

Full Length Research Paper

Cassava Wastewater Treatment by Alkali-Induced Degradation: A Detoxification Strategy

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Accepted 07 October, 2024

Cassava wastewater contains toxic materials that can endanger humans, as well as other living organisms if they are not properly treated before disposal. In order to address this problem, there is an urgent need to develop simple and efficient technologies for management of cassava wastewater, especially in tropical developing countries where cassava is extensively processed, and consumed on daily basis. This study was therefore, aimed at treating cassava wastewater by using alkali hydrolysis. Degradation products of cassava wastewater were characterized using different parameters under static and batch fermentation modes. With batch reactor as a model, hydrolysis of cassava wastewater over 20 days upon with wide range of NaOH concentrations was investigated. With 0.25 M NaOH, cyanide concentration was greatly hydrolyzed (44-fold) in 20 days. Furthermore, the alkali treatment drastically reduced the coliforms and reduced the biochemical oxygen demand in the cassava wastewater. This study apparently indicated that alkali treatment was very efficient in degrading the waste compounds from cassava. This system can be explored further for potential degradation of waste water treatment in tropical developing countries.

Keywords: Cassava, cyanide, hydrolysis, alkali, wastewater.

INTRODUCTION

Cassava belongs to the genus *manihot* and of the natural order of Euphorbiaceae. Cassava was first cultivated in some parts of South America, and later, across the Atlantic in the 17th century, which eventually formed part of diets for Africans and Asians (Olsen and Schaal, 1999). Cassava is a very important food in most tropical developing countries, particularly in Nigeria (FAO, 2005). However, methods for processing cassava and degrading cassava wastewater are still very poor resulting in accumulation of high levels of organic materials and some toxic compounds (Bradbury, 2004; Enyenihi, et al., 2009). Some studies have shown that cassava processing generates solid and liquid residues that are hazardous in the environment (Cumbana, et al.,

2007; Jyothi, et al., 2005). However, the amount of cassava wastes produced would depend on the processing methods and the scale of production. For instance, when cassava is used in homes for culinary purposes, the quantity of wastes generated is very little and thus, will not cause any significant environmental hazards. However, when cassava is used industrially, including small flour factories, the so called "Casa de Farinha", generates a considerable amount of wastes since they are traditionally concentrated in a certain place. Cassava wastewater when discharged on the soil results in environmental pollution. Also, cassava contains cyanogenic glucosides (toxic substances), mainly linamarin (92-98%), which releases hydrogen cyanide after hydrolysis by an endogenous linamarase (Okafor and Ejiofor 1986; Nok and Ikediobi, 1990). Furthermore, the odour from this discharged wastewater is dangerous to human health (Ayenor 1985; Akinrele 1986; Ezeronye 2003). The cassava wastewater also inhibits the growth of vegetations and thus, reduces the entire fertility of the

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Soil. There is therefore, a need to develop efficient processes for degradation of cassava wastewater such that the wastewater can be safe to the environment.

In this work, the effect of degrading cassava waste by alkaline treatment was investigated. The main objective of this study was to degrade and detoxify cassava wastewater, with the ultimate goal of eliminating some toxic substances such as cyanide before they are discharged to the water.

MATERIALS AND METHODS

Cassava wastewater samples

Five-day old fermented cassava samples were used all through the experiments. The experiments were conducted between June 2008 and December 2010. Samples of cassava were obtained periodically from a cassava processing industry located in Onuiyi road, Nsukka, Nigeria. The factory consisted of grinding and fermentation sections. At the fermentation section, the cassava tubers were peeled, washed thoroughly with clean water and fermented in a clean container with sufficient water level for five days. After the fermentation process, the cassava sludge was then removed for "fufu" production leaving behind the cassava wastewater, which was collected and used immediately in this study. Six plastic buckets were filled with cassava wastewater to a capacity of 2 l. Wastewater was also collected from the "garri" processing section (i.e., where cassava tubers were peeled, grinded and dried). All samples were preserved to avoid any significant change in quality between the time of sampling and the actual time. Samples were tested with various concentrations of NaOH (0.05-0.25M).

Biochemical Oxygen Demand (BOD)

Dilution medium is prepared by adding 1 ml of phosphate buffer (pH 7.2), magnesium sulfate (1g), calcium chloride (1g), and ferric chloride solution (1ml) in 1 L of distilled water. 1 ml of wastewater was added to the dilution medium and then saturated with air. The mixed dilution was siphoned into BOD bottles and one bottle was used for dissolved oxygen determination. The other bottles were stored in the incubator for BOD determination.

Coliform MPN test

A series of fermentation tubes were inoculated with appropriate graduated quantities; serial dilutions were carried out in test tubes. The inoculated fermentation

tubes were incubated at $35^{\circ}\text{C} + 0.5^{\circ}\text{C}$. Formation of gas within 48 h in the Durham tubes indicated the presence of coliforms.

Cyanide analysis

Reflux distillation procedure was used to extract soluble cyanide salts and many insoluble cyanide complexes from wastes and leachates. It is based on the decomposition of nearly all cyanides by a reflux distillation procedure using a strong acid and a magnesium catalyst.

A known volume of sample was taken and mixed with 2 ml NaOH. 0.5 ml of paradimethane ethylrhodamine indicator was added to the sample in a conical flask and titrated with silver nitrate. Cranny yellow colour signified the presence of cyanide.

Measurement of cell concentration

Weight of the suspended solids was determined by gravimetry (Ugwu and Aoyagi 2011). Cell concentration was therefore obtained by deducting the weight of the cassava debris from that of the suspended solids.

Measurement of suspended solids (SS)

A beaker with a filter paper inserted into it was dried at a temperature of $103-105^{\circ}\text{C}$ for 1 h. The beaker was allowed to cool in desiccators, and the weight of empty beaker and filter paper was weighed and recorded. Twenty ml of the sample was taken and filtered, using the weighed filter paper and a vacuum device, the filter paper was replaced in the beaker and dried again in oven for 1 h. The filter paper and beaker were reweighed and the difference in weight recorded as suspended solids.

Microbial growth kinetics

Microbial growth was also estimated by following Monod's kinetics. If the biological solids concentration is constant, then the rate of substrate reaction can be calculated as follows;

$$\frac{ds}{dt} = - \frac{K_o X S}{Y(K_m + S)} \quad 1$$

$$\text{Then, it becomes, } - \frac{ds}{dt} = \frac{K_o X_o S}{Y K_m} \quad 2$$

$$\text{Integrating equation (2), we obtained} \quad \frac{\ln S_o}{S} = \frac{K_o}{K_m Y X_o t} \quad 3$$

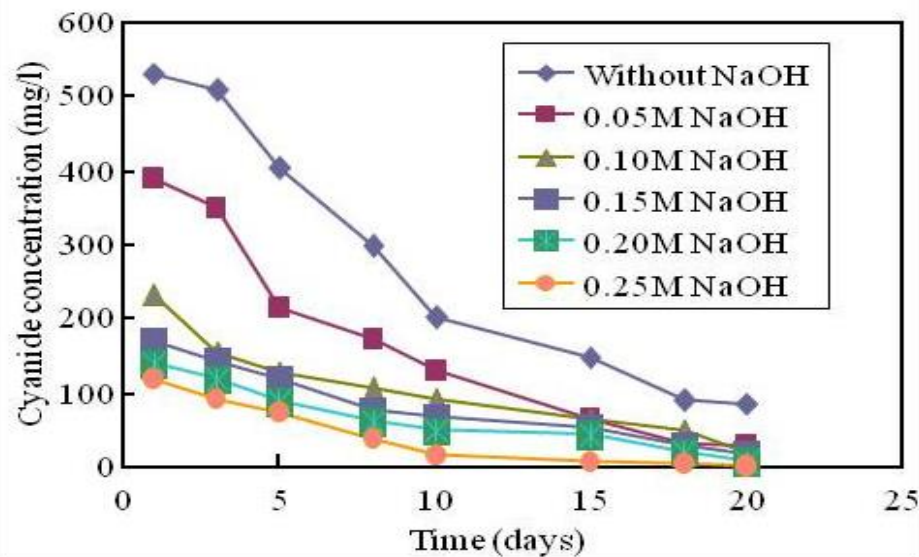


Figure 1. Changes in the cyanide concentration during the degradation of cassava waste water with various concentrations of NaOH.

Where S_0 and X_0 are the initial concentrations of substrate and biomass respectively.

Plotting against time should produce a straight line with a slope of $\frac{dS}{dt}$.

The value of Y can be evaluated from batch data by having $S_0 \gg K_m$ and continuously monitoring the substrate concentration.

Simplifying $\frac{dX}{dt} = \frac{K_o X S}{(K_m + S)}$, the following equation was obtained.

$$\frac{dS}{dt} = \frac{K_o X}{Y} \quad (4)$$

$$\frac{dX}{dt} = K_o X \quad (5)$$

Solving equation (5) and substituting the result into equation (4) and integrating, we have

$$\frac{S_0 - S}{X_0} = \frac{1}{Y} (\exp K_o t - 1) \quad (6)$$

A series of values for K_o are assumed: $\left(\frac{S_0 - S}{X_0} \right)$ was plotted against $(\exp K_o t - 1)$ for each assumed K_o . The points giving the best straight line through the origin will

have a slope of $\frac{1}{Y}$, and determined the correct K_o .

RESULTS AND DISCUSSION

Cassava wastes can be degraded with microorganisms

under acidic conditions (Siller and Winter 1998); however, the process is time consuming and requires technical know-how. In tropical developing countries such as Nigeria where there are few infrastructures, chemical degradation still remains the most efficient means of degrading cassava wastewater. This study was focused on understanding the characteristics of cassava wastewater upon degradation with various concentrations of NaOH. The study was carried out in batch reactors, using six different samples of cassava wastewater. To avoid inhibitory effect of cyanide to cassava wastewater degradation, NaOH (an oxidizing agent) was used for the degradation. The sodium hydroxide decomposed cyanide to cyanate salt and to carbon (IV) and nitrogen. The analysis

included determination of BOD, microbial loads, pH, cyanide concentration and suspended solids. Degradation activity was the best with 0.25M of NaOH solution. Figure 1 shows changes in cyanide concentrations upon treatment with various concentrations of NaOH. At 0 h, cyanide concentrations in samples without NaOH and with 0.25M NaOH were 780 mg/l and 194 mg/l, respectively. However, in 20 days, cyanide level was reduced to 2 mg/l upon addition of 0.25M NaOH. This value (2 mg/l) corresponded to 44-fold reduction compared to the value obtained without NaOH. The results therefore, indicated that

NaOH was very efficient in oxidizing cyanide in cassava wastewater.

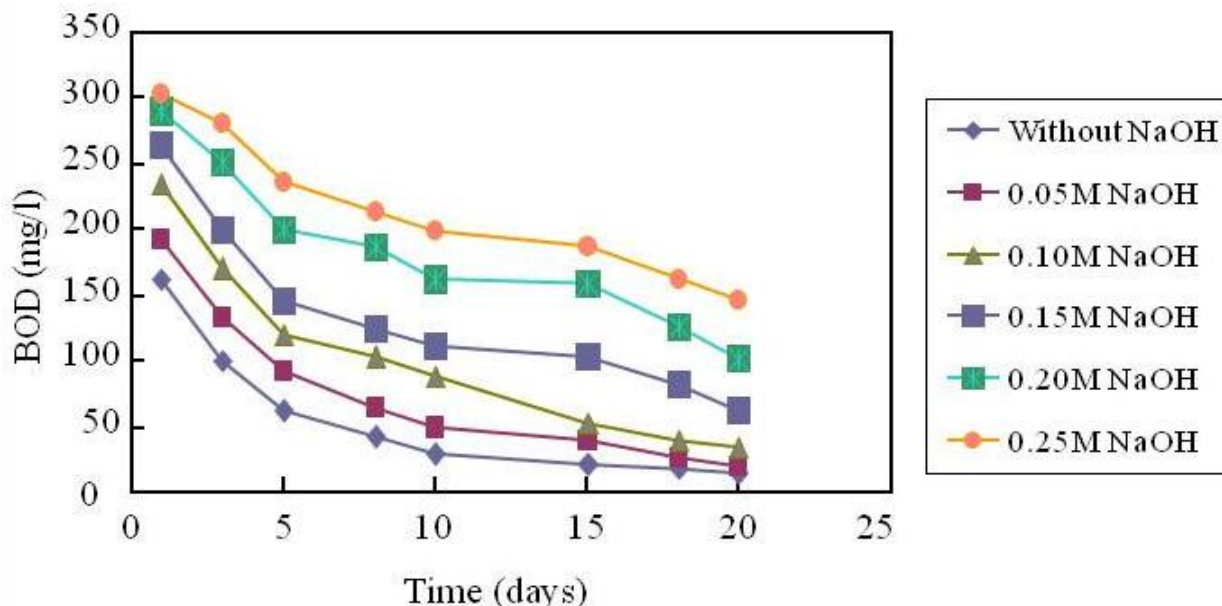


Figure 2. Effect of various concentrations of NaOH on the formation of biochemical oxygen demand (BOD) during the degradation of cassava wastewater.

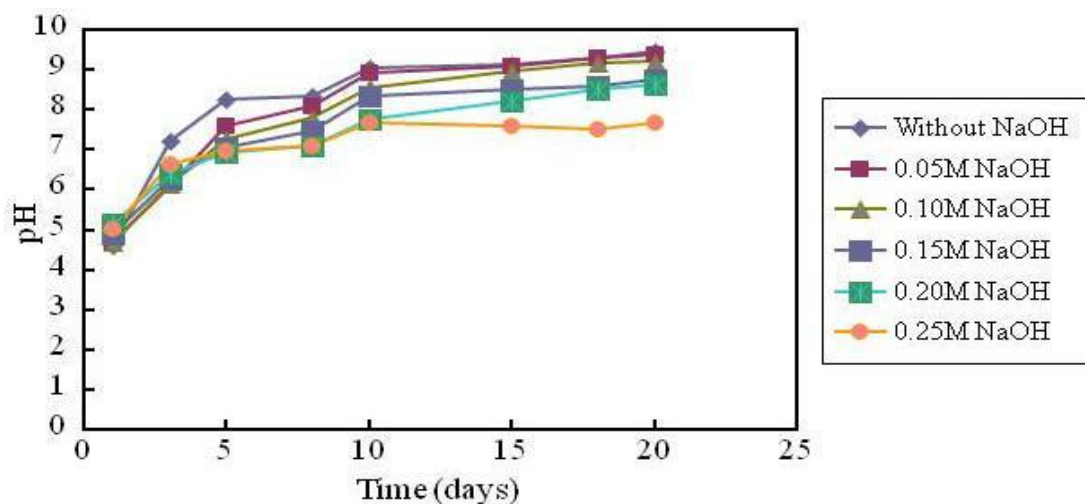


Figure 3. Changes in the pH during the degradation of cassava waste with various concentrations of NaOH.

Biochemical oxygen demand in samples treated with NaOH and those that were not treated with NaOH were evaluated as shown in Figure 2.

Biochemical oxygen demand, an indicator of the amount of oxygen required by bacteria to stabilize decomposable organic matter under aerobic conditions (Agunwamba 2000) was also evaluated. There was about 80% decrease in BOD after 20 days treatment with alkali (data not shown). BOD is a biochemical parameter commonly used for assessing the quality of water since it

reflects the organic load in wastewater (Alaboud 2009; Al-Turki 2010). In other words, a high BOD therefore indicates the presence of a large amount of organic pollutions. Furthermore, studies have indicated that high BOD in effluents constituted some risks to fauna, flora and surface or underground water (Horsfall, et al., 2006, Isabirye, et al., 2007). The pH of the samples varied from 4.5 to 9.5 as the concentration of NaOH was increased from 0.05 to 0.25M (Figure 3). Effect of various concentrations on the level of coliform in cassava

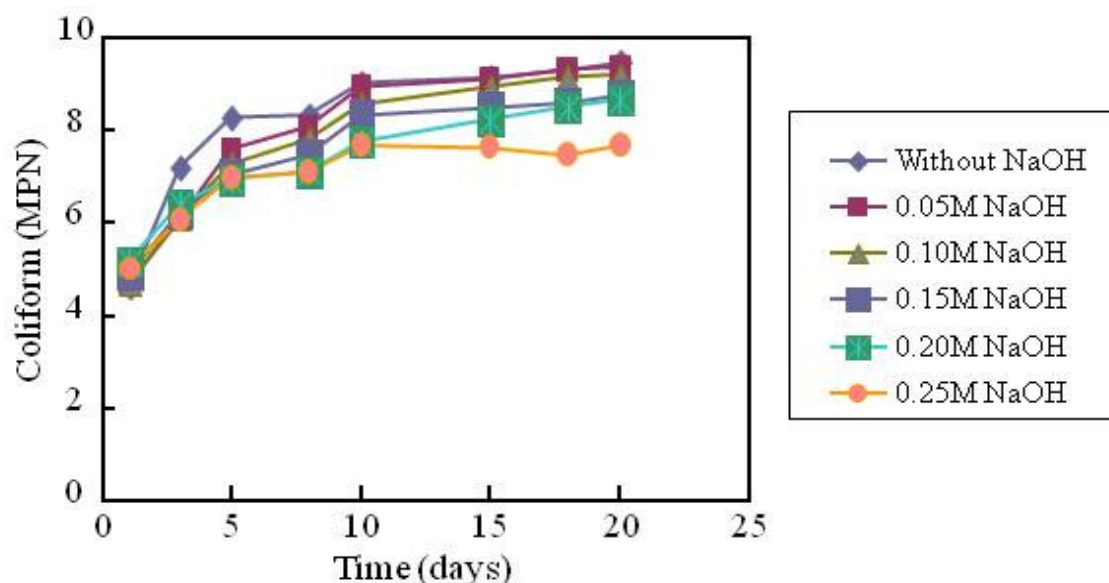


Figure 4. Changes in the number of coliforms during the biodegradation of wastewater with various concentrations of NaOH.

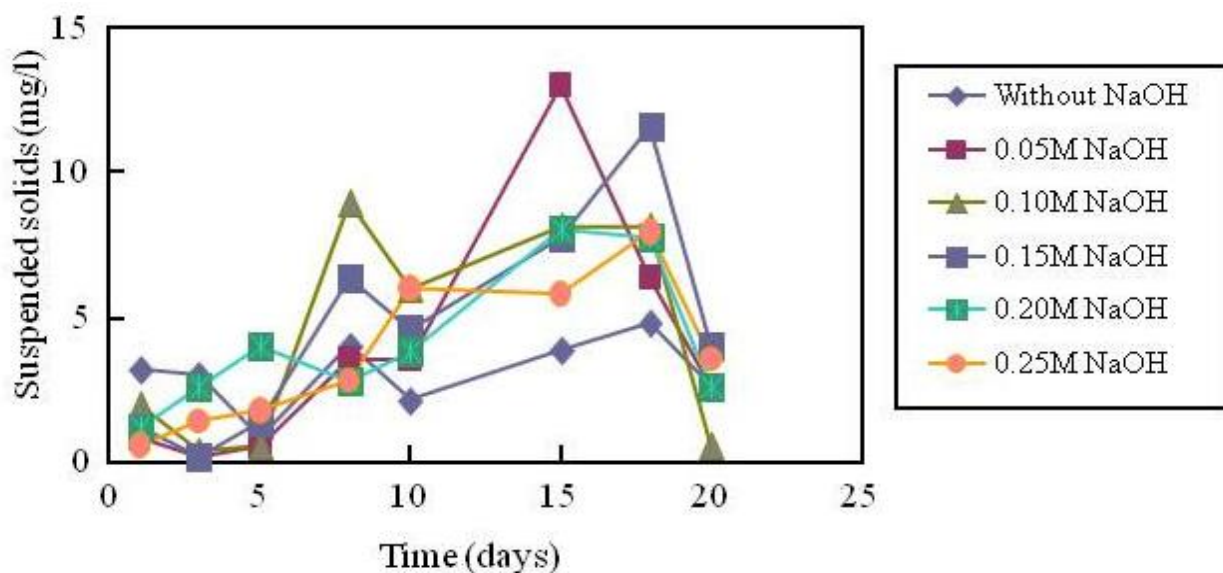


Figure 5. Effect of various concentrations of NaOH on the formation of suspended solids during the degradation of cassava wastewater.

wastewater is shown in Figure 4. Without addition of NaOH on the wastewater, level of coliforms increased with time whereas addition of various concentrations of NaOH, resulted in the decrease in the coliforms. Thus with 0.25M NaOH, there was about 2-fold decrease in coliforms at the 20th day. Higher concentration of NaOH led to increased pH which might favor the growth of alkali

bacteria in the hydrolyzates. Nevertheless, the decrease in the number of coliforms over time signified a reduction in the pollution of the wastewater (Figure 4). Time course for the suspended solids is shown in Figure 5. There was no significance difference between SS of control samples (i.e., without NaOH) and those with NaOH, an indication that the alkali treatment did not reduce the quantity of

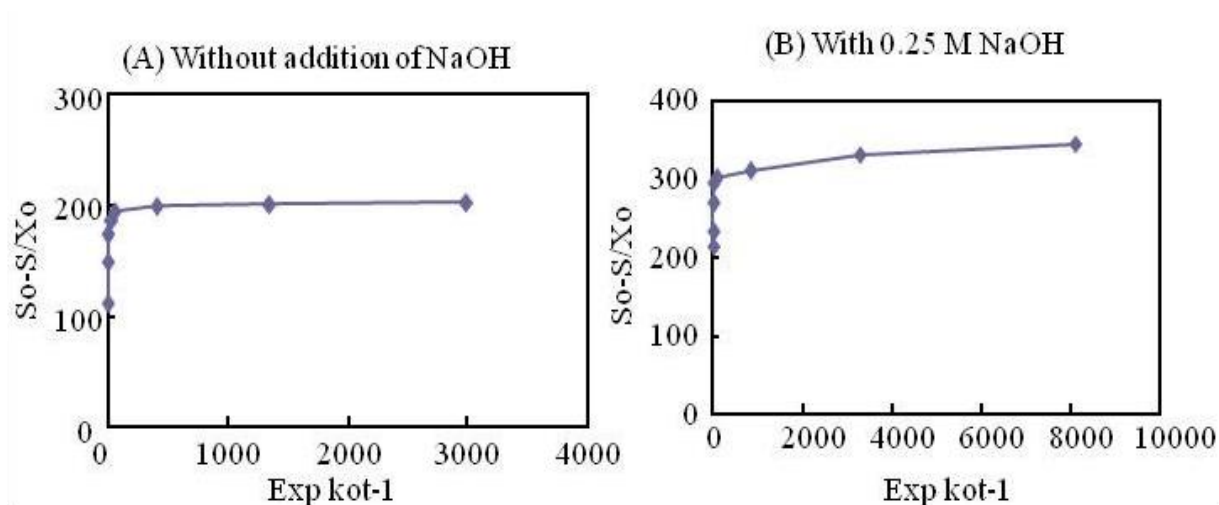


Figure 6. Relationship between $S_o - S/X_o$ and k_{ot-1} when 0.25M NaOH was used for the biodegradation of cassava wastewater.

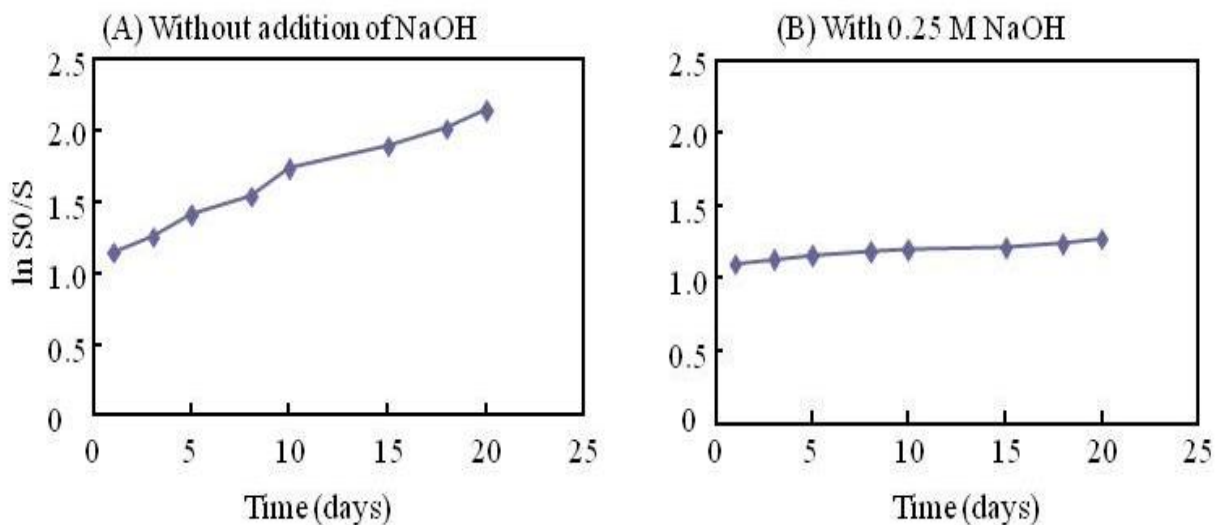


Figure 7. Time course of $\ln S_o/S$ when 0.25M NaOH was used for the degradation of cassava wastewater.

cassava hydrolyzates. However, a close observation showed that the turbidity of cassava wastewater (absorbance reading at 660 nm) reduced with time. Furthermore, maximum specific growth rate constant increased when the concentration of NaOH was increased. Relationship between of $S_o - S/X_o$ and k_{ot-1} with 0.25 M NaOH and without addition of NaOH during biodegradation of cassava wastewater were compared in Figure 6. As shown in the figure, $S_o - S/X_o$ was constant in both conditions all through the degradation period (20 days). A linear increase in $\ln S_o/S$ with time was observed in samples without NaOH whereas steady state or constant condition was observed upon addition of

0.25M NaOH (Figure 7). Table 1 summarizes correlation coefficients in various batch reactor models. Coefficient of correlation varied from 0.958 to 0.999 as the concentration of NaOH was increased from 0.05M to 0.25M.

CONCLUSION

Degradation characteristics of cassava wastewater were studied using parameters such as BOD, pH, cyanide concentration and suspended solids. Our findings indicated that the rate of degradation of cassava

Table 1. Coefficient of correlation for various concentrations of NaOH

Moles of sodium hydroxide (M)	Exp kot-1	Ln So/S
0	0.894	0.845
0.05	0.975	0.958
0.10	0.980	0.975
0.15	0.997	0.988
0.20	0.998	0.998
0.25	0.999	0.999

wastewater increased with time and also with the increase in the concentration of NaOH. Apparently, this alkali treatment method resulted in significant reduction in cyanide content of cassava wastewater. Given that fermentation of cassava would result in the generation of enormous wastewater that contain materials such as cyanide, it is anticipated that this work would provide useful information for the design of efficient treatment plants that can degrade cassava wastewater.

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