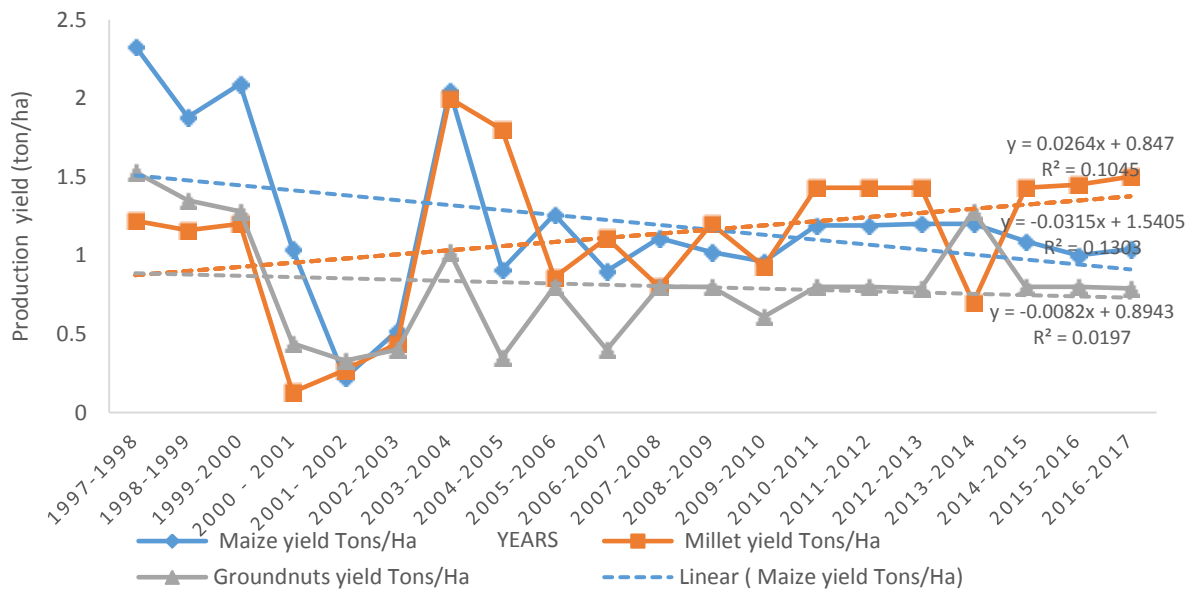


Figure 5. Trends of major crops produced in Manyoni district (1997/1998-2016/2017).
Source: Field data (2017).

by 3.4% of variance observed in Manyoni District. The findings from this study are in line with the findings from Lyimo and Kangalawe (2010) who conducted their study in nearby Shinyanga Rural District and observed that rainfall amount and intensity decreased at a non-significant rate of $R^2 = 0.18$, F probability > 0.47 . Even though such trends were not statistically significant to some extent, they showed a decrease in trend. In addition, Myeya (2013) who conducted a study in Dodoma Region, observed a statistically insignificant decrease in rainfall trends of -3.328 y^{-1} and -2.165 y^{-1} for Mpwapwa and Bahi Districts, respectively.

Moreover, the findings indicate that there had been some variations in terms of rainfall amounts and patterns from 1985 to 2016.

In some years, rainfall appeared to increase while in others, it seemed to decrease (Figure 4). In particular, the study observed that about 12 years in that period had received rainfall below average (577.3 mm). These years are were 1987 (381.6 mm), 1990 (521.4 mm), 1991 (458.4 mm), 1993 (484.1 mm), 1995 (399.6 mm), 1996 (312.3 mm), 2000 (505.3 mm), 2003 (459.1 mm), 2005 (215.0 mm), 2010 (459.6 mm), 2012 (427.9 mm) and 2013 (368.9 mm). In addition, four years appeared to have received very little rainfall. These included 1987, 1996, 2005 and 2013. Meanwhile, 2005 was observed to be the driest year experiencing a total rainfall amount of only 215.0 mm. On the other hand, the rainfall analysis indicates that rainfall was very high in the years 1989 and 1986 which received a total amount of 843.8 and 795.2 mm, respectively. Based on such observations, it can be

argued that the analysis of meteorological data on annual trends and patterns of rainfall and that of smallholder farmers' perceptions on changes of rainfall appear to be in line.

Temperature trends

Figure 5 shows the trends in temperature change in the period of 1985 to 2016, whereby there is a general increase in annual mean temperatures. Moreover, the fitted linear trends indicate that both annual mean maximum temperatures and annual mean minimum temperatures were statistically significant at 0.05 significance level with p value = 0.001. The annual mean minimum temperature showed a higher increase, $y = 0.0399x + 16.473$ as compared to the annual mean maximum temperature, $y = 0.023x + 28.679$. Therefore, this is explained by 66% of observed variance in the annual mean minimum temperature, $R^2 = 0.657$ than the observed 32% in the maximum annual temperature, $R^2 = 0.315$ in the period 1985 - 2016.

The data further indicated that for the period of 32 years, the mean minimum temperature in Manyoni District had increased by 1.3°C , while the mean maximum temperature increased by 1.1°C . Therefore, the annual mean minimum temperatures tend to have increased at a higher rate than the annual mean maximum temperatures which seem to support the concern of the majority of respondents who perceived that temperatures were increasing.

Table 3. Impacts of climate change on crop farming in the study area.

Types of crops	Study Villages								Total %
	Lusilile		Udimaa		Makanda		Magasai		
	N	%	N	%	N	%	N	%	
Damaging crops and persistent of low harvest	102	37.2	68	36	98	38.6	71	35.1	36.7
Reduction of crop varieties and species	40	14.6	44	23.3	46	18.1	47	23.3	19.8
Decrease in soil fertility	15	5.5	11	5.8	17	6.7	10	5.0	5.7
Increase in crop pests and diseases	41	15	31	16.4	47	18.5	33	16.3	16.6
Drying of water sources	76	27.7	35	18.5	46	18.1	41	20.3	21.2
Total	274	100	189	100	254	100	202	100	100

Source: Field data (2017).

Perceived impacts of climate change and variability on crop production system

Damaging of crops and persistence of low yields

It was noted that more than a third (36.7%) of the heads of households who were surveyed pointed out damage of crops and persistence of low yields is the major impacts of climate change and variability. The most mentioned climatic factors impacting agricultural production in all study villages were increasing temperatures and decreasing amounts and intensity of rainfall. For example, it was noted that about 38.6 and 37.2% of the heads of households in in Makanda and Lusilile villages acknowledged crop damage and persistence of low harvests, respectively, while about 36 and 35.1% were reported in Udimaa and Magasai villages, respectively (Table 3). These results collaborated the results of Malley et al. (2009) who observed that productivity of crops in Tanzania was increasingly becoming threatened by increasing drought frequency in semi-arid areas of central Tanzania. The pains of climate change to households in Magasai village were observed to be less as compared to other study villages due to the nature of farming system practiced by agro-pastoralists which gave more weight to livestock keeping than crop farming.

Drying of water sources

Water is an important input essential for crop production, especially in irrigation farming. Decrease in water supply will surely impact crop production as stated by 21.2% of the respondent heads of households who were interviewed in the study area (Table 3). On the other hand, the findings from village analysis revealed that about 27.7 and 20.3% of the heads of households in Lusilile and Magasai villages, respectively, acknowledged that water sources had dried up as a result of increase in temperature and decline in rainfall. Similarly, about 18.5

and 18.1% of heads of households in Udimaa and Magasai villages, respectively, reported drying of water sources as among the impacts of climate change and variability. Information from both focus group discussion and in-depth interviews in Lusilile village revealed that the higher percentage of heads of households in the village who perceived drying of water sources as among the impacts of climate change and variability was due to the presence of many dried water sources such as rivers, natural springs and wells causing shortages of water for domestic activities and for irrigation farming as stated below:

.....“Some years ago before my marriage, it was very difficult to see sands and small stones in the Bubu river and it was hardly to cross over the river, this is because for all seasons, the river was full of water and there were many vegetable farming near the river where farmers used to plant tomatoes, onions, cabbages and spinach and many small scale irrigation farming were established nearby. Unfortunately, currently, the situation has changed because the river has been drying up frequently especially from May to September. Furthermore, even for the remaining months, the river have been receiving a very small amount of water which are insufficient for vegetable growing and irrigation farming that’s why I am experiencing frequent family conflicts due to food shortages but do not give anyone this information” (Key informants, 78 years in Lusilile village).

Reduction in crop varieties and species

One other effect of climate change and variability mentioned by 19.8% of the households interviewed was reduction of crop varieties and species. In terms of specific villages’ analysis, the data showed that reduction in crop varieties and species was higher in Udimaa and Magasai villages than the remaining villages as expressed by 23.3 and 23.3% of the respondent heads of households, respectively (Table 3). The two villages were

Table 4. Analysis of variance of the impacts of climate change on crop farming in the study villages.

Source	Type III sum of squares	Df	Mean square	F	Sig.	Partial Eta squared
Corrected Model	244.573 ^a	12	20.381	26.983	0.000	0.488
Intercept	1058.003	1	1058.003	1400.730	0.000	0.805
Village	0.042	3	0.014	0.019	0.997	0.000
Impacts of climate change	161.905	3	53.968	71.451	0.001	0.387
Village * Impacts of climate change	1.937	6	.323	0.427	0.861	0.007
Error	256.810	340	.755			
Total	7808.000	353				
Corrected Total	501.382	352				

a. R Squared = 0.488 (adjusted R squared = 0.470).
 Source: Field data, 2017.

closely followed by Makanda village with 18.1% and Magasai at 14.6% of the interviewed heads of households.

During focus group discussions, participants were asked the types of crops they produced and if there were any crops that had recently been abandoned. In terms of abandoned crops, the respondent heads of households mentioned beans, onions, bulrush millet, sweet potatoes and some local maize varieties. Different reasons for abandoning such crops were mentioned, including decline in soil fertility and increase in pests and diseases. Farmers, however, pointed out increased drought incidences as the major factor. Other crops that were reported to have been affected by drought conditions were groundnuts, cowpeas, peanuts and sesame. Similar findings were noted by Kangalawe and Lyimo (2013) in their study in Shinyanga Rural and Manyoni Districts.

Increase in incidence of crop pests and diseases

Outbreak of crop as well as animal pests and diseases were mentioned to be among the impacts of climate change and variability. Generally, results from the households survey showed that about 16.6% of the respondent households commented that there had been frequent outbreaks of crop pests and diseases in the study area. The findings revealed that increase in pests and diseases had mostly been due to increase in temperature. The most serious pests and diseases mentioned by the farmers were weevils, birds and stalk borers (*Calidea dregii* locally known as mpipi) attacking maize and millet, and ants (locally known as nkeki) attacking paddy and sesame. Other emerging pests mentioned by smallholder farmers were rodents, armyworms, bollworms, larger grain borers and leaf hoppers. However, it should be noted that though these pests were mentioned by some smallholder farmers as emerging pests, it does not necessarily mean that these

pests were absolutely absent from the area in the past. The fact is that their rate of occurrence had increased with climate change and variability as observed by Kangalawe and Lyimo (2013) in the case of Shinyanga Rural District.

Decrease in soil fertility

Fertile soil is a fundamental element for plant growth. Generally, the findings revealed that about 5.7% of the respondent heads of households acknowledged that soil fertility had decreased (Table 3). During focus group discussions, it was further noticed that majority of the smallholder farmers who acknowledged decrease in soil fertility were associated with the occurrence of floods which washed away soil nutrients and contributed to decline in nutrient supply in the crops grown in those soils. Insufficient nutrient status in arable soil did not only decrease food production for human consumption but also, it increased vulnerability levels to human diseases and food insecurity for the population depending on food produced via such soils. However, it should be noted that decrease in soil fertility per se is not a sole factor for decrease in crop production. There are other contributing factors such as pests and diseases, poor farming skills and poor utilization of insecticides and pesticides.

A two-way analysis of variance was performed to explore the impact of climate change on crop farming and in different villages which were Lusilile, Udimaa, Makanda and Magasai. There was a statistically significant difference at the $P < 0.05$ level in the main effects of impacts on crop farming [$F(3, 362) = 71.451, P = 0.001$], with the effect size of 0.38 (partial eta squared) (Table 4). In addition, Post-hoc comparisons using the Tukey HSD test indicated that the mean score for impacts on the reduction of crop variety and species were statistically different at 0.05 level with mean score impacts of damaging crops and persistent of low yields, also

statistically different from the mean scores impacts of decrease in soil fertility as well as statistically different with the mean score impacts of drying of water sources all the same alpha level. Furthermore, there was a statistically significant difference on the mean scores of impacts of drying of water sources with the means scores impacts of damaging crops and persistent of low yields as well as statistically differences with the mean score impacts of decrease in soil fertility. On the other hand, the main effect for villages was not significant [F (3, 362) = 0.019, P = 0.997] for main effects for villages. Finally, interaction effect [F (4, 362) = 0.427, P = 0.861] did not reach statistical significance.

Statistical analysis of yield trends for maize, millet and groundnuts

An analysis of archival data from the district records were performed in order to observe if they were in coherence with farmers' perceptions on crop yield trends. In this case, the production yields data used covered twenty years/seasons (1997/1998) to (2016/2017). The analysis of production (yield in ton/ha) was done for some selected crops because these were major crops cultivated by the majority in the study area. Figure 5 presents the results of the analysis which revealed that there was a slightly decline in maize and millet yields while millet production showed a slight increase. Decline in maize yields was indicated by a regression equation $y = -0.0315x + 1.540$. The decline is explained by a 13.03% coefficient of determination ($R^2 = 0.1303$). On the other hand, the decline in groundnuts production was indicated by the regression equation, $y = -0.0082x + 0.894$. This decline is explained by a 1.97% coefficient of determination ($R^2 = 0.0197$). Moreover, the slight increase in production yields for millet was indicated by the regression equation, $y = 0.0264x + 0.847$ which is explained by a 10.45% coefficient of determination ($R^2 = 0.1045$). The increase in production of millet yields indicates its high tolerant capacity in semi-arid areas while the decline in trends of maize and groundnuts production yields indicated their low tolerant capacity in semi-arid areas like Manyoni District. Generally, it can be concluded that farmers perceptions on the impacts of climate change and variability on crop production were in consistence with that of the scientific analysis for the two crops, maize and groundnuts.

CONCLUSION AND RECOMMENDATION

This study aimed to assess the impacts of climate change and variability on crop farming systems at community level which were deemed to be often not well documented. Specifically, the study aimed at examining

the perception of farmers on climate change and variability, establishing the trends and patterns of rainfall and temperature and assessing their impacts on crop production in selected villages of Manyoni District, Tanzania. The study concludes that majority of the smallholder farmers perceive climate change and variability through observed decrease in rainfall, increase in temperature and increase in incidences of droughts. Furthermore, the study has established the patterns and trends of rainfall and temperature in the study area by using data accessed from the Tanzania Meteorological Agency in Dar es Salaam for Manyoni District. The data have generally shown a decrease in rainfall amounts and an increase in temperature, which are in conformity with the findings from the farmers' perceptions. Moreover, the study has presented various perceived impacts of climate change and variability on farming systems in the study villages. Crop yield data for maize and ground nuts have shown a decreasing trend while that of millet has shown an increasing trend proving that the crop was indeed versatile enough for this type of climate regime. Therefore, the study recommends that collective efforts from government and other stakeholders should be harnessed and implemented in order to respond to these impacts so as to improve food production and enhance households' food security in the district.

CONFLICT INTERESTS

The authors have not declared any conflict of interests.

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Full Length Research Paper

Equilibrium, kinetic and thermodynamic studies of biosorption of zinc ions from industrial wastewater using derived composite biosorbents from walnut shell

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The biosorption process of Zn (II) ions in industrial wastewater was investigated using derived composite biosorbents from walnut and snail shells. Composite adsorbents were produced by activating walnut shell carbon (WSC) with phosphoric acid to obtain acid-treated walnut shell carbon (AWSC) and WSC and AWSC were independently impregnated on chitosan to produce walnut shell carbon impregnated on chitosan (WSCC) and acid-treated walnut shell carbon impregnated on chitosan (AWSCC) respectively. The removal efficiencies of Zn (II) ions from synthetic wastewater using the prepared adsorbents were determined. The effects of operational parameters on Zn (II) ions adsorption were investigated. The adsorption data of Zn (II) ions were analysed using Langmuir, Freundlich and Temkin isotherms. The Langmuir isotherm fitted the adsorption data excellently for the derived composite biosorbents, giving an indication of monolayer coverage on the derived composite biosorbents and the determination coefficients were close to unity. Also, the maximum adsorption capacities of 3.1104, 3.8052, 16.4474 and 17.6991 mg/g were obtained for WSC, AWSC, WSCC and AWSCC at pH=5, 1 g of adsorbent dosage, Zn (II) ions initial concentration of 30 mg/L, contact time of 2 h, agitation speed of 150 rpm, particle size of 60 BSS and temperature of 30°C. The kinetic modelling of Zn (II) ions adsorption showed that pseudo second-order kinetic model gave the best fit amongst the investigated kinetic models. The adsorption of Zn (II) ions on the prepared adsorbents was film-diffusion controlled. The experimental results of this study showed that acid-treated walnut shell carbon impregnated on chitosan has the potential to be applied as alternative efficient low-cost biosorbent in the remediation of heavy metal contamination in wastewater. The thermodynamic parameters indicated that the adsorption of Zn (II) ions on the derived composite biosorbents was exothermic, endogonic, favourable, non-spontaneous with changes in enthalpy (ΔH , negative), entropy [ΔS , nearly zero (though negative)], and Gibbs free energy (ΔG , positive), for all the prepared adsorbents.

Key words: Adsorption, biosorbents, chitosan, isotherm, kinetic models, film diffusion.

INTRODUCTION

Water pollution is one of the major problems faced globally due to the random release of domestic and urban wastewaters, agricultural wastes and industrial effluents into water courses. The main impact of such pollution is the enormous amount of heavy metals (such as nickel,

lead, copper, zinc, cadmium, etc) in effluents released by industries like electroplating, plastic and paint manufacturing, mining and metallurgical processes, pulp and paper, petrochemical and battery manufacturing industries (Oboh et al., 2009). These metals are toxic and

non-biodegradable, and can cause environmental pollution. Moreover, human health can be adversely affected as these metal ions are highly soluble in water and can be absorbed into the body. Hence, removal of these heavy metals from wastewater is essential for the purpose of protecting the environment and human health.

Trace concentrations of zinc are important for the physiological functions of living tissue and regulation of many biochemical processes. However, like other heavy metals, when zinc is discharged into natural waters at increased concentrations from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants, it can have severe toxicological effects on humans and aquatic ecosystems (Aremu et al., 2002). Zinc is non-biodegradable and it travels through the food chain via bioaccumulation. World Health Organization recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg/L (Hawari et al., 2009).

The orthodox treatment techniques for the heavy metals removal from industrial wastewater include chemical precipitation, membrane filtration, electrolytic reduction, solvent extraction, ion exchange, electro-dialysis, ultra filtration and adsorption on activated carbon (Bhattacharyya et al., 2009; Amadi and Ukpaka, 2015; Babarinde et al., 2016; Babarinde and Onyiaocha, 2016; Iqbal, 2016; Iqbal and Bhatti, 2015b; Iqbal and Khera, 2015; Iqbal and Nisar, 2015; Iqbal et al., 2017; Jamal et al., 2015; Nouren et al., 2017; Patel et al., 2017; Qureshi et al., 2015; Sayed, 2015; Ukpaka and Izonowei, 2017; Ukpaka and Igwe, 2017). However, adsorption has been recognised as a viable technique for removal of heavy metal ions from wastewater (Adesola et al., 2016; Babarinde and Onyiaocha, 2016; Iqbal and Bhatti, 2015a; Iqbal et al., 2016; Iqbal and Khera, 2015; Mushtaq et al., 2016; Rashid et al., 2016) owing to its simplicity, cost effectiveness and feasibility (Foo et al., 2010).

Activated carbon is the most important adsorbent used industrially for the separation and purification of products and also for the treatment of liquid and gaseous effluents owing to its porous surface area, controllable pore structure, thermo-stability and low acid/base reactivity (Mohan et al., 2007). Despite its use in adsorption processes, the biggest barrier in its application by industries is its costly nature and the tediousness of its manufacturing and regeneration processes. Consequently, relatively low cost adsorbents from biomass, called biosorbents, have been developed. Examples of some biological materials used as biosorbents are rice straw, coconut shell, walnut shell, banana pith, beech leaves, orange peels, moss, tree fern, soya cake, cactus leaves and carbonized biomass

products (Bhattacharyya et al., 2004). Moreover, Kauser et al. (2017) compared batch and column adsorption studies for the uranium (VI) ions adsorption onto rice husk waste biomass (RHWB) and concluded that RHWB had potential for removing uranium (VI) ions with batch adsorption more efficient than the column mode. Naeem et al. (2017) carried out uranium adsorption using modified low cost *Vigna radiata* biomass, with maximum uranium removal of 230 mg/g obtained at the optimized process parameters of pH=4, biosorbent dose of 0.05 g, contact time of 60 min and temperature of 40°C using 400 mg/L uranium ions concentration. Akram et al. (2017) showed the efficacy of the prepared biocomposite of mango (*Mangifera indica*) with surfactants and co-metal ions (Na^+ , K^+ , Ca^{2+} , Cu^{2+} , Al^{3+} and Fe^{3+}) for Cr (VI) ions removal from industrial effluents. They also obtained optimum levels of process variables of pH, Cr(VI) ions initial concentration, adsorbent dosage, contact time and temperature as 3, 0.05 g, 30 min, 200 mg/L and 33 °C, respectively for maximum Cr (VI) adsorption onto the prepared biocomposite.

Zarur et al. (2018) investigated the use of agroindustrial waste, corn husk biomass (*Zea mays*) as adsorbent for the removal of Cr (VI) and Hg (II) ions, with a view to carrying out thermodynamic, kinetic and equilibrium studies of the process. In their work, Elovich kinetic model and Freundlich isotherm correlated the experimental data excellently, and the thermodynamic parameters (ΔH^0 , ΔG^0 and ΔS^0) suggested a favourable, spontaneous, reversible and endothermic removal process.

Biosorption can be defined as the passive and non-metabolically simplified process of metal ion binding by dead biomass (Kumar et al., 2006). It is effective, flexible and can remove large amounts of heavy metal ions from industrial effluent using a very simple and straightforward method. Moreover, it is beneficial to the environment as pollutants from both aqueous and gaseous streams can be effectively removed with minimum sludge discharge. Furthermore, biosorption produces treated wastewater of higher purity as compared with the conventional metal removal methods (Kumar et al., 2006). Other advantages of biosorption include high versatility, metal selectivity and overall performance with no concentration dependence, no nutrient requirements, high tolerance for organics and possibility of biosorbent regeneration and reuse (Volesky, 1990). Biosorption is also cost effective as raw materials can be obtained easily in large quantities, mostly from natural or waste materials (Dash, 2010). Therefore, biosorption technology has become an attractive

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alternative for wastewater treatment today.

Biomaterials from agricultural operations have potential to be used as low-cost adsorbents since they are unused, are widely available and environmentally friendly resources (Deans and Dixon, 1992). Walnut shell (*Tetracarpidium conophorus*) is a highly carbonaceous and fibrous material with little or no economic value, and its abundance and low cost makes it a good source for the production of activated carbon. Its disposal is not only costly but also causes environmental problems. Hence, the production of char from walnut shells adds value to the walnut shells. It also helps to reduce the cost of waste disposal, and provides a potentially cheap alternative to the commercial carbonaceous adsorbents (Logan and Rosemarie, 2002). Ahlam et al. (2012), Firas and Aurelia (2015), Ghasemi et al. (2015) and Mahboobeh et al. (2012) have reported processing of walnut shells into char for the treatment of industrial and municipal wastewaters.

Amongst the low cost adsorbents, chitosan possesses the highest sorption capacity for several metal ions (Babel and Kurniawan, 2004; Nomanbhay and Palanisamy, 2005). Chitin, 2-acetamido-2-deoxy- β -D-glucose-(N-acetylglucan), is the second most abundant polymer in nature. It occurs in nature as ordered crystalline micro fibrils forming structural components in the exoskeleton of arthropods (Rinaudo, 2006); its major source is from exoskeleton of sea foods (crab, shrimp, prawn, and lobster shells) that are usually disposed as waste material. Depending on its source, three different crystalline polymorphic forms of chitin have been identified: α -chitin (shrimp and crab shells), β -chitin (squid pen), and γ -chitin (stomach cuticles of cephalopoda) (Jang et al., 2004). Chitosan, 2-acetamido-2-deoxy- β -D-glucose-(N-acetylglucosamine), is a biopolymer with free amine groups that are suitable for the adsorption of heavy metals. It is produced on an industrial level by chemical deacetylation of chitin with NaOH. Chitosan can also be produced by enzymatic deacetylation of chitin using lysozyme, snailase, neutral protease, and chitin deacetylase (Cai et al., 2006). Chitosan is slightly soluble at low pH values and poses problems for development in commercial applications. The active binding sites of chitosan are not readily available for sorption. The sites are reported to be soft and have a tendency to agglomerate or form gel in aqueous solutions. Transport of metal contaminants to the binding sites plays a very significant role in process design. Therefore, it is imperative to provide physical support and increase the accessibility of the metal binding sites for process applications (Amuda et al., 2007; Nomanbhay and Palanisamy, 2005). Some investigators (Bamgbose et al., 2010; Karthikeyan et al., 2004; Muzzarelli, 1977; Schmuhl et al., 2001; Vold et al., 2003; Wana et al., 2010) have reported the use of chitosan as adsorbent for the treatment of industrial and municipal wastewaters. However, impregnation of either char obtained from

carbonaceous materials or of activated carbon on chitosan (Amuda et al., 2007; Ding et al., 2006; Nomanbhay and Palanisamy, 2005; Wu et al., 2002) has resulted in a diversity of adsorbents with far superior adsorption capacity.

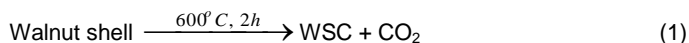
The objectives of this study were to prepare char from walnut shell, perform surface modifications of the walnut shell carbon (WSC) via chemical activation using phosphoric acid to obtain acid-treated walnut shell carbon (AWSC), and the respective impregnation of WSC and AWSC on chitosan to obtain walnut shell carbon impregnated on chitosan (WSCC) and acid-treated walnut shell carbon impregnated on chitosan (AWSCC) with a view to investigating the respective removal efficiencies of Zn (II) ions in aqueous solutions using the prepared adsorbents. The effects of solution pH, adsorbent dosage, initial metal ion concentration, contact time, agitation speed and temperature on the percentage removal of Zn (II) ions in industrial wastewater were also investigated. Three adsorption isotherms (Langmuir, Freundlich and Temkin) and five kinetic models were used to analyse the equilibrium adsorption data and the kinetic data of Zn (II) ions removal respectively. Thermodynamic studies of the Zn (II) ions adsorption on the prepared biosorbents were carried out to determine the spontaneity, exothermic or endothermic nature of the process, and its feasibility.

MATERIALS AND METHODS

All the chemicals used were of analytical grade, purchased from Sigma Aldrich in Germany and used as received. These included zinc (II) tetraoxosulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) (99%) for the synthesis of the industrial wastewater, NaOH (98%) and hydrochloric acid (99%) for the preparation of chitosan, and oxalic acid (99.9%) for the preparation of chitosan gel.

Preparation of char from walnut shell (WSC)

The locally purchased walnut shells were cleaned and washed several times with distilled water to remove surface impurities. After drying, the shells were crushed. To prevent a sticky effect in screening, the samples were dried in an oven at 105°C till constant mass for 4 h prior to screening. The dried shells were screened (sieved) into different particle sizes of 0.80, 0.45, 0.25, 0.20 and 0.15 mm and stored in plastic air-tight containers. The carbonization process was carried out as previously described by Amuda and Ibrahim (2006). The equation for carbonization process is shown thus:



Preparation of acid-treated walnut shell carbon (AWSC)

The activation of the walnut shell carbon (WSC) using phosphoric acid was carried out by the method previously described by Idowu (2015) with a slight modification. Exactly 30 g of the carbonized walnut shell was weighed into a crucible and mixed with 1 M H_3PO_4 . The crucible with its content was heated at 750°C or a period of 5

min. The activated sample was allowed to cool to ambient temperature; the samples were washed several times with deionized water until pH 6-7, filtered with Whatman No. 1 filter paper (150 mm diameter, Cat No. 1001 150) and dried at 110°C for 4 h. The chemical equation for the activation process is shown thus:



Preparation of chitin from snail shell

Snail shells were ground to a smaller particle size, pulverized and screened to a particle size of 1 mm. The method reported by Mohanasrinivasan et al. (2014) was employed for the preparation of chitin with slight modification. 80 g of the powder was mixed with 100 mL of 4 wt% NaOH. The mixture was boiled and stirred at 100°C for 2 h in a water bath. It was then filtered and washed with distilled water. Red litmus was used to check if the base was completely washed away. After washing, the mixture was filtered and the residue was dried at 100°C for 3 h. After deproteinization, the weight of the sample was 62 g. 30 mL of 5 wt% 1 M HCl was added to the deproteinized sample. The mixture was boiled and stirred for 45 min at 100°C in a water bath in order to remove all mineral materials (mainly CaCO₃). Subsequent washing was done with distilled water followed by filtration. The mixture was examined with blue litmus to check the acidity of the mixture. The residue (chitin) obtained was dried in the oven at 100°C for 2 h.

Preparation of chitosan

Deacetylation reaction was used to convert chitin to chitosan according to a revised procedure of Coughlin et al. (1990). Then, a method described by Nomanbhai and Palanisamy (2005) was used for the preparation of chitosan gel. The degree of deacetylation of chitosan was determined by applying the method used by Guibal et al. (1994). The molar mass of chitosan was determined by using the equation of Mark-Houwink-Sakurada for viscosity measurements at different concentrations, given by Paul and Lodge (2007):

$$\eta = kM^{\alpha_1} \quad (3)$$

Where, η and M are the respective intrinsic viscosity and molecular weight of chitosan, k and α_1 are the Mark-Houwink Sakurada constants for a given polymer-solvent temperature system.

Surface modification of WSC and AWSC with chitosan

The surface modification of WSC and AWSC with chitosan gel was carried out using the method described by Babel and Kurniawan (2004). 50 g of the AWSC was slowly added to 100 ml of chitosan gel diluted with 500 ml of water and heated to 50°C and then agitated at 150 rpm for 6 h. The prepared AWSCC was washed with deionized water and dried at 102°C for 2 h. The same process was applied to WSC to obtain walnut shell carbon impregnated on chitosan (WSCC). The AWSCC and WSCC were then soaked in 0.5% NaOH solution till any residual acid was removed. Both adsorbents were rinsed extensively with deionized water and dried in an oven at 102°C for 2 h, cooled at room temperature and stored in desiccator.

Characterization of different prepared adsorbents

Determination of surface area

The specific surface area (S) of the activated carbon was estimated using Sear method (Alzaydian, 2009) by agitating 1.5 g of the adsorbent in 100 ml of diluted hydrochloric acid at a pH of 3. Then, 30 g of NaOH was added while stirring the suspension and the volume was made up to 150 ml with deionized water. The resulting solution was titrated with 0.1 N NaOH to raise the pH from 4 to 9 and the volume, V_{OH} , of NaOH was recorded. The surface area, S , of the adsorbent was calculated thus:

$$S = 32V_{OH} - 25 \quad (4)$$

Determination of ash content

The ash content (AC) of the activated carbon was determined by the method of Jeyakumar and Chandrasekaran (2014), and is given by:

$$AC = \frac{M_1}{M \times (100 - X)/100} \times 100 \quad (5)$$

Where, M is the mass of sample taken for test, M_1 mass of ash, and X the % of moisture content present in sample taken for test.

Determination of bulk density

The apparent or bulk density, ρ_b , of each adsorbent was determined using the tapping procedure described by Ahmeda et al. (1997), and is given by: $\rho_b = W/V_M$, where W is the weight of dry material (g) and V_M the volume of dry material (mL).

Determination of pH

The procedure of Jeyakumar and Chandrasekaran (2014) was used to obtain pH. 10 g of the dried sample was weighed and transferred into a 1 L breaker. 300 mL of freshly boiled water (adjusted to pH 7.0) was added. After digesting for 10 min, the solution was then filtered while hot, rejecting the first 20 mL of the filtrate. The remaining filtrate was then cooled to room temperature and the pH was determined using a pH meter.

Determination of iodine number

The iodine number, I , was determined using the method previously described by ASTM D 4607-94 (2006), and is given by:

$$I = \frac{E \times V_B \times c \times 100}{w_s \times 1000} \quad (6)$$

Where, E is the equivalent weight of iodine (=127), V_B and c the volume and normality of sodium thiosulphate used respectively and w_s the weight of sample used in g.

Fourier-transform infrared (FTIR) analysis

The FTIR analysis of the adsorbents was determined using Shimadzu FTIR-8300 Spectrometer. The corresponding spectra of the chitosan and the derived composite biosorbents were obtained showing the wavelengths in the range 4000 to 400 cm^{-1} of the different functional groups in the samples which were identified by comparison with those in the library.

Preparation of synthetic wastewater

Stock zinc solution of concentration 1000 mg/L was prepared by dissolving 3.93 g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in 1000 mL of distilled water. The range of initial concentration of the prepared metal solutions varied between 10 and 80 mg/L. The stock solutions were further diluted with distilled water to desired concentrations (test solutions). The pH of the solutions was adjusted with 0.1 N H_2SO_4 and NaOH. Blank experiments were conducted to ensure that no adsorption occurred on the walls of the apparatus used.

Batch adsorption experiment

The batch adsorption studies were carried out at ambient temperature using the different adsorbents prepared: WSC, AWSC, WSCC and AWSCC, for the removal of zinc (II) ions in simulated industrial wastewater at the optimum conditions of all factors that influence adsorption: pH, adsorbent dose, initial metal ion concentration, particle size and agitation time. 30 mg/l of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was prepared by diluting 30 ml of 1000 ml ZnSO_4 solution with distilled water in 1000 ml volumetric flask. 100 ml of this aqueous solution was measured into 250 ml Erlenmeyer flasks containing 1 g of each adsorbent. The mixture was mechanically agitated with a basic reciprocating shaker at 150 rpm for 2 h and left undisturbed for 30 min to allow the system to equilibrate. The mixture was filtered, and the concentration of the residual metal ion in the filtrate was determined at $0 \leq t \leq 180$ min using Atomic Absorption Spectrophotometer (Perkins Elmer Model 3100). The equilibrium metal uptake, q_e (mg/g), adsorption percentage, θ , and adsorption capacity values, q_t (mg/g) at time t (min) were calculated using Eqs (7)-(9) respectively:

$$q_e = \left(\frac{c_0 - c_e}{m} \right) V \quad (7)$$

$$\theta = \left(\frac{c_0 - c_e}{c_0} \right) \times 100 \quad (8)$$

$$q_t = \left(\frac{c_0 - c_t}{m} \right) V \quad (9)$$

The distribution ratio, K_d , was determined thus:

$$K_d = \frac{\text{amount of Zn in adsorbent}}{\text{amount of Zn in solution}} \times 100 \quad (10)$$

Erdem et al. (2004) correlated the adsorption percentage, θ , and K_d by the following equation:

$$\theta = \frac{100 K_d}{K_d + V/m} \quad (11)$$

All the adsorption experiments were duplicated to ensure accuracy, reliability and reproducibility of the adsorption data. Relative error did not exceed ± 0.01 .

RESULTS AND DISCUSSION

Fourier Transform Infrared (FTIR) characterization of chitosan

FTIR was performed to confirm the formation of chitosan. The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wave numbers as reported in the literature. Various absorption bands within the 4000-400 cm^{-1} range were recorded in the FTIR spectra of chitosan, prepared from snail shell. The adsorption bands for the prepared chitosan and significant peaks are presented in Table 1.

A characteristic band at 3636.25 and 3348.28 cm^{-1} could be assigned to the stretching vibrations of $-\text{NH}$, $-\text{OH}$, $-\text{NH}_2$ and intermolecular hydrogen bonds which overlap each other. The observed peak at 1815.33 cm^{-1} was due to the presence of the methyl group in NHCOCH_3 . The characteristic $-\text{NH}$ band of the prepared chitosan indicates the presence of a carbonyl group at the observed band at 1657.75 cm^{-1} , which could be attributed to the incomplete deacetylation of chitin to chitosan. The observed peak at 1087.31 cm^{-1} was assigned to $-\text{CN}$ stretch of aliphatic amines. The observed band at 941.28 cm^{-1} was indicative of the presence of β -glycolic linkage. The observed band at 856.07 cm^{-1} was attributed to ring stretching and that observed at 710.06 cm^{-1} is attributed to NH out-of-plane bending (Sneha et al., 2014).

The characteristic absorption bands of the prepared chitosan from snail shells were compared with the standard values obtained from Sigma-Aldrich, as shown in Table 2.

Excellent agreements were obtained with AAD being $\pm 1.10\%$, thus confirming the production of chitosan from snail shell used in this study. Also, a straight line was obtained when the experimental data were plotted against the standard data, with a very high coefficient of correlation, $R^2 = 0.9998$ thereby buttressing the earlier statement made.

Determination of degree of deacetylation of chitosan

The degree of deacetylation (DD) of chitosan is an important parameter to be noted as it affects the solubility, chemical reactivity and biodegradability of chitosan. DD may range from 30% to 95% (Martino et

Table 1. FTIR showing the different bonds present in chitosan.

Wave number (cm ⁻¹)	Functional groups	Reference
3638.25-3348.25	O–H stretching of the hydroxyl group, N–H stretching	Rumengan et al. (2014)
1815.33	C=O in NHCOCH ₃ group (amide I band)	Dilyana and Stoyanka (2010)
1657.70	Primary and secondary amide or C=O group	Rumengan et al. (2014)
1388.77	–NO stretch of nitrogen containing compounds and –CO stretch of carbonyl compounds	Dilyana and Stoyanka (2010)
1087.31	–CN stretch of aliphatic amines	Dilyana and Stoyanka (2010)
941.28	β-glycolic linkages	Sneha et al. (2014)
856.07	Ring stretching	Rumengan et al. (2014)
710.06	NH out-of-plane bending	Sneha et al. (2014)

Table 2. Characteristics absorption bands in the FTIR spectra of standard and experimentally prepared chitosan.

Standard wavelength (cm ⁻¹)	3438	1661	1418	1026	896	752
Experimental wavelength (cm ⁻¹)	3348.25	1657.70	1388.77	1028.31	885.07	750.06
% error	±2.61	±0.20	±2.06	±0.23	±1.22	±0.26

Table 3. Proximate analyses of chitin and chitosan from snail shell.

Materials	Proximate analysis, %			
	Moisture content	Ash content	Protein	Fibre
Chitin	9.00	3.80	10.40	4.09
Chitosan	5.20	6.39	6.14	8.72

al., 2005), depending on the available source and procedure. 100% *DD* is very scarcely obtained, with commercial chitosan with various *DD* in the range of 75–85%. IR technique was used for determining the degree of deacetylation, *DD*, of chitosan, according to the methods described by Domszy and Roberts (1985) and Hiral et al. (1991) using Equation (12):

$$DD = 100 \left(1 - \frac{A_{1657.70}}{A_{3348.25}} \times \frac{1}{1.33} \right) \quad (12)$$

Where, $A_{1657.70}$ and $A_{3349.25}$ are values of absorbance at the wavelengths 1657.70 and 3349.25 cm⁻¹ respectively. From the FTIR analysis of chitosan, the % transmittance of the wavelength 1657.70 and 3349.25 cm⁻¹ was obtained as 95 and 78 respectively. This was then converted to absorbance [$=2 \cdot \log(\% \text{ transmittance})$] to determine the degree of deacetylation of the prepared

chitosan from snail shells as 85.53%, using Equation 12. This value is in the range given by Martino et al. (2005).

Proximate analysis of chitin and chitosan

The proximate analyses of chitin and chitosan prepared in this study are presented in Table 3.

It was found that the moisture content of chitin was higher than that of chitosan owing to the fact that water was removed from the chitin prior to the production of chitosan. The ash content of chitin was lower than that of chitosan as a result of the presence of the acetyl group in the chitin sample. Protein content of the chitin was high after deproteinization of the chitin and this could be attributed to the low degree of acetylation of the chitin, which was found to be 14.47% (that is 100-*DD* of chitosan). The fibre content of the chitosan was higher than that of chitin owing to the fact that the removal of more matter from the chitin to obtain chitosan could have

Table 4. Ultimate and proximate analyses of raw walnut shell.

Ultimate analysis (%)					Proximate analysis (%)			
C	H	N	S	O	Moisture content	Ash content	Volatile matter	Fixed carbon
45.90	5.90	0.25	0.00	47.95	11.60	1.40	70.50	16.50

Table 5. Proximate analysis and physicochemical properties of the prepared adsorbents.

Proximate analysis	Adsorbents			
	WSC	AWSC	WSCC	AWSCC
Moisture content (%)	6.72	5.10	5.56	4.78
Ash content (%)	6.50	1.49	5.60	2.60
Volatile matter (%)	10.56	9.28	8.76	7.54
Fixed carbon (%)	17.08	16.54	17.20	16.71
Physicochemical properties				
Surface area (m ² /g)	620	634	650	890
Bulk density (g/ml)	0.30	0.50	0.40	0.60
pH	9.0	7.6	9.0	5.5
Iodine value (mg/g)	135	168	200	172

led to the presence of more fibre in the chitosan than in chitin. The results of the proximate analysis of chitin and chitosan obtained in this study were consistent with those obtained by Isa et al. (2012) in the extraction and characterization of chitin and chitosan from Nigerian shrimps.

The solubility of chitosan was checked using four different solvents: water, ethanol, NaOH and ethanoic acid. It was found that the chitosan was soluble in acidic condition but insoluble in alkaline, ethanol and neutral solution. The pH value of the chitosan also varied from 6.3 to 8.2, as reported by Sneha et al. (2014) in the extraction and purification of chitosan from chitin isolated from sea prawn.

Ultimate and proximate analyses of raw walnut shell

The results of the ultimate and proximate analyses of the walnut shell are given in Table 4.

From the ultimate analysis, the precursor for the preparation of different adsorbents used in this study has very low nitrogen and no sulphur and thus cannot contribute to environmental issues involving oxides of nitrogen and sulphur. Also, the walnut shells have a high volatile matter content and low ash content, which is essential for pyrolysis and gasification processes.

The lignocellulosic composition of the walnut shell was determined according to the Robertson and Van Soest (1981) method. The % of cellulose, hemicellulose and lignin was found to be 41.40, 20.00 and 17.60 respectively. Thus, the lignin content of the walnut shell

used in this study was least. However, materials with a low content of the lignin fraction are candidates for the production of microporous activated carbon (Daud and Ali, 2004; Gergova et al., 1994).

Characteristics of the prepared adsorbents

Table 5 shows the characteristics of the prepared adsorbents. The moisture content of AWSCC was 4.78%, which was the lowest amongst the prepared adsorbents. Hence, AWSCC could be adjudged the best adsorbent amongst the prepared adsorbents, with excellent adsorption performance since lower moisture content increases the adsorption capacity of carbon by concentrating the action of activated carbon.

The ash content of AWSCC was found to be 2.60%, which was the lowest amongst the investigated adsorbents. The lower the ash content, the better the starting material for removal of heavy metal ions from industrial wastewater (Lin and Wu, 2001). Hence, AWSCC was found to be a better adsorbent than WSC, AWSC and WSCC. Moreover, the least ash content value for AWSCC was favourable because the ash content can interfere with the adsorption process (Khan et al., 2009).

AWSCC has the lowest volatile matter compared to WSC, AWSC and WSCC. This can be attributed to the fact that during thermal activation, most of the non-carbon elements such as hydrogen, oxygen, nitrogen and sulphur might have been eliminated as volatile gaseous products by the pyrolysis.

There is no much difference on the fixed carbon content of WSC, AWSC, WSCC and AWSCC, as the % error between the highest and lowest values for WSCC and AWSC respectively was $\pm 3.84 \pm 5$. Hence, all the prepared adsorbents in this study could be viable options for activated carbon production.

The surface area of an activated carbon is directly related to the porosity of the carbon. From Table 5, the increasing order of surface areas of the prepared adsorbents was WSC < WSCC < AWSC < AWSCC. Therefore, AWSCC could be adjudged the best and highly porous adsorbent. However, the surface areas of these adsorbents conformed to the range for plant adsorbents, which is between 10^2 and 10^3 m²/g.

The results of bulk density of the prepared adsorbents revealed that AWSCC had the highest bulk density, which is indicative of higher quality adsorbent than the other three adsorbents. Therefore, AWSCC could provide better contact with the adsorbate, leading to more effective adsorption process.

The pH parameter is a factor affecting adsorption capacity of heavy metals. It is well known that pH could affect the protonation of functional group on the active sites of the adsorbent, as well as metal chemistry (Tsezos and Bell, 1989). The pH values of WSC, AWSC, WSCC and AWSCC were determined to be 9.0, 7.6, 9.0 and 5.5. These findings were in agreement Cheremisnoff and Ellerbusch (1978) who confirmed that the pH of either raw or carbonized agricultural materials in water suspension can vary between 4 and 12.

Iodine value is a fundamental parameter used to characterize the performance of activated carbons. It is often used to determine the micropore content of the activated carbon and is obtained by the adsorption of iodine from solution by the activated carbon sample (Jeyakumar and Chandrasekaran, 2014). Higher value of the iodine value indicates higher degree of activation. The iodine values of WSC, AWSC, WSCC and AWSCC are given in Table 5. The WSCC had the highest iodine value of 200 mg/g, indicating that its pore surface and structure were the best developed in this study.

Fourier Transform Infrared (FTIR) characterization of prepared adsorbents

The FTIR spectra of the prepared biosorbents were studied in the range of 4000 to 400 cm⁻¹. The FTIR spectra of the WSC and AWSC obtained in this study did not exhibit significant differences in the surface chemistry of these two adsorbents. However, slight differences on the intensity of the bands were detected. The following surface functional groups were identified for WSC and AWSC (González et al., 2009). The wide bands at 3400 cm⁻¹ were related to vibrations $\nu(\text{O-H})$ in water molecules. The weak band was found around 2900 cm⁻¹, which was attributed to carboxylic acids or aliphatic

groups. The band at 2350 cm⁻¹ is generally associated with vibrations in aliphatic bonds. The bands within the region 1400-1800 cm⁻¹ can be attributed to C=O bonds, which is related to the presence of carbonyl groups or aromatic rings. Finally, the weak band detected around 1123 cm⁻¹ was related to $\nu(\text{C-O})$ bonds in lactones, epoxides and ether structures.

For WSCC, the broad band positioned between 3375.99 and 3334.25 cm⁻¹ revealed the existence of -OH stretching of the hydroxyl group, intra molecular hydrogen groups and free N-H. The observed band at 2943.90 and 2360.41 cm⁻¹ was attributed to C-H stretching. The observed band at 2193.00 and 1977.95 cm⁻¹ was as a result -C≡C- (alkyne). The observed band at 1617.55 cm⁻¹ could be attributed to primary and secondary amide or C=O group present in WSCC. The observed band at 1503.37 cm⁻¹ was as a result of N-H deforming. The observed band at 1459.90 cm⁻¹ was attributed C-C stretch (in ring). The observed band at 1374.62 cm⁻¹ was indicative of CH₃ in the NHCOCH₃ group. The observed band at 1317.77 and 1264.49 cm⁻¹ was due to nitrate (NO₂) symmetric stretching vibration. The observed band at 1029.05 cm⁻¹ was as a result of the stretching of the CO bond. The observed band at 886.37 cm⁻¹ was indicative of the stretching of O-O bond and the observed band at 813.95-661.81 cm⁻¹ was as a result of the stretching of halogenated compounds, C-X, where 'X' represents halogens.

For AWSCC, the broad band positioned at 3431 cm⁻¹ revealed the existence of -OH stretching of the hydroxyl group. The 1615.80 cm⁻¹ band was a bend vibration of N-H (Argun and Dursun, 2006). The observed band at 1315.80 cm⁻¹ was as a result of the nitrate (NO₂) symmetric stretching vibration and the observed band at 1056.60 cm⁻¹ was attributed to the vibration C=O=C and O-H in polysaccharides. The observed band at 879.73 cm⁻¹ was due to the C=CH₂ bending and that at 779.26 and 659.06 cm⁻¹ could be attributed to the presence of the SO₃ group and C-S stretching respectively.

Dynamics of Zn II ions adsorption on prepared adsorbents

Effect of pH on the removal of Zn (II) ions

While operational parameters (adsorbent dose, agitation time and initial metal ion concentration) were kept constant and temperature and agitation speed kept at 30°C and 150 rpm respectively, the results of the effect of solution pH ($2 \leq \text{pH} \leq 9$) on the adsorption of Zn (II) ions onto WSC, AWSC, WSCC and AWSCC are shown in Figure 1. It was observed that the adsorption capacities of WSC, AWSC, WSCC and AWSCC for Zn (II) ions removal increased as pH increased until optimum pH value of 5, and then decreased when pH was increased further. This may be due to the formation of soluble

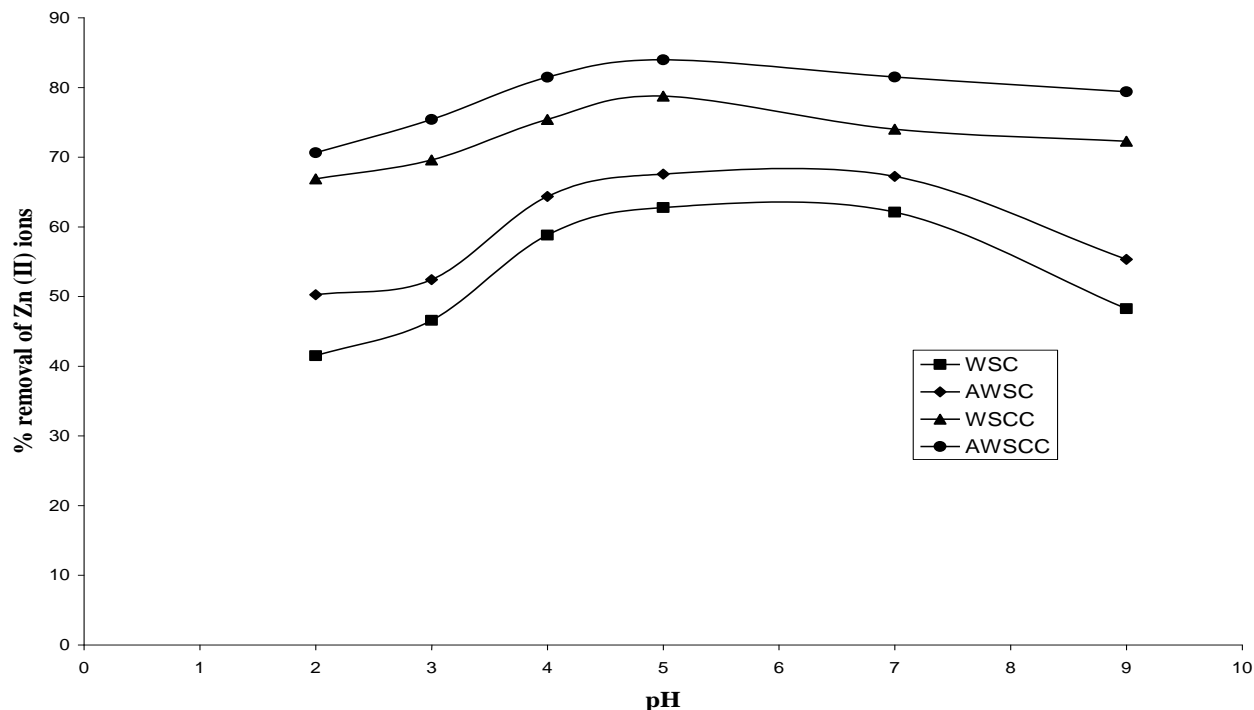


Figure 1. Effect of pH on the removal efficiency of Zn (II) ions using WSC, AWSC, WSCC and AWSCC at $c_0 = 30$ mg/L, dose of each adsorbent=1g, agitation speed=150 rpm, contact time=120 min, particle size=60BSS and temperature of solution=30°C.

hydroxyl complexes. The onset of metal hydrolysis and precipitation begins at $\text{pH} > 5$ (Baes and Mesmer, 1976). Competitive adsorptions between H^+ and Zn^{2+} ions result in low adsorption efficiency of Zn^{2+} as H^+ concentration increases if pH is below 3 (Amuda et al., 2007). At low pH, the amine group on the chitosan is protonated to a varying degree (Nomanbhay and Palanisamy, 2005). The surface acidity was due to the introduction of several oxygen-containing functional groups (Faria et al., 2004). Acid activation of walnut shell carbon using phosphoric acid and subsequent impregnation on chitosan to produce AWSCC improved the electrostatic interaction between chitosan and AWSC. Hence, more active sites were available for the adsorption of Zn (II) ions on AWSCC thereby resulting in the highest metal ion removal efficiency as shown in Figure 1. Therefore, the increasing order of Zn (II) ions removal efficiency at pH between 2 and 9 is $\text{WSC} < \text{AWSC} < \text{WSCC} < \text{AWSCC}$.

Effect of adsorbent dosage on the removal of Zn (II) ions

Figure 2 shows Zn (II) ions removal efficiency as function of adsorbents dosage. The dose of each adsorbent was varied between 5 and 25 g/L, keeping other operational parameters (pH, agitation time, initial ion concentration

and particle size) at the optimum and temperature and agitation speed were kept at 30°C and 150 rpm respectively. Owing to the availability of more binding sites, it was observed that increasing the dose of the each adsorbent increased the removal efficiency of Zn (II) ions. However, increasing the dose of the adsorbents above 15 g/L for WSC, 20 g/L for AWSC, 15 g/L for WSCC and 10 g/L for AWSCC produced no appreciable increase in the Zn (II) ions removal efficiency. The highest Zn (II) removal efficiency for WSC and AWSC was 65.64 and 71.67% respectively at 25 g/L dose of the adsorbent. As it can be seen from Figure 2, 15 g/L and 10 g/L dose of WSCC and AWSCC respectively exhibited 79.76 and 83.81% Zn (II) ions removal efficiency respectively, indicating that surface area of the carbon has significant effect on the removal of Zn (II) from synthetic wastewater. In Table 5, AWSCC had the highest surface area thereby the highest Zn (II) ions removal efficiency. Therefore, the decreasing order of the surface area and thus Zn (II) ions removal efficiency is $\text{AWSCC} > \text{WSCC} > \text{AWSC} > \text{WSC}$. From Figure 2, it can be seen that after a certain dose of adsorbent, no significant amount of ions is bound to the adsorbent. The amount of free ions remains constant even with further addition of the dose of adsorbent (Nomanbhay and Palanisamy, 2005). The difference in the surface

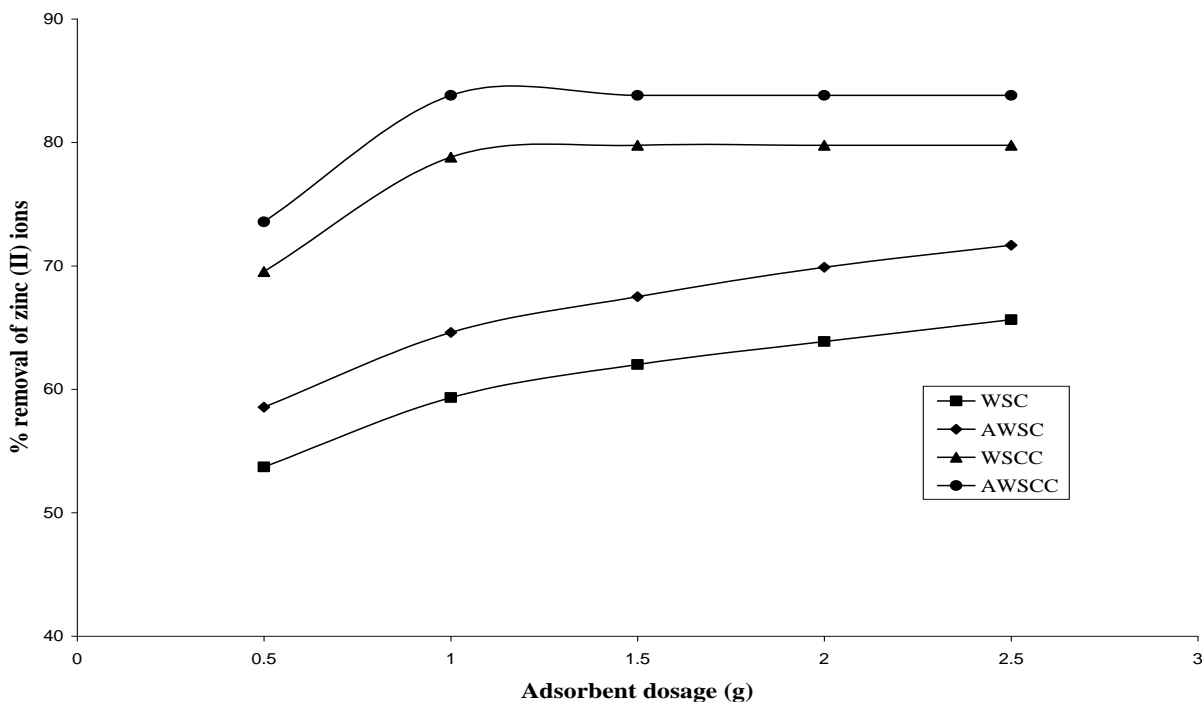


Figure 2. Effect of adsorbent dosage on the removal efficiency of Zn (II) ions using WSC, AWSC, WSCC and AWSCC at $c_0 = 30$ mg/L, pH=5, agitation speed=150 rpm, contact time=120 min, particle size=60BSS and temperature of solution=30°C.

modification of the adsorbents conferred on them different degrees of removal efficiency. The oxidation of WSC with mineral acids has been implicated to introduce more acidic C=O groups on the surface of WSC. This would enhance the electrostatic interaction between chitosan and the more negatively charged AWSCC, thus, preventing agglomeration of chitosan (Amuda et al., 2007). The formation of more acidic surface oxides on AWSCC than WSC, AWSC and WSCC enhanced efficient coating of chitosan, enhanced its hydrophilic character and hence improved the hydrodynamic flow of metal ion to the acidic surface oxides on the carbon surface. This could be responsible for the high adsorption capacity of AWSCC over WSC, AWSC and WSCC.

Effect of initial metal ion concentration on the removal of Zn (II) ions

The percentage removal of Zn (II) ions by the adsorbents initially increased rapidly with increasing Zn (II) ions concentration and stagnates when Zn (II) concentration reached 30mg/L, as can be seen in Figure 3. At lower concentrations, Zn (II) ions in the solution would interact with the binding sites and thus facilitated 100% adsorption (Amuda et al., 2007). At higher concentrations,

more Zn (II) ions were left unadsorbed in solution due to the saturation of binding sites, which was indicative of the involvement of energetically less favourable sites with increasing metal ion concentrations in the aqueous solution. The Zn (II) ion adsorption could be attributed to different mechanisms of ion exchange processes as well as to the adsorption process. During the ion exchange process, Zn (II) ions had to move through the pores of the adsorbent mass, as well as through channels of the lattice, thereby replacing exchangeable cations. Diffusion was rapid through the pores and was retarded when the ions moved through the smaller diameter channels. In this case, the Zn (II) ions sorption could mainly be attributed to ion-exchange reactions in the micropores of the adsorbents (Amuda et al., 2007). The maximum percentage of Zn (II) ions removal of 52.2 and 55.1 was achieved when 75 mg/L Zn (II) ion concentrations was adsorbed with 1 g/100 mL of WSC and AWSC while the maximum percentage of Zn (II) ions removal of 95.4 and 97.8 was achieved when 50 mg/L Zn (II) ion concentrations was adsorbed with 1 g/100 mL of WSCC and AWSCC.

Effect of contact time on the removal of Zn (II) ions

Equilibrium time is another important operational

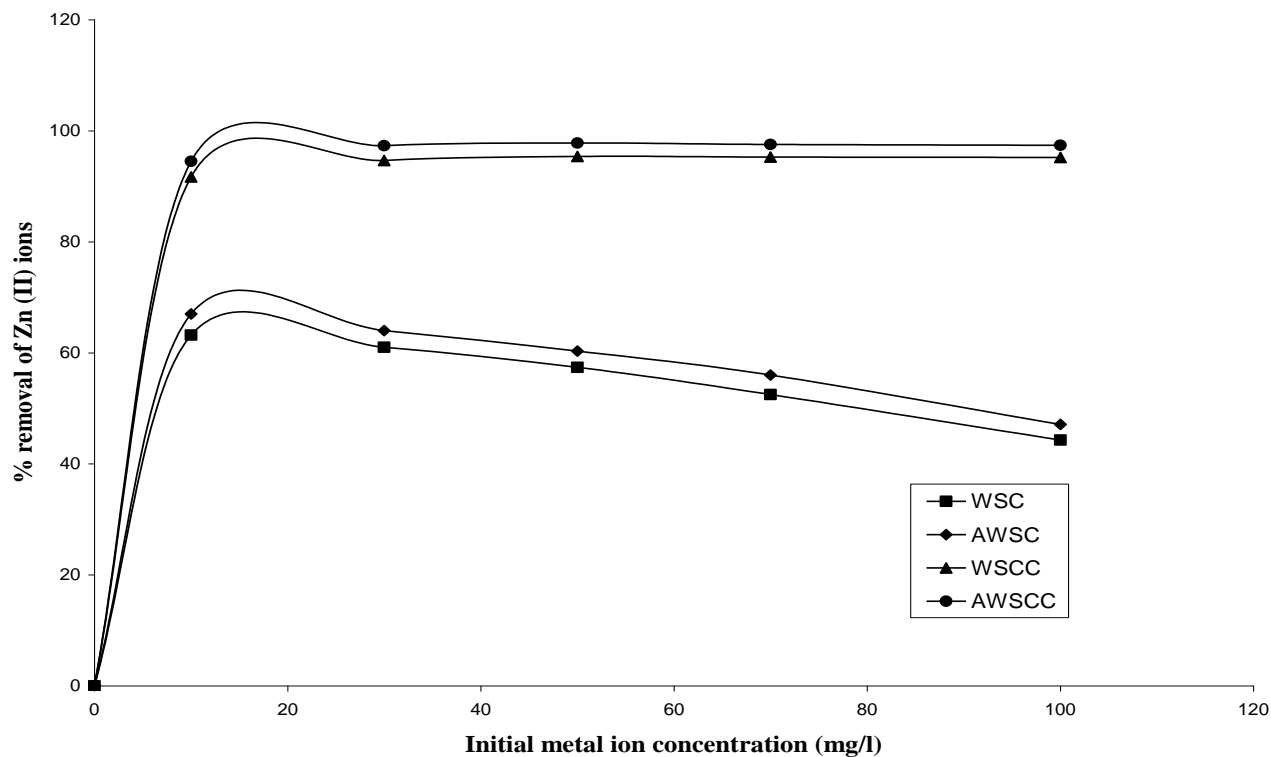


Figure 3. Effect of initial metal ion concentration on the removal efficiency of Zn (II) ions using WSC, AWSC, WSCC and AWSCC at pH=5, dose of each adsorbent=1 g, agitation speed=150 rpm, contact time=120 min, particle size=60BSS and temperature of solution=30°C.

parameter for an economical wastewater treatment process. Figure 4 depicts Zn (II) ions removal efficiency as function of agitation time keeping pH and adsorbent dose at the optimum and temperature and agitation speed at 30°C and 150 rpm, respectively. From the Figure, increase in agitation time increased the removal efficiency of Zn (II) ions until equilibrium adsorption was established. Equilibrium adsorptions were established within 180 min for WSC, AWSC, WSCC and AWSCC with Zn (II) ions removal efficiencies of 62.5%, 68%, 81.8% and 85.4% respectively. This was due to greater availability of various functional groups on the surface of chitosan required for interaction with anions and cations and thus significantly improved the binding capacity and the process proceeded rapidly for AWSCC and WSCC, compared to WSC and AWSC.

Effect of agitation speed on the removal of Zn (II) ions

Figure 5 shows the effect of agitation speed on the percentage removal of Zn (II) ions from industrial wastewater using WSC, AWSC, WSCC and AWSCC as adsorbents, while other parameters such as pH and adsorbents dose were kept at the optimum and

temperature at 30°C. It can be seen that the removal efficiency of Zn (II) ions using the four prepared adsorbents increased as the agitation speed increased until the optimum value and then decreased when the agitation speed further increased. This can be attributed to the fact that an increase in the agitation speed led to improvement in the mixing between metal ions in solution and active binding sites of the adsorbents (WSC, AWSC, WSCC and AWSCC) thereby resulting in an increased removal efficiency of Zn (II) ions. When the mixture of metal ion and the adsorbents (WSC, AWSC, WSCC and AWSCC) was set on a shaker in several Erlenmeyer flasks, the fine particles of WSC, AWSC, WSCC and AWSCC moved rapidly in the metal solution and this led to increased concentration of metal ions near the surface of the active sites. According to Kafia and Surchi (2011), the high shaking speed provided sufficient additional energy to break newly formed weak bonds between the metal ions and binding sites of the adsorbent. Consequently, high agitation speed may lead to the adsorbed metal ions to desorb from the adsorption sites. From Figure 5, at the optimum agitation speed of 150 rpm, the respective value of the removal efficiency of Zn (II) ions was found to be 60.3, 64.1, 82 and 85.4% using WSC, AWSC, WSCC and AWSCC as adsorbents

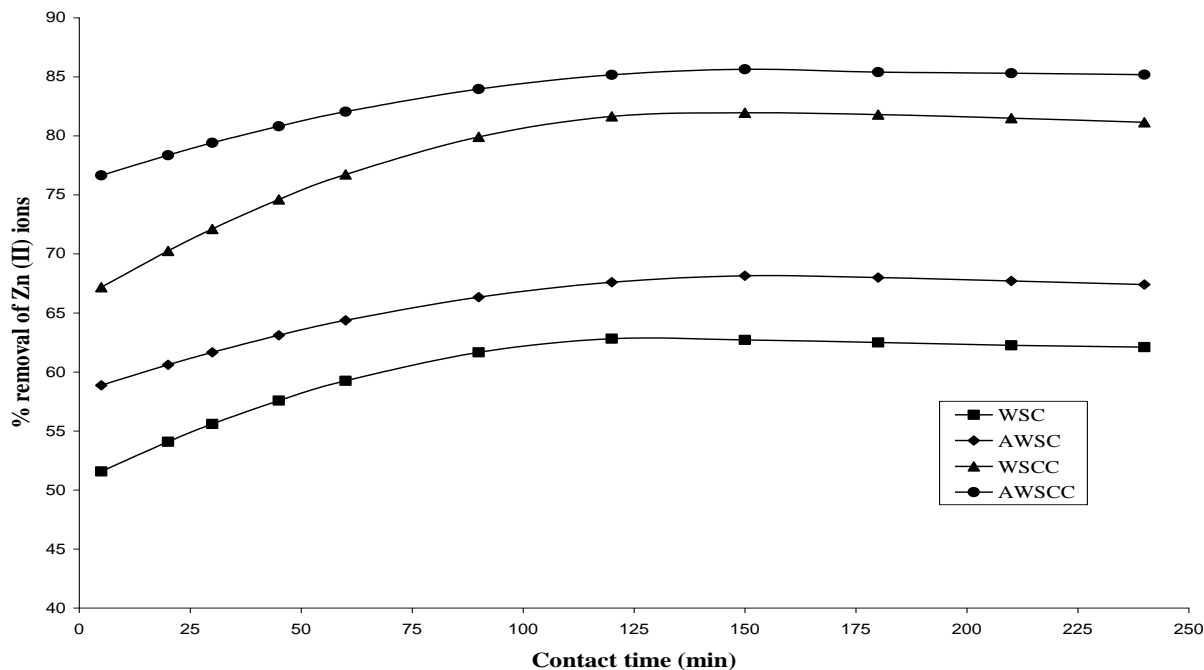


Figure 4. Effect of contact time on the removal efficiency of Zn (II) ions using WSC, AWSC, WSCC and AWSCC at $c_0 = 50$ mg/L, pH=5, dose of each adsorbent=1 g, agitation speed=150 rpm, contact time=120 min, particle size=60BSS and temperature of solution=30°C.

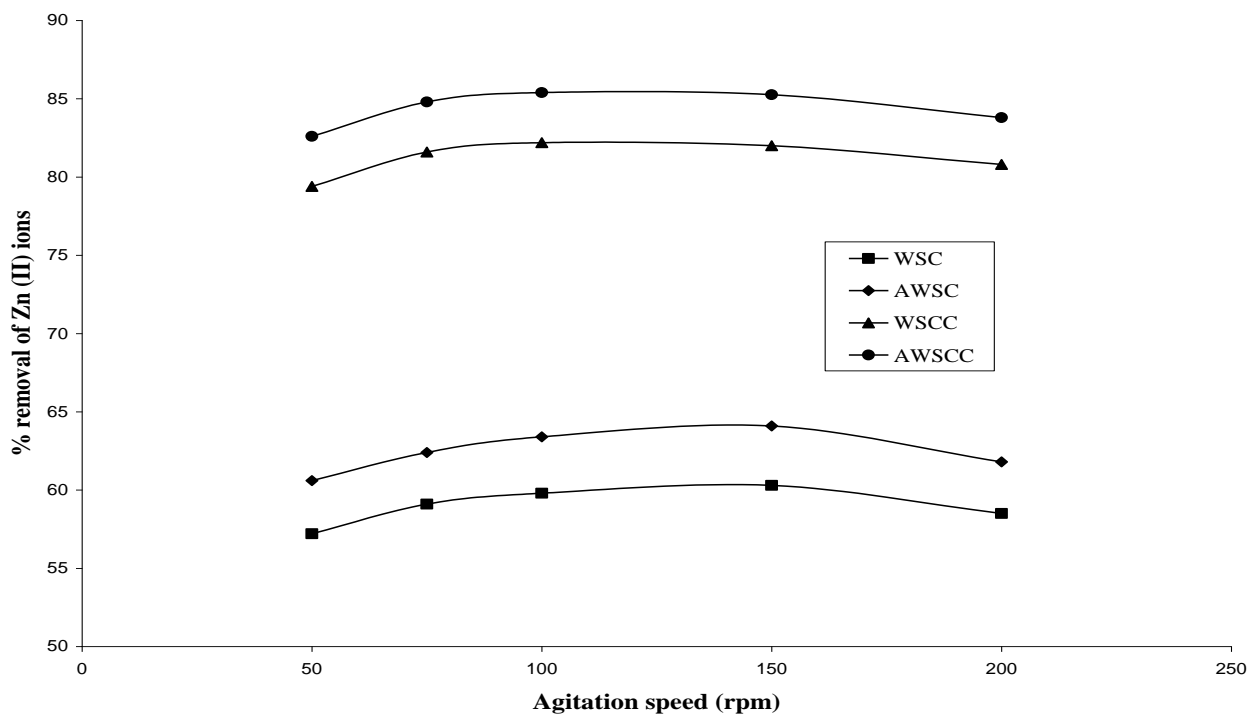


Figure 5. Effect of agitation speed on the removal efficiency of Zn (II) ions using WSC, AWSC, WSCC and AWSCC at $c_0 = 50$ mg/L, dose of each adsorbent=1g, agitation speed=150 rpm, contact time=120 min, particle size=60BSS and temperature of solution=30°C.

thereby giving justification to setting agitation speed to 150 rpm for all adsorption studied in this work.

Correlation of equilibrium adsorption data

The sorption equilibrium data gathered in this study were confronted with the adsorption isotherms of Langmuir, Freundlich and Temkin. These isotherms are given as follows:

$$\text{Langmuir isotherm: } q_e = \frac{q_{\max} K_L c_e}{1 + K_L c_e} \quad (13)$$

Which can be linearized to five different linear forms:

$$\frac{1}{q_e} = \frac{1}{K_L q_{\max}} \frac{1}{c_e} + \frac{1}{q_{\max}}, \quad \frac{c_e}{q_e} = \frac{1}{q_{\max}} c_e + \frac{1}{K_L q_{\max}}$$

$$q_e = \frac{1}{K_L} \frac{q_e}{c_e} + q_{\max}, \quad \frac{q_e}{c_e} = -K_L q_e + K_L q_{\max}, \quad \text{and}$$

$$\frac{1}{c_e} = -K_L q_{\max} \frac{1}{q_e} - K_L$$

The important characteristics of Langmuir isotherm was explained by a dimensionless constant, known as separation factor or equilibrium parameter, R_L , given by Zhai et al. (2004):

$$R_L = \frac{1}{1 + K_L c_0} \quad (14)$$

Using mathematical computations, Zhai et al. (2004) showed that R_L indicates the shape of the isotherm thus: for $R_L < 0$, $0 < R_L < 1$, $R_L = 1$ and $R_L > 1$, we have irreversible, favourable, linear and unfavourable isotherms respectively.

$$\text{Freundlich isotherm: } q_e = K_F c_e^{1/n} \quad (15)$$

Whose linear form is expressed thus:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (16)$$

Where, K_F is a measure of adsorption capacity and n stands for the heterogeneity.

$$\text{Temkin isotherm: } q_e = \frac{RT}{b_T} \ln(A_T c_e) = \frac{RT}{b_T} (\ln A_T + \ln c_e) \quad (17)$$

In these isotherms, necessary linear plots were made, as

shown in Figures 6 to 8, slope and intercept were determined and the inherent isotherm parameters were calculated as shown in Tables 6 and 7.

The coefficient of correlation, R^2 , was the criterion for fitting the experimental data to these isotherms. It should be stressed that all the five linearized forms of Langmuir isotherm were fitted to the experimental data, and they all gave almost the same results. From the R^2 values, Langmuir isotherm correlated exceedingly well the equilibrium adsorption data of Zn^{2+} ions removal using WSC, AWSC, WSCC and AWSCC as adsorbents. The maximum uptake capacities for Zn^{2+} ions were 17.70, 16.45, 3.80 and 3.11 mg/g for AWSCC, WSCC, AWSC and WSC respectively. The Langmuir parameters were also used to predict the affinity of the adsorbents' surfaces toward the Zn^{2+} ions by using dimensionless separation factor, R_L , as expressed in Equation 12. The R_L values obtained were in the range $0 < R_L < 1$ for Zn^{2+} ions concentration studied in this work ($20 < c_0 < 200$ mg/l). This is indicative of a favourable isotherm shape for the adsorption of Zn^{2+} ions onto WSC, AWSC, WSCC and AWSCC in the concentration range studied.

Though $n > 1$ for the four adsorbents using Freundlich isotherm, the R^2 value for AWSC is not that close to unity while promising results were obtained for WSC, WSCC and AWSCC. The n value of Freundlich equation gives an indication of the favourability of sorption. It is generally stated that values of n in the range of 2 to 10 are good, 1 to 2 as moderately difficult and less than 1 as poor sorption characteristic (Chen et al., 2010). Hence, Freundlich isotherm can be used to correlate the adsorption data of Zn^{2+} ions removal using WSC, WSCC and AWSCC as adsorbents, with the best fitted adsorption data obtained for AWSCC.

The estimated values of Temkin parameters and R^2 are presented in Table 7. From the R^2 values, which are close to unity, Temkin isotherm could also be a representative for the Zn^{2+} ions adsorption onto the four adsorbents studied.

In general, Langmuir adsorption isotherm had the best fit for the four adsorbents tested in this study as a result of the highest correlation coefficient. The suitability and applicability of Langmuir isotherm to the adsorption of Zn^{2+} ions on WSC, AWSC, WSCC, and AWSCC reveal the formation of monolayer coverage of the Zn^{2+} ions on the surface of these adsorbents.

Kinetic modelling of Zn (II) ions adsorption

Different kinetic models given in Equations 18, 20, 23, 24 and 26 were used to test the kinetic data for the adsorption of Zn^{2+} ions on WSC, AWSC, WSCC and AWSCC.

The fractional power model, which has the form of

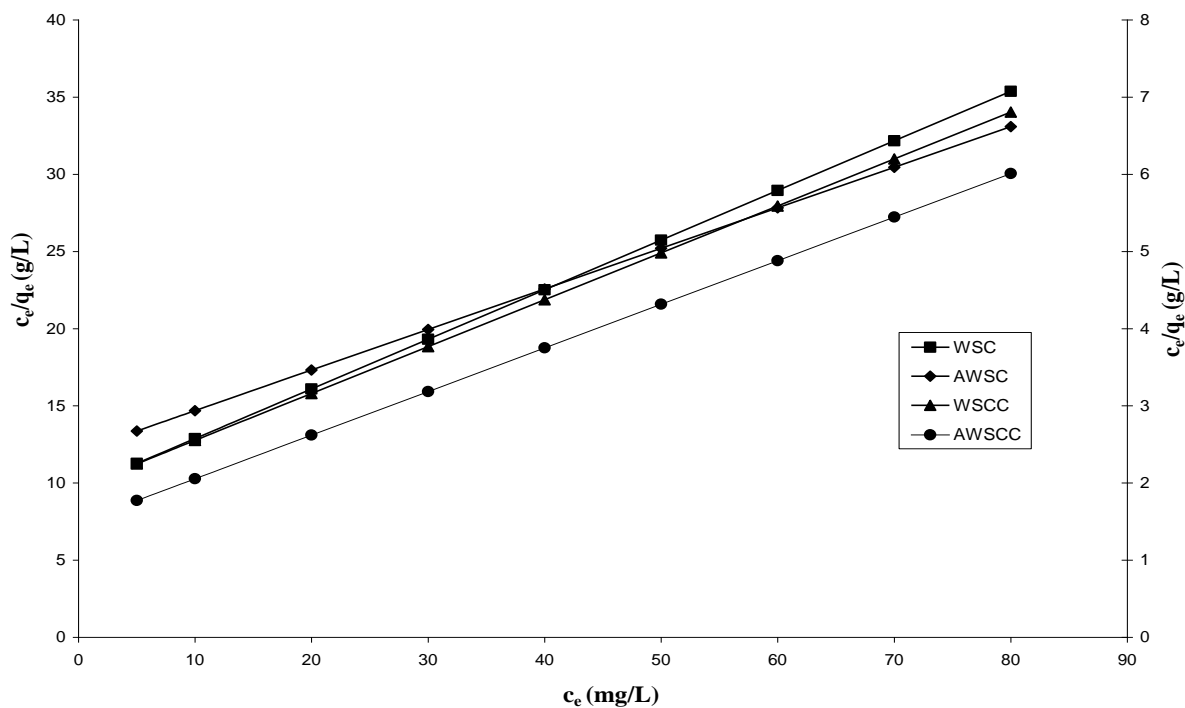


Figure 6. Langmuir adsorption isotherm fitted to the batch equilibrium data of Zn (II) ions adsorption on WSC, AWSC, WSCC and AWSCC as adsorbents.

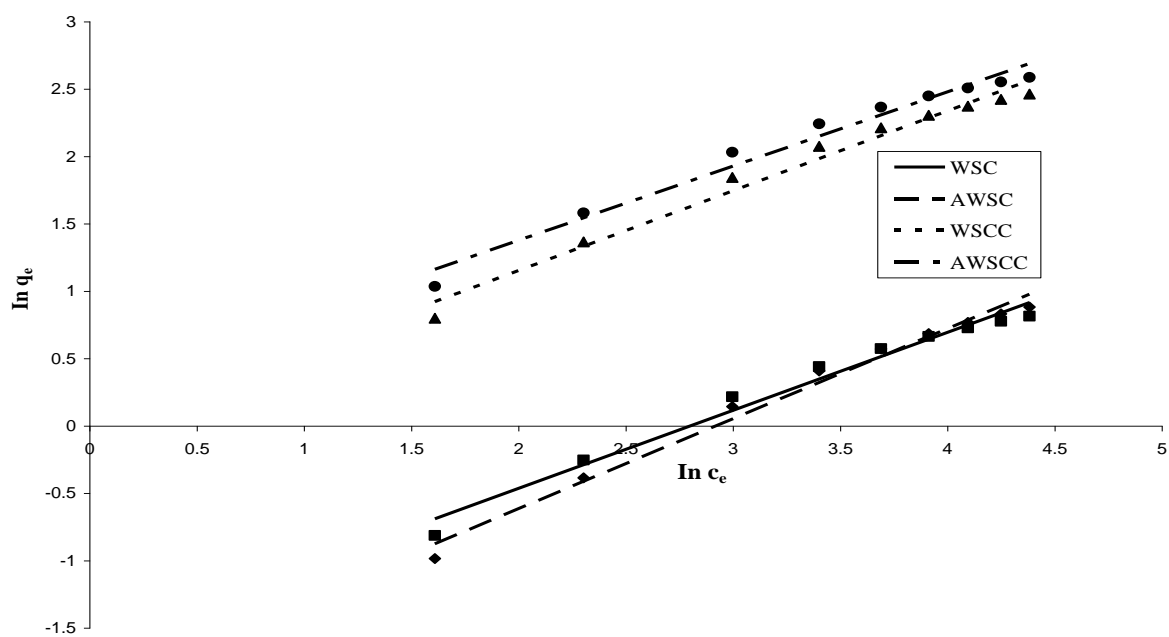


Figure 7. Freundlich adsorption isotherm fitted to the batch equilibrium data of Zn (II) ions adsorption on WSC, AWSC, WSCC and AWSCC as adsorbents.

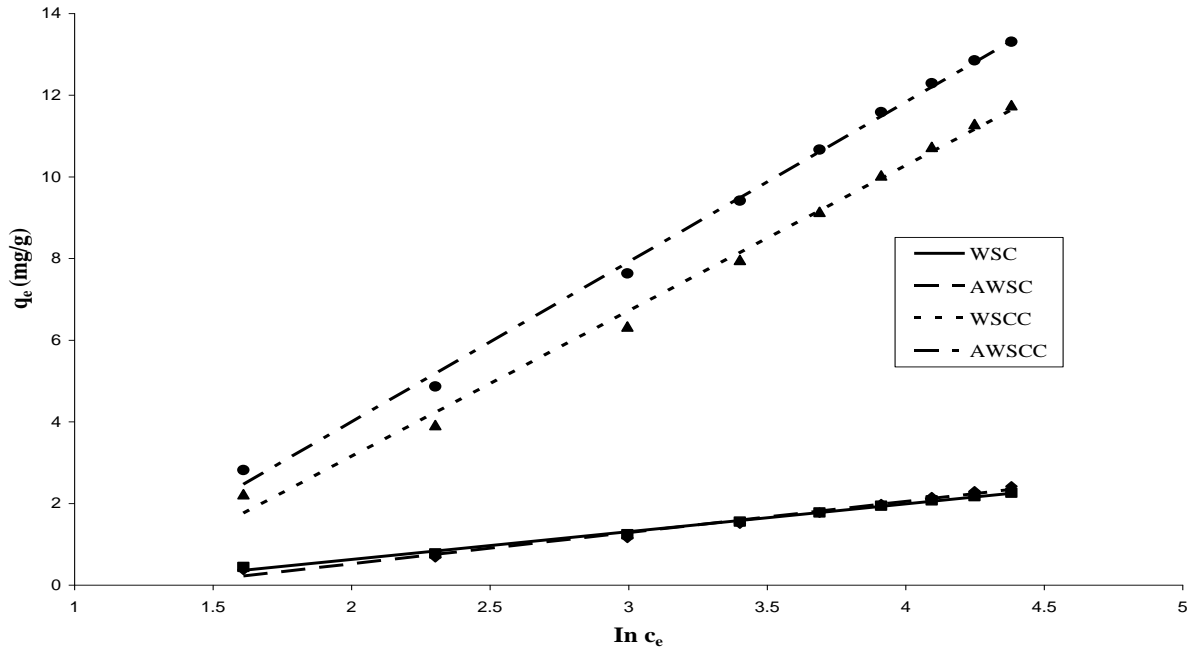


Figure 8. Temkin isotherm fitted to the batch equilibrium data of Zn (II) ions adsorption on WSC, AWSC, WSCC and AWSCC as adsorbents.

Table 6. Langmuir and Freundlich isotherm parameters for adsorption of Zn²⁺ ions by different adsorbents at 30°C.

Adsorbent	Langmuir parameters				Freundlich parameters		
	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2	K_F (mg/g)	n	R^2
WSC	3.1104	0.0333	0.6002	0.9997	2.224	2.9586	0.941
AWSC	3.8052	0.0218	0.6964	0.9998	2.808	2.1505	0.918
WSCC	16.4474	0.0313	0.6150	0.9997	1.0392	1.5952	0.9701
AWSCC	17.6991	0.0379	0.5688	1.0	0.8690	1.6036	0.9754

Table 7. Temkin isotherm parameters for adsorption of Zn²⁺ ions by different adsorbents at 30°C.

Adsorbent	Temkin parameters			
	A_T (L/g)	b_T	$\Phi_1 (= RT/b_T)$	R^2
WSC	0.3422	3710.08	0.6790	0.9753
AWSC	0.2678	3297.74	0.7639	0.9848
WSCC	3.2845	802.63	3.0868	0.9813
AWSCC	3.5570	693.53	2.6950	0.9885

Freundlich equation, indicates the metal uptake increases exponentially with time, and is given by:

$$q_t = k_F t^N \tag{18}$$

Taking natural logarithms of Eq. (16) gives:

$$\ln q_t = \ln k_F + N \ln t \tag{19}$$

Hence, the parameters inherent in the model can be estimated by making appropriate linear plot of $\ln q_t$ against $\ln t$

The Elovich kinetic model is given by:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (20)$$

Where, α and β are constants during an experiment. As $q_t \rightarrow 0$, $dq_t/dt \rightarrow \alpha$, hence α is regarded as the initial rate of adsorption. When $t=0$, $q_t=0$ and $t=t$, $q_t=q_t$, the integrated form of Equation 20 is:

$$q_t = \frac{1}{\beta} [\ln(t + \Phi) - \ln \Phi] \quad (21)$$

Where, $\Phi = 1/(\alpha\beta)$. If $t \gg \Phi$, Eq. (21) simplifies to:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (22)$$

Hence, a linear plot of q_t against $\ln t$ can be made to check if $t \gg \Phi$ for the coefficient of determination, R^2 , should be greater than 1.

The intraparticle diffusion (IPD) (or Weber and Morris) model is used to identify the mechanism involved in the adsorption process. IPD model has the form:

$$q_t = k_{IPD} \sqrt{t} \quad (23)$$

A linear plot of q_t against \sqrt{t} can be used to determine k_{IPD} , with no intercept on q_t axis.

The Lagergren pseudo first-order kinetic model is expressed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (24)$$

The integrated form of Equation (24) is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (25)$$

The specific reaction rate constant, k_1 , for the Lagergren pseudo first-order kinetics is usually obtained by plotting $\ln(q_e - q_t)$ against t , whereby the slope of the straight line obtained is $-k_1$.

The pseudo second-order kinetic model is given by:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (26)$$

The integrated form of equation (26) is:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (27)$$

Which gives different forms when linearized. One of such forms used in this study is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (28)$$

Hence, a plot of t/q_t against t should yield a straight line to enable the determination of q_e and k_2 from slope and intercept respectively.

The goodness of fit was justified based on the fact that the coefficients of determination were close to 1. The models, their estimated parameters and R^2 values are presented in Table 8.

Though the value of the exponent, N , of the fractional power model was less than 1, which indicated the time-dependent of the adsorption of Zn^{2+} ions on WSC, AWSC, WSCC and AWSCC as adsorbents, the fractional power model did not provide a good fit to the kinetic data of the adsorption of Zn^{2+} ions as the coefficients of correlation, R^2 , in all cases of the four adsorbents used in this study, were not close to unity, as presented in Table 8. Moreover, the experimental kinetic data did not show satisfactory fit to Elovich kinetic model since R^2 values for the four adsorbents used were not close to unity. The kinetic plots for the intraparticle diffusion model obtained in this study for the four adsorbents tested were not linear for all the lines did not pass through the origin as expected: they all had intercepts, C , as shown in Table 8. This indicated that the intraparticle diffusion was not the rate-controlling step in the adsorption of Zn^{2+} ions on the prepared adsorbents, and there was some degree of boundary layer diffusion. This was buttressed by the fact that the correlation coefficients are far less than unity. In fact, in all the kinetic models studied, IPD shows the worst fit of the kinetic data. Also, Table 8 depicts the kinetic parameters and the R^2 values for the Lagergren's pseudo first-order kinetic model and the pseudo second-order kinetic model. Although the R^2 values were somewhat high for the former, its theoretical values of q_e in Table 8 were far less than the corresponding experimental values predicted by the latter. This suggested a poor fit between the kinetics data and the Lagergren pseudo-first order kinetic model for the four adsorbents used in this study. These results were in consonance with similar works in the literature (Lodi et al., 1998; Ho and Mckay, 2000) with several natural adsorbents and the same initial concentration values. Excellent agreements were obtained between the

Table 8. Kinetic model parameter values and coefficient of correlation values.

Kinetic model	Parameter values	Adsorbents			
		WSC	AWSC	WSCC	AWSCC
Fractional power law	k_F	2.7665	3.2904	2.5118	3.3814
	N	0.0538	0.0367	0.0844	0.0404
	R^2	0.8368	0.8308	0.8486	0.8321
Elovich model	α (mg/g min)	238671.10	1.07×10^9	286.47	9.76×10^7
	β (g/mg)	5.2493	7.0126	2.9931	6.0827
	R^2	0.8551	0.8435	0.8772	0.8461
IPD model	k_{IPD} (mg/g min ^{1/2})	0.0247	0.0184	0.0437	0.0213
	C (mg/g)	3.2922	3.7059	3.3343	3.8551
	R^2	0.6715	0.6572	0.6997	0.6604
Lagergren's pseudo first-order model	q_e (mg/g)	0.7797	0.5848	2.9029	0.9259
	k_1 (min ⁻¹)	0.0105	0.0108	0.0297	0.0219
	R^2	0.9374	0.9338	0.9671	0.9972
Pseudo second-order model	q_e (mg/g)	3.8655	4.1305	4.11	4.25
	k_2 (g/mg min)	0.0394	0.0557	0.020	0.048
	R^2	0.9998	0.9999	0.9993	1.000

experimental and theoretical values of q_e using the pseudo second-order kinetic model. Moreover, the R^2 values in all cases studied were nearly unity and even unity for AWSCC, which was indicative that the kinetics data fitted exceedingly well the pseudo second-order model for all adsorbents investigated. The pseudo second-order model can be considered as the rate-limiting (or determining) step and probably a chemical adsorption (chemisorption) involving valance forces through ion exchange between each metal ion and the active binding sites existed in WSC, AWSC, WSCC and AWSCC. The pseudo-second order kinetic model was also reported to fit well the kinetic data of the adsorption of Zn²⁺ ions onto pomelo peel (Saikaew et al., 2009), adsorption of Cu²⁺ ions onto Tectona grandis leaves (Kumar et al., 2006), adsorption of Pb²⁺ ions onto pumpkin seed shell activated carbon (Okoye et al., 2010), adsorption of Ni²⁺ ions onto potato peel (Prasad and Abdullah, 2009), and adsorption of Cr (VI) ions onto cooked tea dust (Dhanakumar et al., 2007).

The kinetic data were further analysed using the Boyd kinetics in order to determine the actual rate-controlling step involved in the Zn²⁺ ions adsorption process on WSC, AWSC, WSCC and AWSCC owing to the two mass transfer of solute (both film and pore diffusion). The Boyd kinetics (Boyd et al., 1947) is given by:

$$F = 1 - \frac{6}{\pi^2} \exp(-Bt) \quad (29)$$

$$Bt = -\ln(1-F) - 0.4977 \quad (30)$$

Where, $F (= q_t/q_e)$ is the fraction of solute adsorbed at time, t . The value of B was computed according to Eq. (28) for each value of F for each of the adsorbents used in this study, and then plotted against time to construct the Boyd plots (Ho et al., 2002) for the system under investigation, as depicted in Figure 9. The linearity of these plots was used to distinguish between external transport (film diffusion) and intraparticle transport controlled rates of adsorption (Wang et al., 2006). A straight line passing through the origin is indicative of adsorption process governed by intraparticle diffusion; otherwise it is governed by film diffusion (Mohan and Singh, 2002). From Figure 9, the plots for the four adsorbents studied were neither linear nor passed through the origin, which indicates that in all the adsorbents studied, film diffusion is the rate-determining adsorption process for Zn (II) ions on WSC, AWSC, WSCC and AWSCC as adsorbents. This is in conformity with the earlier result presented in Table 8 that a poor fit of the kinetic data was obtained for the IPD kinetic model.

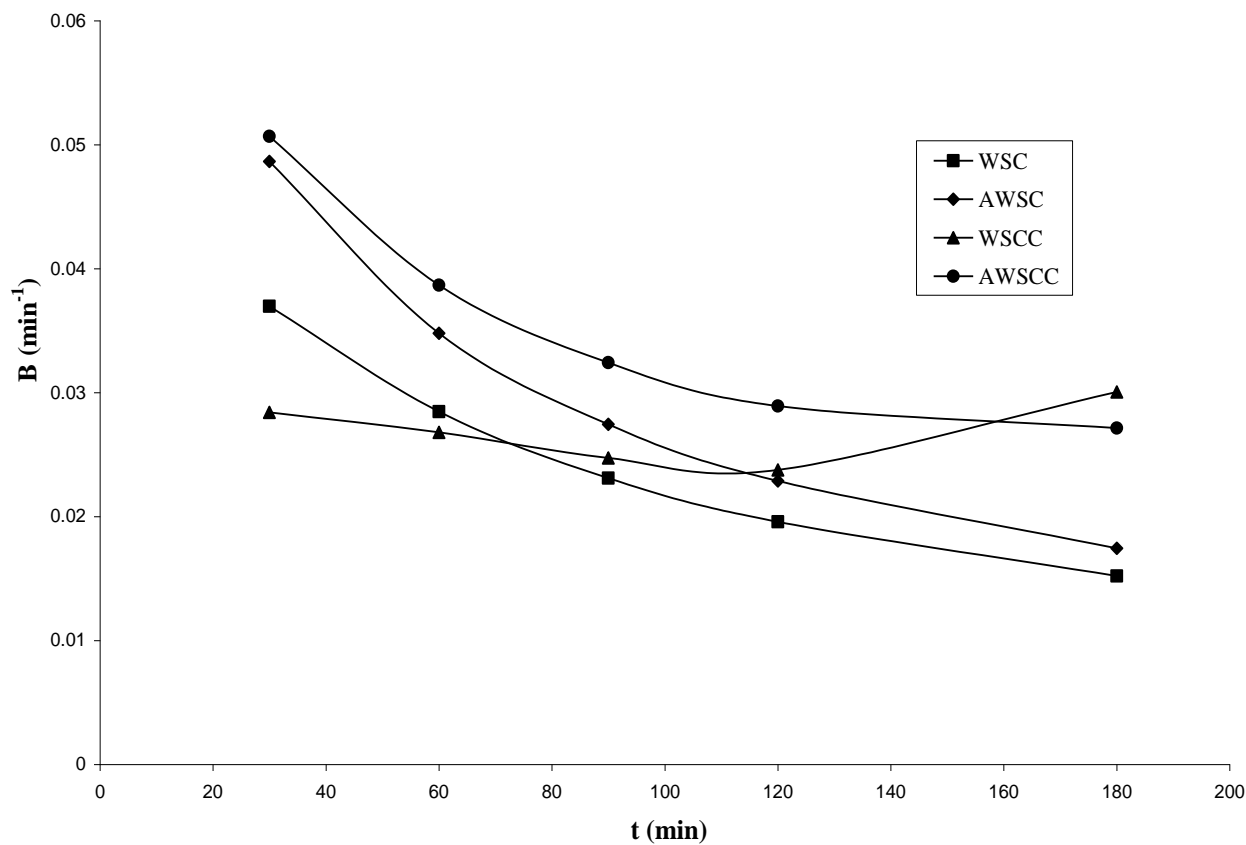


Figure 9. Boyd plots of the kinetic data for Zn (II) ions adsorption on WSC, AWSC, WSCC and AWSCC as adsorbents.

Thermodynamic studies of Zn (II) ions adsorption

Before investigating the thermodynamics of Zn (II) ions adsorption on the derived composite biosorbents from walnut shell, the effect of temperature on the % removal of Zn (II) ions from synthetic wastewater using WSC, AWSC, WSCC and AWSCC as adsorbents was studied. This is an important process for removal of heavy metals from industrial wastewater as effluents are produced at varying temperatures in industrial practice. Table 9 shows the effect of temperature on the % removal of Zn (II) ions, where the % removal of Zn (II) ions and equilibrium biosorption capacity decreased with increasing temperature. Hence, Zn (II) ions adsorption was exothermic in nature.

It was found that low temperature favours the removal of Zn (II) ions from wastewater for all the prepared biosorbents, with maximum % removal being 83.81, 78.81, 64.60 and 59.34 for WSC, AWSC, WSCC and AWSCC respectively at 303 K for pH=5, 1 g of adsorbent dosage, Zn (II) ions initial concentration of 100 mg/L, contact time of 2 h, agitation speed of 150 rpm and particle size of 60 BSS. The equilibrium adsorption capacity decreased at temperature below 303 K, which

suggested the exothermic adsorption nature of Zn (II) ions onto the prepared composite biosorbents (Aksu and Tezer, 2005). Theoretically, % removal of Zn (II) ion on the prepared biosorbents decreases with increasing temperature owing to adsorption of already adsorbed ions (Zubair et al., 2008). The low % removal at higher temperatures may be due to the destruction of active binding sites (Witek-Krowiak, 2011).

Having established the temperature dependence of the Zn (II) ions removal, thermodynamics studies were carried out to comprehend wholly the nature of the adsorption process by computing changes in enthalpy, ΔH , entropy, ΔS and Gibbs free energy, ΔG . This is with a view of confirming the exothermicity of the Zn (II) ions adsorption on the prepared composite biosorbents, non-spontaneity and feasibility of the adsorption process under investigation. The thermodynamic equilibrium constant, K_c , was determined using the relation:

$$q_e = K_c c_e \quad (31)$$

and the change in Gibb's free energy was thus calculated by using:

Table 9. Effect of temperature on % removal of Zn (II) ions and equilibrium biosorption capacity.

T(K)	WSC		AWSC		WSCC		AWSCC	
	θ	q_e (mg/g)	θ	q_e (mg/g)	θ	q_e (mg/g)	θ	q_e (mg/g)
303	59.34	5.9340	64.60	6.4600	78.81	7.8810	83.81	8.3810
308	55.03	5.5000	59.96	6.0000	77.00	7.7000	82.00	8.2000
313	50.10	5.0000	57.02	5.7000	75.04	7.5000	80.00	8.0000
323	43.98	4.4000	52.00	5.2000	69.97	7.0000	76.00	7.6000
333	40.01	4.0000	45.98	4.6000	65.02	6.5000	71.00	7.1000

Table 10. Values of thermodynamic parameters for Zn (II) ions adsorption on prepared composite biosorbents.

TK	ΔG (kJ/mol)			
	WSC	AWSC	WSCC	AWSCC
303	4.8482	4.2853	2.4916	1.6587
308	5.3824	4.8580	2.8021	2.0133
313	5.9920	5.2585	3.1331	2.3844
323	6.8310	5.9685	3.9081	3.0880
333	7.4974	6.8188	4.6610	3.8959
ΔH (kJ/mol)	-21.9539	-20.4117	-19.6535	-20.8050
ΔS (kJ/(mol K))	-0.0888	-0.0818	-0.0730	-0.0741

$$\Delta G = -RT \ln K_c \tag{32}$$

However, $\Delta G = \Delta H - T\Delta S = -RT \ln K_c$

$$\text{so } \ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{33}$$

Setting $Y = \ln K_c$, $X_1 = T^{-1}$, $a_0 = \Delta S/R$, and $a_1 = -\Delta H/R$, equation (33) becomes:

$$Y = a_0 + a_1 X_1 \tag{34}$$

The regression coefficients, a_0 and a_1 were determined using linear regression analysis for each of the prepared composite biosorbents, and the results obtained are as follows:

For WSC, $\ln K_c = 2640.6T^{-1} - 10.682$, $R^2 = 0.9792$

For AWSC, $\ln K_c = 2455.1T^{-1} - 9.8392$, $R^2 = 0.9913$

For WSCC, $\ln K_c = 2363.9T^{-1} - 8.7745$, $R^2 = 0.9979$

For AWSCC,

$\ln K_c = 2502.4T^{-1} - 8.9116$, $R^2 = 0.9990$

Thus, values of ΔH and ΔS were computed for the Zn (II) ions adsorption on WSC, AWSC, WSCC and AWSCC as adsorbents, and the results presented in Table 10.

The ΔG values were positive at all temperatures investigated, which was an indication of the non-spontaneity of the adsorption of Zn (II) ions on WSC, AWSC, WSCC and AWSCC. Hence, the Zn (II) ions adsorption process was endogonic. The negative values of ΔH for all the prepared composite biosorbents was a confirmation of the exothermicity of the Zn (II) ions adsorption process. The negative values of ΔS for WSC, AWSC, WSCC and AWSCC used for Zn (II) ions adsorption suggested that randomness at the solid/solution interface decreased as a result of Zn (II) ions adsorption onto these adsorbents. However, ΔS^0 values for all the prepared adsorbents were nearly zero, implying equilibrium conditions were established during the adsorption experiment, and the limiting value of zero being reached only by a reversible process.

Conclusion

Composite biosorbents were derived from walnut and snail shells for the adsorption of Zn (II) ions from the synthetic industrial wastewater. Chemical activation using phosphoric acid improved the specific surface area of

walnut shell carbon (WSC) while impregnation of WSC and acid-treated walnut shell carbon (AWSC) on the chitosan derived from snail shell enhances further the specific surface areas of WSC and AWSC. The removal efficiencies of Zn (II) ions using the prepared adsorbents were effective in the acidic range. The composite adsorbent of AWSCC exhibited the most effective removal efficiency of Zn (II) ions from aqueous solution. The Langmuir adsorption isotherm fitted excellently the adsorption data of Zn (II) ions on WSC, AWSC, WSCC and AWSCC owing to the highest R^2 value obtained. Moreover, in all the adsorbents (WSC, AWSC, WSCC and AWSCC) used in this study, film-diffusion was the rate-limiting adsorption process for Zn (II) ions and the kinetic data were excellently correlated with the pseudo second-order kinetic model. The uses of walnut and snail shells from renewable resources to produce activated carbon and composite adsorbents potentially provide a less costly and tremendously efficient adsorbent. The thermodynamic studies revealed that Zn (II) ions adsorption on WSC, AWSC, WSCC and AWSCC was non-spontaneous, endogonic, exothermic and favourable at low temperature of 30°C.

Notation

A_T , Temkin isotherm equilibrium binding constant, L/g; b_T , Temkin isotherm constant; c_e , metal ion concentration at equilibrium, mg/L; c_0 , initial metal ion concentration, mg/L; c_t , metal ion concentration at time t , mg/L; C , intercept on q_t axis for IPD model, mg/g; k_{IPD} , intraparticle diffusion rate constant, mg/g min^{1/2}; k_1 , Lagergren's pseudo first-order rate constant, min⁻¹; k_2 , pseudo second-order rate constant, g/mg min; k_F , fractional power kinetic model constant, mg/g; K_F , Freundlich isotherm parameter, (mg/g).(mg/L) ^{n} ; K_L , Langmuir isotherm parameter, L/mg; m , mass of adsorbent, g; n , heterogeneity factor; N , exponent of fractional power kinetic model; q_e , amount of heavy metals adsorbed at equilibrium, mg/g; q_{max} , maximum monolayer coverage capacities, mg/g; q_t , amount of heavy metals adsorbed at time t , mg/g; R , universal gas constant, J/mol K; R^2 , coefficient of correlation; t , adsorption time, min; T , adsorption temperature, K; V , volume of aqueous solution in contact with the adsorbent, α , rate of adsorption at zero coverage, mg/g min; β , extent of surface coverage, g/mg; ρ_b , bulk density of adsorbent, g/mL; Φ_1 , Temkin constant related to the heat

of sorption, J/mol; ω , agitation speed, rpm.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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