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AN EVALUATION OF THE EFFECTS OF LEAD ON THE BIODEGRADATION OF ORGANIC WASTES

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ABSTRACT

This study constitutes an additional step in limiting the concentration of lead in wastewater effluent from waste stabilization ponds. The effects of lead on the biodegradation rate of organic wastes were investigated at lead concentrations of 0, 5, 10, 20, 30, 40, 50, 75, 100, 125, 150, 200mg/l in batch cultures. Several runs were in order to determine temperature effects. A model was proposed to predict deoxygenation rate for different concentrations of lead at various temperatures. The model parameters namely the ultimate BOD, reaction rate constant and lag time were optimized by ordinary least squares (OLS) using the modified Gompertz model. The ultimate BOD and lag time increased as lead concentration was increased. However the deoxygenation rate decreased as lead concentration increased. The deoxygenation rate and ultimate BOD had maximum values at optimum temperature range of 30.15-33.50 ^{o}C.

Keywords: Lead concentrations, biodegradation, organic wastes, biochemical oxygen demand.

INTRODUCTION

Lead is a bluish-white, silvery, grey metal. It is lustrous when freshly cut, with cubic, geometry, crystal structure, and odourless. It is very soft and malleable, easily melted, cast, rolled, extruded, very resistant to corrosion and a poor conductor of electricity. It is a very stable metal although it dissolves in acid. Great care must be taken in handling lead as it is an accumulative poison (Sanders *et al*., 2007).

One characteristic of lead is its tendency to form compounds of low solubility with the major anions of natural water. The amount of lead that can remain in solution in water is a function of the BOD of the water and the dissolved salt content which is about 30μg/l in hardwater and about 500μg/l in softwater (Salvato *et al*., 2003). Much of the lead carried by river water is in the form of suspended solids.

The toxic effects of lead are dependent on the specie of organism, temperature, pH of the wastewater, and valence of lead.

Most industrial wastewaters first pass through a sewage treatment plant. This results in the destruction of bacteria in such plants by trace amounts of lead thereby rendering the treatment plant ineffective (Huan and Diaz, 2009).

The process of oxygen utilization in the degradation of organic constituents present in wastewater or deoxygenation is markedly influenced by the concentration of heavy

metals such as lead (Plunkett, 1987). An understanding of the kinetics of deoxygenation at different concentration of heavy metal is of fundamental importance in water pollution control. It is also essential for efficient design and operation of oxygen utilizing biological treatment processes. Furthermore, since most municipal wastewater treatment facilities use biological treatment processes for stabilization of organic and inorganic substances in wastewater, it is necessary to understand the effects of lead and its toxicity on these processes, with a view to limiting its concentration in wastewater effluent treated in waste stabilization ponds.

In this paper, the effects of lead as a toxic substance on the biodegradation of organic wastes based on experimentation was investigated. The effects of lead on the rate constant, k, the ultimate demand, BOD_u, the lag time and $\lambda$of the monomolecular deoxygenating expression was also examined.

MATERIALS AND METHODS

The wastewater samples were collected from the effluent of oxidation ponds at University of Dar-es-Salaam. The oxidation ponds receive combined sewage from conveniences located in student hostels, staff houses, offices, library, health center, workshops and chemical wastes from laboratories.

Fig. 1 shows a schematic diagram of the waste stabilization ponds at the University of Dar-es Salaam.

Samples were collected from the effluent of the primary facultative pond and analyzed immediately after dosing with a chemical in order to minimize the reduction of BOD values. All laboratory examinations were carried out in accordance with standard methods as laid out in APHA (1992).

BOD for each sample was measured using the manometric BOD measuring devices-OxiTop^{R}IS12. Samples were first incubated at fixed temperature by setting the incubator at the same temperature for each set of samples. Experiments were conducted in dark conditions to prevent anaerobic conditions and photosynthetic reaction of algae as demonstrated by Mara (1974).

Bottles were filled with a wastewater sample of a specified volume. The volume of the sample placed in the bottle was determined by tests depending on the expected BOD and the readings multiplied to the scale factor depending on the sample volume (see Azad, 1976).The bottles were then linked to a top pressure gauge. Oxidation of the sample solution resulted in depletion of the oxygen in the solution which was replaced by oxygen from the gas volume of the sample bottle. As the organic waste was oxidized, CO_2 was formed and this moved to the gas area. This created a negative pressure in the sample, which was recorded on the top pressure gauge. The fall in pressure was proportional to the BOD of the sample. A magnetic stirring rod was inserted in each bottle to ensure oxygen and carbon dioxide exchange and two sodium hydroxide tablets were placed in the rubber quiver in the bottleneck to act as CO_2 absorbent. The BOD was read off from the calibrated top manometer in mg/l while the actual BOD values were the displayed measured values multiplied by the dilution factor.

In order to minimize the insufficiency of nutrients in the primary facultative pond, the same test sample was employed throughout

the duration of the investigation in form of diluted sample. Lead solution was added to the diluted water at different concentrations as shown in Table 1. These were thoroughly mixed together to form a uniform dispersion of the nutrients and lead.

To examine the effects of lead on the depletion of oxygen, the mixture of diluted water and lead was introduced into the samples as 30% of the total volume (250ml). The incubator was set at 35^{o}C. A second run was done to determine the influence of lead concentrations at different temperatures. The samples were divided into sixty portions of 250ml each. Out of sixty portions of samples, five groups were selected. Each group contained twelve equal portions of diluted samples of 250ml. Each group was dosed with varying concentrations of lead ranging from 0-200mg/l. In each single group, each sample was kept at constant temperature of 20, 25, 30, 35 and 40^{o}C. Each test run was carried out for up to 12 days and records of BOD concentrations were taken every 2-6 hours.

Table 1: Measurements of the sample, dilution water and lead solution

70% of the total volume sample (ml)	30% of the total volume		Lead concentration (mg/l)
	Dilution water (ml)	Lead solution (ml)	
175	75.00	0.00	0
175	73.75	1.25	5
175	72.50	2.50	10
175	70.00	5.00	20
175	67.50	7.50	30
175	65.00	10.00	40
175	62.00	12.50	50
175	56.00	18.80	75
175	50.00	25.00	100
175	43.70	31.30	125
175	37.50	37.50	150
175	25.00	50.00	200

Modelling process

A FORTRAN Program was used to predict the BOD rate based on the modified Gompertz equation below.

$$BoD=BoD_u \exp\{-\exp[k.e/BoD_u (-\lambda t)+1]\} \quad (1)$$

The Gompertz model (also see Linton *et al.,* 2006) uses three parameters namely, the ultimate biochemical oxygen demand, the rate constant and the lag time. The model was run with each concentration of lead applied giving consideration to the effects of temperature on BOD rate.

The objective function for the model was to minimize the sum of square of differences, F between the experimental and the estimated rate constants and the summation taken as

$$F= \sum_{i=1}^{n} (y-y^1) \quad (2)$$

F = index of residual error
y^1 = model output estimate
y = experimental output.

The Nash and Sutcliffe model efficiency, R^2 was used to analyze the performance of the proposed model.

and $$R^2 = F_o\text{-}F/F_o \quad (3)$$
where

$$F_o = \text{Initial variance} = \sum_{i=1}^{n} (y_i - \bar{y})^2 \quad (4)$$

and

$\bar{y}$ is the mean of experimental data.

The reaction rate constant k was obtained from the Arrhenius expression as

$$K= A^1 e^{(-E_1/RT)}/[1+Ke^{(-E_2/RT)}] \quad (5)$$

where A^1 = Constant, day^{-1}
E_1= Activated energy of the growth limiting reaction J/mole
T= Absolute temperature, ^oK
E_2= enthalpy change for enzyme inactivation reaction (J/mole)
K= dimensionless constant

RESULTS AND DISCUSSION

A non-linear analysis was used to fit a model for the BOD rate described in equation (1) for the range of 0-200mg/l lead concentrations. The BOD rate was determined for control sample (without lead) at 25^{o}C (Fig 2). It was observed that there was a sudden increase in the rate of deoxygenation up to a BOD value of 170mg/l. Beyond this value, the deoxygenation rate was nearly zero. At 20^{o}C and 125mg/l, BOD uptake was rapid in the early stages but no further uptake was observed after 50mg/l of organic material was biodegraded. No significant lag time was observed (Fig 3).

Fig 4 shows deoxygenation rate for a control sample at 40^{o}C. The behaviour was similar to results obtained at 25^{o}C and 20^{o}C. However the ultimate BOD at 40^{o}C was considerably lower than the same at other temperatures. Lag time was observed to be larger when the lag time increased to 70.6hours from 25.9 hours in the absence of lead at the same temperature. In fact, lag time increased exponentially with increase in lead concentration.

The results showed that uptake of dissolved oxygen decreased as dosage of lead was increased. It was also observed that deoxygenation rate and ultimate BOD increased as lead concentration increased.

Lag phase was clearly evident when unfavorable temperature and high lead concentrations were applied. This may be attributed to the fact that lead even at low concentrations, significantly reduces the population of hetetotrophic bacteria in a batch culture (Lester *et al.*, 1979).

At 40^{o}C, there was no deoxygenation activity in the sample with lead concentration of more than 75mg/l.

Fig 6 shows the relationship between the lag time, λ and lead concentrations at temperature 35^{o}C. It was observed that as lead concentration increased, the lag time became smaller.

Fig 7 shows the effects of lead concentration and temperature on the lag time. It was evident that the minimum lag time occurred at a temperature of about 30^{o}C. It is probable that at about 30^{o}C, the temperature is optimal for growth of microorganisms. It was also evident that lag time increased sharply when temperature was raised to 40^{o}C particularly at higher lead concentrations.

Figs. 8 and 9 show the goodness of fit between the predicted and observed BOD rates at 35^{o}C and 40^{o}C respectively for lead concentrations of 50mg/l. It was evident that the predicted BOD rate compared favourably with the experimental data.

The values of BoD_u, k,& λat 35^{o}C were then substituted in Gompertz equation (Equation 1). The resulting model was obtained as

$$BoD_c = 243.95(1+c)^{-0.27}[\exp\{-\exp(0.0286(1+c)^{0.15})(—\lambda t)+1\}]$$

where c= concentration of lead

The efficiency R^2 of the model was found to be 0.95. The predicted and observed BOD rate are shown in Figs. 8 and 9.

Equation 5 was used to model the effect of temperature on the rate of deoxygenation. Based on this the optimum temperature was obtained from

$$Topt = E_2/R \ In[k(E_2/E_1-1)]$$

This was found to be in the range of 30-33^{o}C.

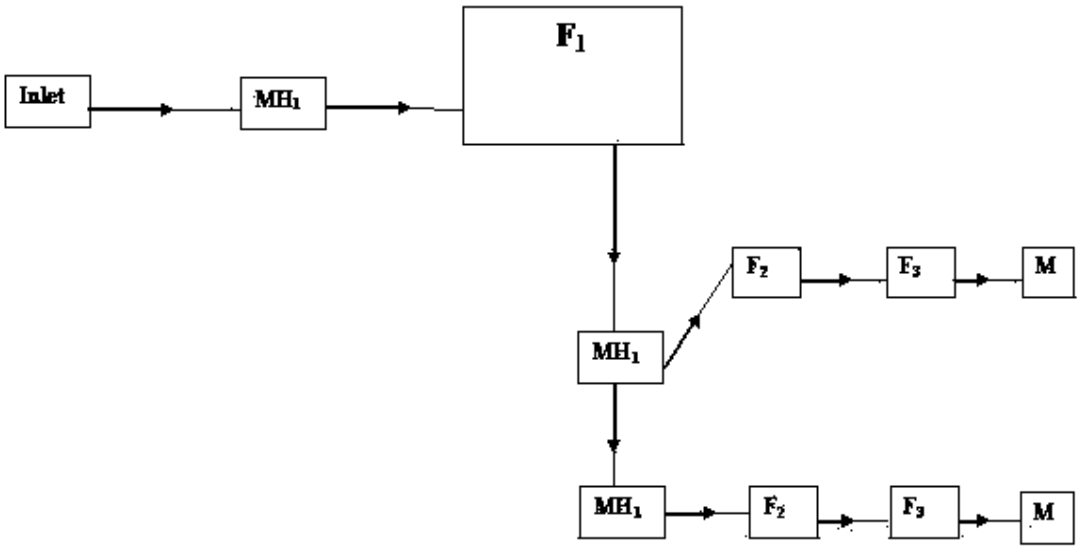

Figure 1: Schematic diagram of the waste stabilization ponds at the University of Dar-es-Salaam

MH_1, MH_2, MH_3 –manholes 1,2 and 3.
F1- primary facultative pond.
F2 & F3- secondary facultative ponds
M- maturation ponds.

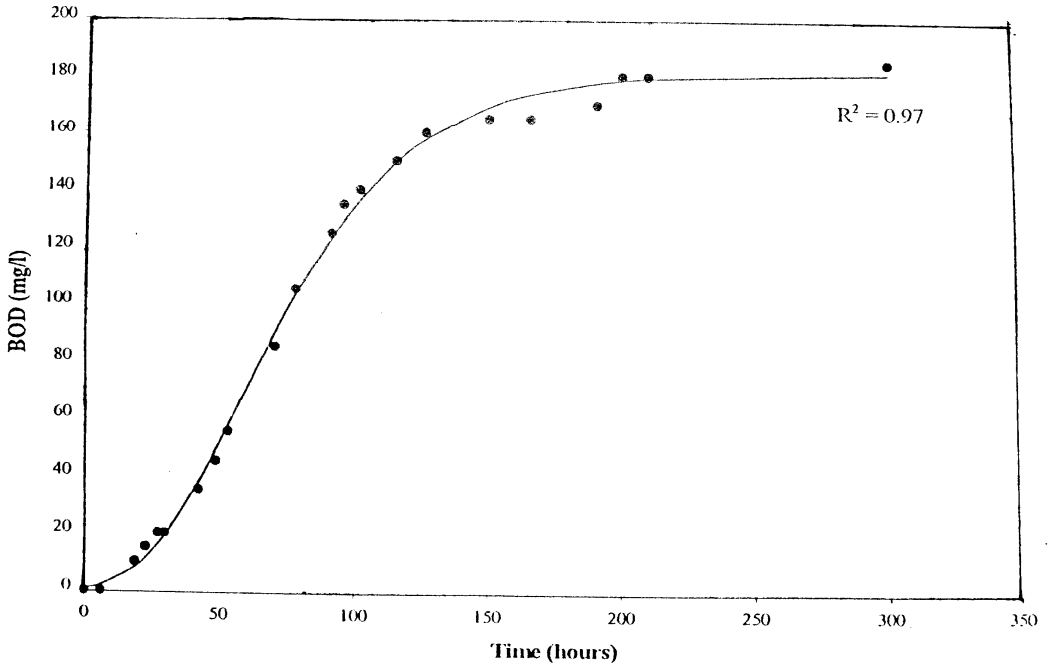

Figure 2: BOD at 25°C

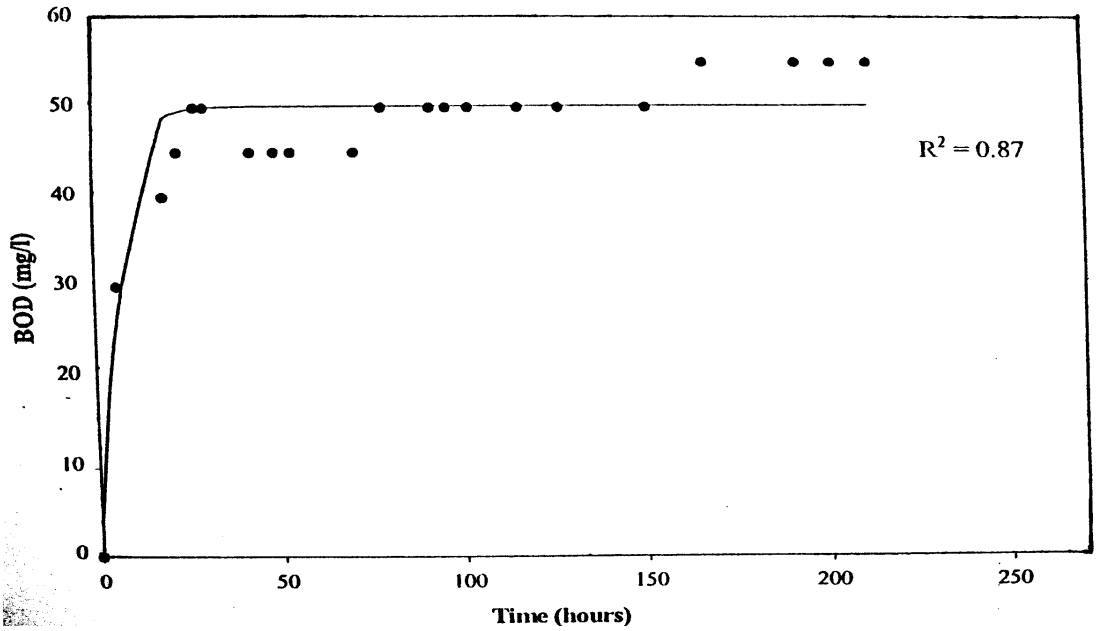

Figure 3: Effect of 125mg/l on BOD at 20°C

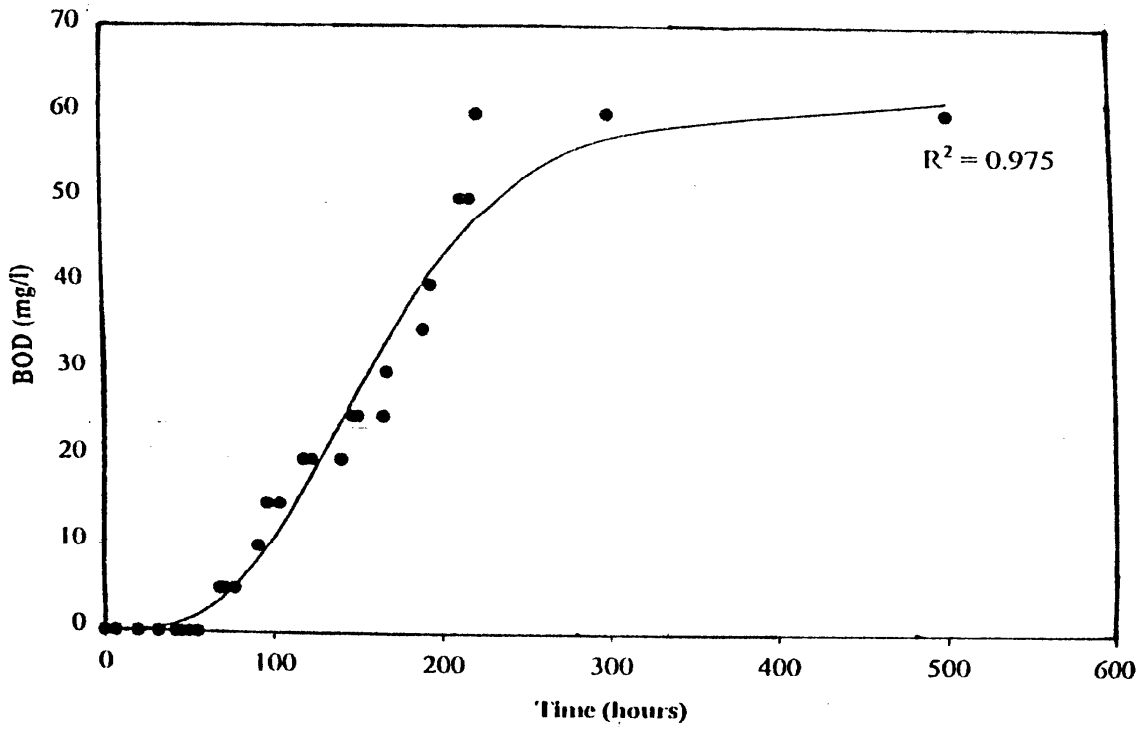

Figure 4: Effect of 30mg/l lead on BOD at 40°C

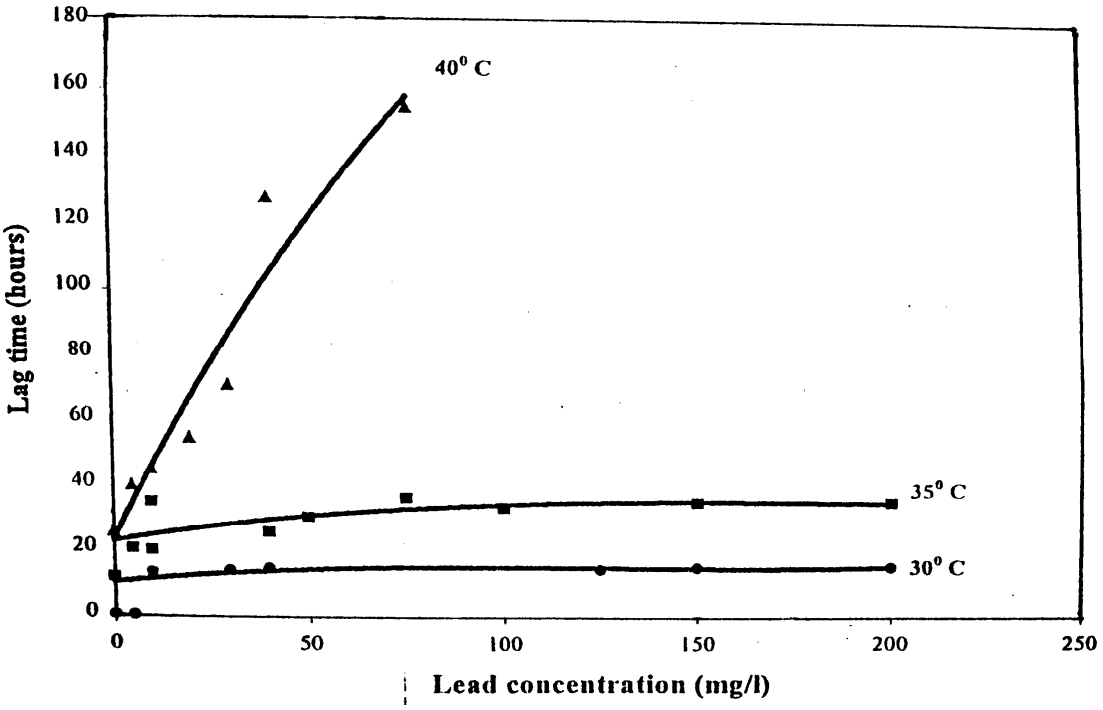

Figure 5: Lag time against lead concentrations at 30, 35 and 40°C

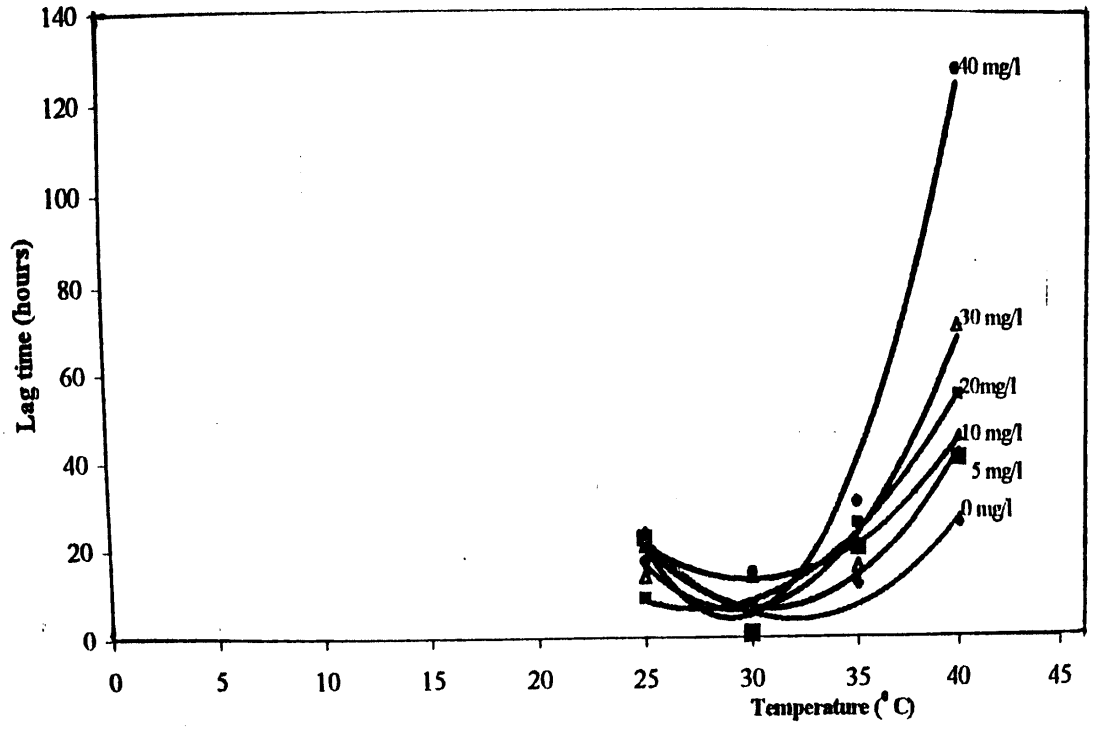

Figure 6: Lag time versus temperature at varying lead concentrations

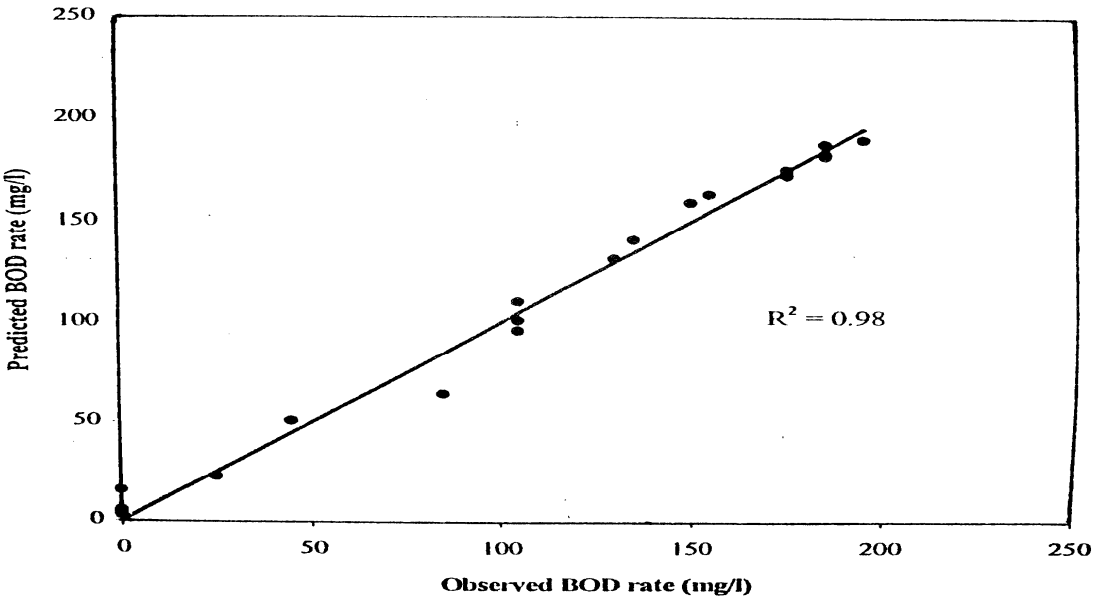

Figure 7: Scatter plot of the predicted versus observed BOD rate at 35°C and lead concentrations of 50mg/1

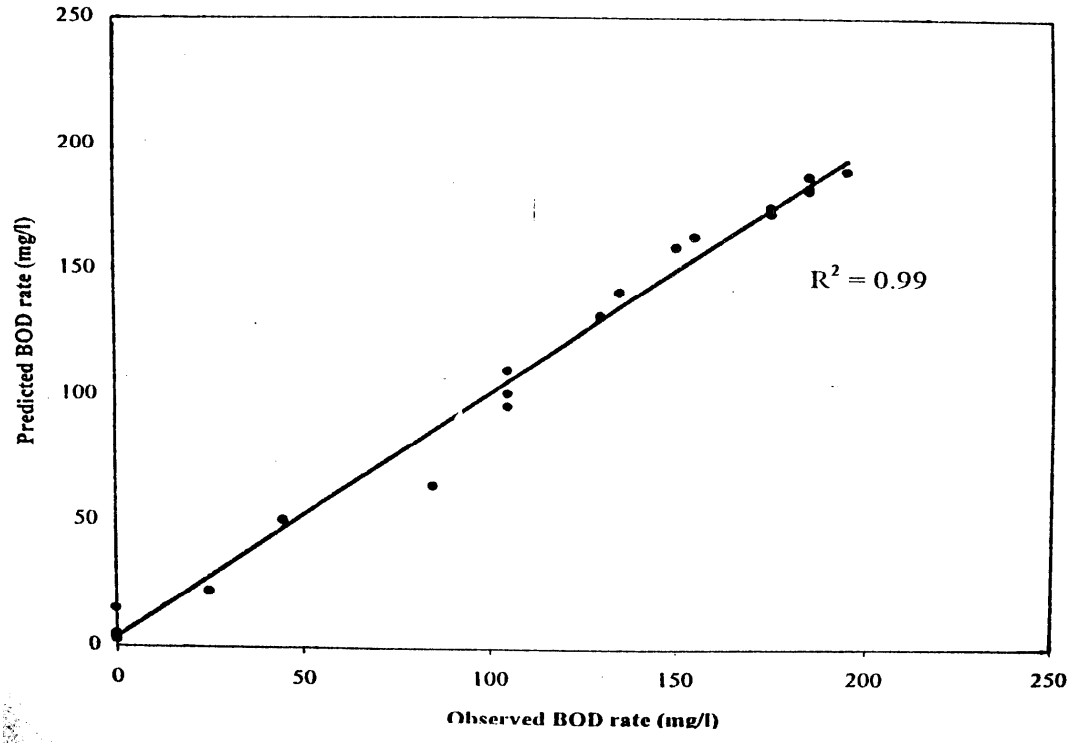

Figure 8: Scatter plot of the predicted versus observed BOD rate at 40°C and lead concentrations of 50mg/1

CONCLUSION

Biodegradation rate of organic wastes due to varying lead concentrations was investigated. The model below proposed for a temperature of 35°C is of the form:

$BoD_c = 243.95(1+c)^{-0.27}[\exp\{-\exp(0.0286(1+c)^{0.15})(—t)+1\}]$

The BOD rate predicted compared with the experimental data with a model efficiency of 95%. Due to increase in lead concentration, there was a decrease in ultimate BOD, and deoxygenation rate k and an increase in lag time λ during the initial stages of incubation.

The optimum temperature was determined to be in the range of 30.15-33.50°C.

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