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Analysis of inhibition of cassava wastewater degradation by cyanide

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Abstract

This research aimed at analyzing the inhibition of cassava wastewater degradation by cyanide. The investigation was carried out in the sanitary engineering laboratory using six different buckets containing samples of cassava wastewater. The present of cyanide content inhibits the degradation of cassava wastewater drastically. Sodium hydroxide was used as an oxidizer to reduce the cyanide content in the waste. Monod kinetic constants and the inhibition constant KI were determined using the Line Weaver Burk equation and statistical regression analysis. The results from the analytical experiments show the different forms of inhibition involved at the different grams of the sodium hydroxide added and its inhibition constant. The results obtained for the inhibition constant were given as 591.954mg/l, 398.980mg/l, 358.554mg/l, and 259.254mg/l respectively for the competitive inhibition, non-competitive and mixed inhibition (competitive non-competitive inhibition). The results from this research will be useful in the design of treatment plants.

Keywords: Cyanide; cassava wastewater; fermentation; inhibition; degradation

1. Introduction

Cassava is a source of carbohydrate and is the main carbohydrate source in the diet of the teeming population of the third world countries where it is largely grown. Banjoko et al, (2008) posited that cassava is a supplementary staple food of more than 200 million Africans aside from its uses as livestock feed particularly for monogastrics. Cassava is the most widely distributed major food crop with a high content of cyanogenic glycosides. It is also known as Manioc (manihot esculentz), yuca tapioca, or guacamate. Other foods such as sweet potatoes, yams, maize, millet, bamboo sugarcane, peas and beans, as well as kernel of almond, lemon, lime, apple, pear, cheery, apricot, prune and plum (Fiksel et al, 1981) contains cyanide. Cassava as an important root crop in the tropics, widely grown throughout the tropical Africa, Asia, and South America contains 1mg/g of cyanide while cereals and grains contain cyanide of 0.001 to 0.45µg/g, 0.07 to 0.3µ/g for Soya proteins, 0.1to 3mg/g for lima bean (Honig et al, 1983).

Cyanide is both widely available and easily accessible throughout the world. The compound is not frequently encountered, as it is a potential terrorist agent, used as poison and contaminant in the past. It has the ability to cause significant social disruption and demands special attention to public health preparedness. Cyanide refers to the anion radical and the compounds capable of releasing cyanide may be inorganic or organic in nature. Inorganic compounds may be simple (eg AgCN, KCN) or complex (eg. A[CN]y, A[M]x[CN]y). Organic compounds may be glycosides or nitriles. It is toxic to humans and is a substance that is formed in combination with other chemicals in the environment. In a drinking water maximum acceptable concentration of 0.2mg/l (200µg/l) for free cyanide has been set. Free cyanide is defined as the sum of the cyanide present as either HCN or CN^-. Hydrogen cyanide is a colorless liquid with an odor characteristic of bitter almonds and a vapor pressure of 107.6 KPa at 27.7^{o}C; it is completely miscible in water. Cyanide is both man-made and naturally occurring substance found in food and water. Cassava wastewater causes environmental pollution and aesthetic nuisance. The wastes are gotten from italic gari production. Borgstorm (1968) considered the scope of bioconversion of cassava and its by-product through fermentation as the oldest form of food biotechnology, in which cassava wastewater can be generated strongly. Therefore the cassava starch is then either dehydrated or submitted to natural fermentation for the production of sour cassava starch to reduce it cyanide content. The cyanogenic glycoside are two forms known as linamarin (93%)and lotaustralin (7%), and were decomposed by linamarase, a naturally occurring

enzyme in cassava liberating hydrogen cyanide (HCN). According to Iyayi et al (1997), the utilization of most of the agro-industrial by-products is plagued by their high level of structurally as non-starch polysaccharide (NSP). These NSP include cellulose, hemicelluloses, pectin and lignin. Cassava by-products are also reputedly high in anti-nutrients like hydrogen cyanide (HCN) polyphenels (tannis) and Phyate and low in protein (Akpan and Ikeneboneh, 1995). The fallout of these constraints on the animals includes low digestibility, poor feed intake and reduced animal performance (Alawa and Amadi, 1990; Adegbola and Oduozo, 1992). The general agreement that overestimate the actual cyanide toxicity to aquatic organisms and the analytically determination of HCN concentration in cyanide polluted water, is considered to be the most reliable index of toxicity (Irwin, 1997). Cyanide acts through the inhibition of cytrochome oxidase in the respiration electron transport chain of the mitrochondria, impairing both oxidative metabolism and the associated process of oxidation phosphorylation (Holland, 1983; Dreisenbach et al, 1987). Its outward acute effects resemble those of acute hypoxia. Interference in the oxidation process may also give rise to cardiac disturbance, seizures, unconsciousness and ultimately death to living organisms.

2. Experimental detail and analysis

The cassava wastewater was poured in six different plastic buckets at 2.0l capacity. The buckets were labeled and arranged in order of A_1, A_2, A_3, A_4, A_5, and A_6. The sample in A_1 was left as control. while some grams of chemicals known as Sodium Hydroxide were added to A_2 – A_6 at different percentage intervals, starting with 2%, 4%, 6%, 8%, and 10% respectively. The concentration of Cyanide, Biochemical Oxygen Demand (BOD), Suspended Solid (SS), Coliform and pH level were measured for 0hour, 1 hour (0.042 day), 6 hours (0.25 day), I day, 3 days, 5 days, 8 days, 10 days, 15 days, 18 days and 20 days. The values obtained for the Cyanide, BOD, SS, Coliform and pH were plotted against time. Graphical method and statistical regression analysis were used to determine the Monod constants, K_m, K_0, K_d, and Y using equation 1 and 2 below and the use of equation 3-6 was used to determine the inhibition constant K_1.

$$\frac{S_0-S}{X} = \frac{K_d\theta}{Y} + \frac{1}{Y} \quad (1)$$

Graphically plotting $(S_0 - S)/X$ versus Θ is linear while the K_d/Y is the slope and 1/Y is the intercept.
By inversion the equation becomes

$$\frac{X\theta}{S_0-S} = \frac{YK_m}{K_0} 1/S + \frac{Y}{K_0} \quad (2)$$

For determination of K_m and K_0.

The specific growth rate K, was determined using equation 3 below

$$\frac{1}{K} = \frac{K_m}{K_0}(1/S) + \frac{1}{K_0} \quad (3)$$

Line weaver-bulk plot equation
Then substituting for K in the equation 4-6 and evaluating them properly K_i was obtained for the different types or forms of the inhibition involved in the experimental results.

$$\frac{1}{K} = \frac{K_m}{K_0}(1 + \frac{I}{Ki})\frac{1}{S} + \frac{1}{K_0} \quad (4)$$

$$\frac{1}{K} = \frac{K_m}{K_0}(1+\frac{I}{Ki})\frac{1}{S} + (1+\frac{I}{Ki})\frac{1}{K_0} \quad (5)$$

$$\frac{1}{K} = \frac{K_m}{K_0}(1/S) + \frac{1}{K_0} \quad (6)$$

Where k_m is substrate saturation constant, K_0 is maximum specific growth rate constant, K_d is death rate, Y is the growth yield, Θ is time, S_0 is initial substrate concentration, S is substrate concentration, X is biomass concentration and K is specific growth rate, and K_i is the inhibition constant.

3. Results and discussion

Bacteria are favored by the pH level between 6.5 and 8.5. Respect to this the pH of the sample varies with time, as it increases and decreases showing it effect to converge to it neutral state in Fig. 1. The BOD values in Fig. 2 decreases with time showing the reduction of the pollutants as it is exposed to air in effect reducing the cyanide contents with interval of time enabling degradation. In Fig. 3 the suspended solid in the wastewater was observed to be reducing; resulting to the decrease in turbidity of the water and in Fig. 4 the coliform results indicates that in each day there is reduction of pollution of the wastewater. Again, the introduction of sodium hydroxide as an oxidizing agent reduces the amount of cyanide as it decreases with time in Fig. 5 allowing the degradation of biological activities.

Figure 6-17 below show the graphical analytical results for the Monod kinetic constant. The growth yield "Y", death rate "K_d", maximum Specific growth rate constant "K_0" and Substrate Saturation constant "K_m" which enable the achievement of the Specific growth rate result K biological activities in the reactor.

Progression of these results using Line weaver Burk plot models lead to the summarized result in table 1 below showing different forms of inhibition determined at different concentration of the oxidizing agent added using regression analysis. The inhibition constant also varies with the increase in variation rate of the oxidizing agents added to reduce cyanide concentration for biodegradation. Two competitive inhibitions were observed from the graph at the addition of 2g and 10g of sodium hydroxide to the waste for the reduction of the concentration of the inhibiter, indicating that the substrate concentration is low at 2g NaOH which make the inhibitor to compete favorably with the substrate,

resulting to high degree of inhibition, but at 10g NaOH the substrate concentration is high making the inhibitor to be much less successful in competing with the substrate, then the inhibition degree becomes lower.

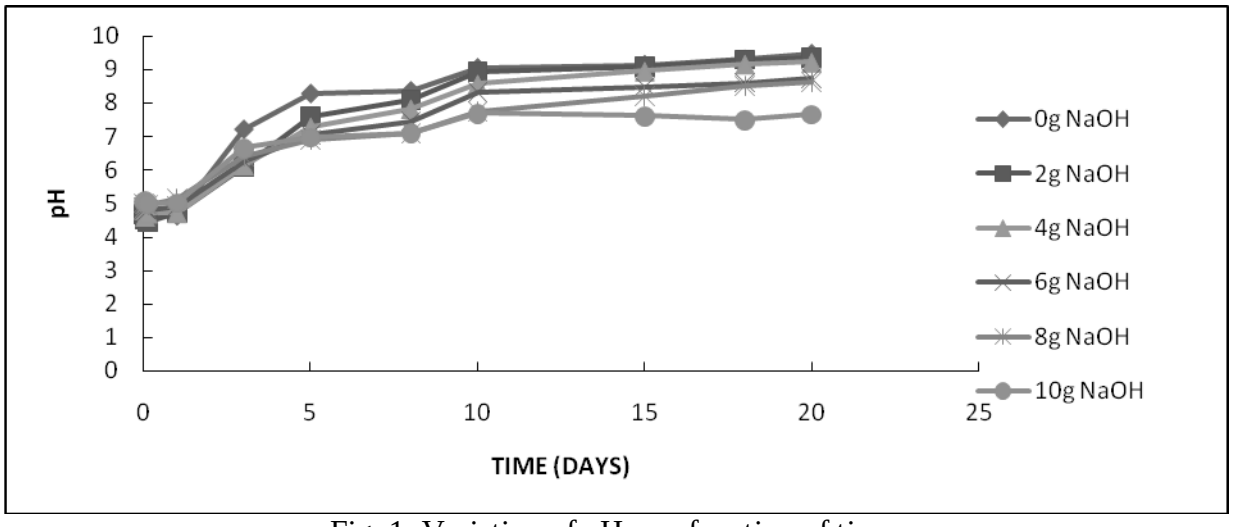


Fig. 1. Variation of pH as a function of time.

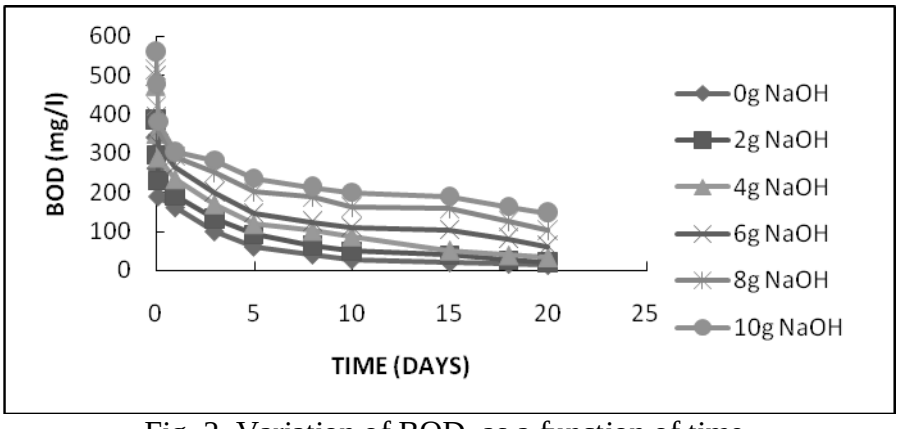


Fig. 2. Variation of BOD_5 as a function of time.

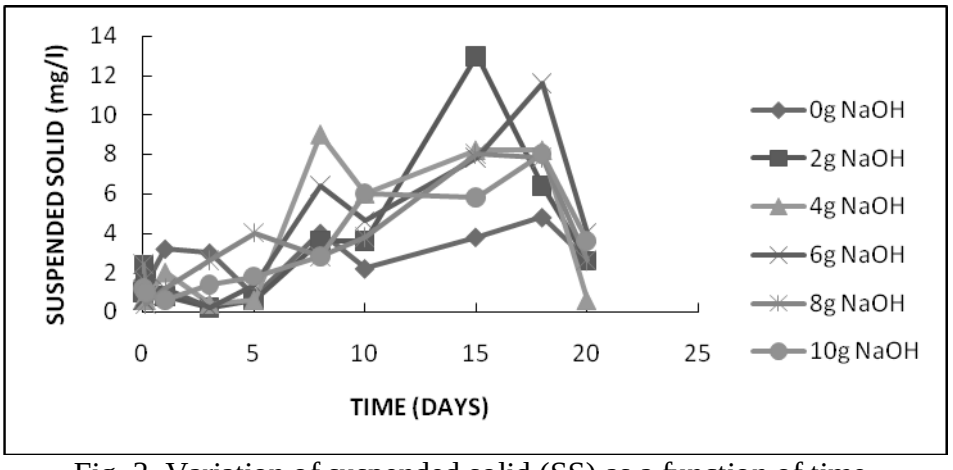


Fig. 3. Variation of suspended solid (SS) as a function of time.

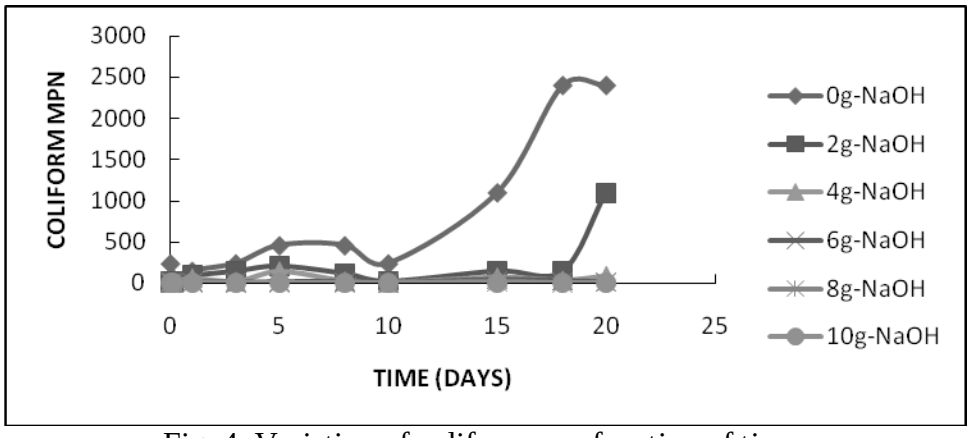


Fig. 4. Variation of coliform as a function of time.

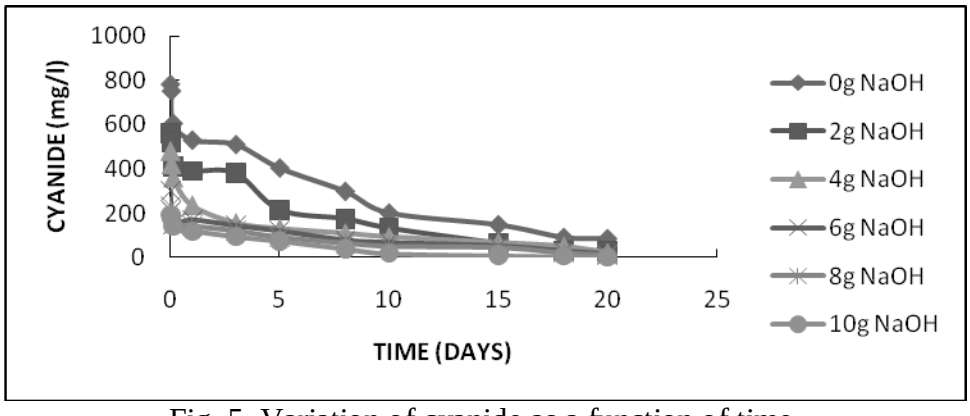


Fig. 5. Variation of cyanide as a function of time.

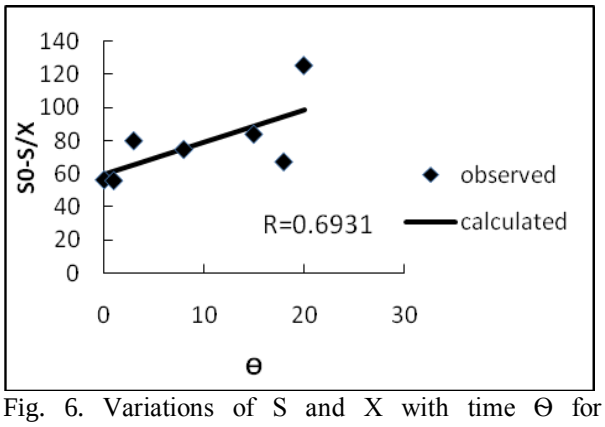


Fig. 6. Variations of S and X with time Θ for determination of Y and K_d for 0g of NaOH.

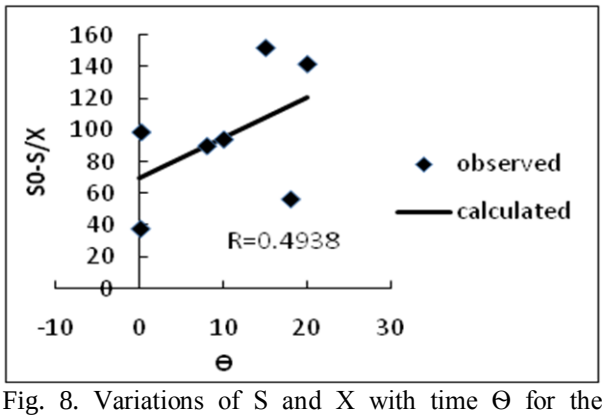


Fig. 8. Variations of S and X with time Θ for the determination of Y and K_d for 2g of NaOH.

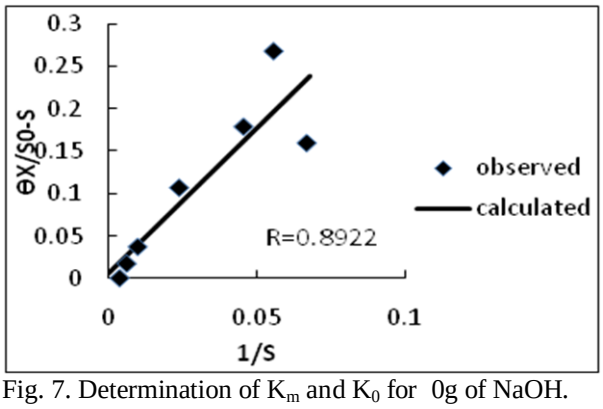


Fig. 7. Determination of K_m and K_0 for 0g of NaOH.

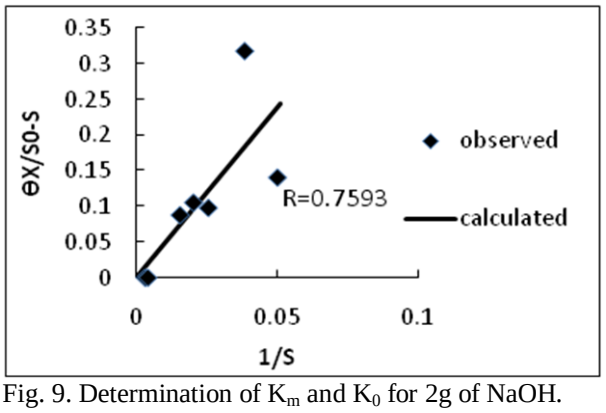


Fig. 9. Determination of K_m and K_0 for 2g of NaOH.

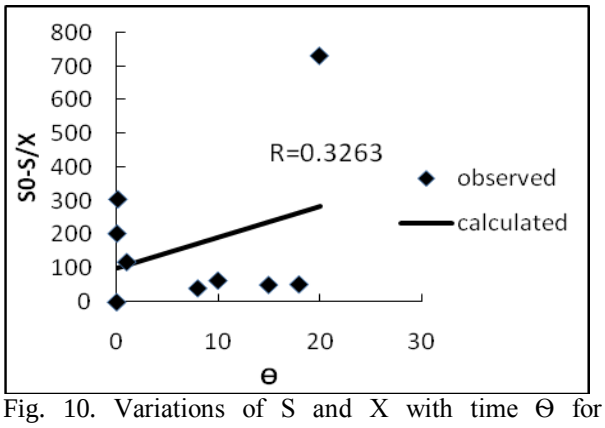


Fig. 10. Variations of S and X with time Θ for determination of Y and K_d for 4g of NaOH.

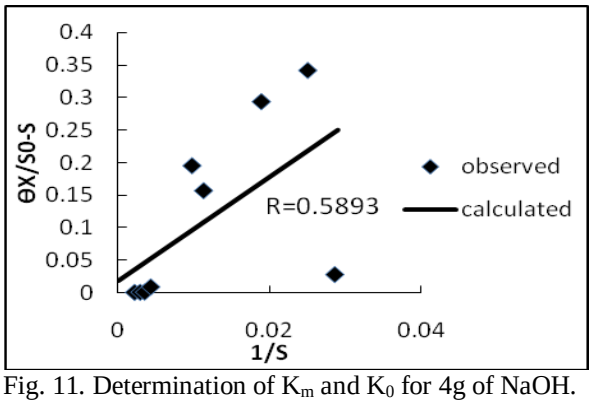


Fig. 11. Determination of K_m and K_0 for 4g of NaOH.

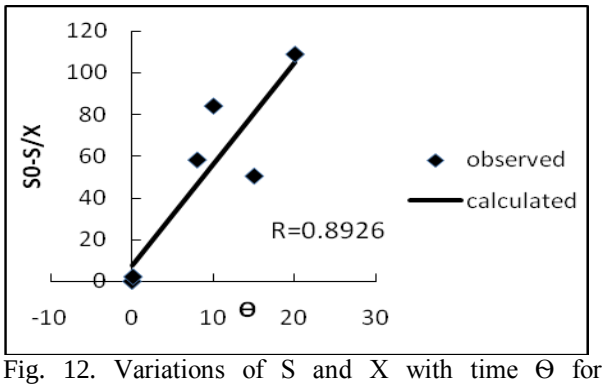


Fig. 12. Variations of S and X with time Θ for determination of Y and K_d for 6g of NaOH.

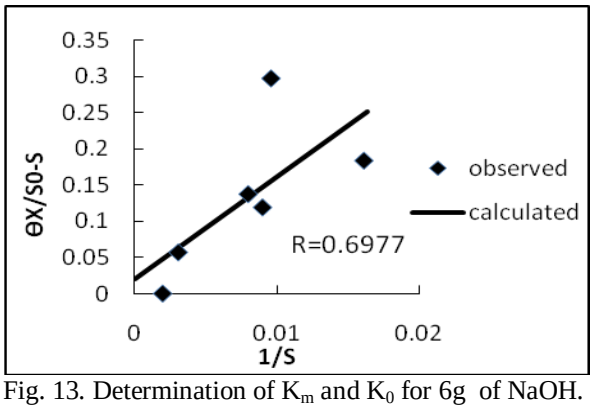


Fig. 13. Determination of K_m and K_0 for 6g of NaOH.

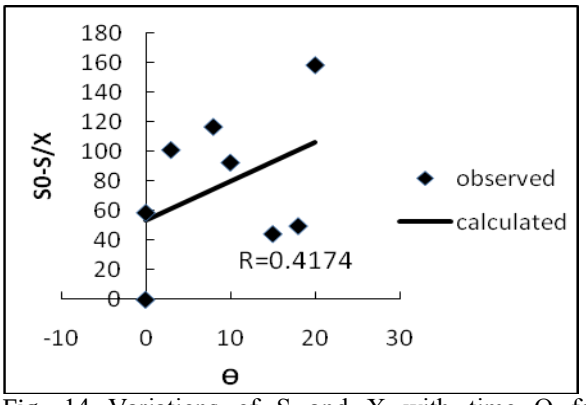


Fig. 14 Variations of S and X with time Θ for determination of Y and K_d for 8g of NaOH.

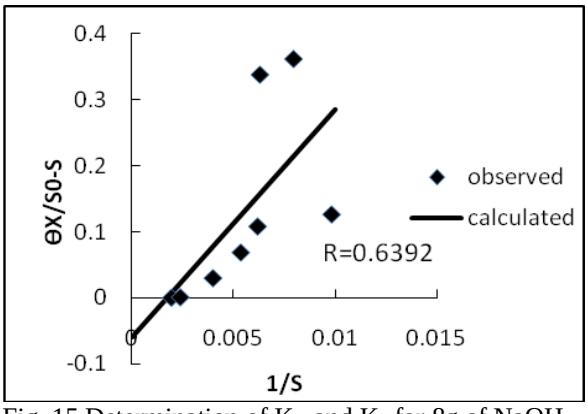


Fig. 15 Determination of K_m and K_0 for 8g of NaOH.

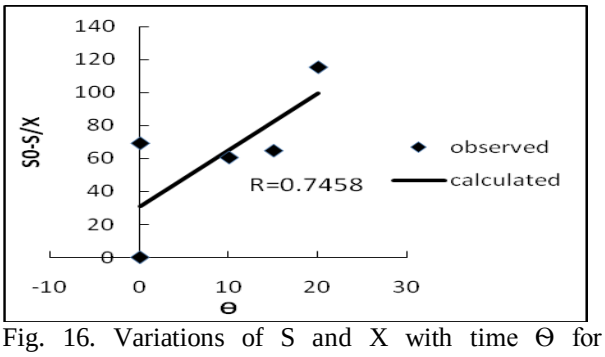


Fig. 16. Variations of S and X with time Θ for determination of Y and K_d for 10g of NaOH.

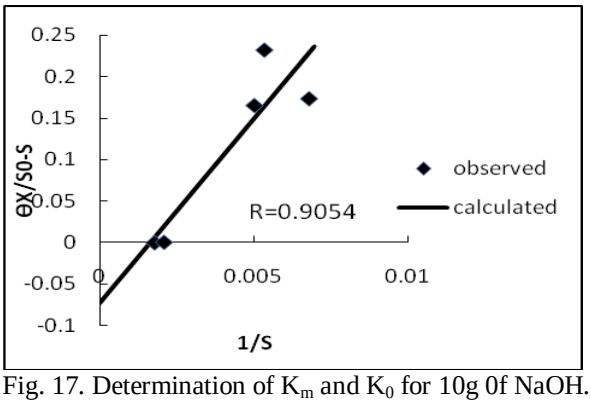


Fig. 17. Determination of K_m and K_0 for 10g 0f NaOH.

For 4g and 6g of the oxidizing reagent, mixed inhibition and non-competitive inhibition was observed respectively from the plotted graph that show the variation of 1/k with 1/S below in figure 19 and 20. The non-competitive inhibition produces an ideal end complex since the inhibitor combines with an enzyme molecule not minding whether a substrate molecule bound or not, (i.e. the presence of the inhibitor on the enzyme does not prevent that complex from reacting with the substrate). This is because the substrate does not affect the inhibitor binding, thereby the total enzyme concentration was effectively reduced by the inhibitor, decreasing the value of K_0 and not altering K_m. The observed mixed inhibition form is known as competitive non-competitive inhibition showing that from the graph K_I(slope) is greater than K_I(intercept) i.e. $K_I > K_1$ and the plots cross to left of the 1/k axis, and is above the 1/S axis.

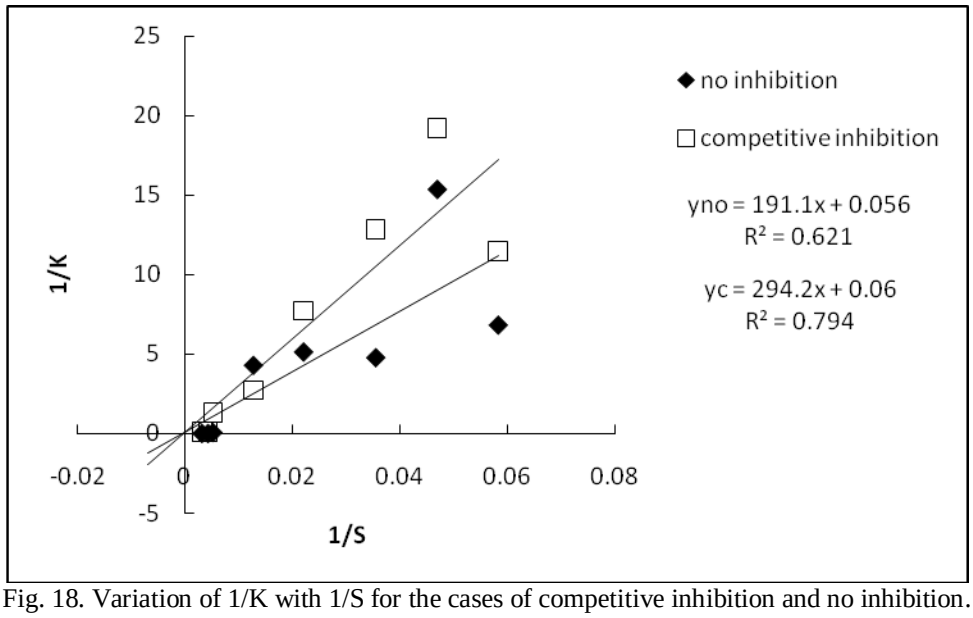


Fig. 18. Variation of 1/K with 1/S for the cases of competitive inhibition and no inhibition.

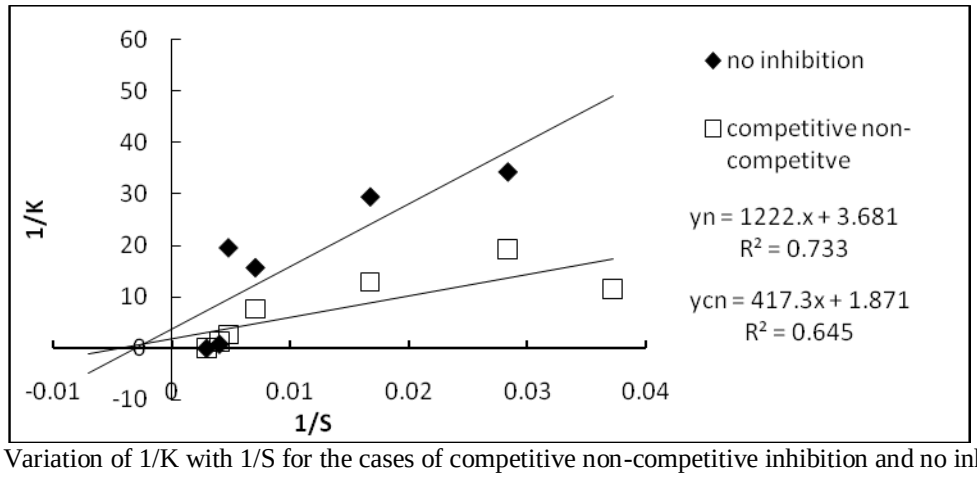


Fig. 19. Variation of 1/K with 1/S for the cases of competitive non-competitive inhibition and no inhibition.

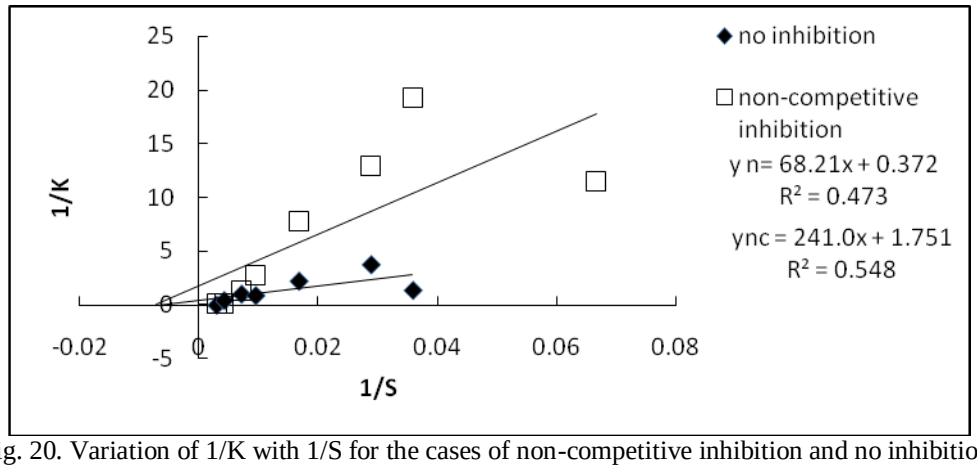


Fig. 20. Variation of 1/K with 1/S for the cases of non-competitive inhibition and no inhibition.

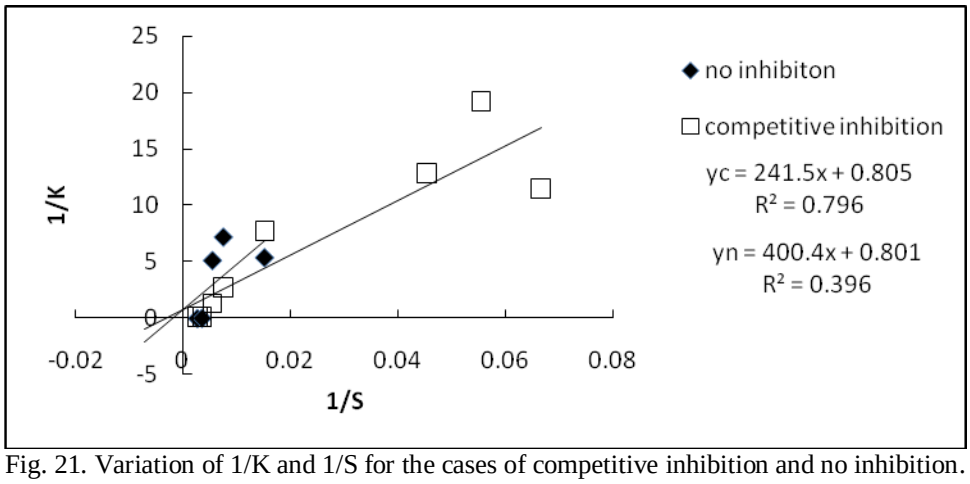


Fig. 21. Variation of 1/K and 1/S for the cases of competitive inhibition and no inhibition.

Summary of results

Table 1
Forms of inhibition and its constant values.

Inhibition types	Competitive	Mixed	Non-competitive	competitive
NaOH (g)	2g	4g	6g	10g
K_I	591.954	358.554	398.980	259.254

4. Conclusion and recommendation

This research made it possible to analyze the chemical component of cassava wastewater and the effect of cyanide on its degradation. The wastewater was subjected to laboratory test and sodium hydroxide was added to ensure effective degradation. Positively using the statistical regression and the Line weaver Burk plot equation, the inhibition forms involved in the experiment and inhibition constants K_1 was identified and achieved. The results show that the inhibition constants K_1 vary at different increase of the oxidizer and the cyanide contents reduce with time.

The analytical result of this research is useful and noteworthy for the design of treatment plants. Untreated sewage from cassava industries should not be used for irrigation or in fish ponds, and should not be discharged to the river untreated. It has to undergo proper treatment to avoid chromosomal aberration in some plant and prevention of self purification of the receiving water bodies which result to massive aquatic deaths.

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