Performance stability of reactors in disseminating COD and ammonium in domestic wastewater contaminated with pharmaceutical residues

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Abstract. Currently, the use of PPCP products has increased significantly. Personal Pharmaceutical Care Products (PPCPs) enter the environment through human activities and residue from hospital and community use. The effect of increasing the concentration of amoxicillin as a pharmaceutical residue on bacterial growth and removing COD and ammonium was investigated on the intermittent and continuous reactor's performance. The study was started with seven days of seeding acclimatization and running for twenty days. An increase in the concentration of pharmaceutical residue pollutants was carried out every five days. The sediment used came from the septic tank sediment and used artificial waste with an initial COD of 100 mg/l and an initial Ammonium of 80 mg/l. The results showed that the increase in the concentration of pharmaceutical residual pollutants in the operational reactor affected COD removal efficiency and ammonium efficiency. The efficiency of COD reduction at increasing concentrations of amoxicillin 0 mg/l, 5 mg/l, 10 mg/l and 20 mg/l were 58.06%, respectively; 48.48%; 41.18% and 35.14%. Meanwhile, the highest ammonium reduction rate was when the increasing amoxicillin concentration to 5 mg/l with the ammonium reduction rate of 3.98 NH₄⁺-N/l.day.

1. Introduction

Currently, the use of PPCP products has increased significantly. Drugs and personal products, well known as PPCP (Pharmaceutical Personal Care Products), are substances individually used for personal health, cosmetic reasons, and personal cleanliness. PPCP can be divided into two groups, namely Pharmaceutical Products and Personal Care Products. The presence of this pharmaceutical product will leave behind pharmaceutical compounds or commonly known as pharmaceutical residues. Pharmaceutical Compounds (PCs) enter the environment after humans activity and then produce waste such as residue from the hospital and public facility. Medicines are often not completely processed by the human body. Through disposal, the drug can enter the environment once excreted. As a result, active medicinal components have been found in many environments worldwide, where they are thought to have harmful effects on aquatic life.

Wastewater treatment technology is the key to maintaining environmental sustainability. Various wastewater treatment techniques to remove pollutants, such as physical, chemical and biological treatment, have been tried and developed. According to Said (2001), in general, there are five groups of
biological wastewater treatment processes, namely aerobic processes, anaerobic processes, aerobic and anaerobic combination processes, anoxic processes, and processes with lagoon or ponds [1].

The concentrations of COD and ammonium in wastewater vary depending on the activity of producing wastewater. Ammonium can be removed by various processes, biologically (nitrification and denitrification) and ion exchange. In Goh Chin Ping (2008), Steve stated that the attached biomass system had better microorganism activity than the suspended biomass system. The better activity of the microorganisms that form the biofilm layer has a low substrate concentration and provides a higher probability of reaction with nutrients outside the substrate [2].

This study will discuss the reactor's stability in removing COD and ammonium from domestic waste contaminated with pharmaceutical residues. This study's objectives are assessing the fluctuation of COD and ammonium concentrations from reactors, which are operational in the long term with increasing concentrations of pharmaceutical pollutants (products/care). Besides, analyzing the stability of the reactor's performance in removing COD and ammonium from domestic waste contaminated with pharmaceutical residues.

2. Methodology

This research was conducted with an experimental method using a laboratory-scale reactor. Observations in experimental research are carried out under artificial conditions set by the researcher. The advantages of laboratory-scale experimental methods are that there is the possibility of controlling from relatively perfect conditions, using random division, and manipulating one or more independent variables, resulting in a level of accuracy or precision of research results that are generally high when done with proper research procedures.

This research continues the previous research by Sudarno et al., where the bacteria extracted from the septic tank sediment were proven able to remove ammonium and COD; even though the concentration of pharmaceutical residues in the waste was relatively high. This research was finished in 27 days by operating the reactor continuously. The parameters measured were pH and temperature, while the parameters tested were the concentration of ammonium, COD, nitrite and nitrate. The microorganisms' sources were tested for initial characteristics, including temperature, pH, COD, ammonium, nitrite, and nitrate. The wastewater used is artificial wastewater made in the Environmental Engineering Laboratory of Undip. Artificial wastewater was prepared with ammonium concentration 80 mg/l and COD concentration 100 mg/l. This research was started with acclimatization seeding and continued with the running stage.

![Anaerobic continuous reactor](image)

**Figure 1.** Anaerobic continuous reactor.
3. Results and discussions

3.1. The effect of increased amoxicillin concentration on COD and ammonium removal

At this stage, it is core research that consists of two stages. The first stage is the seeding and acclimatization stage, carried out for seven days on the Anaerobic Batch Reactor. The second stage is the running stage for 20 days on the Anaerobic Intermittent and Continuous Reactor.

3.1.1. pH. In the anaerobic process, pH is one of the essential parameters because methane bacteria are susceptible to changes so that the pH must always be conditioned in the 6.5-7.5 range. However, the process can still run in the pH range of 6.0-8.0. Low pH and excess acid production will act as inhibitors for methanogenic bacteria [3]. Sodium Bicarbonate is used to control pH in anaerobic treatment.

![Figure 2. pH Value.](image)

At this stage, the pH for 20 days of running is 7.04 to 7.68. The pH conditions in this range are still in the optimum pH range for anaerobic bacteria's growth. Following the viewpoint of Tchobanoglous (2003), in anaerobic conditions, an optimal pH condition is needed, namely the range of 6.0-7.6 [4]. On the first day to day ten, an increasing concentration of amoxicillin 5 mg/l made the pH fluctuates. However, the increase of amoxicillin concentration to 10 mg/l causes the pH to increase slightly. While, if the amoxicillin concentration increased to 20 mg/l cause the pH decreases.

3.1.2. temperature. The addition to pH measurements, temperature measurements are also carried out every day during the running stage. Anaerobic processes can occur at temperatures of 25 °C - 40 °C so that bacteria can degrade organic matter. Meanwhile, anaerobic processes can take place in the mesophilic temperature (25°C–40°C) and the thermophilic (55°C–60°C). Thus, the reactor's temperature is still in the optimum range for the growth of microorganisms, namely 28°C–31°C.

Each unit of Wastewater Treatment Plant (WWT) has a processing capacity of up to 15 m³/day. Nevertheless, technical considerations then will only use capacity up to 10 m³/day. Wastewater treatment 100 m³/day requires ten units of Wastewater Treatment Plant (WWT), then the necessary for the placement of the entire Wastewater Treatment Plant (WWT) is 10 x 90 x 54 x 52 cm (5 m²).

The figure below showed that the temperature is relatively the same from the first day to the end of the running process. The reactor temperature ranges from 28 °C-31 °C, which indicates the optimal temperature for bacterial growth.
3.1.3. COD

The graphic above showed that the reactor’s initial COD concentration fluctuated and was influenced by an increased concentration of amoxicillin pharmaceutical residue. Each concentration was running for five days with a residence time of 2.5 days so that it was able to remove COD contained in the artificial wastewater influent used. The activity of microorganisms in the septic tank sediment could remove COD. It occurs cause of the microbial metabolic process, which is the microorganism that needs high carbon as an energy source to adapt and grow, resulting in a decrease in the COD value. The microorganisms from the septic tank degrade organic material contained in wastewater optimally with an average COD removal rate of 12.67 mg/l.day, 10 mg/l.day, 8 mg/l.day, and 6.67 mg/l.day for each increase in the concentration of amoxicillin in the intermittent and continuous reactor.

The removal efficiency and the rate of reduction in COD concentration were different due to an increase in amoxicillin concentration as a pharmaceutical residue. The addition of 20 mg/l of amoxicillin resulted in the lowest removal compared to other reactors. Based on the Monod equation, it is \( \mu = \mu_{\text{max}} \frac{S}{K_s + S} \), a substrate (S) is a function of the growth rate (\( \mu \)). A small substrate limits the rate of waste degradation. The low substrate causes the growth rate (\( \mu \)) to be directly proportional to the substrate (S) so that the growth rate is slowed, and the steady-state is achieved longer. More substrate will accelerate the bacterial growth phase for longer. With fewer substrates, the bacterial growth phase will be slower, and the stationary phase is achieved longer so that COD removal is lower than the higher organic load.

3.1.4. Ammonium \((NH_4^+ - N)\). Ammonia is also the parameter tested in this study. Testing of ammonia parameters is carried out every day with a spectrophotometer using the Nessler method according to SNI 06-2479-1991.
Figure 5. Ammonium (NH$_4^+$-N) concentration.

The figure above showed that ammonia reduction's efficiency was the highest for the pharmaceutical residue with an ammonia concentration in the reactor. The higher the pharmaceutical residue added to the reactor will cause a decrease in ammonia, which is lower. The residence time and processing process affect ammonia removal; in addition to that, the operational conditions and the presence of inhibitors such as pharmaceutical residues are essential things that need to be considered in this study.

There are some causes that reducing the concentration of ammonia in this study is unstable, namely:

- Organic matter contained in wastewater is degraded by unstable heterotrophic bacteria so that it will affect the concentration of ammonia [5].
- The dissolved oxygen contained in liquid waste for the nitrification process is lacking [1]. The dissolved oxygen needed in the nitrification process is > 1 mg/l [5]. However, based on visual observations made, there was a darkening change in the wastewater color. According to Gray (2004), the wastewater should turn brown then change color to yellowish-brown according to the day's length. If all the oxygen in the wastewater is used for treatment, the wastewater will undergo anaerobic conditions, causing the wastewater to darken. The process of ammonia oxidation to nitrite can be seen in the following reaction:

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\text{NH}_4^+ + \frac{1}{2} \text{O}_2 + \text{OH}^{-} \rightarrow \text{NO}_2^- + \text{H}^+ + \text{H}_2\text{O}.
\]

- The turbidity of wastewater affects the ammonia removal process by microorganisms attached to the substratum layer [6].

4. Conclusion

The efficiency of COD reduction at increasing concentrations of amoxicillin 0 mg/l, 5 mg/l, 10 mg/l and 20 mg/l were 58.06 %, respectively; 48.48 %; 41.18 % and 35.14 %. Meanwhile, the ammonium reduction rate when the amoxicillin concentration was increased was 3.81 mg NH$_4^+$-N/l/day; 3.98 mg NH$_4^+$-N/l/day; 3.07 mg NH$_4^+$-N/l/day, and 2.21 mg NH$_4^+$-N/l daily. So it can be concluded that an increase in the concentration of amoxicillin in the intermittent and continuous reactor disrupts the reactor's stability and affects the removal of COD and Ammonium.

References

[1] Said N I and Tresnawaty R 2001 Fakultas Teknik Universitas Trisakti
[2] Suarbaua T 2013 Anaerob Fixed Bed Reaktor untuk Menurunkan COD, Fosfat (PO$_4$) dan Deterjen (Jatim: UPN)
[3] Sawyer, Clair N and Perry L Mc Carty 1978 Chemistry for Environmental Engineering (Mc. Graw Hill International)
[4] Tchobanoglous G, Burton F L dan Stensel H D 2003 *Waste Water Engineering: Treatment and Reuse* (New York: Metcalf & Eddy Inc)

[5] Gray N F 2004 *Biology of Wastewater Treatment* (Ireland: Imperial College Press University of Dublin)

[6] Herlambang A, Widayat W, Suprihatin 2010 *Penyisihan Amonia dalam Upaya Meningkatkan Kualitas Air Baku PDAM-IPA Bojong Renged dengan Proses Biofiltrasi Menggunakan Media Plastik Tipe Sarang Tawon* (6)