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RESEARCH ARTICLE

KINETIC MODELLING OF VITAMIN C (ASCORBIC ACID) DEGRADATION IN TOMATO AND PAWPAW UNDER MARKET STORAGE CONDITIONS

*Nwakaudu, M. S., Nkwocha, A. C., Madu, I. K., Enwereji, C. B and Ireaja, I. E.

Department of Chemical Engineering, Federal University of Technology, P.M.B 1526, Owerri, Nigeria

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ABSTRACT

Vitamin C (ascorbic acid) is one of the most important and popular vitamins, and is contained in most fruits and vegetables; the problem with vitamin C is its easy degradation during storage. In this study, the degradation kinetics of vitamin C was determined in tomato and pawpaw, and the market storage methods considered were: open air (ambient) storage and sack (jute bag) storage for six days. Iodometric method of analysis was employed in analyzing the concentration of vitamin C in fruit samples. The vitamin C content of the fruit samples during storage were determined daily for the duration of 6days. The rate constants were calculated for both fruits under the two storage methods using the integrated law method; half-life was also calculated. Loss of ascorbic acid in tomato and pawpaw under the two storage conditions followed the first-order kinetic model, as the coefficient of determination (R^2-value) was greater than 0.95. The rate constant of ascorbic acid degradation for pawpaw stored in open air and jute bags were 0.1909day^{-1} and 0.1963day^{-1} respectively; while the rate constant for tomato stored in open air and jute bags were 0.1331day^{-1} and 0.1969day^{-1} respectively. The half-life of both fruits ranged from 3 – 6days. The most appropriate method of storage is open air because the rate constants depicted from the model equations were lower, and the half life longer, hence, slower rate of degradation.

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INTRODUCTION

Cultivated papaya, *Carica papaya*, popularly known as pawpaw, is a fast-growing tree-like herbaceous plant in the family Caricaceae, and is available throughout the year. It is a rich source of three powerful antioxidants - vitamin C, vitamin E, and vitamin A, as well as magnesium, potassium, folate and fibre. The extracts of unripe *C. papaya* contain terpenoids, alkaloids, flavonoids, carbohydrates, glycosides, saponins, and steroids (Aravind *et al.,* 2013). Leaves, fruits and bark of this tree are traditionally employed in several regions as foodstuffs and for medicinal purposes. Tomato (*Solanum lycopersicum*) is a short-lived perennial plant, grown as an annual plant, in the Solanaceae or nightshade family. Though, it is botanically a berry, a subset of fruit, tomato is nutritionally classified as vegetable. The fruit is an edible, brightly coloured (usually red, from the pigment lycopene) berry that has both nutritional and medicinal values. It contains a wide array of beneficial nutrients and antioxidants, and is a rich source of vitamins A and C, folic acid, alpha-lipoic acid, lycopene, choline, beta-carotene and lutein (Nichols, 2014).

Corresponding author: Nwakaudu, M. S.
Department of Chemical Engineering, Federal University of Technology, P.M.B 1526, Owerri, Nigeria.

Vitamin C (ascorbic acid, AA) is an important component of our nutrition. It prevents scurvy and protects the body from oxidative stress which might lead to cancer, inflammation, cardiovascular diseases, asthma and arteriosclerosis (Maria, 2007; Vasanth *et al.,* 2013). Plants can make it themselves as can some animals, but humans do not have the right enzyme (gulonolactone oxidase) to synthesize this vitamin, hence, ascorbic acid has to be supplemented mainly through fruits and vegetables. Ascorbic acid is known to be a vitamin sensitive to a number of factors, including pH, moisture content, light, oxygen and temperature (Lee and Coates, 1999). Its degradation proceeds in both aerobic and anaerobic pathways (Johnson *et al*., 1995), and depends upon many factors such as oxygen, light, heat, storage temperature and storage time (Fellers, 1988). Oxidation of ascorbic acid occurs mainly during the processing of juices, whereas, anaerobic degradation mainly appears during storage (Abioye *et al*., 2013).

The nutrient quality of food during storage has become increasingly important. The loss of some nutrients such as vitamin C during storage might be a critical factor for the shelf life of some products such as juice concentrate, since vitamin C content of fruits undergo destruction during storage (Burdurlu *et al*., 2006). Therefore, a deep knowledge of vitamin C degradation such as the kinetic order, and rate constants are the basic requirements to define the shell life of fruit juice (Derossi *et al*., 2010), and related products. Numerous analytical techniques are available for the determination of the vitamin C content in various fruits and vegetables, amongst them are Iodometric titration, chromatographic methods, enzymatic methods, and electrochemical methods (Abraha *et al*., 2014; Gunjun and Mangla, 2012; Iwase, 2000; Vermeir *et al*., 2008). Kinetics can be defined as the rate at which reaction occurs. Changes occur at certain reaction rates. Kinetic modelling enables to describe these changes and their rates quantitatively.

Kinetic modelling also enables us understand the basic reaction mechanisms vital for quality modelling and control. The degradation kinetics of ascorbic acid in model systems conform to first order kinetics, however, in food systems the kinetics is somehow complex (Liao and Seib, 1988). The complexity of the degradation mechanisms hinders the development of mechanistic models, and pseudo-kinetic model such as zero order, first-order or second-order kinetics are often applied in order to obtain a good fit to the experimental data. The model that gives the highest coefficient of determination value (R^2 value) is regarded as the best fit for the analysis. The objectives of this study were (i) to determine the rate of degradation of vitamin C in pawpaw and tomato under the market storage methods prevalent in Nigeria – ambient storage in open air and sack storage, so as to recommend the best; (ii) to develop kinetic models for predicting vitamin C degradation in pawpaw and tomato under the studied conditions.

MATERIALS AND METHODS

Sample preparation

Pawpaw and tomato were sourced ripe and fresh from a relief market in Owerri, Nigeria. Each fruit sample was divided into two groups and stored using the two market storage methods common in Nigeria. The first group of the fruit samples were stored in jute bags and isolated, while the second group were put in trays and exposed to air and ambient temperature. Both groups were stored for a period of 6 days. Samples were withdrawn on daily basis (that is, every 24hrs) for analysis.

Preparation of standard solution

Starch solution was prepared by dissolving 0.5g soluble starch in 50ml near boiling distilled water, while vitamin C solution was prepared by dissolving 0.25g of standard vitamin C in 100ml of distilled water, and the solution was diluted to 250ml with distilled water. 5g of potassium iodide (KI) and 0.268g of potassium iodate (KIO_3) were dissolved in 200ml of distilled water, and 300ml of 3M sulphuric acid (H_2SO_4) was added to obtain standard iodine solution.

Preparation of Fruit juice extracts

The fruit juice from the pawpaw and tomato samples were prepared by cutting 100g of the fruit samples into small pieces and blending with 50ml of distilled water. The pulp was strained using a filter cloth and the residue rinsed with 10ml of distilled water. The washings were collected and added to the filtrate. Distilled water was added to make up the final extract volume to 100ml. Ascorbic acid is susceptible to oxidation by atmospheric oxygen over time; for this reason, the fruit juice samples prepared were analyzed immediately.

Sample analysis

The iodine solution was titrated with 25mi of the standard vitamin C solution, and then with 25mi of prepared fruit juice samples using starch indicator. Triplicate samples were analyzed and the average titre used for calculation.

a) Calculation of the mass of vitamin C present in fruit sample- The mass of vitamin C contained in each of the samples was calculated from this relationship:

$$\frac{\text{volume of iodine solution required to react with standard vitamin C sample}}{\text{mass of standard vitamin C used}} = \frac{\text{volume of iodine solution required to react with vitamin C in fruit sample}}{\text{mass of vitamin C in fruit sample}}$$

b) Calculation of the Concentration of vitamin C present in fruit sample

$$\text{Concentration of vitamin C} = \frac{\text{mass of vitamin C in fruit sample}}{\text{volume of fruit juice sample used}}$$

Kinetic modeling

The degradation of vitamin C was modelled using the integrated rate law. Different models were developed using the integral method of analysis. The integral law equation stated below;

$$\frac{dC}{dt} = -k[C]^n \qquad \text{......................(1)}$$

was used to develop three models based on concentration (for order of reaction n = 0, 1 and 2) and their associated half lives ($t_{1/2}$).

Zero order model (n = 0):

$$C = C_0 - kt \qquad \text{...................(2a)}$$

$$t_{1/2} = {C_0}/{2k} \qquad \text{...................(2b)}$$

First order model (n = 1):

$$\ln(C) = \ln(C_0) - kt \qquad \text{....................(3a)}$$

$$t_{1/2} = {\ln(2)}/{k} \qquad \text{....................(3b)}$$

Second order model (n = 2):

$$\frac{1}{C} = \frac{1}{C_0} + kt \qquad \text{...................(4a)}$$

$$t_{1/2} = {1}/{kC_0} \qquad \text{...................(4b)}$$

where, k = rate constant

C_0 = initial concentration of vitamin C in sample
C = concentration of vitamin C in sample at time t
$t_{1/2}$ = half-life of vitamin C in sample

Concentration or a function of concentration was plotted against time for each model and regression analysis was used to determine the 'Goodness of fit' employing Matlab software (Version 8.2, Mathworks Inc., USA). Goodness of fit is characterized by coefficient of determination (R^2), sum of squared errors (SSE), and root mean sum of errors (RMSE). The model with maximum R^2 and minimum RMSE is adjudged the best (Silva *et al*., 2011; Mitra *et al*., 2011).

RESULTS AND DISCUSSION

The variations in vitamin C concentration of fruit samples during storage is presented in Tables 1 and 2, Tables 3 and 4 summarize the results of kinetic model regression analysis, while Table 5 compares vitamin C first order kinetics degradation parameters for the samples under different storage methods. As can be observed in Table 1 the concentration of vitamin C decreased steadily with time during storage in all the samples. This confirms the fact that vitamin C in fruits degrades during storage.

Table 1. Vitamin C concentration in pawpaw during storage

Time (day)	Concentration (g/l)	
	Open air	Sack
1	1.78	2.01
2	1.44	1.63
3	1.17	1.33
4	0.98	1.10
5	0.83	0.98
6	0.68	0.72

Table 2. Vitamin C concentration in tomato during storage

Time (day)	Concentration (g/l)	
	Open air	Sack
1	1.68	1.40
2	1.52	1.29
3	1.33	1.02
4	1.10	0.76
5	0.98	0.64
6	0.87	0.57

Table 3. Results of kinetic model statistical analysis for pawpaw

Storage Method	Kinetic order (n)	R^2	Adjusted R^2	SSE	RMSE
Open air	0	0.9692	0.9615	0.002567	0.08011
Sack	0	0.9738	0.9657	0.02857	0.08455
Open air	1	0.9983	0.9974	0.001070	0.01635
Sack	1	0.9896	0.9870	0.007109	0.041216
Open air	2	0.9857	0.9821	0.008114	0.04504
Sack	2	0.9495	0.9369	0.025910	0.08044

Table 4. Results of kinetic model statistical analysis for tomato

Storage Method	Kinetic order (n)	R^2	Adjusted R^2	SSE	RMSE
Open air	0	0.9856	0.9820	0.00665	0.04077
Sack	0	0.9638	0.9548	0.02168	0.07362
Open air	1	0.9880	0.9850	0.00377	0.03073
Sack	1	0.9791	0.9738	0.01451	0.06023
Open air	2	0.9804	0.9755	0.00443	0.03330
Sack	2	0.9751	0.9689	0.02267	0.07528

Table 5. Comparison of first order kinetic parameters and proposed model

Fruit samples (Storage method)	Rate constant k (day^{-1})	Half life $t_{1/2}$	Proposed model
Pawpaw			
Open air	0.1909	3days 15hrs	$\ln(C) = \ln(C_0) - 0.1909t$
Sack	0.1963	3days 12hrs	$\ln(C) = \ln(C_0) - 0.1963t$
Tomato			
Open air	0.1331	5days 5hrs	$\ln(C) = \ln(C_0) - 0.1331t$
Sack	0.1969	3days 12hrs	$\ln(C) = \ln(C_0) - 0.1969t$

This confirms the fact that vitamin C in fruits degrades during storage. The vitamin C concentration of the fruit samples with respect to time decreased during storage, but in different degrees, depending on the method of storage. This is in agreement with the report of earlier workers on citrus and strawberry fruit juices (Burdurlu *et al*., 2006; Derossi *et al.*, 2010) and in accordance with the degradation kinetics of ascorbic acid in model systems as put forth by Liao and Seib (1988).

Besides, in a recent investigation by Dereje and Girma (2015), the ascorbic acid content in a given mass of pawpaw was found to be greater than that in an equal mass of tomato. This is confirmed by this study; as the concentration of vitamin C in pawpaw is greater than that in tomato for the same mass of sample.

A visual inspection of the kinetic plots of models (2a),(3a) and (4a) presented in Figures 1-3 for pawpaw, and in Figures 4-6 for tomato, shows that the first order model fitted the kinetic data best in all fruit samples. This is confirmed by the goodness of fit data in Tables 3 and 4. The first order kinetics exhibited R^2 values; 0.9983, 0.9896 and RMSE values; 0.01635, 0.041216 for pawpaw under open air and sack storage respectively, R^2 values; 0.9880, 0.9791 and RMSE values; 0.03073, 0.06023, for open air and sack respectively for tomato. These R^2 values were the highest and RMSE values the lowest. Thus, the vitamin C degradation kinetics in pawpaw and tomato can be best described by a first order kinetics. This implies that the rate of degradation at any time is dependent on the initial concentration of vitamin C in the fruit. Furthermore, the rate constant of fruit samples stored in sacks were higher than those kept in open air.

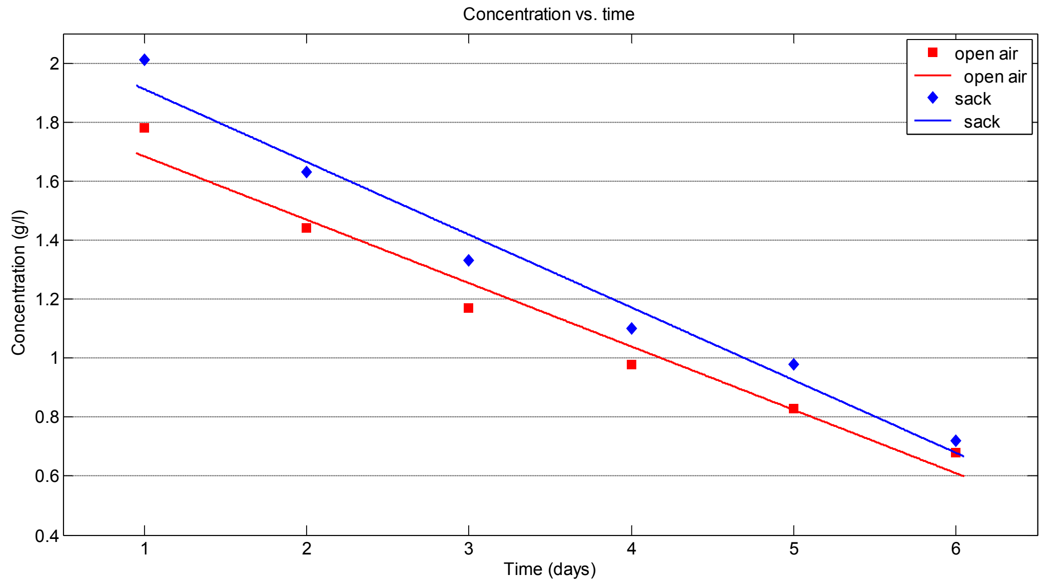

Figure 1. A plot of zero order kinetics for pawpaw (concentration vs. time)

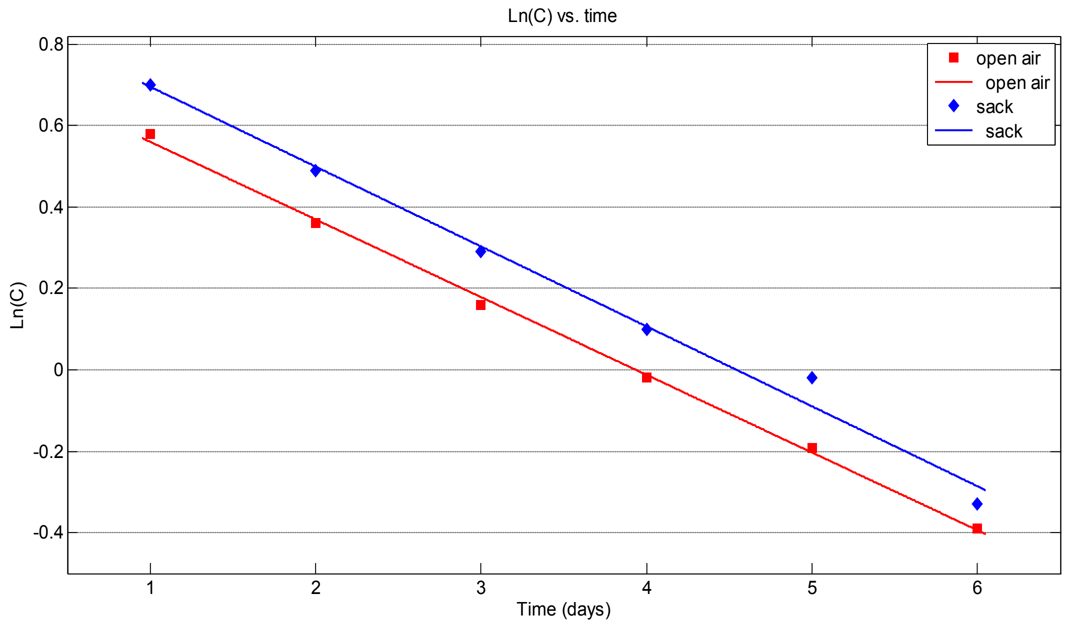

Figure 2. A plot of first order kinetics for pawpaw (Ln C vs. time) C = concentration

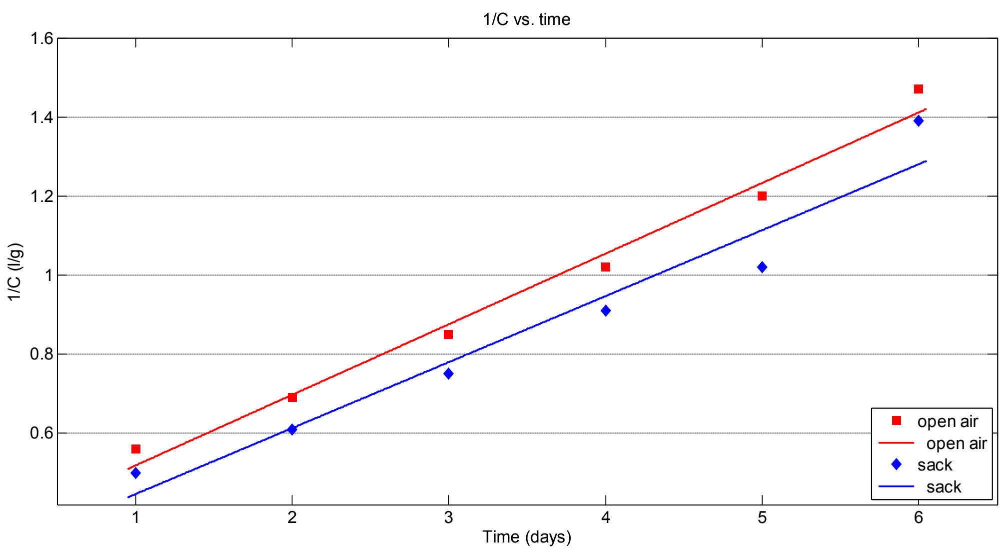

Figure 3. A plot of second order kinetics for pawpaw (1/C vs. time)

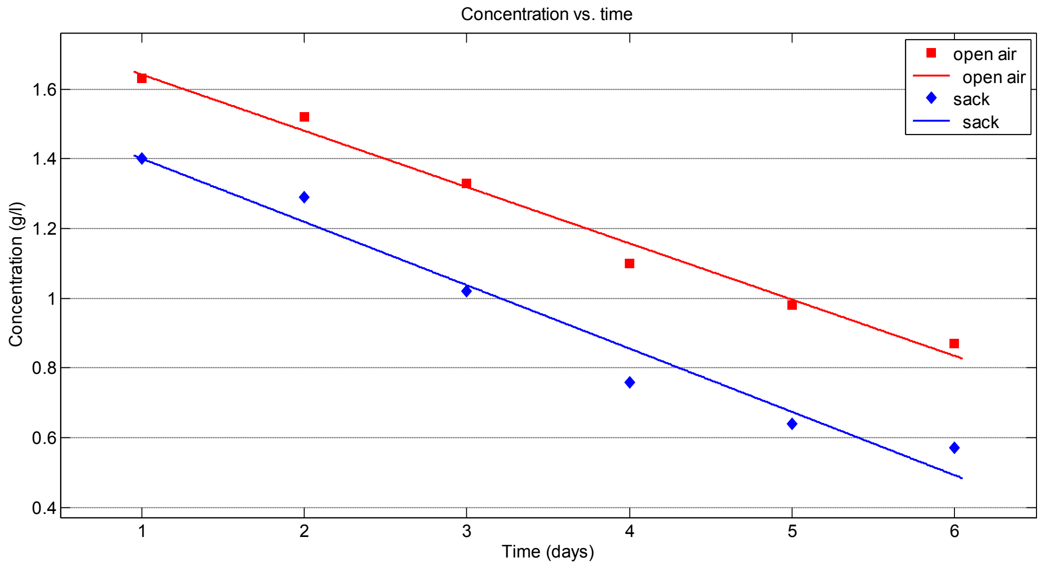

Figure 4. A plot of zero order kinetics for tomato (concentration vs. time)

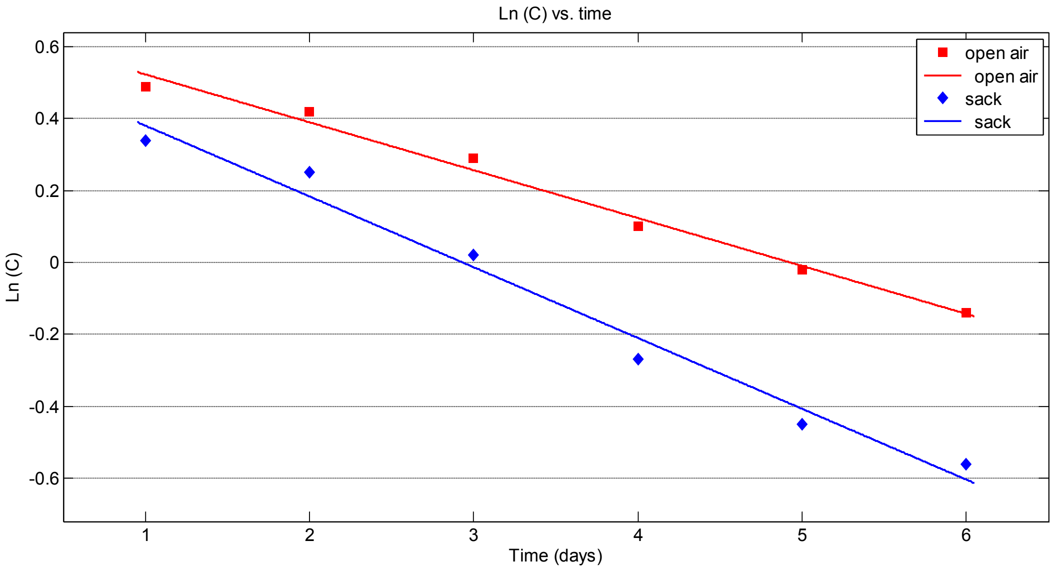

Figure 5. A plot of first order kinetics for tomato (Ln C vs. time)

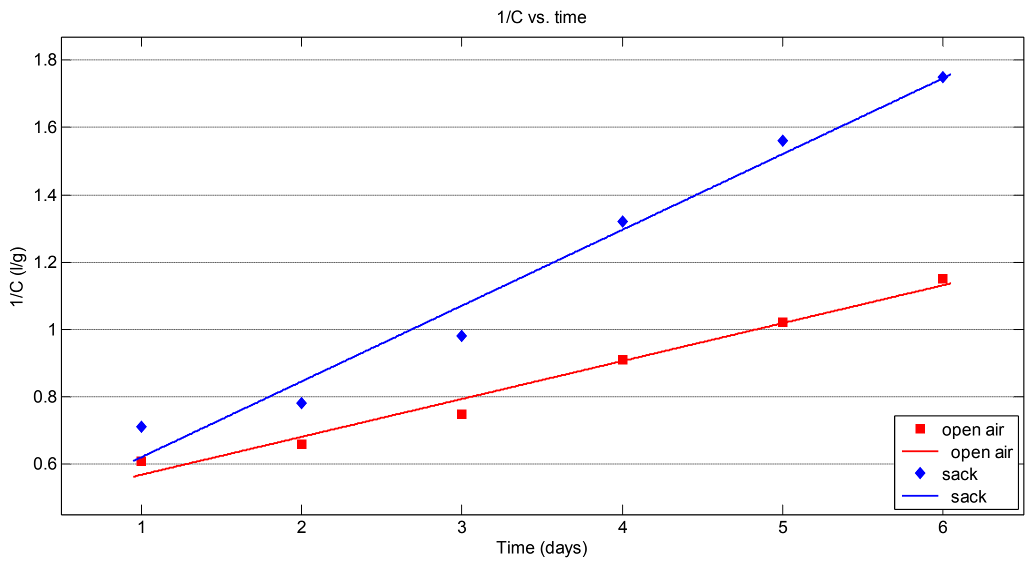

Figure 6. A plot of second order kinetics for tomato (1/C vs. time)

Tomato and pawpaw samples stored in sacks exhibited rate constants of 0.1969 and 0.1963day^{-1} respectively, which were the highest. Since the magnitude of the rate constant is a reflection of the rate of reaction, the inference is that degradation of vitamin C occurred faster in samples stored in sacks than in those exposed to the air. This trend manifested in the half life of the samples which gives further credence to this fact. The time at which the concentration of vitamin C in the samples reduces to half of its original amount (half life) was shorter in sack stored samples than in the exposed samples. This implies that the exposed samples will be expected to have longer shelf life than the sacked ones. Open air stored tomato samples recorded the longest half life of 5days 5hrs, while sacked tomato and pawpaw had the shortest half life of 3days 12hrs.

Conclusion

The rate of vitamin C degradation in the pawpaw and tomato samples under the two storage methods investigated in this study followed a first order reaction kinetics. This indicates that the rate of degradation is dependent on the concentration of the vitamin C present in both fruits. In addition, the storage of the fruits in sacks (jute bags) resulted in faster rate of degradation of vitamin C than in open air. This impresses the fact that the open air storage of fruits and vegetables is more preferable in terms of vitamin C retention than sack storage, hence, is recommend for the storage of fruits and vegetables in Nigeria local markets, especially in situations where cold storage facilities are not available.

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