Kinetics of Biological Reduction of Chemical Oxygen Demand from Petroleum Refinery Wastewater

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ABSTRACT: Petroleum refinery wastewater contains various hazardous contaminants which need to be removed before being discharged into the environment. Chemical oxygen demand (COD) is the parameter that measures the level of pollutants in wastewater. Biological method is one of the effective, cheaper and environmentally friendly methods of removing these pollutants. In this work, *Bacillus subtilis* and *Micrococcus luteus* isolated from Kaduna petroleum refinery, Nigeria, were employed in the COD reduction. *Bacillus subtilis* reduce COD by 82.9% while *Micrococcus luteus* reduced it by 76.5%. 76.5%. The COD reduction process from the refinery wastewater is described by Michaelis-Menten kinetics whereby it was initially zero order at high substrate concentration and then changed to first order at moderate to low substrate concentration. The rate constants for the COD reduction by *Bacillus subtilis* were 29.37 mg/l.d and 0.0654 d^{-1} for the zero order and first order regions respectively, whereas the reduction by *Micrococcus luteus* had constants 30.4 mg/l.d and 0.0.0776 d^{-1} for the zero order and first order regions respectively. This work showed that the two bacteria used have the potential to be utilized in COD reduction processes. [Researcher. 2009; 1(2): 17-23]. (ISSN: 1553-9865).

Key words: Biological; Chemical oxygen demand; kinetics; Petroleum Refinery

INTRODUCTION

Water is employed in the refinery processes for cooling system, distillation, hydro-treating, desalting, equipment flushing and tank drains (Abdulkarim *et al.*, 2005). Therefore, Wastewater released from petroleum and petrochemical industries contain hazardous substances due to the number of sources it came into contact with (Lentech, 2008; Hazardous substance research centers, U.S.A, 2003). The wastewater is characterized by presence of toxic organics (phenols, aromatics and polycyclic aromatics), heavy metals (lead, chromium and cadmium) and in-organics (sulphides) which need to be removed before discharge.

Biological treatment is preferred over physicochemical as the former is cost effective, efficient and environmentally friendly (Ojo, 2006). The wastewater may be treated by physicochemical or biological methods. The most rational way of decontamination of the environment loaded with petroleum derivatives is an application of methods based mainly on metabolic activity of microorganisms (Bogusiawska *et al.*, 2005). Bacteria that have prior exposure and adaptation to petroleum hydrocarbons exhibits higher biodegradation rate (Leahy and Colwell, 1990). Biotreatment is assessed by increase in biomass growth and reduction in the substrate. *Bacillus subtilis* and *Micrococcus luteus* have been found to have high biomass growth and substrate reduction among group of bacteria isolated from petroleum contaminated wastewater (Hamza *et al.*, 2008)

Chemical oxygen demand (COD) which measures the oxygen equivalence of the constituents in the wastewater is used as a measure of substrate composition (Tchobanoglous *et al.*, 2003). The COD and BOD are gross overall indicators of sewage composition and they therefore do provide a measure which relates to the potential environmental damage of a wastewater. Though, COD has advantage over BOD of being measurable in about 2 hours by conventional methods or in a few minutes using sophisticated instruments (Bailey and Ollis, 1986), if large amount of chemicals enter wastewater chemical reaction occur which consume large amount of oxygen (i.e high COD). On the other hand, if the oxygen level of water drops too much fish and other aquatic life may not survive (Wisconsin department of natural resources, 2006).

A variety of microbial growth and biodegradation kinetics models have been used for removing both organic and inorganic materials from aqueous solution. Such model allows the prediction of amount of chemicals that remain at a given time and the calculation of the time required to reduce chemicals to a certain concentration (Okpokwasili and Nweke, 2005). Knowledge of bio-kinetics is also essential for biological wastewater system design and optimization of operational conditions (Nakhla *et al.,* 2005). Biokinetic coefficients are usually obtained either by observing substrate depletion with time in batch experiments, and then fitting the data with an appropriate model or by respirometric studies (Morgenroth et al., 2002).

Sand bioreactors could achieve 90% COD removal from sanitary sewer overflow with peat having the lowest of 75% COD removal (Tao *et. al.,* 2007). Up-flow anaerobic sludge blanket reactor (UASB) reactor was demonstrated to have, COD removal efficiency of 75-85% at a Hydraulic Retention Time (HRT) of 5 days with an influent COD concentration of about 40 gL-1 and Organic Loading Rate (OLR) = 7-8 g CODL-1.d-1 (Sobhi *et al*., 2005). Many industrial wastewaters, including food processing wastes, invariably contain colloidal and particulate organics that undergo hydrolysis prior to biodegradation. Morgenroth et al. (2002) have reviewed the kinetic modeling of hydrolysis in municipal wastewater treatment and noted that the most widely used kinetic model was first order with respect to particulate substrate. Biodegradation kinetics of high oil and grease rendering wastewater was found to obey Monods and Haldane kinetic model (Nakhla, 2005).

This work is aimed at obtaining the kinetics of COD removal using bacteria in a suspended growth biological system.

MATERIALS AND METHODS

Sample Collection

The wastewater for this study was collected using sterile plastic containers at the bio-filter (unit for the removal of organic substrates) inlet of Kaduna Petroleum Refinery, Nigeria. The wastewater was preserved at low temperature before the commencement of the experiment.

Isolation and Identification of the Bacteria

The source *Bacillus subtilis* and *Micrococcus luteus* used in this experiment from the biofilter inlet and effluents wastewater samples of Kaduna Petroleum Refinery, Kaduna, Nigeria. The two bacteria were isolated by spread plate technique; they were further identified by their morphological features, gram reactions, motility, fermentation reactions and enzyme production (Hamza *et al.*, 2008).

Refinery Wastewater Treatment and COD Determination

The COD was determined by reactor digestion method (Hach Company manual, 2007). The wastewater samples (4.5 liters) were poured into two suspended growth plastic bioreactor (6.8 liters). Pure cultures of *Bacillus subtilis* and *Micrococcus luteus* were inoculated into the two bioreactors. Air was supplied into the bioreactor through a sparger. The biotreatment studies was conducted at room temperature (30-35 ^{0}C). The substrate removal was measured by monitoring the COD reduction at the interval of two days.

RESULTS AND DISCUSSIONS

The biomass growth was indicated by increase in the optical density of the cultured sample (Figure 1). The substrate consumption was measured by reduction in the chemical oxygen demand (Figure 2).

The two isolates were able to grow in wastewater cultured samples, this indicate their ability to be utilized substrates therein as source of nutrients (Oboh *et al.,* 2006). The optical density of *Micrococcus* increases from 0.12 to a maximum of 0.85 while that of *Bacillus subtilis* increases from 0.13 to 0.69. None of the bacterial culture exhibit lag phase (Figure 1). This could be attributed to their prior exposure and adaptation to petroleum contaminated environment (Leahy and Colwell, 1990). *Micrococcus luteus* exhibits all the other three phases (Figure 1): exponential, stationary and death phase. *Bacillus subtilis* exhibits only two phases (Exponential and Stationary). This could be due to the ability of *Bacillus* to form endospores which enables it to withstand deleterious conditions such as radiation, heat, cold and lack of nutrients (Lindquist, 2007).

The substrate consumption was indicated by the reduction in chemical oxygen demand (COD). The COD was reduced from 595 to 102 mg/l by *Bacillus subtilis* and it was reduced from 595 to 140 mg/l by *Micrococcus luteus* (Figure 2). It is obvious that the rate of COD removal is divided into rapid removal and moderate removal stage (Guan bao *et al*., 2003). The results showed that the two bacteria are capable of reducing the COD from refinery wastewater.

The kinetics of the COD reduction was determined by fitting the COD data trough different kinetic models. The data fitted into zero and first order kinetic models as shown in Figures 3 to 6.

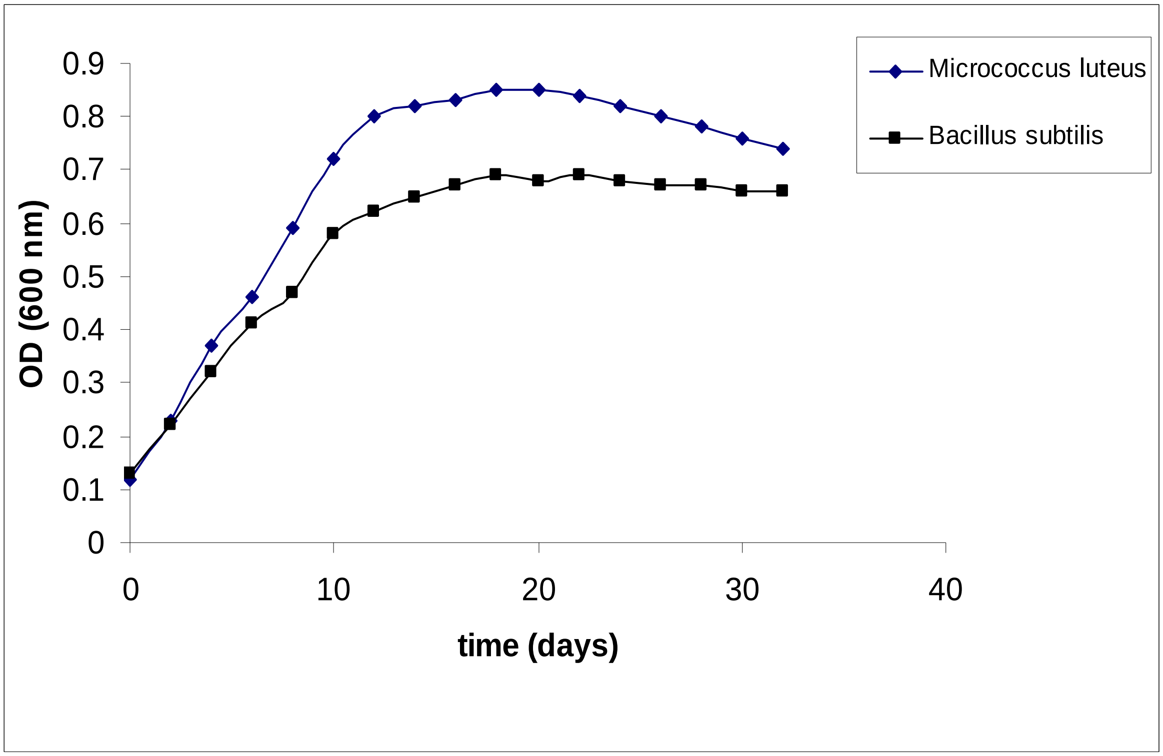

Figure 1: Growth Profile of *Bacillus subtilis* and *Micrococcus luteus* on Refinery Wastewater

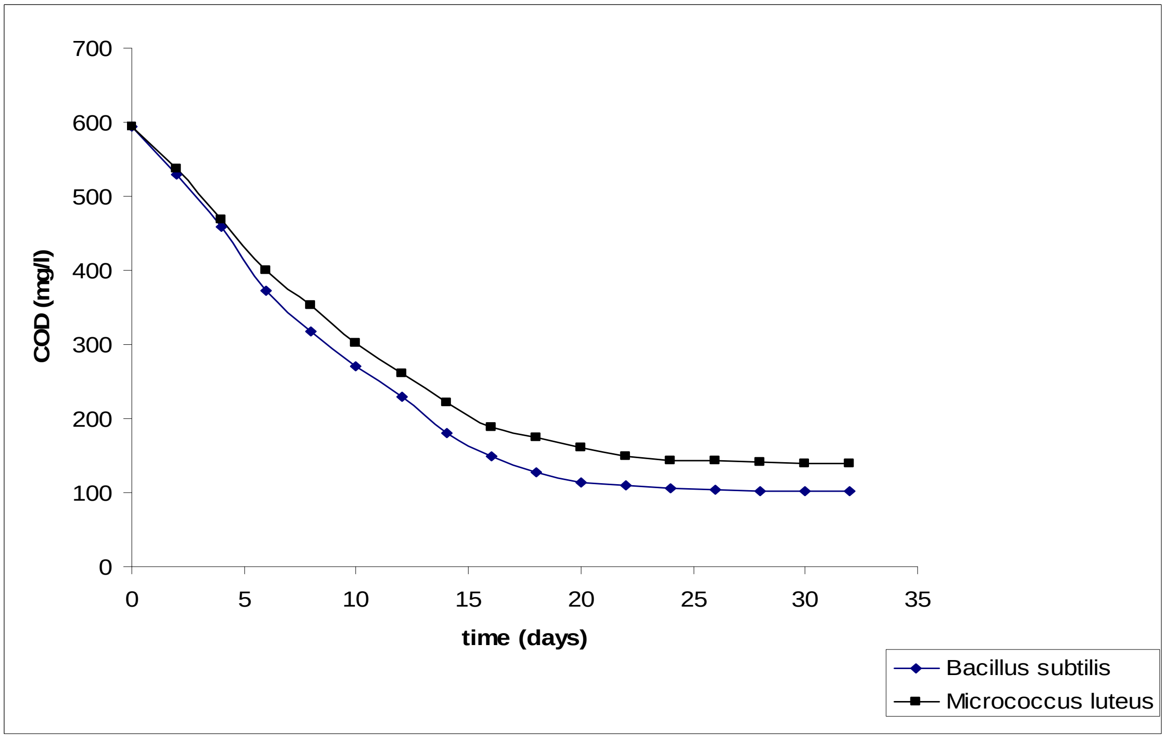

Figure 2: COD Reduction by *Bacillus subtilis* and *Micrococcus luteus*

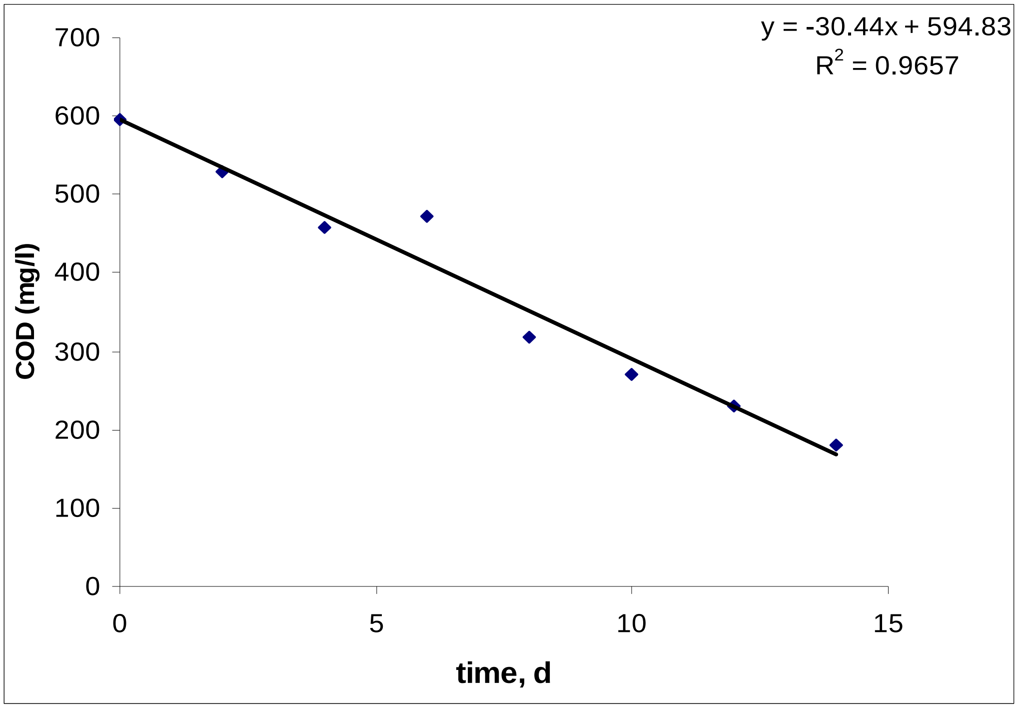

Figure 3: Testing Zero Order Kinetics for COD Removal by *Micrococcus luteus*

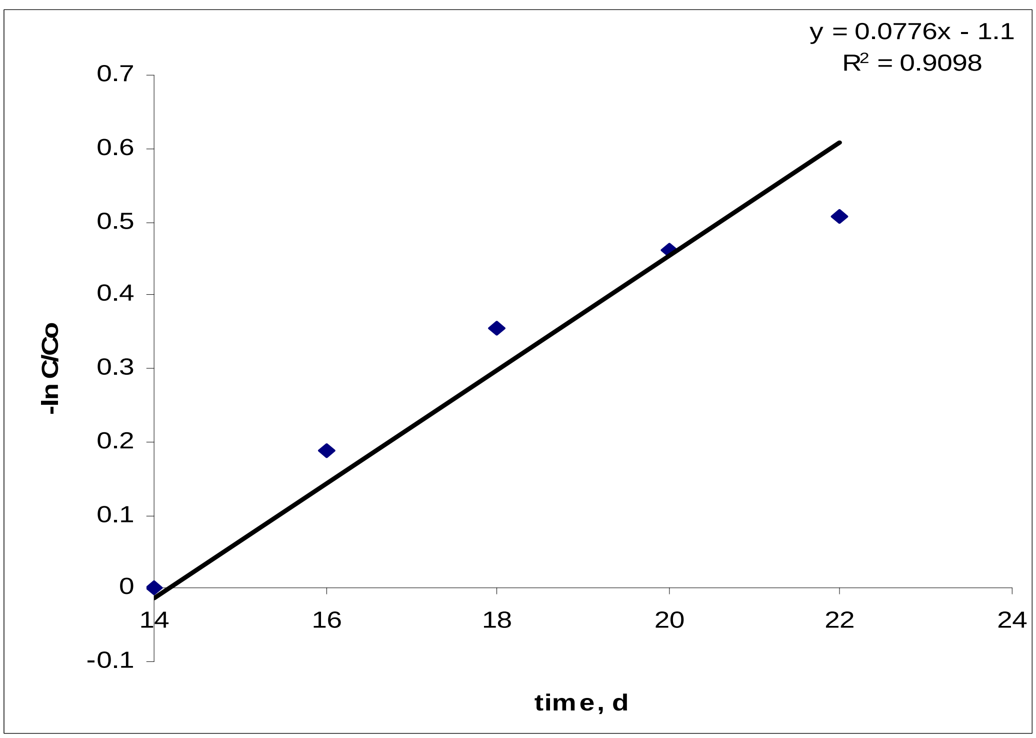

Figure 4: Testing First Order Kinetics for COD Removal by *Micrococcus luteus*

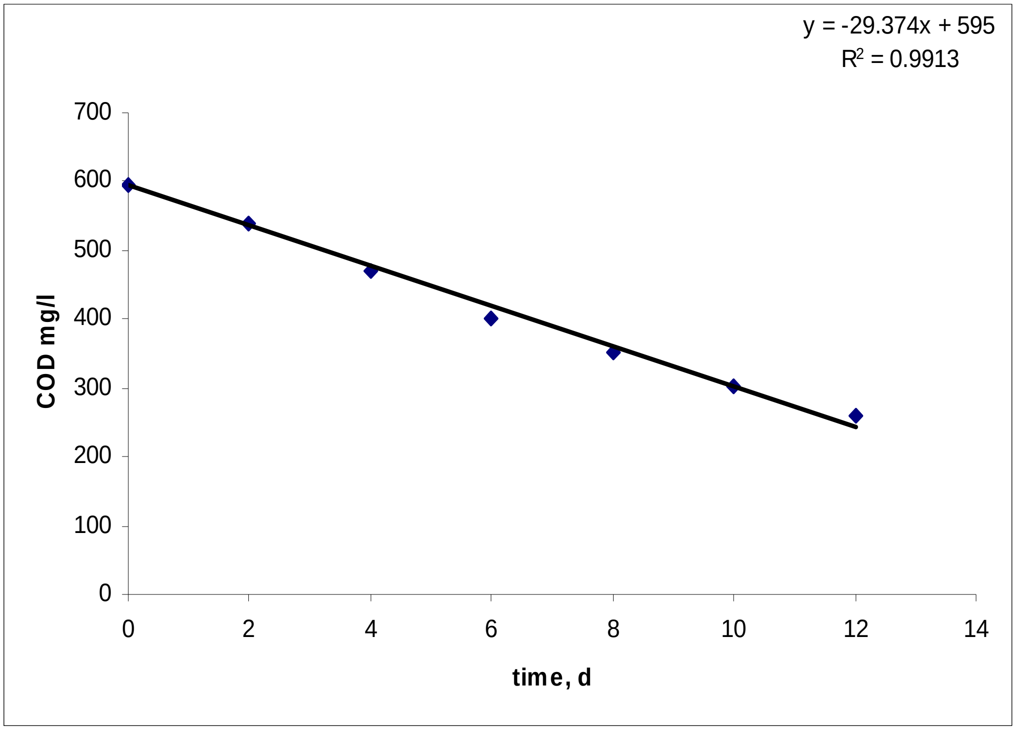

Figure 5: Testing Zero Order Kinetics for COD Removal by *Bacillus subtilis*

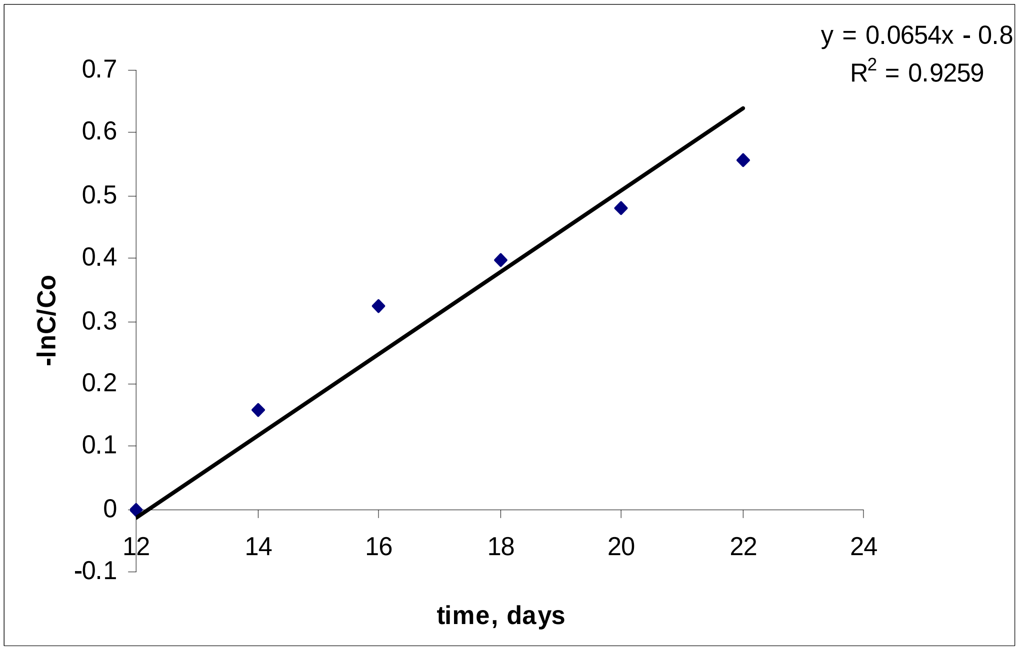

Figure 6: Testing First Order Kinetics for COD Removal by *Bacillus subtilis*

Micrococcus rate of COD removal is zero order from 595 to 181 mg/l (Figure 3), and then first order from 181 to 109 mg/l (Figure 4). *Bacillus subtilis* rate of COD removal is zero order initially at high substrate concentration (595 to 260mg/l) (Figure 5), and then first order subsequently at moderate to low COD concentration (260 to 149 mg/l) (Figure 6). It is obvious that the rate of COD removal is divided into rapid removal and moderate removal stage (Guan bao *et al*., 2003).

Substituting the value of the constants (rate constant, k and initial COD concentration, C_o) from the above plots into the integrated rate expression for zero order (equation 1) and for first order (equation 2), the kinetic models were obtained (Table 1)

$C = C_o - kt$ …………………………………………………………………………………………… 1

$C = C_o e^{-kt}$ …………………………………………………………………………………………… 2

Table 1: Summary of COD Removal Kinetic Models

Parameter	**Order**	
	Zero	**First**
COD removal (Micrococcus luteus)	594.8 – 30.4t	$181e^{-0.0776t}$
COD removal (Bacillus subtilis)	595.4-29.3745t	$260e^{-0.0654t}$

In all of the above cases, it can be observed that the rate of substrate reduction is zero order initially at high substrate concentration and then first order at low substrate concentration. This substrate reduction behaviour is exhibited by data that obeys Michaelis Meten kinetics (Okpowasili, 2005 and Levenspiel, 1999). The reason for this behaviour was because at high substrate concentration every site of the organism is saturated with the substrate that made the rate to be constant (i.e. zero order). As the substrate concentration decreased only few available site of the organism was covered and that made the rate of reaction to be proportional to the substrate concentration i.e. first order (waterloo, 2006).

CONCLUSIONS

From the results obtained, it showed that *Bacillus subtilis* and *Micrococcus luteus* have high ability to reduce chemical oxygen demand from refinery wastewater. The amount COD removal by *Bacillus subtilis* and *Micrococcus luteus* were respectively 82.9% and 76.5. The kinetics of the COD reduction obeys Michaelis Menten kinetics, meaning it is zero order at high substrate concentration and first order at low substrate concentration.

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