PERFORMANCE OF AERATED SUBMERGED FIXED-FILM BIOREACTOR FOR TREATMENT OF ACRYLONITRILE-CONTAINING WASTEWATER

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ABSTRACT
Acrylonitrile is used as the main raw material for manufacturing acrylonitrile butadiene styrene resin. It is usually found as pollutant in the petrochemical wastewater. In this research an aerated submerged fixed-film reactor was developed to treat a synthetic acrylonitrile butadiene styrene unit wastewater containing acrylonitrile. Laboratory experiments were conducted using a bioreactor with 44.2 L capacity operated at different hydraulic and organic loading rates. Stationary submerged biofilms were attached to net-type media (polypropylene) under diffused aeration. The specific surface area and porosity of media were 324 m$^2$/m$^3$ and 87%, respectively. In the first phase the reactor was operated in hydraulic retention times of 9, 7, 5 and 4 h with soluble chemical oxygen demand of 300 mg/L. Then the experiments were continued with the constant retention time of 4 h and variable chemical oxygen demand concentrations of 350, 400 and 450 mg/L. In stable condition of operation and loading rates of 0.8 to 2.4 kg/m$^3$/d the removal efficiencies of reactor for soluble chemical oxygen demand reached to 95 to 99%. At the organic loading rate up to 2.4 kg/m$^3$/d the soluble chemical oxygen demand was less than 50 mg/L which was lower than the Iranian national discharge standards (chemical oxygen demand<60 mg/L). The increase of organic and surface loading to 2.7 kg/m$^3$/d and 23.16 g/m$^2$/d, respectively, caused the system becoming unstable and the soluble chemical oxygen demand removal efficiency decreased to 66%. Finally, the kinetic coefficients of the aerated submerged fixed-film reactor for treating of acrylonitrile were determined using a separate pilot unit. According to the results, it was concluded that the aerated submerged fixed-film reactor can be used as suitable approaches for treating of petrochemical effluents contain acrylonitrile.

Key words: Acrylonitrile; acrylonitrile butadiene styrene resins; Aerated submerged fixed-film reactor; Petrochemical wastewater; Biological treatment

INTRODUCTION
The manufacturing of acrylonitrile butadiene styrene (ABS) resin is one of the most important units in Tabriz Petrochemical Complex in the northwest of Iran. The ABS manufacturing wastewater contributes to high total Kjeldahl nitrogen to chemical oxygen demand ratio (TKN/COD) that indicates biodegradation refractory characteristics (Table 1). High-strength organic-nitrogen wastewater has major harmful effects upon the environment and public health (Wang and Lee, 2001). Acrylonitrile (AN), ($CH_2=CH-CN$), is an important industrial raw material frequently used in the manufacturing of ABS resin. AN is emitted from the industrial plants in the form of vapors and aqueous effluents. It is the third item in the
EPA list of 129 priority pollutants (Kumar et al., 2008). AN is classified as highly toxic due to its cyanide effect and there are also indications of carcinogenic and teratogenic activities (Martínková et al., 2009).

Available methods for ABS resin wastewater treatment consist of adsorption on activated carbon, chemical oxidation and microbial degradation, with their merits and limitations in applications (Chang et al., 2006a). In addition, high operational cost associated with chemical methods such as ozonation and photocatalytic oxidation and harsh reaction conditions in generating secondary pollutants have often made them not a desirable choice (Li et al., 2007). However, the ABS wastewater is generally treated using activated sludge process based on environmental and economic considerations, but it is inefficient due to the presence of recalcitrant and/or inhibitory aromatic compounds and nitriles (Hu and Kung, 2000). Therefore, finding an alternative method for treating ABS resin wastewater has become a critical issue to satisfy the effluent discharge standards.

During the last two decades, attached growth bioreactors are increasingly being used in place of suspended growth ones because of their resistance to short-term toxic loads, ability to perform at low influent substrate concentrations, and high volumetric biomass concentrations, which allow to have small reactor volumes (Riefler et al., 1998). However, new versions of attached growth bioreactors have been developed. Aerated submerged fixed-film reactor (ASFFR) is a novel system in which total submerged fixed media is used to support biomass growth as a thin biofilm on their surfaces. Diffusers are also used to provide air bubbles for both aeration and turbulence. Turbulence created this way prevents the excessive biofilm growth.

There have been several reports on the application of ASFFR process for both municipal and industrial wastewater treatment.

Practical kinetic approach for interpreting an ASFFR was described by Hamoda (Nabizadeh and Mesdaghinia, 2006). An experimental study using lab-scale ASFFRs for treating petrochemical wastewater was shown 91.8% to 96.6% removal efficiencies of soluble COD (SCOD). It exhibited efficient and stable performance at organic loading rates (OLR) of 1.02 to 6.21 kg/m³.d (Park et al., 1996). Satisfactory application of an ASFFR in removing high ethylene glycol loads was also reported (Nabizadeh et al., 2000). High solids retention time of the ASFFR provides more appropriate conditions for nitrifying bacteria, so the system was used for simultaneous carbon and nitrogen removal. It has been shown that the ASFFR was able to handle the increase in continuous severe OLR from 5 to 120 g/m².d of biological oxygen demand (BOD) with a slight decrease in organic removal efficiency from 97.9 to 88.5% for BOD and 73.6% to 67.8% for COD (Hamoda and Al-Sharekh, 1999).

Performance of an ASFFR was evaluated under organic and ammonia loading rates of 1.93 to 5.29 g/m².d and 116 to 318 mg.NH₄-N/m².d, respectively. It has been shown that with OLR up to 3.97 g/m².d, complete nitrification was achievable while high organic loading such as 5.29 g/m².d could cause nitrification to be stopped (Nabizadeh and Mesdaghinia, 2006).

In another development, an ASFFR was used to treat an artificial wastewater based on crude oil. It has been shown that the system was able to achieve 83.1% to 97% removal efficiencies of SCOD in the OLR of 0.84 to 9.41 g/m².d (Izanloo et al., 2006). In another study, the aerobic submerged biofilter has been used to biodegradation of AN. Experimental results have shown that the upper limit of AN loading to the biofilter for the ultimate degradation of the influent AN was about 2 to 2.2 kg/m².d (Hu et al., 1998).

ASFFR has been proven to be an effective process for treating various industrial pollutants. However, the treatability information of AN-containing wastewater by the ASFFR is relatively limited in

Table 1: Typical values for an ABS unit wastewater (Wang et al., 2001)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.8–7.4</td>
</tr>
<tr>
<td>COD, mg/L</td>
<td>4282–6985</td>
</tr>
<tr>
<td>BOD, mg/L</td>
<td>75–3700</td>
</tr>
<tr>
<td>BOD₅/COD</td>
<td>0.23–0.51</td>
</tr>
<tr>
<td>Acrylonitrile, mg/L</td>
<td>185–292</td>
</tr>
<tr>
<td>Organic N, mg N/L</td>
<td>478–880</td>
</tr>
<tr>
<td>TKN, mg N/L</td>
<td>626–949</td>
</tr>
<tr>
<td>Total P, mg P/L</td>
<td>0.2–0.3</td>
</tr>
</tbody>
</table>
the literature. Hence, an adequate understanding of the effects of changing operational parameters on the ASFFR performance is essential for developing effective AN control strategies. So, the major purpose of this study was to investigate the performance of ASFFR for treating AN-containing wastewater under different hydraulic retention times and influent AN concentrations. In addition, biofilm kinetics of ASFFR was determined to describe the characteristics of the reactor.

MATERIALS AND METHODS
Specifications of the ASFFRs
In this study, two lab-scale ASFFRs were used with the specifications described in Table 2. The reactors were covered by black paper to minimize algal growth. Schematic diagram of experimental system with specifications of the packing media are shown in Fig. 1 and Table 3, respectively. Air was supplied through a fine-bubble diffuser at the bottom of the reactors and the wastewater was co-currently fed to the reactors by a peristaltic pump which was calibrated according to the desired wastewater flow rates. The air flow rate was controlled by a flow-meter and was also adjusted using a valve to keep the dissolved oxygen higher than 2 mg/L.

Startup period
Return activated sludge from wastewater treatment plant of Tabriz petrochemical complex was taken as seed sludge in the experiments. The reactor was first operated on batch mode with clean supporting media to develop attached microbial films. Then the operation was changed to the continuous mode with flow rate of 3.01 L/h. The startup period was continued for about 2 months in order to achieve stable operation as constant effluent SCOD. The artificial wastewater was prepared using glucose, NH₄Cl and KH₂PO₄ as a source of carbon, nitrogen and phosphorus, respectively to have COD:N:P ratio of 100:5:1. The average TCOD and pH range of the influent were 550 mg/L and 7.4 to 7.9, respectively. To avoid sharp pH changes in the reactor, the alkalinity of influent was adjusted to 500 mg/L as CaCO₃. The air flow rate was maintained constant at 4 L/min and the liquid temperature varied from 23 to 25°C. Influent and effluent wastewater samples

![Fig. 1: Schematic diagram of the experimental system](image-url)
were daily analyzed for SCOD, total suspended solids (TSS), volatile suspended solids (VSS), alkalinity, nitrate, soluble phosphorus and pH.

**Operational details of experimental procedure**

The experimental program lasted for more than 5 months during which the wastewater temperature was in the range of 19 to 30°C. Seven experimental runs were subsequently carried out, where the conditions of each run is summarized in Table 4. In all runs, AN was used as the sole organic substrate which the COD:N:P ratio was maintained as 100:5:1. At the first four runs, the reactor was loaded to provide hydraulic retention times (HRTs) of 9, 7, 5 and 4 h with soluble COD of 300 mg/L. The experiments were continued with the constant HRT of 4 h and variable COD of 350, 400 and 450 mg/L at runs 5, 6 and 7, respectively. Overall, the OLR were provided in the range of 0.8 to 2.7 kg/m³d. Each experimental run lasted about 3 to 4 weeks of stable operation with about 3 to 5 days between successive runs to allow for adaptation to new conditions.

Dissolved oxygen (DO) levels were kept at a minimum of 2 mg/L throughout the experimental runs. During the period of stable operation of each runs, influent and effluent samples were daily taken. The collected samples were filtered using Whatman’s filter paper with pore size of 0.45 μm for analyzing COD, AN, NH₄-N, soluble P, nitrate and alkalinity. Unfiltered samples were used to determine TSS and VSS. The attached biomass weight was determined by scraping the biofilm from the supporting media surface and weighing the dried biomass gravimetrically.

**Experimental set-up for determining of kinetic coefficients**

Specifications of the reactor are given in Table 2 as ASFFR2. Startup phase of the reactor was similar to ASFFR1 with COD of 300 mg/L. At steady state conditions, different OLRs were applied with constant HRT of 5.78 h. Three pilot runs were performed with AN concentrations of 100, 250 and 400 mg/L to provide OLRs of 0.415 to 1.66 kg/m³d. During the period of stable operation of each runs, influent and effluent SCOD, effluent VSS and attached biomass were daily analyzed. Finally, the values of kinetic coefficients including, Kₛ, k, Y, K_d and μ_max were determined using the equations 1 to 3, based on the kinetic model described by Hamoda (1989).

\[
\frac{1}{S} = \frac{k}{K_s} \left( \frac{AX}{Q(S_0 - S)} \right) - \frac{1}{K_s} \quad (1)
\]

\[
\frac{(S_0 - S)}{X} = K_d \left( \frac{AX}{Y} \right) + \frac{1}{Y} \quad (2)
\]

\[
\mu_{max} = kY \quad (3)
\]
Where, \( S_0 \) and \( S \) are the concentrations of substrate in the influent and effluent (g/m^3), respectively; \( Q \) is the flow rate (m^3/d); \( A \) is the microbial growth surface area (m^2); \( X \) is the concentration of effluent VSS (g/m^3) and \( X' \) is the attached microbial mass (g VS/m^2).

**Analytical techniques**

COD, pH, DO, TSS and VSS, \( \text{NH}_4^+ \)-N, \( \text{NO}_3^- \)-N, \( \text{PO}_4^{3-} \)-P, alkalinity and AN were measured according to Standard Methods (APHA, 2005). AN concentrations were analyzed using a gas chromatograph (Shimadzu-2010, Japan) equipped with a Shimadzu CBP-20 capillary column and a flame ionization detector. The injector was kept at 170°C; the column was programmed from 40 to 230°C at 40°C/min increments (3 min hold), and the detector was set at 230°C.

**RESULTS**

**Startup period**

The biofilm growth on the clean supporting media surfaces in the reactor was visually observed after 12 days of batch mode operation and the biofilm started to expand gradually during the continuous operation of the reactor. The stable biofilm was observed on the whole of the media surfaces at the steady state condition. Based on the results, the pH remained in the range of 6 to 8.11 throughout the experiments and there were no significant changes in pH of the effluent due to feed sufficient alkalinity.

After 21 days, the pilot reached a steady state condition based on the effluent SCOD concentrations, where the average value and removal efficiency of SCOD were 30 mg/L and 94.5%, respectively. During the steady state conditions, DO was in the range of 3 to 5 mg/L. In addition, the average value of TSS in the steady state condition was 65.2 mg/L. At the end of 8 days of the startup period, the average values of nitrate and alkalinity in the effluent were equal to 23.7 and 276 mg/L, respectively, which indicated the achievement of nitrification, since there was no nitrate source in the feed.

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**Table 4: Experimental conditions of different pilot runs**

<table>
<thead>
<tr>
<th>Pilot run</th>
<th>Influent flow (L/h)</th>
<th>Air flow (L/min)</th>
<th>Influent COD (mg/L)</th>
<th>HRT (h)</th>
<th>Organic loading (kg/m^3.d)</th>
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<tbody>
<tr>
<td>1</td>
<td>4.91</td>
<td>4</td>
<td>300</td>
<td>9</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>6.31</td>
<td>6</td>
<td>300</td>
<td>7</td>
<td>1.03</td>
</tr>
<tr>
<td>3</td>
<td>8.84</td>
<td>8</td>
<td>300</td>
<td>5</td>
<td>1.44</td>
</tr>
<tr>
<td>4</td>
<td>11.05</td>
<td>10</td>
<td>300</td>
<td>4</td>
<td>1.8</td>
</tr>
<tr>
<td>5</td>
<td>11.05</td>
<td>12</td>
<td>350</td>
<td>4</td>
<td>2.1</td>
</tr>
<tr>
<td>6</td>
<td>11.05</td>
<td>15</td>
<td>400</td>
<td>4</td>
<td>2.4</td>
</tr>
<tr>
<td>7</td>
<td>11.05</td>
<td>20</td>
<td>450</td>
<td>4</td>
<td>2.7</td>
</tr>
</tbody>
</table>

**Fig. 2: Variation of effluent SCOD at different OLR**

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Performance of the ASFFR

The reactor was operated at variable OLR ranging from 0.8 to 2.7 kg/m³·d. Effect of OLR on ASFFR performance was evaluated at runs 1 to 4 by HRT stepwise decreasing from 9 to 4 h with a constant influent COD of 300 mg/L, subsequently at runs 5 to 7 by influent COD stepwise increasing from 350 to 450 mg/L with a constant HRT of 4 h. The operational conditions were not changed until steady state conditions were reached. The reactor was assumed to be operating at steady state when the measured effluent COD concentrations did not show variations higher than 10% at least for the last five measurements.

The experimental runs were started with HRT of 9 h which was equivalent of OLR of 0.8 kg/m³·d. The variation of effluent SCOD according to the OLR is shown in Fig. 2. The difference in the effluent SCOD varied 18 to 166 mg/L at OLR ranging from 0.8 to 2.7 kg/m³·d. Fig. 3 depicts the variation in COD removal efficiency and COD removal rate with different influent OLR at steady state condition. The COD removal efficiencies in the reactor for 0.8 to 2.4 kg/m³·d OLR were nearly 87.5% to 93.7%. However, the efficiency of COD removal decreased at highest OLR to 66.2%. On the other hand, the rate of COD removal increased from 0.75 to 2.1 kg/m³·d at the OLR values up to 2.4 kg/m³·d which was then, decreased to 1.79 kg/m³·d at the highest OLR of 2.7 kg/m³·d.

Fig. 4 presents the effluent SCOD and AN concentrations recorded throughout the experiments. The effluent AN concentration presented slight variations as the influent concentration was increased and AN removal efficiencies of more than 95% were reached, except in the last run. In addition, at the organic loading of below 2.4 kg/m³·d, the effluent SCOD resulted in acceptable values of <50 mg/L.

Fig. 5 shows the variation of effluent TSS with OLR. The difference in the effluent TSS varied 75 to 141 mg/L at OLR ranging from 0.8 to 2.7 kg/m³·d. Fig. 6 presents the effluent TSS and VSS at the steady state conditions with respect to OLR. The effluent TSS and VSS were 38 and 25 mg/L, respectively, at OLR of 0.8 kg/m³·d with corresponding HRT of 9 h. Up to OLR=1.8 kg/m³·d, the effluent TSS concentrations were maintained considerably below 100 mg/L. However, the effluent TSS and VSS concentrations increased rapidly when the OLR was higher than 1.8 kg/m³·d. As OLR was increased to 2.7 kg/m³·d, the TSS and VSS at steady state conditions were increased to 353 and 316 mg/L, respectively. The high TSS content of effluent denoted the wash out phenomena at high OLRs. It should be mentioned that the washed out sludge had good settling property because the TSS of the settled treated wastewater with various OLR was measured to be less than 8 mg/L.

The effluent ammonium, nitrate and alkalinity concentrations as a function of OLR at steady state conditions are shown in Fig. 7. The results indicate that at OLR values less than 1.44 kg/m³·d, efficient nitrification was achieved in the reactor.
The values of required air at different OLRs allowing for supply of proper DO contents in the reactor, is shown in Fig. 8. It should be noted that the the average values of DO throughout the experiments were higher than 2 mg/L and that there was no indication of oxygen limitation. Furthermore, the pH of the effluent from ASFFR was found to be in the accepted operational range for biological treatment systems ranging from 7.3 to 8.14 throughout the experimental runs. The effective pH for most biological oxidation systems cover the range of 5 to 9 with the optimum rates occurring over the range of 6.5 to 8.5.

**Determination of kinetic coefficients**

Values of parameters $Y$, $k$, $K_S$, $K_d$, and $\mu_{max}$ must be available to use biological kinetic models. Experimental data collected at steady state conditions of ASFFR given in Table 5 were used to determine these coefficients. Coefficient of $K_S$ and $k$ were determined by plotting the term $(1/S)$ versus $[A \bar{X}/Q(S_0 - S)]$. The $y$-intercept equals $(1/K_S)$ while the slope of the curve equals $(k/K_S)$. This gave the value of $K_S$ as 63.29 mg/L and $k$ as 1.21 (1/d), respectively. The values for coefficients $Y$ and $K_d$ were determined by plotting the term $[(S_0 - S)/X]$ versus $(A \bar{X}/QX)$. The $y$-intercept equals $(1/Y)$ while the slope of the...
curve equals \( (K_d/Y) \). The value of the coefficient \( \mu_{\text{max}} \) was determined using equation 3. These gave the value of \( K_d \) as 0.146 (1/d), \( Y \) as 0.748 g.VS/g. COD and \( \mu_{\text{max}} \) as 0.91 (1/d).

**DISCUSSION**

According to the results, ASFFR can be used as a process for treatment of AN-containing wastewater. However, the drop in COD removal efficiency at OLR values above 2.4 kg/m³.d (Fig. 3) indicated the insufficient elimination capacity because of inhibitory effects of hardly

<table>
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<tr>
<th>( S_0 ) (mg/L)</th>
<th>( S ) (mg/L)</th>
<th>( X ) (mg/L)</th>
<th>( \bar{X} )</th>
<th>( A \bar{X}/Q(S_0 - S) )</th>
<th>( 1/S )</th>
<th>( A \bar{X}/QX )</th>
<th>( (S_0 - S)/X )</th>
</tr>
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<tbody>
<tr>
<td>100</td>
<td>19</td>
<td>18</td>
<td>12.1</td>
<td>3.6</td>
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<td>16.2</td>
<td>4.5</td>
</tr>
<tr>
<td>250</td>
<td>31</td>
<td>93</td>
<td>21.5</td>
<td>2.4</td>
<td>0.032</td>
<td>5.57</td>
<td>2.36</td>
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<tr>
<td>400</td>
<td>43</td>
<td>146</td>
<td>32.3</td>
<td>2.2</td>
<td>0.023</td>
<td>5.33</td>
<td>2.45</td>
</tr>
</tbody>
</table>

\( A = 1.48 \) m²; \( V = 14.8 \) L; \( Q = 0.0614 \) m³/d

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![Graph](image1.png)

Fig. 6: Effluent TSS and VSS vs. OLR at steady state conditions

![Graph](image2.png)

Fig. 7: Effluent alkalinity, ammonium and nitrate concentrations vs. OLR at steady state conditions

Table 5: Experimental data at steady state conditions of ASFFR to determine kinetic coefficients
biodegradable AN and its intermediates as well as the limitation in oxygen mass transfer and media surface area for attached microorganisms. As a similar result, Hamoda and Abd-El-Bary have reported 88.9% to 97% COD removal at OLR ranging from 12.6 to 90 g/m².d using an ASFFR in treatment of wastewater containing sucrose (Hamoda and Abd-El-Bary, 1987). According to Hu et al., in order to ultimate degradation of AN in an aerated submerged biofilter, the system should be operated at OLRs lower than 2 to 2.2 kg/m³.d (Hu et al., 1998). Also, Park et al., have obtained 91.8 to 96.6% COD removal efficiencies at OLR ranging from 1.02 to 6.21 kg/m³.d using an ASFFR in treatment of petrochemical wastewater (Park et al., 1996). Furthermore, the comparison of the performance of different systems in treatment of AN-containing wastewater is presented in Table 6. According to the results, at OLR values up to 2.4 kg/m³.d, SCOD was less than 50 mg/L which was lower than the Iranian national effluent discharge standards (COD<60 mg/L) (Iranian Environmental Protection Regulations and Standards, 2004). However, the effluent SCOD and AN concentrations increased as the OLR increased. On the whole, the biodegradation of AN was found to be suitable for all the influent concentrations assayed. It should be mentioned
that, although no experimental tests were conducted, the removal of AN by air stripping in the reactor was considered negligible. This assumption was based on the studies of Hu et al., who reported only 2% of abiotic AN removal in an aerated submerged biofilter, and Chang et al., who reported 2% to 10% BOD removal by air stripping in submerged membrane bioreactor treating ABS industry wastewater (Hu et al., 1998; Chang et al., 2006b).

In addition, it is clear (Fig. 7) that the ammonium concentration increased as the OLR increased, while nitrate concentrations in the effluent decreased with increasing the values of OLR. In another words, the nitrification rate decreased as the HRT values were decreased in the ASFFR.

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