Integration of upflow anaerobic sludge blanket and constructed wetlands for pharmaceutical wastewater treatment

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Abstract. Pharmaceutical wastewater is a critical issue for environmental and human safety due to its resistance in character and toxicity. Studies reported that pharmaceutical residue and several drug metabolites have been detected in the aquatic environment and pose a high risk to humans and the ecosystem. Many technologies are ranging from conventional methods, such as activated sludge, anaerobic digestion, and aerobic membrane bioreactors (MBR), to advanced treatment, such as advanced oxidation process (AOP), or integration of more than one method. Integration of Upflow Anaerobic Sludge Blanket (UASB) and constructed wetlands was applied for pharmaceutical wastewater treatment discharged by one of Semarang's pharmaceutical industry. The performance of UASB and constructed wetlands were evaluated. Up to 75% and 94% of COD removal efficiency was achieved in UASB and constructed wetlands, respectively. An average of 95% of pollutant removal was achieved by the system, indicating the stability and potential of UASB and constructed wetland integration in pharmaceutical wastewater treatment.

1. Introduction

Pharmaceuticals are considered as basic needs and widely used in daily life. However, pharmaceutical industries generate quite a large sum of wastewater and discharge it to the ecosystem. Generally, the wastewater is originated from utility washing process, laboratory activity, and production process. Thus, wastewater discharged may contain solvent, catalysts, additives, and reactants and has a high value of Chemical Oxygen Demand (COD) [1]. Based on their characteristics, pharmaceutical wastewater is considered toxic and contain persistent pollutants.

In contrast, antibiotic-containing pharmaceutical wastewater may pose a high risk on the aquatic environment and human, therefore, needs to be treated before discarded to the environment. The previous studies have applied flocculation, coagulation, flotation, filtration, sedimentation, ion exchange, adsorption, and biological process as pharmaceutical wastewater treatment [2]. Ozonation was applied effectively to remove pharmaceuticals in Japan [3], while nanofiltration and reverse osmosis were also applied, ranging from lab scale to full scale [4]. However, the high investment cost is still the main problem hindering advanced technology in pharmaceutical wastewater treatment. In contrast, physical and chemical treatment show low efficiency in removing dissolved pollutants. High COD value and dissolved persistent pollutants in pharmaceutical wastewater indicate that anaerobic digestion may be suitable for treatment.
Anaerobic digestion has been widely applied in various wastewater treatment, ranging from bakery to municipal wastewater [5,6] and is mostly known as a highly effective method for soluble COD removal. Anaerobic digestion is superior in wastewater treatment, especially with high Organic Loading Rate (OLR), making it a dependable primary treatment and extensively studied. It is reported as a robust and highly efficient method, with the potential of generating renewable energy in the form of methane [7]. Previous studies reported the application of an up-flow anaerobic stage reactor, anaerobic suspended film reactor, and fluidized bed reactor as anaerobic treatment of pharmaceutical wastewater. While, as a form of the modern anaerobic process, Upflow Anaerobic Sludge Blanket (UASB) has been extensively reported as a suitable technology for wastewater treatment. UASB also can be applied for synthesis-based pharmaceutical wastewater treatment with high efficiency, due to operational advantages, and superior to the other form of anaerobic treatment.

Aside from UASB, this study also applied constructed wetland (CW) as a secondary treatment for further degradation of soluble contaminants contained in pharmaceutical wastewater. CWs are treatment systems imitating the natural ecosystem with high sustainability[8]. CWs have been developed extensively as industrial wastewater treatment, such as the coffee processing industry, titanium sponge industry, and pharmaceuticals. They can be constructed in various configurations to improve treatment performance [9–14]. They are reported as a low-cost alternative to replacing conventional wastewater treatment technology.

A combination of the anaerobic digester and constructed wetland has been applied before as a solution to avoid clogging in constructed wetlands. Clogging is regarded as the main problem in constructed wetlands due to the accumulation of solids in wastewater, leading to decreasing system performance. Anaerobic digestion application as the primary treatment and constructed wetlands as finishing treatment has been commonly used as wastewater treatment and considered very advantageous. The anaerobic process will remove most suspended solids and organic load, while constructed wetlands will process remaining contaminants with less possibility of clogging. As the organic load decreased, CW's required area will also reduce and lead to a lower investment cost [15]. The integration will resulted in a low cost and a highly efficient system with simple operation and maintenance.

This paper will evaluate the application of the integration system of UASB and CW for pharmaceutical wastewater treatment in a lab-scale system. The UASB and CW performance will be evaluated separately based on organic loading rate (OLR) and hydraulic retention time (HRT), indicated by COD removal efficiency. The system performance and effluent concentrations were monitored and evaluated. This paper will evaluate the whole system, in terms of effluent quality and stability.

2. Methodology
Pharmaceutical wastewater used in this study was obtained from one of the formulations of pharmaceutical industries' raw influent. Immobilized anaerobic culture was used as a seed for the UASB reactor, while Nitrogen and Phosphor were used as macronutrients. A laboratory-scale UASB reactor with a 190 mm diameter, 380 cm height, and 5.2 L working volume was used, as depicted in figure 1. UASB reactor was made of acrylic with a pyramid-shaped bottom as an influent channel. Peristaltic pump (Cole Palmer Masterflex L/S 7518-62) was connected to the influent point to feed raw wastewater to the UASB reactor. Influent to UASB reactor was set to high and low OLR, 1.1–2.0 kg COD/m³ day and 0.5–0.8 kg COD/m³ day, respectively, by adjusting the flow rate of the peristaltic pump. The effluent point of UASB was located at one side of the reactor and equipped with a partition to avoid suspension washout.
This study's constructed wetland system comprised two series of reactors with 17 L working volume and set based on horizontal subsurface flow constructed wetland (HSSFCW), with the wastewater level below the media surface. Each CW reactor was loaded with gravel and planted with Typha angustifolia, cyperus papyrus, and heleconia, and equipped with influent and effluent distribution pipe. Influent flowrate was set manually to adjust the hydraulic retention time. Plants were acclimated in the CW reactor in a circulated system continuously for two weeks. After the acclimation period, CW reactors were then fed by UASB effluent continuously.

The sample was collected from influent and effluent of UASB and CW reactors for COD measurement according to Standard Method. At the same time, pH was measured with a digital pH-meter at UASB influent and effluent points, starting from seeding, acclimation, and steady-state of the anaerobic process. Stable condition of anaerobic digestion in the UASB reactor was indicated by increasing pH to neutral value and an optimal COD removal in a minimum fluctuation (less than 10%, pseudo-steady-state) [1]. All chemicals used for COD measurements were pro analysis, and the analysis was carried out using Shimadzu spectrophotometer UV-Vis.

3. Results and discussion

3.1. Wastewater characteristics
Wastewater used in this research was in the same batch and had the same characteristics as reported in our previous study [16]. It was turbid and yellowish with a normal temperature. Wastewater discharged shows a fluctuate COD, ranging from 1100 to 3708 mg/L.

| No | Parameter | Result (mg/L) |
|----|-----------|---------------|
| 1. | TSS       | 126           |
| 2. | BOD       | 278           |
| 3. | COD       | 1976          |
| 4. | pH        | 7.4           |
| 5. | Total-N   | 12.25         |
| 6. | Phenol    | 0.782         |
3.2. Performance of UASB reactor

The anaerobic process operated continuously at various OLR (COD up to 1310,13 mg/L). An average HRT of 18 h reduced COD to 288.98 mg/L with COD removal efficiency up to 75%. Continuous operation of UASB was carried out for 25 days after the acclimation period (performance of UASB at the acclimation period was not presented). COD removal efficiency and overall performance of the UASB reactor at experimental conditions were described in figure 2.

![Figure 2. Performance of the UASB reactor at continuous operation.](image)

After the acclimation period, 100% of pharmaceutical wastewater was fed continuously at a constant HRT of ±18 h. Increasing OLR was achieved by increasing wastewater COD concentration. As described in figure 2, anaerobic digestion removed COD up to 75%, with an average removal of 48.98%. It is observed that anaerobic digestion's performance was fluctuating, possibly due to the presence of less biodegradable compounds contained in pharmaceutical wastewater. The COD removal efficiency was about 30-45% during the initial period, with an average OLR of 0.64 kg COD/m³/day and started to show an increasing trend and achieved 73.96% after day 8. However, the efficiency was found to decrease at an increased OLR of 1.12 kg COD/m³/day. Reactor performance was recovered within five days, and 60-75% removal efficiency was achieved. These results indicated that anaerobic digestion had adapted to decreasing COD and achieved a pseudo-steady state as in the initial period. Another study used a hybrid upflowed anaerobic sludge blanket reactor for chemically-synthesized pharmaceutical wastewater treatment and reported a similar result with an average COD removal efficiency of 70% and HRT of 2 d [1].

3.3. Performance of constructed wetland (CW)

CW reactor was operated at a relatively constant OLR (0.12 kg COD/m³ day) due to the relatively stable performance of UASB. As shown in figure 3, CW removal performance at the initial period of the experiment was relatively stable at 92 – 94%. The COD removal efficiency was dropped to 40 – 69%, possibly due to the instability of UASB at increased OLR, leading to the low quality of UASB effluent or CW influent. However, the CW unit improved on day 15 and achieved a stable and high COD efficiency of 90 – 92%. The primary pollutant removal mechanisms in CW are microbial processes, such as nitrification and denitrification, in addition to physicochemical processes, such as fixation of phosphate by iron and aluminum in gravel media [17].

Furthermore, CW is also a superior technology because plants can tolerate high concentrations of organic compounds and heavy metals and accumulate them in their tissues. The result also indicates that
CW, as a secondary unit, is mainly dependent on prior unit performance, which is UASB in this experiment. Thus, it is essential to choose a suitable and robust technology to anticipate shock loading and ensure system performance. It can be concluded that UASB is suitable as a pretreatment of CW, as UASB is able to reduce organic loading, shows high COD removal efficiency, and has a high potential to recover from shock loading. It is in accordance with the result of another study [8], which reported high suspended solids removal efficiency when treating winery wastewater.

**Figure 3.** The COD removal efficiency of constructed wetland (CW).

3.4. **Performance of the integrated system**
The results mentioned above agree with the total system performance, as shown in figure 4. It is found that the system performance was high from the beginning of the experiment (90 – 94%), though showed a fluctuation in the process, the system was recovered and achieved a stable and high cod removal efficiency of 93 – 96%. This result supports the potential of UASB and CW as an integrated technology for wastewater treatment.

**Figure 4.** Performance of integration of UASB and constructed wetland (CW).

4. **Conclusion**
Upflow anaerobic sludge blanket reactor showed high performance of pollutant removal efficiency in pharmaceutical wastewater treatment. Constructed wetland unit as a secondary treatment also achieved a high removal and was able to support UASB. The UASB reactor was operated at HRT for approximately 18 h and removed up to 75% of COD. The CW was operated continuously at a relatively
low OLR of 0.64 kg COD/m³ day, due to the high performance of UASB, and found to be efficiently effective in removing remaining pollutants. Integration of UASB and CW shows promising potential as a low cost and effective wastewater treatment with COD removal efficiency ranges between 90 and 96%.

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