Treatment of Pulp and Paper Wastewaters in an Upflow Anaerobic Sludge Fixed Film Bioreactor


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Abstract: The performance of a UASFF (Upflow Anaerobic Sludge-Fixed Film) reactor for treating pulp and paper wastewater were investigated. The COD, COD_{lab}, COD_{ad}, COD_{mep}, pH, MLSS and alkalinity were evaluated for continuous operation in duration of 113 days. Initially the system was operated at HRT of 24h till the system reached steady state condition. In the next stage, experiments were carried out with variation of HRT 24, 18, 12 and 8h for duration of four weeks. Since the system was sensitive to accumulated toxic compounds, partial recirculation of the effluent was applied to dilute fresh feed. The recirculation rate (10% of fresh feed) slightly improved the removal efficiency. Effect of HRT was investigated, while HRT was reduced from 24 to 8 h, the average COD_{lab} removal efficiency dropped from 71 to 45%. At HRT of 24 hours maximum soluble COD removal of 82% was achieved. As the organic loads were gradually increased from 1.6 to 7.9 gCOD m^{-1} d^{-1}. The COD removal was dropped to 35%. The HRT was affected on OLR, as HRT decreased the OLR was increased but the performance of the bioreactor was decreased.

Keywords: UASFF · Pulp and paper wastewater · COD_{lab}, OLR · Granulated particles · Anaerobic treatment

INTRODUCTION

Industrial wastewaters are highly pollutants to environment, treatment plants are designed to deliver clean effluent with permissible composition for discharge of industrial effluents. Based on nature of wastewater suitable treatments are employed. Biological treatments are considered as the most economical process with waste minimization aspects [1-3]. Pulp and paper wastewater is riched with lignocellulosic and aromatic compounds [4-7]. Simple oxidation ponds are unable to deteriorate the ring structure of effluents originated from pulp digesters. The black liquor from paper mills generate varieties of pollutants depending upon the type of the pulping process [5, 8, 9]. The Kraft process may create high pollutants and is responsible for large discharges of highly polluted effluents. Such effluents have high toxicity and low biodegradability, because of their tannins, lignins, resins and chlorophenolic compounds. The composition of these effluents, which has a great influence on mechanisms of treatability, may vary considerably, depending on the raw material and manufacturing process utilized. It also may worth to be mentioned that the liquids from alkaline, wood resins and tannins are potentially toxic to methanogenic Archaea. Moreover, the degradation of lignin by the anaerobic consortium is limited to low molecular weight fraction [4-6, 10-12].

An anaerobic pre-treatment of industrial wastewaters can greatly enhance the final effluent quality and is currently being used in some plants [4, 13]. It was clearly understood that aerobic process might be very deficient to degrade aromatic compounds even the process is considered as fast and simple. Most pulp and paper mills are benefited from activated sludge plants and aerated lagoons to treat their wastewater. One of the main disadvantages of aerobic plants is the production of large amounts of sludge that requires disposal and energy for aeration [5, 13, 14]. However, due to lower operational costs and potential to degrade some recalcitrant compounds, the anaerobic treatment process is the most suitable alternative to handle pulp and paper wastewater [1, 2, 5, 13].

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Anaerobic process has been successfully applied in the treatment of nontoxic and easily biodegradable wastewaters from pulp and paper plants. However, the high toxicity of the effluents from chemical, semi-chemical and chemo-thermomechanical pulping have restricted the application of the anaerobic process for the treatment of these effluents. However, the biological treatment of bleached pulp and paper wastewater has been reported in the literature [1, 2, 5, 15]. One of the major disadvantages of anaerobic treatment process having long HRT and also has limited capacity; unable to handle massive amount of pulp and paper wastewater. UASB has the potential to degrade aromatic compounds but it requires long duration for adaptation and biogranulation core metrics in the sludge bed [12, 16, 17].

The upflow anaerobic sludge fixed film bioreactor (UASFF) combines the advantages of the upflow anaerobic sludge blanket (UASB) and upflow anaerobic fixed film (UAFF) concepts. A novel anaerobic processes used for high rate reactors such as UAFF have been applied to the treatment of a wide variety of industrial wastewaters with a high soluble COD content, including paper-pulp liquors, spent sulphide liquors and those from the food industry. A hybrid system of UASB and upflow anaerobic packed bed reactors (UAPB) have been successfully applied to the partial treatment of fiberboard manufacturing wastewaters distillery spentwash water and slaughterhouse effluent. The hybrid system is known as UASFF reactors could also become a preferred option for certain chemical synthesis-based pharmaceutical wastewaters due to several operational advantages over other reactor configurations. It has been reported that UASFF has successfully been used for the treatment of palm oil mill effluent, pharmaceutical wastewater [9, 18-23].

The main objective of the present work was to demonstrate the performance of an UASFF reactor treating pulp and paper wastewater from Mazandaran pulp and paper factory. The investigations were conducted on variation of HRT, OLR and several process operation conditions. The results obtained from UASFF were promising for scale-up. The findings are useful for biological treatment of pulp and paper wastewater.

**MATERIALS AND METHODS**

**Wastewater Characteristics:** The fresh wastewater was supplied from the effluent of stabilization tank of the primary treatment unit, Mazandaran pulp and paper factory (Sari, Iran). This plant has capacity of production for 90000, 42000 and 32000 tons per year of Kraft paper, newspaper and printing papers, respectively.

**Table 1: Main characteristics of wastewater of Mazandaran pulp and paper factory**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily volume (m³ d⁻¹)</td>
<td>16416</td>
</tr>
<tr>
<td>Flow rate (m³ h⁻¹)</td>
<td>684-1080</td>
</tr>
<tr>
<td>pH</td>
<td>Generally slightly alkaline</td>
</tr>
<tr>
<td>Temperature (oC)</td>
<td>35-55</td>
</tr>
<tr>
<td>SS (mg l⁻¹)</td>
<td>600-1100</td>
</tr>
<tr>
<td>Volatile suspended solids/suspended solids (VSS/SS)</td>
<td>0.6-0.7</td>
</tr>
<tr>
<td>COD₉₅ (mg l⁻¹)</td>
<td>2200-2900</td>
</tr>
<tr>
<td>COD₉₅ (mg l⁻¹)</td>
<td>1200-1700</td>
</tr>
<tr>
<td>COD₉₅ (mg l⁻¹)</td>
<td>1000-1700</td>
</tr>
<tr>
<td>COD₉₅ (mg l⁻¹)</td>
<td>120-180</td>
</tr>
<tr>
<td>COD₉₅ (mg l⁻¹)</td>
<td>300-700</td>
</tr>
<tr>
<td>BOD₅ (mg l⁻¹)</td>
<td>1025-1280</td>
</tr>
<tr>
<td>N₉₅ (mg l⁻¹)</td>
<td>6</td>
</tr>
<tr>
<td>P₉₅ (mg l⁻¹)</td>
<td>1</td>
</tr>
<tr>
<td>Resin acids (mg l⁻¹)</td>
<td>40-220</td>
</tr>
<tr>
<td>Sulfur, SO₂ and SO₃ (mg l⁻¹)</td>
<td>100-200</td>
</tr>
<tr>
<td>DTPA</td>
<td>20-50</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>40-100</td>
</tr>
</tbody>
</table>

The characteristics of the plant effluent were summarized in Table 1. The nature of pulp and paper wastewater is its toxicity which was the effluents collected from number of paper producing units and the effluent contained xenobiotic compounds, which are formed and released from various stages of papermaking. Generally the pulp and paper plants may generate 20-70 m³ wastewater per ton of paper.

The wastewater was weekly collected from the plant and transported to the laboratory, refrigerated and stored at 4°C to avoid acidification and any changes of the chemical composition of the wastewater.

The supplied fresh feed was diluted and pH was adjusted to 7.0 with 0.1M NaOH solution. Supplementary nutrients such as urea and phosphorous (KH₂PO₄) were added to maintain COD:N:P ratio of 250:5:1.

**Experimental Set-up:** The schematic diagram of the pilot scale UASFF bioreactor is shown in Figure 1. The reactor was fabricated with an internal diameter of 2.76 cm and a height of 160 cm. The total volume of the reactor was 960 ml. The column was randomly packed with seashell. The voidage of the packed bed reactor was 85 percent. A 1000 ml funnel shaped gas separator was used to liberate the generated biogas from the effluent and then the gas was led to the gas collector. The gas tank was a cylindrical glass pipe ID 40mm and volume of 1250 ml. The liberated gas was frequently measured for a fixed HRT and the gas volume was recorded with respect to time. The UASFF reactor was operated at a fixed
temperature (37°C). The reactor temperature was controlled by external circulation of hot water bath. The feed from pulp and paper wastewater as a suitable substrate was continuously fed to the reactor using a peristaltic pump (SR25 adjustable flow rate, Thomas, Germany). The feed was introduced from the bottom of the column and it was distributed through the column using a perforated plate. The effluent was collected from the top of the column in a 20 liter polyethylene container.

Seeding Sludge: The inoculum for seeding was a mixture of sludge taken from the existing wetland, cow dung and Pseudomonas putida supplied from stock culture in biotechnology research lab (Babol UT, Iran). The sludge was initially passed through a screen to remove debris.

Reactor Operation: In order to evaluate the system’s characteristics, experiments were initially conducted under anaerobic batch operations. The granulation column was fabricated with a glass tube with an internal diameter of 2 cm and a height of 40 cm. The prepared seeding sludge was transmitted into the granulation column with addition of glucose, yeast extract, K₂HPO₄ in a one liter medium with a COD:N:P ratio of 150:5:1. The system was operated in a closed recycle loop. The core formation and granulation period was prolonged for three weeks.

For UASFF operation the produced granulated sludge were transmitted into the reactor for start-up operation. Fresh feed was gradually pumped into the column. The wastewater was added to the reactor with an HRT of 24 h for duration of 20 days.

The experiments were performed in two different stages. In the first stage the experiments were conducted without recirculation for duration of 28 days for several HRTs such as 24, 18, 12 and 8 hours. Samples were often withdrawn for COD, pH and MLSS analysis. In the second stage, the experiments were conducted with recirculation ratio of 0.1.
Analytical Methods: A colorimetric method using closed reflux system was developed for measurement of COD. Spectrophotometer (Unico2100, USA) at wavelength 600 nm was used to measure the light absorbance of COD samples. Based on standard method, potassium hydrogen phthalate (KHP) standard solution was prepared in the range of 0 to 1000 mg L⁻¹ as the wastewater sample had a high COD range. Therefore 425 mg of KHP was dissolved in 500 ml of distilled water. KHP has a theoretical COD value of 1.176 mg O₂ mg⁻¹. Thus, the standard KHP solution, 1000 mg L⁻¹ has a theoretical COD value of 1176 mg O₂ L⁻¹. The standard KHP solution was used for the preparation of COD calibration curve. The biogas was measured by displacement of water in the gas tank and pH of the effluent was measured by a pH meter, HANNA Model 21 (Italy).

For process follow-up and performance total COD (CODₜ) and filtered COD (CODₚₐ) (also referred as SCOD in Paper) typically were analysed and for CODₚₐ both Schleicher and Schuell GF50 and Whatman GF/A filters were used. Both filters have an approximate pore size of 1.6 μm. Soluble COD (CODₚₐ) samples were filtered with a 0.45 μm 21 Schleicher and Schuell membrane filter and pre-filtered with GF/A or GF50 filters. COD was also characterized into more detailed fractions, such CODₚₐ, suspended COD (CODₚₐ₈₉₂₉), colloidal COD (CODₚₐ₉₉₉₉) and CODₚₐ, of which CODₚₐ₈₉₂₉ and CODₚₐ₉₉₉₉ were calculated values. CODₚₐ₈₉₂₉ is the difference between CODₚₐ and CODₚₐ₉₉₉₉. Also CODₚₐ₉₉₉₉ is the difference between CODₚₐ and CODₚₐ. Other parameters, such as COD, suspended solids (SS), volatile suspended solids (VSS) and alkalinity were analyzed using procedures outlined in Standard Methods [24].

Operational and Performance Parameters: A hybrid system for the anaerobic treatment was performed that system was incorporated with acidogenesis and methanogenesis process. For the treatment of pulp and paper wastewater, the UASSF was operated under optimum operating conditions. In order to obtain optimum results, the system was experimented with several HRT and organic loading rate (OLR).

RESULTS AND DISCUSSION

The UASFF pilot system was under operation in order to investigate several influential parameters on performance of the process. The HRT was initially set at 24h and the pulp and paper wastewater was gradually introduced into the column. The organic load was stepwise increased as the HRT was maintained at constant value. Once the system was very stable and operated at steady state condition, the HRT was reduced. Then the performance of UASFF was evaluated for each set of HRT; the fluctuating OLR was another set of variables in UASFF. As the OLR was increased to 7.9 kg COD m⁻³ d⁻¹, the COD removal rate was decreased.

Acclimation to Pulp and Paper Wastewater: Prior to start-up, the UASSF reactor was inoculated with approximately 500 ml of granular sludge from granulation process. The UASSF was successfully operated for duration of 113 days.

Glucose is a readily degradable as soluble carbohydrate never caused any limitation for the rate of anaerobic biodegradation. It produces readily measurable intermediary metabolites in anaerobic digestion and is commonly used as a carbonaceous substrate in many experimental studies. Glucose was, therefore, used as a sole source of energy during the initial acclimation phase. In the latter stages of experiment, glucose was gradually replaced with pulp and paper wastewater.

Accordingly, the hybrid reactor was initially fed with glucose at an OLR of 3 kgCOD m⁻³ d⁻¹ with a hydraulic retention time (HRT) of 24 hours, which was then gradually increased to 7 kgCOD m⁻³ d⁻¹. The hybrid reactor performed well at an OLR of 1.73 kgCOD m⁻³ d⁻¹ at which point 44% COD removal efficiency was achieved. Variations in COD removal efficiency was minimized in the range 10% for a period of at least four HRTs. That was considered as stability of the system had reached a pseudo steady-state condition. A summary of the operational schedule with operating conditions applied to the hybrid UASB reactor is given in Table 2.

After the completion of acclimation stage, the glucose in the feed stream was gradually replaced by pulp and paper wastewater. In the first week, the reactor was fed with an influent COD of 2500 mg L⁻¹ (OLR = 2.63 gCOD L⁻¹ d⁻¹). The proportion of the pulp and paper wastewater in the feed stream was in stepwise increased, with the proportion of 10, 30, 70 and 100% (w/v) pulp and paper wastewater (Table 2). Throughout this transition, the OLR was maintained at 7 kgCOD m⁻³ d⁻¹ and the HRT was kept at 24 hours. Introducing 10, 30 and 70% (w/v) pulp and paper wastewater caused decrease in COD removal efficiency. At the end of the feeding with 100% (w/v) pulp and paper wastewater, the COD removal efficiency dropped to the lowest value of 36%. The influent COD was fluctuated and COD of
Fig. 2: COD removal efficiency during start-up period

Fig. 3: COD\textsubscript{tot} and COD\textsubscript{filt} removal efficiency (%) with respect to HRT

Fig. 4: Variation and removal efficiency of COD\textsubscript{sol}

Fig. 5: MLSS and OLR variations

Fig. 6: Alkalinity variations in influent and effluent

Fig. 7: pH variations of effluent
Table 2: Summary of operational schedule of the hybrid UASB reactor.

<table>
<thead>
<tr>
<th>Stage no</th>
<th>Operation mode</th>
<th>Time (d)</th>
<th>Feeding strategy</th>
<th>Influent COD (mg l⁻¹)</th>
<th>OLR (gCOD l⁻¹ d⁻¹)</th>
<th>HRT (h)</th>
<th>Temperature °C</th>
<th>RF*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Batch</td>
<td>8</td>
<td>Wastewater</td>
<td>2900</td>
<td></td>
<td></td>
<td>24</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Osmosis</td>
<td>21</td>
<td>Glucose</td>
<td>4000-6000</td>
<td>1.3</td>
<td>4</td>
<td>24</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>Acclimation</td>
<td>1-20</td>
<td>10% (v/v) wastewater</td>
<td>1500</td>
<td>6</td>
<td>24</td>
<td>37</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>90% (v/v) glucose</td>
<td>5400</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>21-33</td>
<td>10% (v/v) wastewater</td>
<td>1700</td>
<td>6</td>
<td>24</td>
<td>37</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>70% (v/v) glucose</td>
<td>6000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>34-44</td>
<td>70% (v/v) wastewater</td>
<td>1900</td>
<td>7</td>
<td>24</td>
<td>37</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>80% (v/v) glucose</td>
<td>4500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Operating without recirculation</td>
<td>45-52</td>
<td>100% (v/v) wastewater</td>
<td>1500</td>
<td>7</td>
<td>24</td>
<td>37</td>
<td>0.9</td>
</tr>
<tr>
<td>5</td>
<td>Operating with recirculation</td>
<td>53-81</td>
<td>100% (v/v) wastewater</td>
<td>1500-2500</td>
<td>6-8</td>
<td>24-8</td>
<td>37</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*RF: Recirculation/Feed

The effluent COD after 7 days were gradually recovered and reached to 44%. After 10 days of operation the system was fed with the low value of COD in order to recover the COD removal. The system was successfully passed through the start up period absolutely acclimated to pulp and paper wastewater in duration of 52 days. Figure 2 represents the fluctuation of effluent COD and COD removal efficiency in the period of start-up and acclimation. The actual pulp and paper wastewater was treated in the UASFF with COD in the range of 5000 to 6950 mg l⁻¹.

The influent CODin concentration was stepwise increased 1045 to 2200 mg l⁻¹ and remained for 7 days. It is clear from the illustrated data increase in influent COD (1045 to 2200 mg l⁻¹) caused reduction in CODremoval efficiency. These observations were attributed to the sudden increase in COD loads which was resulted in organic shocks to the microbial consortia. In case high organic shocks and for the new environment, additional acclimation time was required.

Continuous Operation at Steady State Condition:
After the completion of the acclimation period the UASFF was ready for continuous operation for the treatment of pulp and paper wastewater. To demonstrate the high performance of UASFF for maximum COD removal, the OLR was gradually increased from 3 kgCOD m⁻³ d⁻¹ to 9 kgCOD m⁻³ d⁻¹.

Figure 3 shows the COD removal from day 53 to 113. In this duration the HRT was 24, 18, 12 and 8 h. This HRT variation was repeated for the reproducibility of data. When the HRT was set at 24 h with OLR 1.46 kgCOD m⁻³ d⁻¹, the removal efficiency was 80%. Once HRT reduced to 18, 12 and 8 the removal efficiencies dropped to 70, 56 and 44%, respectively.

Figure 4 depicts soluble COD with respect to HRT. The effluent COD concentration and COD removal had similar trend as discussed in Figure 3. For HRT of 24, 18, 12 and 8 h the soluble COD removal efficiencies with recirculation were 82, 63, 61 and 56, respectively. Recirculation of effluent has enhanced the COD removal efficiencies by 12%.

Figure 5 represents MLSS and OLR for the HRT of 24, 18, 12 and 8 h. The MLSS concentration was retained about 360 mg l⁻¹ while at HRT of 8 h the MLSS drastically dropped to less than 50 mg l⁻¹. The OLR at HRT of 8 h sharply increased to 7.98 g COD l⁻¹ d⁻¹. The trend for MLSS is opposite to OLR, as the OLR increases the MLSS decreases. At HRT 24 h for the second round OLR of the effluent has decreased. The MLSS was reported more than 380 mg l⁻¹.

The alkalinity of the influent and effluent are shown in Figure 6. Variation of alkalinity shows the intermediate products were formed.

Figure 7 of shows the effluent pH variations of anaerobic media. The acidification may be due to
incompletion of digestion cycle as the organic matters are hydrolyzed and acidified. Finally, at latest stage of UASFF, methane formed. Short HRT may caused slightly acidic conditions. Overall pH represent almost stable at about pH value of 7.

The COD removal with and without recirculation are shown in Figures 8 and 9. The total COD removal, COD\textsubscript{th}, and soluble COD with and without recirculation are shown 50-60, 55-65 and 70-80, respectively. The recirculation showed slightly improvement in the treatment process.

CONCLUSIONS

The UASFF was successfully operated for stepwise increase in OLR from 1.6 to 7.9 kg COD m\textsuperscript{-3} d\textsuperscript{-1}. The COD removal efficiency without recirculation for pulp and paper wastewater for HRTs 8, 12, 18 and 24 h in UASFF were 44, 52, 54 and 59%, respectively. The COD removal efficiency was improved 13%. The maximum soluble COD removal efficiency for HRT 24 h was 80%. The filtrated COD removal was much higher than total COD removal. It was concluded that the optimum condition with circulation for UASFF at HRT of 24 h, influence COD of 2800 mg l\textsuperscript{-1}, pH value of 7, OLR 2.92 kg COD m\textsuperscript{-3} d\textsuperscript{-1}, resulted maximum soluble COD removal of 82%.

REFERENCES