Nigerian Journal of Engineering
Faculty of Engineering
Ahmadu Bello University
Samaru - Zaria, Nigeria

Vol. 25, No. 2, Dec. 2018
ISSN: 0794 - 4756

CHEMICAL OXYGEN DEMAND REDUCTION KINETICS IN CO-DIGESTION OF MUNICIPAL SOLID WASTES WITH COW DUNG

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ABSTRACT
This work investigated the use of laboratory batch anaerobic digester to derive chemical oxygen demand (COD)reduction kinetic parameters for anaerobic co-digestion of the organic fraction of municipal solid waste (OFMSW) with cow dung (CD) by mixing the substrates to achieve optimum carbon to nitrogen ratio (C/N) of 30:1 for a hydraulic retention time of 18 days at ambient mesophilic temperature of 37°C and pH of 6.9.A consortium of Staphylococcus aureus Bacillus species, Micrococcus, Pseudomonas aureus, Streptococcus and Escheria coli isolated from the OFMSW and Coliform, Staphylococcus aureus, salmonella, Streptococcus, Bacillus species and Escheria coli isolated from CD were employed in the COD reduction. Co-digestion of OFMSW and CD reduce COD by 86.47% while OFMSW reduced it by 61.3%. The COD reduction process is described by Michaelis-Menten kinetics. The rate constants for the COD reduction by Co-digestion of OFMSW and CD were –239.21 mg/L.day and 0.1315/day for the zero order and first order regions respectively, whereas the reduction by OFMSW alone had constants -36.01 mg/L.day and 0.0567day-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.
Keyword: *Chemical oxygen demand, Anaerobic, Co-digestion, Kinetics, Digester.*

INTRODUCTION
The organic fraction of municipal solid wastes and other easily biodegradable solid substrates (e.g., agro-waste) have to be conveniently treated to reduce their environmental impact and to recover energy and material while massive disposal treatments (e.g., landfill or incineration) should be avoided. An obvious choice to achieve this goal is given by the anaerobic digestion andco-digestion processes for methane production. Anaerobic fermentation is an effective bioprocess for the production of volatile fatty acids and other low weight organic compounds such as alcohols or lactic acid (David, *et al.,* 2005).

These can then be used for the production of methyl-and ethyl-esters to be added to gasoline because of their high octane number (between 103 and 118), as a low-cost external carbon source for the production of biopolymers, like poly-hydroxyl-alkanoates, for sustainment of the biological processes for nutrients removal in wastewater treatment plants, or, still, for anaerobic fermentation with a high hydrolysis rate being the first step of the anaerobic digestion process for biogas production when treating organic wastes with a high biodegradability (David, *et al.,* 2005).

Anaerobic digestion (AD) is a bacterial fermentation process that operates without free oxygen and results in a biogas containing mostly methane and carbon dioxide. It occurs naturally in anaerobic niches such as marshes, sediments, wetlands, and the digestive tracts of ruminants and certain species of insects. AD systems are employed in many wastewater treatment facilities for sludge degradation and stabilization, and are used in engineered anaerobic digesters to treat high-strength industrial and food processing wastewaters prior to discharge (Joshua *et al.,* 2008). There are also many instances of AD applied at animal feeding operations and dairies to mitigate some of the impacts of manure and for energy production. According to Joshua *et al.* (2008), AD of municipal solid waste (MSW) is used in different regions worldwide to reduce the amount of material being land filled, stabilize organic material before disposal in order to reduce future environmental impacts from air and water emissions and to recover energy.

Singh and Singh (2012) reported that the COD test is commonly used to indirectly measure the amount of organic compounds in waste; they also observed that COD is a useful measure of waste degradation rate. The COD also provide a measure which relates to the potential environmental damage of a wastewater; if large amount of chemicals enter wastewater, chemical reaction occur which consume large amount of oxygen (high COD), if the oxygen in the water is depleted too much aquatic life may not survive Hamza *et al.* (2009). Agulanna *et al.* (2012) used the Fenton's reaction model based on leachate COD reduction in first order kinetics, to determine the rate of reaction (k) which was taken as a measure of the rate of biodegradation of OFMSW.

The aim of this work is to derive COD reduction kinetic parameters for anaerobic co-digestion of the organic fraction of municipal solid waste (OFMSW) with cow dung.

Rapidly biodegrade putriscible organic fraction of municipal solid wastes (OFMSW) using readily available nutrients in cattle dung (CD) and the microbes in putrescible as reagents.

DIGESTION PROCESS DESCRIPTION
The anaerobic digestion of organic material is accomplished by a consortium of microorganisms working synergistically. Digestion occurs in a four-step process: hydrolysis, acidogenesis, acetogenesis, and methanogenesis.
1. Large protein macromolecules, fats and carbohydrate polymers (such as cellulose and starch) are broken down through hydrolysis to amino acids, long-chain fatty acids, and sugars.

2. These products are then fermented during acid genesis to form three, four, and five-carbon volatile fatty acids, such as lactic, butyric, propionic, and valeric acid.
3. In acetogenesis, bacteria consume these fermentation products and generate acetic acid, carbon dioxide, and hydrogen.
4. Finally, methanogenic organisms consume the acetate, hydrogen, and some of the carbon dioxide to produce methane. Three biochemical pathways are used by methanogens to produce methane gas.

The pathways along with the stoichiometries of the overall chemical reactions are:
a. Acetotrophicmethanogenesis: $4CH_3COOH \rightarrow 4CO_2 + 4CH_4$
b. Hydrogenotrophicmethanogenesis: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
c. Methylotrophicmethanogenesis: $4CH_3OH + 6H_2 \rightarrow 3CH_4 + 2H_2O$

Methanol is shown as the substrate for the methylotrophic pathway, although other methylated substrates can be converted. Sugars and sugar-containing polymers such as starch and cellulose yield one mole of acetate per mole of sugar degraded. Since acetotrophicmethanogenesis is the primary pathway used, theoretical yield calculations are often made using this pathway alone.

MATERIALS AND METHODS

Sample Collection and Preparation

Municipal Solid Wastes (MSW) was collected from central dumpsites located in communities around the Ahmadu Bello University, Zaria, Nigeria following the guidelines of Sampling Methodology by ASTM International (2011). The MSW was sorted, mixed and blended properly as described by Carboo and Forbil (2005).The CD was collected from the National Animal Production Research Institute (NAPRI), Shika, Kaduna State, Nigeria.

Identification and Isolation of the Bacteria

The identification of the inherent microbes in the samples was conducted at the Department of Microbiology, ABU, Zaria, Nigeria. Standard spread-plate dilution method described by Ogunmwonyi *et al.* (2008) was adopted to identify the microbial contents of the OFMSW and the CD. Each sample was mixed, and a suspension of one gram (dry weight equivalent) in ten millimetres of sterile water was prepared. 1 ml of the suspension was then diluted serially (ten-fold). To inhibit fungi growth, nutrient agar containing 0.015% (w/v) nystatin was used for bacteria isolation and incubation at 37^oC for 24 hours.

Physico-Chemical Analyses of OFMSW

The shredded OFMSW sample was analyzed for various physical, chemical and biological characteristics and the parameters observed are shown in Table 1.

Experimental

A total of three biodigesters each of 4litres working volume were constructed as adopted and modified from Bayard *et al.* (2005).Three layers of heat-insulating materials were employed to prevent loss of conductible heat as adopted and modified from Li *et al.* (2009). A valve was placed at the bottom of the reactor to collect the leachates. The digesters were also equipped with a layer of gravel and a wire mesh at the bottom for leachate collection and to prevent waste saturation and a layer of wire mesh at the top of the digester for the homogenous escape of the gases from the top as adopted from Bayard *et al.* (2005). Two perforations were made on the cover of the digester through which the gas hose and thermometer were tightly fixed. The gas delivery tubing was made to pass the evolved gas from the digester into an inverted 250 ml graduated gas jar cylinder filled with saline water. The gas cylinder was held in position in a trough containing the saline water by a clamp mounted on a retort stand; the setup is shown in Figure 1.

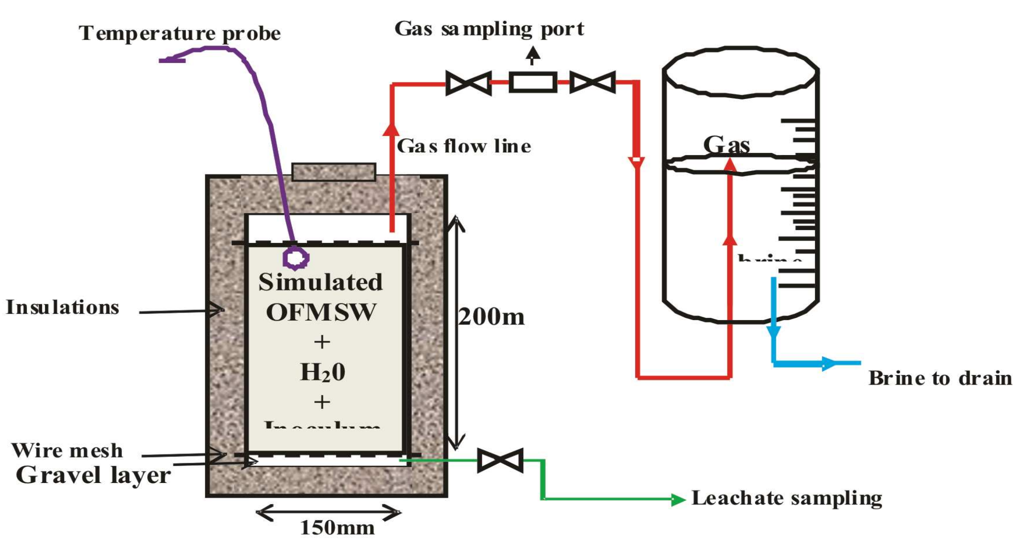

Figure 1: Experimental set-up adapted and modified from West *et al.* (1998)

COD Determination

Measurement of leachate COD was conducted at the Department of Chemical Engineering, ABU, Zaria, Nigeria using the dichromate method by utilising the closed reflux, 5220C, titrimetric method as described in the Standard Methods for Examination of Water and Wastewater; APHA, AWWA, WEF (2012). The substrate removal was measured by monitoring the COD reduction at the interval of two days.

RESULTS AND DISCUSSION

Table 1**:** Physicochemical properties of simulated organic fraction of municipal solid wastes and cattle manure

S/No.	PARAMETERS	OFMSW	CATTLEDUNG
	Particle size	1-2 mm^2	1-2 mm^2
	Bulk density: (kgm^{-3})	342.73	-
	pH	6.47	7.63
	Moisture content (wet weight) (%)	47.06	52.7
	Moisture content (dry weight) (%)	67.3	ND
	Total solid (wet weight) (%)	52.94	30.0
	Total solid (dry weight) (%)	32.7	NIL
	Volatile solids (%)	92.9	NIL
	Ash (%)	7.1	NIL
	Total organic carbon, C (%)	46.1	37.2
	Total hydrogen (%)	5.9	NIL
	Total oxygen (%)	39.5	NIL
	Total Nitrogen (%)	1.02	2.86
	Total sulphur (%)	0.2	0.04
	Available phosphorus, P (%)	0.20	0.52
	C/N	45:1	13:1
	Ca (%)	0.55	NIL
	Mg (%)	0.20	NIL

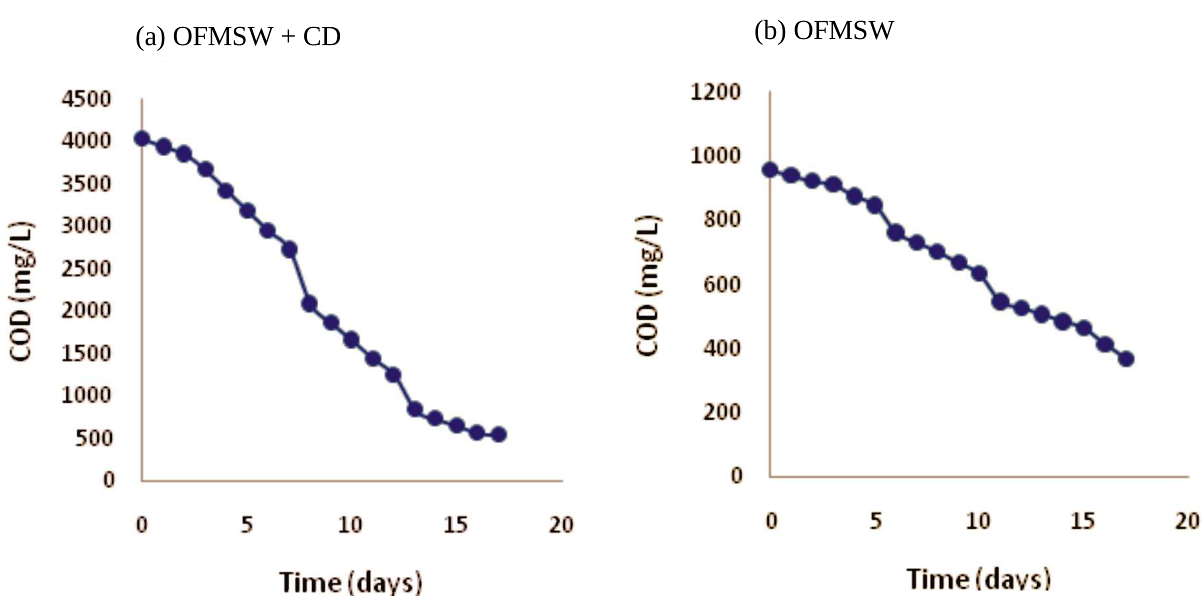

Figure 2: COD reduction by OFMSW/CD and OFMSW systems

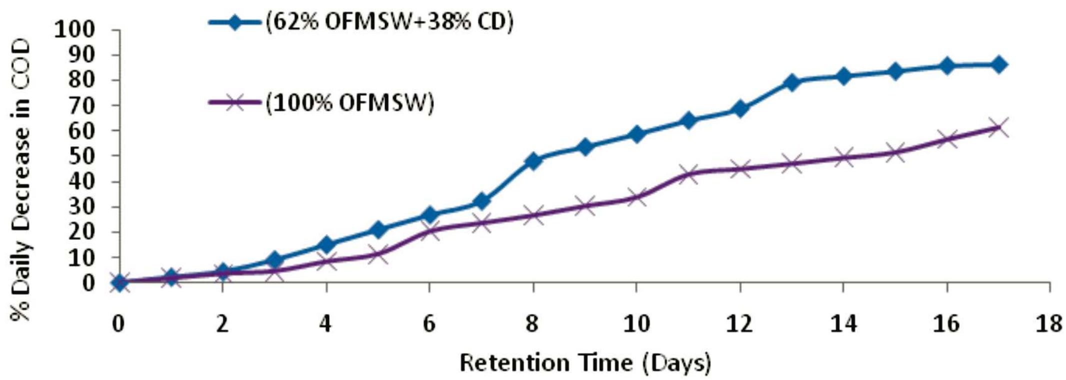

Figure 3: Daily % reduction in leachate COD

Figure 2a and 2b shows the COD reduction by OFMSW/CD and OFMSW systems respectively; the reduction in the chemical oxygen demand gives an indication of the substrate consumption (Hamza *et al.*, 2009). The two profiles show a similar trend with Figure 2a showing a steep slope indicating rapid degradation of the substrate because of the addition of CD.

Figure 3 shows the daily COD percentage reduction profiles. It can be seen that from day "0" to day "2", there was no significant change observed, probably the bacteria are adapting to the environment, in what was called lag phase, (Yates and Smotzer2007). Afterwards, the rate of COD removal was more with the CD enhanced system; at day 10 for instance the percentage removal for OFMSW/CD and OFMSW were 59 and 34% respectively. Similarly, at day 15, the removal were 84 and 52% respectively. The bacterial consortium in both samples under investigation exhibit lag and exponential phases but the stationery phase can only be visualised for the mixed substrate i.e. 62% OFMSW & 38% CD. In general the curves are similar to those obtained by Surajudeen and Mustapha (2015)

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 4 to 7.

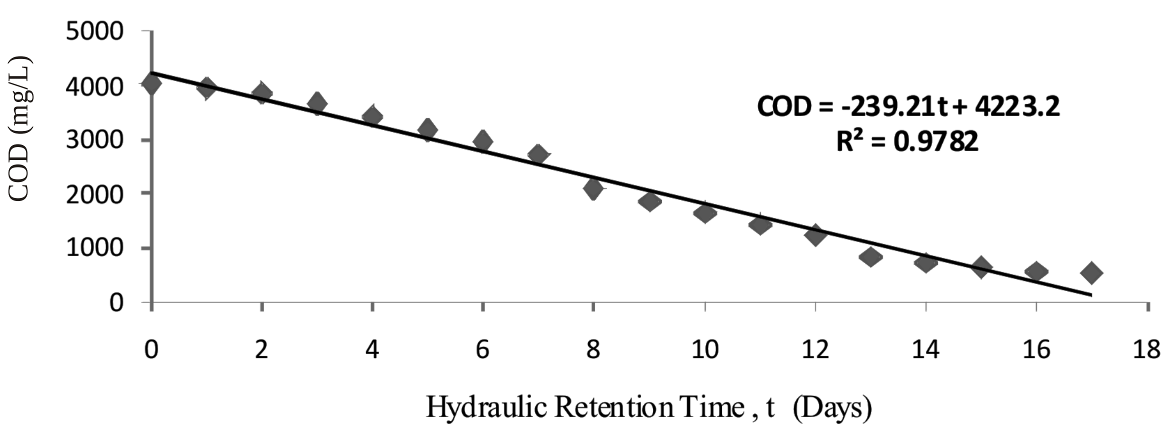

Figure 4: Testing zero order kinetics for COD (OFMSW with CD)

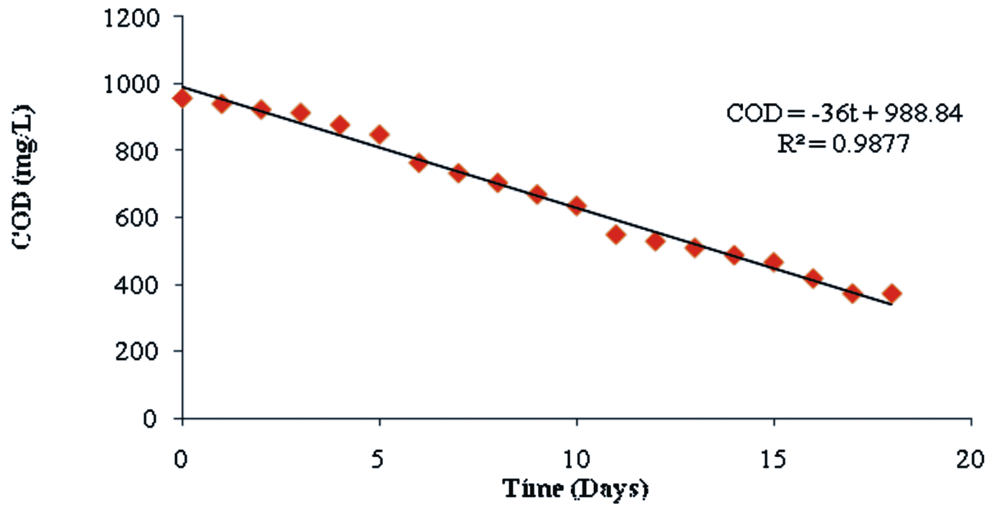

Figure 5: Testing zero order kinetics for COD (OFMSW)

Figures 4 and 5 shows zero order kinetics for OFMSW/ CD and OFMSW respectively, the constant, k_o, was found to be -239.21 and -36 mg/L.day for OFMSW/CD and OFMSW respectively. Since the more negative the value of k_o, the faster the rates of removal of the biodegradable fractions (Tsunatu 2014), it showed that the biodigester with the fastest reaction was the enhanced OFMSW/CD while the slowest was the control, OFMSW.

This finding is in agreement with reports from Hamza *et al.* (2009) who reported that the reaction is zero order at high substrate concentration and first order at low substrate concentrations and (Jeremy *et al.*, 2002) who explained that at high substrate concentration every site of the organism is saturated with the substrate that made the rate to be constant, that is zero order and that 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 which is first order.

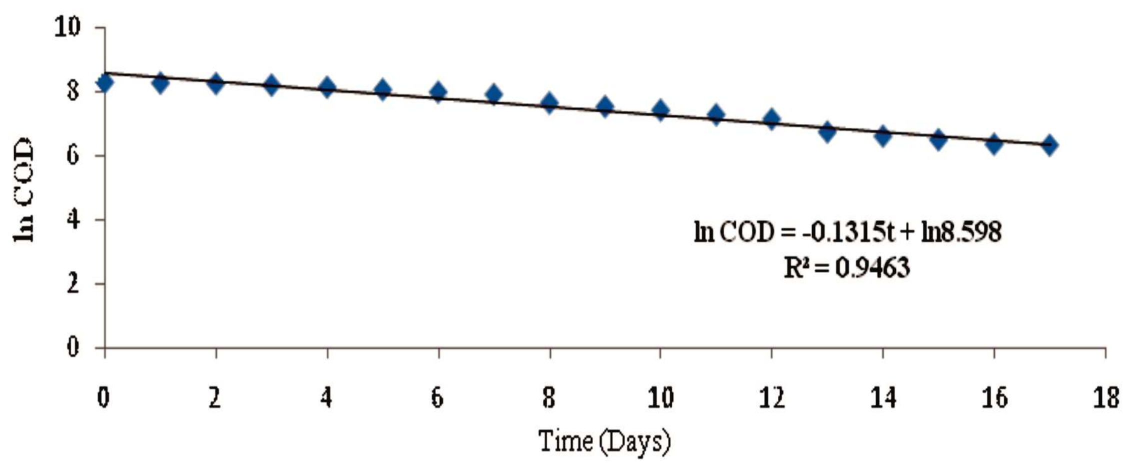

Figure 6: Testing fenton's first order kinetics for OFMSW/CD

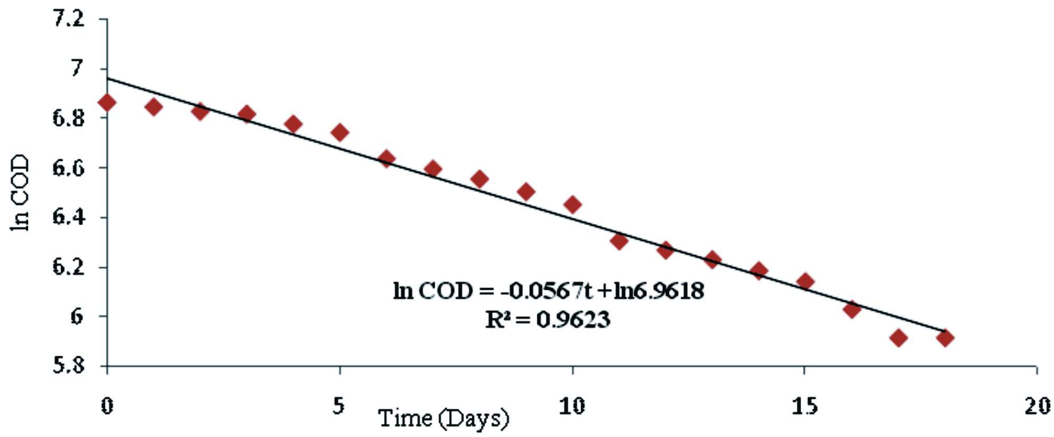

Figure 7: Testing fenton's first order kinetics for OFMSW

Figures 6 and 7 shows first order Kinetics for OFMSW/ CD and OFMSW respectively, the rate constant, k_1, was found to be -0.1315 and -0.0567mg/L.day for OFMSW/CD and OFMSW respectively. Since the more negative the value of k_1, the faster the rates of removal of the biodegradable fractions (Tsunatu 2014), it showed that the biodigester with the fastest reaction was the enhanced OFMSW/CD while the slowest was the control, OFMSW.

The slope of the plots of lnCOD against time is a linear graph with the slope representing the rate constants k_1 while the intercept on the vertical axis represents lnCOD at time zero. The more negative the value of k_1, the faster the rates of removal of the biodegradable fraction while the more positive the value of k_1, the slower the rate of removal of biodegradable fractions as reported by Yusuf *et al.* (2011). It can be inferred that the rate of COD removal is divided into rapid removal and moderate removal stage (Guan bao *et al.*, 2003).

In all of the above cases, it can be observed that the rate of substrate (COD) reduction is zero order initially at high substrate concentration and then first order at low substrate concentration. This substrate reduction behaviour is exhibited by the data obtain obeys MichaelisMenten kinetics (Gujjala *et al.*, 2016and Okpowasili, 2005).

Table 2: A Summary of the COD Removal Kinetic Models

Digester	Zero Order		First Order	
	Kinetic Model	R^2	Kinetic Model	R^2
OFMSW/CD	$COD = 4223.2 - 239.21t$	0.9877	$lnCOD = 8.5980 - 0.1315t$	0.9463
OFMSW	$COD = 988.84 - 36.00t$	0.9877	$lnCOD = 6.9618 - 0.0567t$	0.9623

CONCLUSIONS

It can be concluded from the results obtained that OFMSW/CD system exhibit the highest capability in chemical oxygen demand (COD) removal. The COD removals by OFMSW/CD and OFMSW were 86% and61% respectively. The kinetics of the COD reduction obeys MichaelisMenten kinetics, meaning it is zero order at high substrate concentration and first order at low substrate concentration. All the plots showed very good R^2 values ranging from 0.9463 to 0.9877.

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