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RELATIONSHIP BETWEEN BOD/COD RATIO AND OCTANOL/WATER PARTITION COEFFICIENT FOR GLUCOSE, LACTOSE, SUCROSE, FORMALDEHYDE, ACETIC ACID AND OXALIC ACID

Latifa Mirzatika Al-Rosyid and Sarwoko Mangkoedihardjo*
Department of Environmental Engineering, Institut Teknologi Sepuluh Nopember (ITS), Surabaya, Indonesia
*Corresponding author

ABSTRACT

The purpose of this study was to obtain a relationship between the ratio of BOD/COD and partition coefficient octanol/water (Pow) for glucose, lactose, sucrose, formaldehyde, acetic acid and oxalic acid. This relationship was supported by the toxicity test of each organic material on fish. The results show that the lower the BOD/COD ratio, the higher the Pow coefficient, which means more organic matter leads to biomass. Among the organic materials studied, formaldehyde has the lowest BOD/COD ratio (<0.1) and highest Pow (>4) and was supported by the results of its toxicity in fish having the lowest LC-50 (24 mg/L). Whereas lactose has the highest BOD/COD ratio (>0.9) and lowest Pow (<0.7) with the highest LC-50 (851 mg/L). The rest of the organic substances have characteristics in the range of lactose and formaldehyde.

Keywords: BOD/COD Ratio, Octanol/Water Partition Coefficient, Organic Matter, Toxicity test.

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1. INTRODUCTION

The use of fossil fuels in various activities and energy industry release various of organic matter. The more amount of organic matter in the water, the more difficult it will be in

management because some substances are difficult to be broken down by microorganisms in the water. The quality of wastewater containing organic matter can be expressed as Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD). Both of these parameters represent many variations of compounds that can be formed in line with the development production of organic compounds. In line with the quantity complexity, organic matter has the complexity of the quality of wastewater (Zaman et al, 2017). The BOD/COD ratio indicates biodegradability of wastewater, the higher the ratio, the lower the biodegradability of waste water (Papadopoulos *et al*, 2001). The substance tendency to produce bioconcentration is related to its persistence and its lipophilic properties as measured by the octanol/water partition coefficient (Pow). Pow is used to determine the tendency of a substance, whether to water or biota. Analysis of BOD_5, COD and Pow was used to determine the quality status of organic matter (acceptable, biodegradable and non-biodegradable) to the relationship between BOD_5, COD and Pow at different concentrations and classes of compounds, aliphatic and aromatic. The results of the study were verified by toxicity tests LC_{50}-96h on *Brachydanio rerio* (zebrafish).

Organic substances used in this study are: Glucose, Lactose, Sucrose, Formaldehyde, Acetic Acid, and Oxalic Acid. It is based on the exposure level of the six organic substances, because it is often used, so it wasted much into the environment. Pow is the partition coefficient of n-octanol and water, which represents the ratio of substances entering the organic carbon phase and the water phase. Solubility, absorption characteristics, and organic biodegradability have empirically correlated with octanol water partitioning. Octanol is a chemical that is used as a representation of biota according to the European Standard. The relationship between Pow and BOD/COD ratio has never been studied.

This research was conducted to obtain quality status of organic matter on the relationship between BOD/COD ratio and Pow at different concentrations and classes of compounds, namely aliphatic and aromatic and to carry out toxicity test using *Brachydanio rerio* as verification results of laboratory analysis.

2. MATERIALS AND METHODS

2.1. Analysis of BOD_5, COD dan Pow.

Analysis of BOD_5 uses the Winkler method. The principle is using iodometric titration. COD analysis was carried out with closed reflux spectrophotometry and Analysis of water octanol (Pow) partition coefficient using gas chromatography. In this study using 3 variations of concentration namely 10 mg/l, 100 mg/l and 1000 mg/l, with each of three repetitions. This is because the potential of a substance will move. It can be different for BOD_5 and COD status at different concentrations.

2.2. LC_{50}-96h Toxicity Test on *Brachydanio rerio*

Toxicity tests were carried out as a verification of theoretical concentration based on the results of laboratory analysis as an implementation of this research on organisms. *Brachydanio rerio* is used as a representation of freshwater organisms in toxicity tests. *Brachydanio rerio* is commonly used in ecotoxicological studies, because the biological and reproductive properties of zebras (short generation intervals and spawning) are suitable as test fish for toxicological research (Meinelt *et al*, 2000).

In each series, in addition to the control tank, the concentration of substances is set from the lowest to the highest concentration. Static test design is used to compare the concentration of various substances. In a static flow system, the organism is immersed in a medium/silent

solution with varying concentrations of substances used throughout the duration of exposure, which is 96 hours. In this study 3 concentrations were used with 1 control tank, namely C0 (control tank without substance) = 0 mg / l; C1 = 10 mg / l; C2 = 100 mg / l; and C3 = 1000 mg / l with 6 types of organic substances namely Glucose, Lactose, Sucrose, Formaldehyde, Acetic Acid and Oxalic Acid with a total series of 24 tanks. Each contains 10 fish (USEPA, 2002). The LC50 toxicity test results can be accepted if 90% of the test animals in the control at the end of the observation are still alive (OECD, 1992).

Determination of LC50 value was carried out using probit analysis (Conell dan Miller, 1995). Probit analysis is commonly used in toxicology to determine the relative toxicity of organic substances for living organisms. This is done by testing the response of organisms below the various concentrations of each of these organic substances and then comparing the concentration until the results are obtained (Vincent, 2008). The relationship of the logarithmic value of the concentration of the test material with the probit value of the percentage mortality of the test animal is a linear function of $y = a + bx$ (Hendri *et al*, 2010).

3. RESULTS AND DISCUSSION

3.1. Correlation Retween BOD/COD Ratio and Pow

By looking at the overall results of the analysis of BOD and COD, the tendency of aliphatic organic substances namely Glucose, Lactose and Sucrose, is biodegradable and the tendency of aromatic groups namely Formaldehyde, Acetic Acid and Oxalic Acid, is non-biodegradable (Table 1). Comparison of very low BOD and COD is <0.01 indicating that the incoming organic pollutants are difficult to decompose (non-biodegradable). For the acceptable category, only Lactose is present at a concentration of 10 mg/l which is equal to 0.925.

The results showed that organic matter with the smallest BOD/COD ratio was formaldehyde at 0,082 at a concentration of 1000 mg/l so that it was included in the non-biodegradable category. Organic substances with the highest BOD/COD ratio are lactose of 0,797 at a concentration of 100 mg/l so that it is included in the biodegradable category. Large BOD and COD values indicate that the substance has enough carbon to degrade. Formaldehyde is a strong and accumulative reducing agent. This can reduce the activity of microorganisms (Cahyadi, 2008). Lactose is a disaccharide consisting of glucose and galactose composed of β-D-galactose and α-D-glucose molecules that are linked by 1,4′-β bonds, which are carbon sources for microorganisms (Solomons, 2002).

Table 1. Biodegradability Level of Organic Substances

Organic Matter	Concentration (mg/l)	BOD/COD Ratio	Pow	Biodegradability
Lactose	10	0.925	0.66	biodegradable
	100	0.797	0.68	biodegradable
	1000	0.780	0.77	biodegradable
Sucrose	10	0.774	0.69	biodegradable
	100	0.617	0.74	biodegradable
	1000	0.519	1.35	biodegradable
Glucose	10	0.662	0.67	biodegradable
	100	0.503	0.73	biodegradable
	1000	0.422	1.06	biodegradable

Acetic Acid	10	0.258	0.68	non-biodegradable
	100	0.200	1.06	non-biodegradable
	1000	0.178	1.58	non-biodegradable
Oxalic Acid	10	0.329	1.07	non-biodegradable
	100	0.144	1.53	non-biodegradable
	1000	0.103	2.33	non-biodegradable
Formaldehyde	10	0.174	0.71	non-biodegradable
	100	0.145	2.39	non-biodegradable
	1000	0.082	4.54	non-biodegradable

The Pow value of the six types of organic matter studied, showed a tendency to biomass. For non-biodegradable organic substances, namely Formaldehyde, Acetic Acid and Oxalic Acid, more concentrated towards biomass. This is because the average value of Pow > 1, compared to organic substances that are biodegradable. The more non-biodegradable a substance, the more it tends to biomass, is not wasted through water, urine or other disposal systems (only a small portion). So that if we consume a lot of formaldehyde, it will accumulate a lot in the human body, little will come out through the discharge (urine), compared to glucose.

The higher the toxicity level of organic matter, the higher the Pow value of the substance. In other words, Pow is directly proportional to the level of toxicity (toxicity level) of a substance. While the more toxic the concentration of a substance, the lower the BOD/COD ratio. So that the relationship is obtained that the Pow is inversely proportional to the BOD/COD ratio. This means that the more toxic a substance is, the more it tends to biota.

3.1. LC_{50}-96h Toxicity Test on *Brachydanio rerio*

Lethal concentration fifty for 96 hours (LC_{50}-96h) values of non-biodegradable organic substances are lower than biodegradable organic substances (Table 2). This shows that non-biodegradable organic substances are more toxic than biodegradable organic substances and tend to lead to biomass. The value of LC_{50}-96 hours of formaldehyde obtained for *Brachydanio rerio* was 23,99 mg/l (Table 2). The lower the LC50, the more toxic the compound (Meyer *et al*, 1982); A substance is said to be very toxic if it has a small LC50 value and vice versa (Imono, 2001). *Brachydanio rerio* response to formaldehyde concentration showed the highest mortality.

Table 2. LC_{50}-96h Organic Substance in *Brachydanio rerio*

Organic Matter	LC50-96h value (mg/l)	Estimated Probyt Line
Glucose	371.53	m = 0.087x - 5.39
Lactose	851.14	m = 0.052x - 2.77
Sucrose	685.49	m = 0.082x - 2.09
Formaldehyde	23.99	m = 0.104x + 2.69
Acetic Acid	30.19	m = 0.102x + 2.33
Oxalic Acid	41.69	m = 0.049x + 31.66

m = mortality of test organisms and x = concentration of organic matter

The results of the LC50 toxicity test of the Probyt method show probyt line m = 0,104x + 2,69, where m is the dependent variable which shows 96-hour test organism mortality. The value of a is the y axis intersection value of 2,69 and b is the slope of the regression line whose value is 0,104. Then x is the concentration of organic matter. In formaldehyde, probyt line m

= 0,104x + 2, 69 is obtained. Positive regression coefficients indicate that the higher the concentration of organic matter, the higher the mortality of organism test. For lactose, probyt line m = 0,087x - 5, 39 is obtained, a constant/intercept (a) of -5.39. Negative constants are found in biodegradable organic substances, namely glucose, lactose and sucrose. This is because the organic matter is a carbon source that is not toxic, so the LC50 value is greater than the non-biodegradable organic matter category. In other words, biodegradable organic substances do not support the LC50, so that negative constants are obtained.

From the observations, it was seen that the clinical symptoms of formaldehyde appeared in fish after 24 hours of exposure, especially at concentrations of 100 and 1000 mg/l. Where fish are often on the surface of the water, swim irregularly and then die. These symptoms are responses that occur when substances interfere with the process of cells or subsel in living things to a limit that causes death directly (Conell dan Miller, 1995). Fish that are exposed to toxic substances can be seen from the behavior of the fish, which is hyperactive, floundering, and paralyzed (Shah, 2010). This is thought to be a way to minimize the poisoned biochemical processes in the body, so that lethal effects occur more slowly.

The entry mechanism of toxins into the biota can occur directly and can enter from the environment which then enters the body of the biota. The entry mechanism of toxins into the biota directly on *Brachydanio rerio* is due to the entry of formaldehyde into the body through direct absorption through the skin and extraction from water through the gill membrane. This is due to the presence of CO or aldehyde groups. Inhaled formaldehyde will be absorbed by the upper respiratory tract but not distributed throughout the body because of the detoxification process so that it is metabolized quickly (Heck *et al*, 1985). In addition, fish mortality is also caused by formaldehyde capable of causing stimulation of the central nervous system, causing seizures. Formaldehyde that enters the body of the fish will disrupt the balance of sodium (Na) and potassium (K) in nerve cells so that the nervous system is unstable which results in fish not being able to control muscle contractions as a result of excessive brain stimulation which causes convulsions.

The mechanism for the entry of toxics from the environment into the body of biota can also occur biologically and physically-chemically, varying based on the nature of each substance that is put into the water. Biologically, in biodegradable organic substances, namely glucose, lactose and sucrose, when added to these organic substances with high concentration, the aerobic bacteria in the water will eat the glucose so that it requires high oxygen. This results in dissolved oxygen (DO) in the water becoming increasingly low, causing the fish to die. Formaldehyde is a toxic organic matter, where Pow increases with increasing levels of toxicity from a substance. So that the higher the toxicity of a substance can cause the biota to die. In acetic acid and oxalic acid, the concentration of high acid content in the water causes the pH to become acidic. Where fish prefer to be in a neutral pH environment. This can also cause the fish to die.

The LC50 test results on *Brachydanio rerio* have verified laboratory analysis carried out namely BOD_5, COD, and Pow. Formaldehyde has the smallest LC_{50}-96h, which is 23, 99 so that the Brachydanio rerio response with the highest mortality is obtained. This is in accordance with the biodegradability of formaldehyde included in the non-biodegradable category. Lactose with the largest LC_{50}-96h value is 851, 14 and is included in the biodegradable category in laboratory analysis. This is also in accordance with lactose biodegradability which is included in the biodegradable category. Thus, the LC_{50}-96h value of organic matter is obtained by using the Probit Method based on the level of toxicity of the most toxic are: Formaldehyde, Acetic Acid, Oxalic Acid, Glucose, Sucrose and Lactose. This verifies the results of laboratory analysis that has been carried out.

4. CONCLUSION

Overall results of the analysis of BOD/COD ratio showed that aliphatic organic substances namely Glucose, Lactose and Sucrose, were biodegradable, and the aromatic groups namely Formaldehyde, Acetic Acid and Oxalic Acid, were non-biodegradable. The Pow value showed a tendency to biomass for non-biodegradable organic substances, namely Formaldehyde, Acetic Acid and Oxalic Acid. This result was supported by a toxicity test, which showed that the three were more toxic than the biodegradable substances.

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