Study of COD Removal Rate in Tapioca Wastewater Treatment by Sequencing Batch Reactor (SBR)

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ABSTRACT

Industrial wastewater treatment using Sequencing Batch Reactor (SBR) can improve effluent quality at lower cost than that obtained by other biological treatment methods. Further optimization is still required to enhance effluent quality until it meets standard quality and to reduce the operating cost of treatment of high strength organic wastewater. The purpose of this research was to determine the effect of pretreatment (pH adjustment and prechlorination) and aeration time on effluent quality and COD removal rate in tapioca wastewater treatment using SBR. Pretreatment was done by (1) adjustment of tapioca wastewater pH to control (4.92), 7, and 8, and (2) tapioca wastewater prechlorination at pH 8 during hour using calcium hypochlorite in variation dosages 0, 2, 4, 6 mg/L Cl₂, SBR operation was conducted according the following steps: (1) Filling of pre-treated wastewater into a bioreactor during 1 hour, and (2) aeration of the mixture of tapioca wastewater and activated sludge during 8 hours. Effluent sample was collected at every 2-hours aeration for COD analysis. COD removal rate mathematical formula was got by first deriving the best fit function between aeration time and COD. Optimum aeration time resulting in no COD removal rate. The value of COD effluent and its removal rate in optimum aeration time was used to determine the recommended of operation condition of pretreatment. The result is shows that chosen pH operation condition is pH 8. Prechlorination can make effluent quality which meets standard quality and highest COD removal rate. The chosen Cl₂ dosage is 6 mg/L.

Keywords: Aeration time; COD; pH; prechlorination; SBR

INTRODUCTION

The washing and extraction process for every ton of cassava in starch production process can produce 23 m³ tapioca wastewater (Okunade and Adekalu, 2013). The waste is an organic material with a Chemical Oxygen Demand (COD) range between 4,000 – 12,000 mg/L (Liu et al., 2010). The total suspended solids content of the wastewater where level pH in the range of 4.5–5 is high, between 4,200-7,600 mg/L. The toxic compound, cyanide (CN-), is also found with a level between 19–28 mg/L (Indrayatie et al., 2013). The Central Java Provincial Government Regulation No. 5 Year 2012 about tapioca wastewater quality stated that pH between 6-9; maximum COD 300 mg/L; maximum total suspended solids 100 mg/L; and maximum CN- 0.3 mg/L are the environmental friendly conditions.

The BOD/COD ratio value of tapioca wastewater, which is between 0.6-0.7, has indicated the high level of biodegradability (Pandian and Meenambal, 2017). Furthermore, the characteristics of wastewater with BOD/COD > 0.5 also recorded as easy to process through biological processing (Chan et al., 2009). Compared with other biological processing, the aerobic method can produce more significant reduction of organic compound levels in the waste in the shortest time. Activated sludge process with 170 minutes of aeration time can reduce the COD concentration in tapioca wastewater up to 96.3% (Nguyen and Nguyen, 2016). However, the high concentration of organic materials reported can...
create a difficulty in the application of aerobic method, either economically or technically (Jern, 2006). Viewed from the economical aspect, around 1,100 - 2,400 MJ of electricity is needed for treating each 1,000 m³ of wastewater using activated sludge process (Au et al., 2013). The technical restraint in its application is caused by activated sludge process inability to reduce organic material content in wastewater having concentration more than 4,000 mg/L COD into effluent which meets the quality standard (Chan et al., 2009).

The anaerobic-aerobic combined method is generally applied to the processing industrial wastewater with high organic content as an effort to fulfill effluent quality to the standards (Jern, 2006). The process of organic materials removal in the anaerobic reactor will reduce aeration cost needed. However, the low microorganisms growth rate causes the longer hydraulic retention time (Chan et al., 2009).

Results of previous researchers proved that adjusting pH can significantly reduce pollutant concentration in tapioca wastewater in a short time. Adding 5 g NaOH into wastewater can spontaneously eliminate 35.71% suspended solids, 39.13% BOD, and 75% CN (Jideofor, 2015). The increasing of efficiency can be performed by adjusting pH of tapioca wastewater using Ca(OH)₂ solution 1% becoming 8. The removal efficiency of suspended solids and Biological Oxygen Demand (BOD) reached 73.01% and 44.69%, respectively (Mulyani et al., 2012).

Chlorination application has proven effective to eliminate pollutants in tapioca wastewater. The chlorine addition based on reaction stoichiometry (mole ratio Cl⁻;CN⁻ 1:1) at pH 8 can remove 79.85% suspended solids and 77.92% BOD in tapioca wastewater (Mulyani et al., 2012).

Furthermore, increase of mixed liquor volatile suspended solids (MLVSS) and reduction of COD in tapioca wastewater resulted from prechlorination effluent can take place along with retention time addition of activated sludge process. Moreover, increase of chlorine dose will further decrease effluent COD concentration in activated sludge process and required aeration time. However, the best effluent COD concentration which still reached 1,538 mg/L (Mulyani and Pamungkas, 2016) shows that further pretreatment optimization is still needed.

Next, in order to make organic materials removal take place optimally, contact between pollutant in the wastewater and microorganisms in the activated sludge must also be maintained at sufficient time and O₂ supply. The longer the contact time between organic material in the wastewater and microorganisms, the bigger the COD degradation level obtained. However, on the other hand, the longer the aeration period, the bigger operational cost that must be spent. Therefore, optimization is needed to obtain aeration time which can produce maximum microorganism growth and COD concentration reduction.

Sequencing batch reactor (SBR) is an appropriate activated sludge treatment method for processing high strength organic industrial wastewater. This treatment is economically qualified because the operational cycle which include filling, aeration, settling, and discharge of the effluent happens in one reactor. The usage of SBR can save more than 60% cost if compared with conventional activated sludge process (Elmolla et al., 2012). Wastewater treatment using SBR can also produce better effluent quality than the other biological treatment methods (Ibrahim, 2017). The arrangement of each stage of cycle time can increase the performance of COD reduction. The filling stage facilitates the process of selection and enrichment of aerobic microbe population. Aeration stage sufficiency is needed to create efficient microorganism growth and COD reduction. The settling stage is needed to maximize COD reduction.

This research aims to recommend aeration stage operational conditions of SBR treating tapioca wastewater with the application of pretreatments (pH adjustment and prechlorination) which produces highest COD removal rate and best effluent quality. Pretreatment application will reduce the energy consumption for aeration process. Optimization of initial pH, CI, dosage applied, and aeration time are expected to obtain a tapioca wastewater treatment technology development which produces effluent that meets wastewater discharge quality standards in a short time at a low cost.

**RESEARCH METHOD**

**Materials**

The main materials used for treatment process include wastewater from tapioca industry in Wonogiri, activated sludge from tapioca industry wastewater treatment plant (WWTP) in Wonogiri, calcium hypochlorite technical (Tjiwi Kimia, 60%), and Ca(OH)₂ technical. Materials used for analysis process include potassium dichromate p.a (Merck, min 99.9%), sulfuric acid p.a (Merck, 95-97%), HgSO₄ p.a (Merck, min 99%) Ag₂SO₄ p.a (Merck, min 98.5%), and potassium hydrogen phthalate p.a (Merck, min 99.5%).

**Equipments**

The main equipment for treatment process is consist of pretreatment tank and SBR basin made from a plastic bucket with 30 L capacity. The bucket for
pretreatment is perforated with a 5 mm diameter hole at 1/3 of the height (13 cm) from the base for adjusting SBR influent flow rate. For SBR tank requirement, the bucket is equipped with a tap at 1/3 of the height from the base to discharge the treated wastewater. The main tools used for analysis processes include a two-hole aquarium aerator (Amara), pH meter (ATC), chlorine comparator (Hanna Inst), COD reactor (Hach), spectrophotometer uv vis (Thermo Scientific), and furnace (Thermo Scientific).

Research Design

The approaches used to achieve research objective are experiment and optimization methods. The experiment method is used to determine the influence of each pretreatment type variation (pH adjustment and pre-chlorination) on the observed variable (COD effluent of SBR treating tapioca wastewater) for aeration time of 0, 2, 4, 6 and 8 hours. The independent variables tested are the pretreatment operational conditions which will be optimized, they consist of pH values (control; 7; 8) in the SBR system variation with the application of pH adjustment and Cl₂ dose applied (0; 2; 4; 6 mg/L) in the pre-chlorination process. Optimization is used for effluent COD concentration data analysis to determine the pretreatment operational conditions (Cl₂ dose; pH) and the recommended aeration time in SBR system.

Research Method

Pretreatment

Pretreatment variations studied for their influence in this research are pH adjustment and pre-chlorination. The pH adjustment is performed by mixing tapioca wastewater with a 1% Ca(OH)₂ solution with Cl₂ dose variations 0; 2; 4; 6; and 8 mg/L Cl₂, and 1% Ca(OH)₂, until the pH reaches 8. Pre-chlorination effluent not contain free Cl₂ again by the test using chlorine comparator can be used as SBR influent.

SBR System Operation

The SBR process stages is consist of inoculation, acclimatization, and SBR operation. The inoculation process is carried out by introducing 8 L of activated sludge into the SBR basin. After that, acclimatization is accomplished to allow the stable and optimal work of microorganisms in the activated sludge. The acclimatization process is performed by operating the SBR system following cycle stages:

- (1) Filling of 16 L of pre-treated wastewater into a bioreactor during 1 hour,
- (2) aeration of the mixture of tapioca wastewater and activated sludge during 8 hours, and
- (3) settling for 30 minutes, and
- (4) treated wastewater discharge. Then, SBR is operated again according to same stage cycles as acclimatization. In the second operation of SBR, a 100 mL of mixed liquor sample is taken with a 2-hour aeration time intervals for COD analysis purposes using the method of SNI 6989.2:2009 and MLVSS analysis using APHA 2540 E-2005 method.

Data Analysis

Data is analysed using an optimization method. This method is usually used to determine design variable values which resulted in the best performance in process and design operation of a plant. The first step for optimization purposes is a process needs to be represented in an mathematical equation that correlate between the design variable and performance indicator parameter of operation for determination of minimal and maximal function value. The optimum design variable value is the first derivative of these mathematical equation (Kiusalaas, 2005). After that, the equation root value determination can be done by using zero subroutine if the equation derivation is a non-polynomial function and roots subroutine if the equation is a polynomial function (Yang et al., 2005).

In this research, optimization is used to estimate aeration time value which obtain minimal effluent COD concentration and highest COD removal rate. Data analysis is processed through several stages: (1) determining mathematics equation between aeration time and effluent COD concentration with the highest \( R^2 \) values, (2) formulating COD removal rate equation, (3) estimating optimum aeration time and effluent COD concentration produced, and (4) calculating optimum COD removal rate for each run variation of SBR operation.

\[
COD\ effluent = f(t)
\]

\[
COD\ effluent^\prime = \frac{dCOD\ effluent}{dt} = 0
\]

(Chapra and Canale, 2015)

COD removal rate equation \( \frac{dCOD\ effluent}{dt} = 0 \) is the first derivative of mathematics equation between aeration time and the chosen COD effluent concentration. The optimum aeration time is reach when the COD removal rate is equal to zero. To determine it, a subroutine to find fzero/roots equation root in Matlab 7.1 program is used. The optimum effluent COD is the estimation of
COD value at the time of optimum aeration calculated by substituting the optimum aeration time value into its mathematical equation of the correlation between aeration time and effluent COD concentration with the highest $R^2$ value. Later, the optimum COD removal rate is determined based on the equation 3.

\[
\text{Optimum COD removal rate} = \frac{mg \text{ COD}}{L \text{ hour}}
\]

\[
\frac{mg}{L} \text{ optimum effluent COD} - \frac{mg}{L} \text{ influent COD} = \frac{mg}{L} \text{ optima aeraiton time (hour)} (3)
\]

The chosen operation condition is the pH and Cl$_2$ dose which produce the lowest effluent COD and the highest COD removal rate in SBR operation using optimum aeration time.

**RESULTS AND DISCUSSIONS**

**The Influence of pH Adjustment on COD Removal in Tapioca Wastewater**

In this research, the pH adjustment by Ca(OH)$_2$ addition is proven can become an alternative tapioca wastewater pretreatment method. Table 1 shows that pH adjustment can decrease COD concentration in tapioca wastewater. This phenomenon can occur because dissolved organic compounds are eliminated through precipitation by adding Ca$^{2+}$. Next, suspended organic compounds which resulted from precipitation can be easily removed by settling. The other research result also shows that 32.5% COD removal percentage in the waste can happen due to applying 10 mg/L Ca$^{2+}$ (Gunasekara, 2011).

Table 1 also shows that the effluent COD decreases by increasing pH. The pH increase, which in this research is obtained by adding Ca(OH)$_2$, will increase Ca$^{2+}$ concentration in the wastewater. The increase of Ca$^{2+}$ concentration until reach a certain level will enhance formation of flocs that can be settled rapidly by themselves (Avessa et al., 2016; Isyuniarto et al., 2007). A positive correlation can be seen between the pH increase and the COD removal efficiency by precipitation (Gunasekara, 2011; Isyuniarto et al., 2007). Previous researches have mentioned that 0.6% Ca(OH)$_2$ solution (Isyuniarto et al., 2007) and pH 8 are optimum conditions for precipitation process in order to remove suspended solids (Avessa et al., 2016), COD, and BOD in wastewater (Isyuniarto et al., 2007).

**Pre-Chlorination Influence on the COD Removal in Tapioca Wastewater**

Table 2 shows that calcium hypochlorite addition can reduce COD concentration in tapioca wastewater. This phenomenon is possible because organic compound oxidation process can take place quickly with the addition of Cl$_2$ compound in the waste (Pickup, 2010).

In this case, Cl$_2$ addition in tapioca wastewater as SBR pretreatment didn’t have the negative effect on COD analysis accuracy. The existence of chloride (Cl$^-$) in the sample can disturb the performance or silver sulfate catalyst (Ag$_2$SO$_4$) and be oxidized by potassium dichromate (KCr$_2$O$_7$) if the concentration reaches 800 mg/L (BSN, 2009). In fact, as presented in Table 2, the highest Cl$_2$ levels applied in the waste was 6 mg/L. Other efforts to eliminate Cl$^-$ presence in the sample has also taken. The measurement of effluent COD concentration of pre-chlorination process is done after the sample is confirmed no contain Cl$^-$ residue using chloride comparator test. By ensuring that the sample no longer contain Cl$^-$ ion, the effort to prevent Cl$^-$ ion presence as the result of Cl$_2$ hydrolysis when diluted in water (Crittenden et al., 2012) has been done. Moreover, adding mercury sulfate (HgSO$_4$) in the sample is also applied before adding other reagents. With HgSO$_4$ addition, Cl$^-$ ion will bind Hg$^{2+}$ ion to form HgCl$_2$. Consequently, Cl$^-$ ion concentration becomes too low so that it does not disturb organic substance oxidation in COD analysis. Additionally, COD analysis procedures according to SNI 6989.2:2009 stated that Cl$^-$ disturbance in COD analysis can be solved by adding HgSO$_4$ if the existence of Cl$^-$ ion in the sample does not exceed 2,000 mg/L (BSN, 2009).

Table 2 also shows that the COD effluent has a negative correlation with Cl$_2$ dosage addition applied in the prechlorination. It is consistent with previous research which stated that the increase of Cl$_2$ dosage from 60 mg/L Cl$_2$ to 300 mg/L Cl$_2$ will reduce industrial

<table>
<thead>
<tr>
<th>Table 1. Effluent COD levels in tapioca wastewater pH adjustment process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (pH = 4.92)                            pH = 7      pH = 8</td>
</tr>
<tr>
<td>COD (mg/L)                                    7,266.667  5,166.667  4,041.667</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Tapioca wastewater effluent COD data of pre-chlorination process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$ dose = 2 mg/L                                       Cl$_2$ dose = 4 mg/L   Cl$_2$ dose = 6 mg/L</td>
</tr>
<tr>
<td>COD (mg/L)                                           7,933.333  5,066.667  3,483.333</td>
</tr>
</tbody>
</table>
wastewater effluent COD concentration from 356 mg/L to 247 mg/L (Jain and Khambete, 2013).

The Influence of pH Adjustment on COD Removal Rate in SBR Treating Tapioca Wastewater

Tapioca wastewater effluent COD profile at each aeration time in SBR process under various pH is presented in Figure 1. Aeration phase in SBR system at every pH variations tested can work properly. This is seen from the tendency of effluent COD decrease along with the increase of contact time between activated sludge and the wastewater. The bigger chance for microorganisms to degrade carbon source in the wastewater in longer aeration period. This statement is also consistent with the results of research by Titiresmi (2007) and Purwita & Soewondo (2010) which stated that COD concentration reduction in the wastewater using activated sludge aeration process will get bigger along with the increase of aeration time.

Figure 1 also shows that increasing pH addition as pretreatment will effect in COD effluent of tapioca wastewater degradation in SBR system. In this case, the COD concentration removal is calculated by the difference of COD concentration between 0 to 8 hours of aeration time. The pH factor gives a significant impact on wastewater biodegradation and COD removal efficiency in SBR. The high pH has proven to contribute to increasing SBR ability especially in COD removal (Yan et al., 2013). The biodegradability of wastewater is indicated by increasing BOD/COD ratio along with the increasing pH (Mulyani et al., 2012). Applying precipitation using Ca(OH)₂ solution has also been proven in previous researches that it can improve COD removal in biological wastewater treatment (Gunasekara, 2011).

The lowest influent pH variation (4.92) will produce the lowest COD effluent concentration. It is probably due to the fact that acidic condition is one of the main inhibition in the process of carbon source utilization and substrate degradation by microorganisms. The optimum pH for wastewater treatment by activated sludge process is between 6.5-9. In acidic condition, COD concentration removal in biological treatment of dairy products drastically drops (Kheiredine et al., 2014). The high influent COD under various pH cause inhibition of substrate decomposition by microorganisms. It also has been found that the efficiency of COD concentration reduction will tend to decrease along with the increase of organic loading rate (Aygun et al., 2008).

The kinetics is important aspect to quantifying performance and stability of COD removal in biological treatment (Purwaningsih et al., 2008). Furthermore, the selection of operation conditions which can obtain the best COD removal and in the shortest time is a strategic to increase effluent quality and to reduce operational cost of a wastewater treatment system. For that purpose, Figure 2 displays the correlation between aeration time and COD removal rate. In this case, the COD removal rate is represented by the first derivative of correlation approach between aeration time and effluent COD concentration, as seen in Figure 1.

The lowest COD removal rate in SBR process had reached at pH 4.92. In the same condition, the COD removal rate is also seen decrease along with the increase of aeration time. It is mainly caused by the low number of microorganisms in SBR operation at acidic pH condition especially in the beginning of process. This is indicated by the low MLVSS value as presented in Figure 3. In general, MLVSS is represent the number of microorganisms in activated sludge process tank (Glymph, 2005).

Furthermore, the most stable pH is 8. Figure 2 shows that value in this SBR operation has the tendency to increase along with the rising of aeration time until it reach stability. This phenomenon happens because tapioca wastewater influent COD in SBR at pH 8 has the lowest value, as presented in Table 1. The previous research on upflow anaerobic sludge blanket system

![Figure 1. Effluent COD profile in SBR treating tapioca wastewater at various pH during aeration time](image1)

![Figure 2. Profile of COD removal rate in SBR process aeration phase at various pH](image2)
treating domestic wastewater, by Yazid et al. (2012) stated that the lowest influent COD concentration is required to achieve the best COD removal.

The determination of optimum aeration time, concentration of COD effluent and COD removal rate in tapioca wastewater treatment using SBR is presented in Table 3. The table also shows the optimum COD removal rate will increase along with the rising of pH. However, aeration time optimization in wastewater treatment by SBR with the pH adjustment still unable to obtain COD effluent which met the quality standard. The COD effluent concentration is still far above 1,000 mg/L causes the aerobic biological treatment method does not work efficiently (Chan et al., 2009).

The Influence of Pre-Chlorination on COD Removal Rate in in SBR Tapioca Wastewater Treatment

The profile of COD tapioca wastewater effluent in each aeration time by SBR process with pre-chlorination in variation of pH is presented in Figure 4. This figure shows the quality of effluent in process SBR with pre-chlorination is better process without pre-chlorination or the process just by the pH adjustment. The higher the Cl₂ dose addition, the lower the COD effluent resulted in tapioca wastewater treatment by SBR system. As explained by Mulyani et al. (2012), this phenomenon is mainly caused by the decrease of BOD/COD ratio of tapioca wastewater due to chlorine addition. The reduction of BOD/COD ratio is commonly used indicator of the higher degree of biodegradability of the wastewater.

The reason of the lowest COD effluent in SBR system with the highest dosage of chlorine addition is the COD removal rate phenomenon. Figure 5 presents the COD removal rate at SBR process with pre-chlorination application at the dosage of Cl₂ 6 mg/L become increase along with aeration time. As presented in Figure 6, this phenomenon indicates that microorganisms will continuously grow along with aeration time addition.

Furthermore, Table 4 presents that optimum COD removal rate can be reached in tapioca wastewater treatment by SBR with the increasing of chlorine dosage in the influent. The effluent COD concentration in

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**Table 3. pH adjustment effect on COD removal rate in SBR treating tapioca wastewater**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH = 4.92</th>
<th>pH = 7</th>
<th>pH = 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimum aeration time (hour)</td>
<td>0.9753</td>
<td>3.2402</td>
<td>7.8109</td>
</tr>
<tr>
<td>Optimum effluent COD (mg/L)</td>
<td>7,490.578</td>
<td>4,211.982</td>
<td>1,284.342</td>
</tr>
<tr>
<td>Optimum COD removal rate (mg COD/L/hour)</td>
<td>-185.151</td>
<td>286.4075</td>
<td>354.2048</td>
</tr>
</tbody>
</table>

**Table 4. Prechlorination effect on COD removal rate in SBR treating tapioca wastewater**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cl₂ dosage = 2 mg/L</th>
<th>Cl₂ dosage = 4 mg/L</th>
<th>Cl₂ dosage = 6 mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimum aeration time (hour)</td>
<td>7.3464</td>
<td>4.131</td>
<td>7.5011</td>
</tr>
<tr>
<td>COD optimum effluent (mg/L)</td>
<td>6,346.054</td>
<td>3,614.034</td>
<td>276.7343</td>
</tr>
<tr>
<td>Optimum COD removal rate(mg COD/L/hour)</td>
<td>217.5142</td>
<td>351.4805</td>
<td>431.3055</td>
</tr>
</tbody>
</table>
optimum aeration time of tapioca wastewater treatment by SBR with 6 mg/L Cl₂ addition can fulfill the quality standard. The quality standard of COD in tapioca wastewater according to the Central Java Provincial Government Regulation No. 10 Year 2004 is maximum 300 mg/L.

CONCLUSION

The increasing pH is proven to increase the effluent quality and COD removal rate in tapioca wastewater treatment by SBR system. Pre-chlorination can further increase effluent quality and COD removal rate. The higher the Cl₂ dosage addition, the higher the COD removal rate and effluent quality in the SBR process. The addition of 6 mg/L Cl₂ can obtain COD effluent that fulfill the quality standards.

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