The Effect of Cr (VI) Metal On Aerobic Stability of (WWTP) Process CED UGM Laboratories

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Abstract. Chemical Engineering Department, Gadjah Mada University, has a wastewater treatment plant to process wastewater produced by its laboratories. The WWTP consists of equalization, anaerobic, aerobic and phytoremediation ponds. WWTP operates with the adding of starch as substrate and NPK as nutrient. However this WWTP could not treat wastewater which contained a variety of chemical compounds, so that it did not operate properly. Therefore WWTP revitalization should be done in order to make it operate optimally. The purposes of the research are to determine the effect of Cr on the WWTP stability conditions, and the performance of aerobic activated sludge. The experiment was done by controlling substrates flow as much as 3 litters per day to the aerobic pond in a laboratory scale pond made from plastic with the capacity of 10 litters. The pond was run continuously, the samples of wastewater was taken to measure its BOD, COD, MLSS andMLVSS along with the waste feeding. The results showed that the higher Cr concentration the longer time required by aerobic bacteria to degrade it into Cr. Aerobic bacteria are able to reduce the BOD - COD of waste-water that contains Cr up to 50% on various concentrations.

1. Introduction

Laboratory is an important part of a university especially engineering faculty, in more specifically in chemical engineering. In this laboratory, activities produce waste which can lead to environmental pollution if not managed properly.

In the laboratory waste treatment efforts Chemical Engineering Department (CED), University of Gadjah Mada (UGM), has a wastewater treatment system to treat waste from all laboratories at CED UGM. However, the WWTP is not able to process waste containing various types of chemical compounds, so it is no longer in operation. It is necessary for the revitalization of the WWTP, in order to make operate optimally again. Based on the survey data, there are known that the most common pollutants found in wastewater laboratory is Cr. Therefore, the presence of Cr becomes a major concern in the wastewater treatment process. Some research [1-3] showed that Cr(VI) in low concentration can be reduced in activated sludge
Activated sludge is a biological treatment process that has been applied widely for treating wastewater. The process becomes an option because it has the effectiveness and efficiency of the process as well as has low operating costs [4].

The research premeditated the core of Cr (VI) on the aerophilic bacteria stableness in the wastewater treatment process using activated sludge at laboratory scale WWTP.

2. Literature Review

2.1. Laboratory wastewater Characteristic

The operational activities of Laboratory generate waste consists of solid, liquid and gas. Liquid waste containing big metals much as Hg, Ag and Cr can harm the environment because they are toxic to animal and human [5]. According ref [6], laboratorial waste generally contains more complex pollutants comparing with industrial waste.

2.2. Wastewater Processing Technology

Wastewater treatment technologies are very widely, depending on the water-waste characteristics, the desired quality of processed product and operational costs. According to [7], the techniques of water-waste treatment are generally divided into three methods that are:

a. Physical Wastewater Treatment
b. Chemical Wastewater Treatment
c. Biological Wastewater Treatment

2.3. Laboratorial Wastewater Treatment with Aerobic Suspended Culture

Based on the technique of microorganisms controlling in growth media, biological wastewater treatment can be divided into [8]:

a. Attached Growth Processes
b. Suspended Growth Processes

2.4. Activated Sludge

Activated sludge method is one of biological treatment types where the microorganisms are in suspended growth. It is aerobic process that requires oxygen for aerobic biological reactions. In the biological system, the microorganisms live and grow in colonies that form easily sedimented clumps [9]

2.5 Aerobic Bacteria Stability on Waste Treatment Using Activated Sludge Method

Microorganism’s stability is strongly influenced by the availability of nutrients and environmental conditions, especially degree of acidity (pH) and dissolved oxygen (DO). According to [10], the degree of acidity values for aerobic bacteria in activated sludge systems ranged from 6.5 to 8.5. To maintain aerobic conditions in the floc core of the dissolved oxygen concentration, it takes approximately 4-6 mg / L [11].
2. 6. The Effect of Chromium (Cr) Addition on Aerobic Bacteria Stability in Activated Sludge Wastewater Treatment

The effect of chromium (Cr) addition on aerobic bacteria stability in water-waste treatment described as: Cr (VI) in the cell membrane is rock-bottom to Cr (III) and reacts with intracellular bimolecular. Cr6+ concentration on activated sludge that has concentration above 25 mg/L can inhibit the growth of activated sludge, and the lethal dose of the activated goo has concentrations supra 150 mg/L [1].

2.7. Theoretical Basis

The main principles of wastewater treatment by aerobic process is the supply of oxygen in the wastewater treatment ponds, the appropriate ratio of substrate composition and substrate feeding period to keep the bacteria remaining in a stable condition. Stability of the bacteria will be disrupted if there is a foreign substance whether deliberately or not inserted in aerobic pond. The research will be added K2Cr2O7 as Cr (VI) substance that will act as an inhibitor for aerobic bacteria.

In order to Cr (VI) can be degraded by aerobic bacteria optimally, it is necessary to make Cr (VI) acclimatization. Acclimatization process intended to aerobic bacteria, so aerobic bacteria can adapt to the presence of Cr (VI).

The Effects of Cr (VI) (as chromate, [CrO4]2−) include efficient absorption by the cells through the anion (such as sulfuric line), and subsequent responses with intracellular reduction attorney (such as glutathione, ascorbate, or NADPH), which lead to intermediate phase that can damage DNA and organic radicals [12].

3. Experimental Method

3.1. Equipment

Equipment’s used are: rectangular plastic tubs which has 10-liter capacity, pump U-9900 220-240V. The apparatus set is shown in Figure 1.

![Figure 1. Aerobe bacteria growth medium](image)

Description:
1. Aeration tank
2. Aerator pipe
3. Aerator

Analysis tools used are: UV-Vis spectrophotometer GBC Scientific Equipment with serial No. V4131, Lutron pH meter pH-201, Lutron DO meter 5501, oven (memmert 854 schwabach type) 220V that has Tmax 220°C, furnace mod L51/s that has Tmax 1100°C 220V, analytical scale ohaus type PA214C max cap: 210 gram.
3.2. Material Procedure

The materials used are: Waste milk from the Waste Water Treatment Plant (WWTP) PT. Sari Husada Yogyakarta, Aerobic bacterial culture inoculums of Waste Water Treatment Plant (WWTP) PT. Sari Husada, Yogyakarta, urea as a source of natural phosphorous and nitrogen source K$_2$Cr$_2$O$_7$ as Cr (VI) source.

3.3. Research Procedure

The steps performed are:

a. Aerobic bacterial cultures.

b. Dairy wastewater as substrate included in the aeration basin as much as 3 liters / day.

c. In the process of aeration, wastewater is put in aeration pond, further the transfer of air from the aerator is given. Phosphate and Nitrate was added as microorganism’s nutrient. Operating conditions are pH between 6.5 to 8.5, and temperature (25°C). besides, the aeratin process had to be controlled to avoid the sediment on the base of the ponds.

d. The volume f the wastewater is kept constant by taking and adding with the same amount of 3L along with the nutrient adding with the ratio of BOD : N : P = 100 : 5 : 1 once a day. The bacteria in aeration pond were aclimated for ± 20 days in order to make the bacteria abe to adapt the new environment, indicatd from constant COD reduction efficiency value.

e. The addition of K$_2$Cr$_2$O$_7$ as an inhibitor as 0.05 grams was added. The feeding is done intermittently. The process is done until the value of BOD, COD and chromium levels obtained are constant. After Cr concentration was constant, it was then followed by the addition of K$_2$Cr$_2$O$_7$ 0.025 gram with the same analytical procedure.

3.4. Samples Analysis

Determination of Cr (VI) concentration using UV-Vis spectrophotometer with difenilkarbazid method, BOD analysis used BOD5 method, COD analysis used open reflux method, mixed liquor suspended solids (MLSS) is done by evaporation and drying of biomass at temperatures of 103-105°C, Mixed liquor volatile suspended solid (MLVSS) performed by heating biomass at a temperature of 600°C.

3.5. Product Analysis

Sampling of waste water in the reactor was conducted to determine the concentration of COD and BOD in wastewater. The data are used to determine the effect of Cr (VI) addition on aerobic bacteria stability in degrading organic substances. Analysis of the MLSS and MLVSS also conducted to determine the decreasing of aerobic bacteria after addition of Cr (VI).

4. Result and Discussion

4.1. The Effect Of Cr(VI) Adding Toward Activated Sludge

This reserch was devided into to steps, those are aerobe bacteria acimatization and K$_2$Cr$_2$O$_7$ adding. In aclimatizin process the mmicroorganisms in the reactor were grown for ± 20 days. After the breeding of microorganisms in the reactor run well, K$_2$Cr$_2$O$_7$ as an inhibitor as 0.025 grams was added. After Cr concentration was constant, it was then followed by varying the addition of Cr (VI) to 0.05 gram. After Cr concentration was constant subsequently the K$_2$Cr$_2$O$_7$ adding was variated as 0.025 gram and so on.

Total suspended solid concentration which contains in the waste is measured from MLSS level. Th analysis result of the solid during the waste treatment is shown on Figure 2. The wastewater treatment
which contains Cr(VI) using aerobic bacteria can reduce MLSS level. This phenomenon occurred because it is difficult for aerobic bacteria to reduce the waste which contains Cr(VI).

![Figure 2. The effect of K$_2$Cr$_2$O$_7$ addition as the function of time to MLSS level](image)

MLVSS is the suspended solid level which only consist of bacteria component. MLVSS measurements by a further heating for the filtered solids MLSS, with high heat the components of microorganisms will break down and evaporate. The difference in weight before and after a heated indicates the number of microorganisms [13]. Basically the value of MLVSS is proportional to the value of MLSS. Figure 3 shows the K$_2$Cr$_2$O$_7$ additional to produced MLVSS level. MLVSS level in reactor without Cr addition is higher compare to the addition of Cr.

![Figure 3. The effect of K$_2$Cr$_2$O$_7$ addition as the function of time to MLVSS level](image)

4.2 The Effect Of K$_2$Cr$_2$O$_7$ Adding Toward Cr(VI) Concentration

This is due to high levels of Cr (VI) were feed as influent to be treated by aerobic bacteria are not comparable with the levels of aerobic bacteria that will process the metal, the measured data obtained for the addition of Cr (VI) 0.025 grams with the lowest measurement data which is equal to 4.614 mg/L and a decrease in the highest concentration of 2.064 mg/L.
Figure 4 shows that the calculated initial concentration of Cr (VI) in liquid was greater than the concentration of Cr (VI) final measurement results it is because in the bacterial cell the Cr has been reduced into Cr (III) through sulphate stream [14].

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} & \rightarrow 2\text{Cr}_2\text{O}_4^{2-} + 2\text{H}^+ \quad \text{(outside of cell)} \\
\text{Cr}_2\text{O}_7^{2-} + 4\text{H}_2\text{O} + 3e^- & \rightarrow \text{Cr(OH)}_3 + 5\text{OH}^- \quad \text{(inside cell)} \\
\text{Cr(OH)}_3 & \rightarrow \text{Cr}^{3+} + 3\text{OH}^- \quad \text{(inside cell)}
\end{align*}
\]

4.3. The Effect Of Cr(VI) Toward The Ability Of Aerob Bacteria To Reduce COD Of Wastewater

COD is an analysis to measure the oxygen demand of the organic substances which are difficult to be destroyed by oxidation, so that it needs support from a strong oxidizing agent in acid [15-16]. In this research, the treatment for wastewater by using aerobe bacteria showed the COD concentration decreasing with the initial concentration as 56.23 mg/L became 25.16 mg/L. Figure 5 shows the comparison of COD concentration before and after K₂Cr₂O₇ adding as 0.05 g and 0.025 g.

Figure 5. Wastewater COD value declining as a function of time before and after K₂Cr₂O₇ adding
Decreased levels of COD is caused by the degradation of organic matter due to a simple component of bacterial [15]. The chart shows that constant COD levels was obtain on the day of 18, 19 and 20 as 25.16 mg/L. So it can be followed by adding \( K_2Cr_2O_7 \) into the pond. In the \( K_2Cr_2O_7 \) adding as 0.05 g showed the fluctuate value of COD, with the highest value as 127.18 mg/L and the lowest value as 5.54 mg/L. Meanwhile at the \( K_2Cr_2O_7 \) adding as 0.025 g, the value of COD obtained was tend to be constant with the highest value of COD as 78.31 mg/L and the lowest as 35.77. This constant condition is because the adding of \( K_2Cr_2O_7 \) as 0.025 g dis not give significant effect toward bacterial activity.

4.4 The Effect Of Cr(VI) Toward The Ability Of Aerobe Bacteria To Reduce BOD Of Wastewater

The ability of aerobic bacteria in wastewater treatment was considered good, because it fulfill the requirement of wastewater as environmental ministry No. 03 year 2010 the maximum BOD of wastewater as 50 mg/L. This is proofed by the value of BOD has been reduced from 84 mg/L into 4.5 mg/L.

The BOD decreasing due to the oxygen used by bacteria to degradeate organic compound as its nutrient. the aerobe bacteria can reduce wastewater BOD which contains up to 94%. Figure 6 show a comparison of wastewater BOD levels before and after the addition of \( K_2Cr_2O_7 \).

![Figure 6](image)

**Figure 6.** Wastewater BOD value declining as a function of time before and after \( K_2Cr_2O_7 \) adding

4.5. Acidity (pH)

From the pH analysis in sludge in the reactor with the various resident times was shown in Figure 7.

![Figure 7](image)

**Figure 7.** The effect of \( K_2Cr_2O_7 \) as function of time toward the pH of solution before and after \( K_2Cr_2O_7 \) adding
From Figure 7, there was an increased pH in the aeration to 55, 56, and 78 day and a decrease in pH on day 43. A decrease and an increase in the pH value is not significant, which still remains in the range of pH for aerobic bacteria in activated sludge systems, which are in the range of 6.5 to 8.5 [16].

5. Conclusion

On the addition of $K_2Cr_2O_7$ 0.05 g it shows that it inhibit the growth of microorganisms indicated from MLSS and MLVSS analysis results which shows the microorganism was reduced for about 35%. The time required to obtain a new stable state with the addition of $K_2Cr_2O_7$ 0.05 g of $K_2Cr_2O_7$ and 0.025 g were 14 days and 12 days to reach a constant point.

There is no information on the repeated use of a maximum of sludge that requires further research on the characteristics of the sludge on a few times it is used. It is necessary to know the trend of change in sludge characteristics associated with the ability of aerobic bacteria in reducing waste especially waste metal.

Further optimization of the operating unit can be done, for example by using a variation of the concentration of other metals, the contact time optimization for wastewater produced continuously in large quantities and need to be processed continuously, the continuous assessment needs to be done for the optimization process.

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