JBAAR
Journal of Basic And Applied Research
ISSN 2413-7014

Kinetic Potentials of the Effect of Ethanol on Calcium Content of Ashed Palm Bunch (*Elaeis guinensis*)

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Received: 20-4-2016
Revised: 19-5-2016
Published: 22-5-2016

Keywords:
Kinetics,
Oil Palm bunch,
Elaeis guinensis,
Calcium,
Ethanol

Abstract: The effect of ethanol on the calcium content of ashed palm bunch (*Elaeis guineensis*) was studied. The palm bunch residue was subjected to pre-treatment processes such as drying, grinding and ashing. The calcium content of the filtered extract of the ash was determined titrimetrically and a concentration of 73.33 mg/l of calcium was recorded. Kinetic studies were carried out on the mixture of local ethanol and the ash extract and the effect of ethanol on calcium concentration was monitored using titrimetric method at 10 minutes interval. The ethanol led to a gradual decrease in the concentration of calcium with increase in time, the rate constant value was 0.67 mgdm^{3}min^{-1} and half life of 54.97 minutes. Analysis of the kinetic data showed that the reaction was zeroth order as it fitted into the zeroth order integrated rate law. The average pH of the reaction mixture was alkaline (10.57)

1. INTRODUCTION

1.1. The Oil Palm (*Elaeis guinensis*)

The oil palm (*Elaeis guinensis*) is a major source of edible oil which is extracted from its fruits (Etukudo *et al.,* 2014). It is a tropical plant that is widely grown and is a valuable economic crop in Nigeria. The oil palm empty fruit bunch is a lignocellulose source which belongs to the famiily *Palmae*, a distinct group of the monocotyledons (Akpakpan *et al.,* 2012) and is available as a substrate in cellulose production (Rajoka and Malik, 1997). The Plant ash is a powdery residue that remains after the plants are burned. Chemically, the ash is alkaline (pH > 10) and composed primarily of calcium carbonate, and secondarily, most often, of potassium chloride. Palm ash is reportedly a desirable component in artisanal soap making. Palm ash has established ritual roles in Jewish and Christian ceremonies (Jewish encyclopedia, 2002; Catholic Encyclopedia, 1996-2010). African oil palm (*Elaeis guineensis*) is the most industrialized palm in the world, with extensive areas under plantation cultivation. The empty fruit bunch ash is used often as an organic fertilizer. The ash contains a high percentage of potassium which is one of the minerals required for plant growth. A mixture of the ash with decanter cake (which contains a high amount of nitrogen) has been used as a palm-based bio-fertilizer (Haron *et al*., 2008). Oil palm ash has also been used as a partial substitution in Portland cement (Tangchirapat *et al.,* 2009). It was noted that the compressive strength of concrete containing oil palm ash increased after 28 days and exhibited a higher value than that of ordinary Portland cement. This was attributed to the additional Calcium silicate hydrate bond formed between the silica in oil palm ash and $Ca(OH)_2$ contained in cement, enhancing the interfacial bonding between the aggregates and pastes. Oil palm ash has also been used as an absorbent for sulfur dioxide (Mohamed *et al.,* 2005). A study by Zainudin *et al.,* (2005) revealed that oil palm ash slurry mixed with calcium oxide and calcium sulphate demonstrated 100% removal of sulphur dioxide. It has also been used as an adsorbent material for removing colour dyes such as disperse blue, disperse red, and acid green-25 dye from aqueous solution (Hameed *et al.*, 2007; Isa *et al.*, 2007). The filtrate obtained from the mixture of oil palm bunch ash and water is known to emulsify oil. The filtrate is used in Annang of Akwa Ibom State in preparing a local delicacy known as “Otong” which is used in eating meat, drinking palm wine, and can be used to spice soup (Udoetok, 2012).

Chemical analysis of the ash made from oil palm empty fruit bunch revealed that it contains metals such as chromium, zinc, calcium, potassium, sodium and magnesium with the following concentrations: 0.088 mg/kg, 0.38 mg/kg, 146.15 mg/kg, 139.35 mg/kg, 0.63 mg/kg and 1.68 mg/kg, respectively. It also contained anions such as phosphate, nitrate, sulphate and chloride (Israel and Akpan, 2007).

1.2. USEFULNESS OF CALCIUM IN THE BODY

Calcium is known to be most abundant element in the body and accounts for about 2% of body weight, which is equivalent to 1200g of calcium

(Ilich and Kerstetter, 2000). It is an essential nutrient, not only for mineralization of bones and teeth but for regulating intracellular events in most, if not all body tissues. The majority (99%) of calcium is found in the skeleton and teeth, mainly as hydroxyapatite, an inorganic crystalline structure made up of calcium and phosphorus [$Ca_{10}(PO_4)_6(OH)$], which provides rigidity. The remainder is present in soft tissues and body fluids, and account for less than 1% of total body calcium. The roles calcium plays in the body include: strengthening bones and teeth, regulating muscle functioning such as contraction and relaxation, regulating heart functioning, blood clotting, transmission of nervous system messaging and enzyme function.

1.3. DEFICIENCY OF CALCIUM AND EFFECTS

Since calcium is an essential for bones, the deficiency of calcium affects the bones the most severely. Some of the symptoms of calcium deficiency include: muscle cramps which is the initial alarm towards the decrease of calcium in the body; muscle ache, especially those of the thighs, arms, and underarms while moving or walking around; insomnia, tooth decay, poor bone density which is a serious condition for children as it may lead to easy fracture, vascular aches, spasms, and in extreme cases rickets; late sign of puberty in adolescent females and weak/brittle nails.

1.4. EFFECT OF ALCOHOL IN THE BODY

The effect of alcohol on human capacities is attracting much attention, especially in its relation to motoring. Alcohol tends to impair skill and cloud judgment, though the extent of these effects depends on the individual and his alcoholic tolerance. Large quantities of alcohol in the system lead to lack of muscular control like the drunken stagger, and ultimately to coma, the state of dead-drunk. A sufficiently large alcoholic consumption taken over a long period causes liver deterioration and accelerates death.

In terms of metabolism, ethanol within the body is converted into acetaldehyde by alcohol dehydrogenase and then acetic acid by acetaldehyde dehydrogenase. The product of the first step of conversion, acetaldehyde, in the human body is more toxic than ethanol (Bill, 2001). Acetaldehyde is linked to most clinical effects of alcohol. It has been shown to increase the risk of developing cirrhosis of the liver, multiple forms of cancer and alcoholism. Ethanol can interact with drugs by intensifying the sedation caused by other central nervous system depressant drug such as barbiturates, benzodiazepines, opium, and phenothiazine (David and Yost, 2002). Also, frequent drinking of alcoholic beverages has been shown to be a major contributing factor in cases of elevated blood levels of triglycerides. Ethanol is not a carcinogenic. However, the first metabolic product of ethanol, acetaldehyde, is toxic, mutagenic, and carcinogenic.

The aim of this work is to determine the amount of calcium in ashed empty palm bunch and to determine the kinetic potentials of the effect of ethanol on calcium content of ashed palm bunch.

2. MATERIALS AND METHOD

2.1. Sample Collection

The empty palm bunch wastes were obtained from a local oil palm mill in Nung Udoe Itak in Ikono Local Government Area of Akwa Ibom State, Nigeria.

The palm bunches were chopped into pieces, sundried for two weeks to ensure adequate removal of moisture from the sample and was ground into powder. The powdered sample was ashed in a crucible in a temperature controlled furnace for 6 hours at 450^0C

2.2. EXTRACTION OF CALCIUM FROM THE ASHED PALM BUNCH

The ashed empty palm bunch (40g) was leached with 200 cm^3 of distilled water, shaken thoroughly and was made up to 1000 cm^3 solution. The leached sample was allowed to stand for 24 hours to ensure equilibrium leaching. The leached suspension was then filtered using Whatman filter paper of 125 cm to obtain a clear extract. The filtrate was labeled and kept for titrimetric analysis.

2.3. DETERMINATION OF CALCIUM PRESENT IN THE ASHED PALM BUNCH EXTRACT

The concentration of calcium content of ashed empty palm bunch was determined using titrimetic method of analysis. The filtered palm bunch extract (10 ml) was measured into a 500 ml conical flask and 2 ml of Ammonia buffer solution and a tablet for total hardness was added to the extract and a purple solution was obtained as blank. The mixture was titrated against 0.02N of ethylenediamine tetraacetic acid (EDTA) to give a blue colour end point. Also, 10 ml of the mixture of the extract and 1 molar ethanol was measured into a 500 ml conical flask, ammonia buffer solution and a tablet for hardness was also added. The mixture was titrated against 0.02N EDTA to give a blue colour end point.

Table 2.1: kinetic data for the reaction of ethanol with ashed palm bunch extract

Time (mins)	0	10	20	30	40	50	60	70	80	90
pH	10.73	10.52	10.55	10.57	10.58	10.55	10.55	10.55	10.55	10.55
[Ca^{2+}] (mg/l)	73.33	66.67	60.00	53.33	46.65	40.00	33.32	26.64	20.00	13.33

The Average titre at every 10 minutes interval was calculated and then divided by the volume of the sample to get total hardness which is made up of calcium and magnesium ions using the following equation.

$$\text{Total hardness} = \frac{V_2 \times 10^3}{V_1} \qquad 2.1$$

where V_2 = Average titre, V_1 = volume of palm bunch extract with ethanol

Since calcium is two-third of total hardness, concentration of calcium in the ashed palm bunch was obtained by concentration of

$$[Ca^{2+}] = \frac{2}{3} \times \text{ total hardness} \qquad 2.2$$

2.4. KINETIC MEASUREMENT OF THE EFFECT OF ETHANOL ON THE CONCENTRATION OF CALCIUM IN ASHED EMPTY PALM BUNCH EXTRACT

The percentage purity of the local ethanol was obtained to be 30 percent. Based on the percentage purity and relative density of ethanol (789 kg/m^3), the required volume of local ethanol which contained one mole was determined. Here, 194cm^3 of ethanol was measured and diluted to 1000 cm^3 of solution. This dilution gave a 1M solution of local ethanol in solution. Equal volumes (200 cm^3) of the palm bunch extract and ethanol solution were reacted in a 500 cm^3 beaker and a stop watch started simultaneously. At every 10 minutes interval, the reaction mixture was bled out using injection syringe and the concentration of calcium remaining in the mixture was determined using titrimetric method. The pH of the reaction mixture was also taken at every 10min interval.

3. RESULTS AND DISCUSSION

Table 2.1 and figure 3.1 records the effect of ethanol on the concentration of calcium extract. The table reveals a steady decrease in the concentration of calcium in the calcium extract with increasing time.

3.1. EFFECT OF ETHANOL ON THE CONCENTRATION OF CALCIUM IN THE PALM BUNCH EXTRACT

Table 2.1 and fig. 3.1 records the effect of ethanol on the concentration of calcium in the palm bunch extract. The table reveals a decrease in the concentration of calcium in the extract with increasing time interval. This shows that ethanol actually reduces or destroys the quantity of calcium present in a bio-system and thereby weakens the strength of the biological system.

It was observed that the original calcium content in the ashed empty palm bunch extract was 73.33 mg/l. after 10 minutes of the reaction of local ethanol with the calcium extract, tha calcium content reduced to 66.67 mg/l. at 30 minutes interval, the concentration of calcium was found to reduce to 53.33 mg/l. the decrease in calcium content continued gradually with increasing time as the ethanol persisted in the solution. At an interval of one hour (60 minutes), the original calcium content (73.33 mg/l) had reduced to 33.32 mg/l. at the end of 90 minutes of the measurement period, the calcium content left in the reaction mixture was 13.33 mg/l.

It is suggested that the gradual decrease in calcium content could lead to a weakening of the body structure. The trend could lead to the estimation of half life of the calcium content and the estimation of the full life which shows the time of complete depletion of the calcium content as a result of the intake of an estimated amount of alcohol.

The various rates of reaction obtained at each time interval for the reaction of ethanol and calcium content of the ashed palm bunch extract is shown in table 3.1. The values obtained showed that the rate of reaction was steady as the reaction progressed with the average rate constant obtained to be 0.66 $mgl^{-1}min^{-1}$.

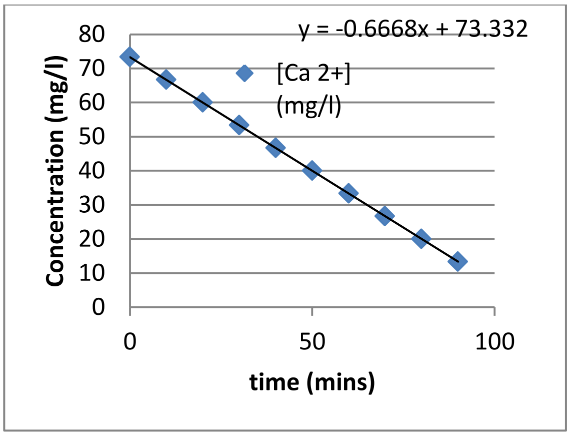

Fig. 3.1: A plot of concentration versus time for the reaction of ashed oil palm bunch with ethanol

. **Table 3.1: Rate of reaction and concentration of calcium with ethanol**

Time (mins)	0	10	20	30	40	50	60	70	80	90
Log $\frac{a_0}{a_0 - x}$	-	0.041	0.09	0.14	0.196	0.26	0.34	0.44	0.56	0.74
Log C	-	1.82	1.78	1.73	1.67	1.60	1.52	1.43	1.30	1.12
Log R	-	-0.18	-0.18	-0.18	-0.18	-0.18	-0.18	-0.18	-0.18	-0.18

3.2. ORDER OF THE REACTION

The order of the reaction was obtained through half life method by appropriate substitution from the integrated rate law. Generally, half life ($t_{1/2}$) is inversely proportional to the initial concentration raised to the order of the reaction n, minus one, where the proportionality constant may vary depending on the type of order. The half life obtained was directly proportional to the initial concentration, signifying that the reaction is of zeroth order. Also, a plot of log R versus log C produced a straight line parallel to the horizontal axis, where the slope for horizontal lines is zero. The value of zero for the slope represents the order of the reaction.

For zeroth order, $t_{1/2} = \frac{a_0}{2k}$ 3.1

By appropriate substitution, the half life $t_{1/2}$ for the zeroth order reaction was 54.97 minutes. This value shows that if the original calcium, concentration in the body was 73.33 mg/l, by consuming 200cm^3 of 1M local ethanol, it will take 54.97 minutes for the original calcium concentration to reduce to half the concentration. The full life of the calcium concentration shows that at 109.94 minutes after consumption of the alcohol, the original concentration of the calcium in the blood would have been depleted by the alcohol leading to exhaustion as experienced by most alcohol addicts.

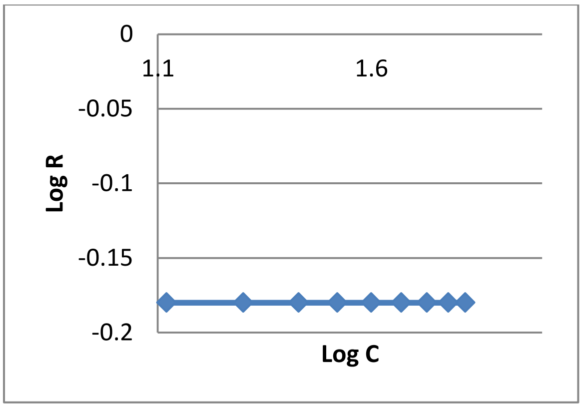

Figure 3.2: A plot of Log R against Log C for the kinetics of the reaction of ashed empty palm bunch extract with ethanol

3.3. RATE CONSTANT OF THE REACTION

The concentration-time data obtained from the titrimetric measurement was subjected to various integrated rate laws. The data substitution fitted properly into the zeroth order kinetic model which produced a constant value for the rate constant according to the equation

$$k = \frac{a_0 - (a_0 - x)}{t} \quad 3.2$$

The average rate constant obtained for the hydrolysis of the calcium extract was 0.667 mgdm^{-3}min^{-1}. The value confirmed that the rate of the reaction of the alcohol molecules with calcium is moderately fast and portends danger at high rate of consumption.

3.4. THE pH OF THE REACTION MIXTURE

Ethanol's hydroxyl group, -OH is like the hydroxyl group of water (Morrison and Boyd, 1972). Like water, it causes the molecules to be slightly basic. It is almost neutral like water. The pH of 100 percent ethanol is 7.33, compared to 7.00 of water. The pH of the ashed empty palm bunch extract was 10.73 being alkaline. With the addition of ethanol, the hydroxyl group causes the mixture to be slightly less basic. The average pH was obtained as 10.57 and was almost constant throughout the time interval of the measurement (90 minutes). Literature reveals that ethanol is a neutral molecule and the pH of a solution of ethanol in water is nearly 7.00, hence, the measured value of the pH of the mixture not being close to neutral is far from expectation.

It is suggested that the calcium ions (Ca^{2+}) present in the palm bunch extract is being precipitated out by the ethanol to produce calcium hydroxide, hence, the alkaline solution of pH 10.57.

$Ca^{2+} + 2C_2H_5OH \rightarrow Ca(OH)_2 + 2C_2H5$ - 3.3

The ethene vapour generated also weaken the cells of the biological system

4. SUMMARY AND CONCLUSION

The kinetic test confirmed that the reaction of local ethanol with calcium extract obtained from ashed empty palm bunch follows a zeroth order reaction. The ashed palm bunch extract was found to the rich in calcium content up to 73.33mg/l, with the original calcium content decreasing with increasing time on addition of local ethanol. The interaction of the local ethanol with the ashed palm bunch extract revealed a half life of 54.97 minutes. The reaction progressed under alkaline condition with a pH of 10.57 and the reaction progressed moderately with average rate of reaction of 0.67 mgl^{-1}min^{-1}. This study has confirmed the deleterious effect of alcohol on the calcium content which relates to human capacities as it is attracting much contemporary attention, especially in its relation to motoring. By destroying the calcium content of the body, the study has offered some clues as to the reason why alcohol tends to impair skill and cloud judgment, though the extent of the effects depends on the individual and his alcoholic tolerance. This study has revealed how quantities of alcohol may probably lead to lack of muscular control of muscular control as noticed when the drunk stagger, or reach ultimate coma or dead drunk. The hale life/full life measurements have shown that excessive consumption of alcohol could sap the body nutrients to lethal level which may cause many to die prematurely. The study has further revealed that alcohol has depleting effect on the calcium content of the organs of the mammalian body. It reduces the level of concentration of calcium with increase in time as it persists in the body. The study also reveals that the order of reaction of alcohol with the concentration of metal depends on the pH of the body. At near neutral pH, the reaction follows a second order kinetic. In basic medium, the study reveals that first or zeroth order kinetics may be favoured.

ACKNOWLEDGEMENT

The authors wish to thank Emem Martina Joseph, a final year undergraduate student of the department of chemistry, University of Uyo for her painstaking effort to collect and screen the palm bunch ready for ashing. We are also grateful to Gerald Inoh, the Director of Science in Akwa Ibom State Ministry of Science and Technology and his team of laboratory staff for the spectrophotometric and titrimetric analysis.

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