Abstract This study investigated the aerobic treatment of two different types of wastewaters emanating from manufacture of pyrethroid and organophosphorus pesticides in dual media biofilm reactors packed with polyurethane foam and Pall ring. Two dual media reactors were employed: one reactor treating a pyrethroid pesticide wastewater containing 4000–4400 mg/L of chemical oxygen demand (COD) and 135–200 mg/L of ammonia and the other an organophosphorus pesticide wastewater containing 6400–7200 mg/L of COD and 50–160 mg/L of ammonia. Over 84% of COD and 97% of ammonia were removed in the reactor receiving the pyrethroid pesticide wastewater with 48 h of hydraulic retention time (HRT). Conversely, with 72 h of HRT the reactor treating the organophosphorus pesticide wastewater demonstrated a limited treatment capability, achieving a lower COD removal efficiency of 77% and exhibiting no ammonia removal.

Keywords biofilm reactor; immobilized cell bioreactor; pesticide wastewater; polyurethane foam

1 Introduction

The innate propensity of microorganisms to adhere to and proliferate on surfaces in contact with aqueous systems has been exploited in various biofilm reactors that utilize an inert carrier to immobilize large amounts of biomass through natural attachment. Such biofilm reactors can be employed to remediate challenging industrial effluents. Since reactor performance is linked to effective formation of a biofilm on a solid support, selecting a suitable support media for biomass development is of critical importance. Among commercially available synthetic support media, polyurethane foam has been found to be an excellent scaffold for colonization of pollutant-degrading microorganisms owing to its attractive attributes such as high specific surface area, huge void volume and long service life.

A variety of biofilm reactor configurations (e.g., fixed bed, fluidized bed, sequencing batch biofilm reactor or SBBR, rotating biological contactor or RBC and moving bed biofilm reactor or MBBR) utilizing polyurethane foam as the biofilm support media have been employed to treat industrially produced wastewaters under aerobic, anoxic, or anaerobic conditions. Continuous-flow fixed biofilm reactors are appropriate for the treatment of complex industrial wastewaters due to their high biomass concentration within the reactor, short hydraulic retention times, high removal efficiency and ability to withstand hydrodynamic variations and toxic effects of shock loadings. Real olive mill [15], tannery [19] and L-lysine plant [12] wastewaters were successfully treated using fixed biofilm reactors filled with polyurethane foam. Fixed biofilm reactors packed with a proprietary polyurethane media were used, either alone or in combination with other treatment technologies, to remediate various industrially produced effluents including coke plant [9,10,22], yellow ginger processing [21], Dioscorea zingiberensis C.H. Wright production [3], bromoamine acid [5] and molasses wastewaters [20].

However, some process limitations still remain in the use of fixed biofilm reactors packed with polyurethane foam. For example, a major drawback of polyurethane foam is that it is compressible, which would cause compaction of the fixed bed reactor such that channeling of liquids and gas is enhanced, which may reduce reactor performance. Another operational limitation often associated with fixed biofilm reactors is clogging induced by excessive biomass formation, leading to a build-up in pressure drop and flow channeling [1,16,17]. To alleviate the problem of reactor clogging, periodic backwashing is a useful technique but this leads to increased operating costs and complex operating procedures.

A novel solution to the problems of reactor compaction due to media compressibility and reactor clogging induced by excessive biomass accumulation is to blend compressible polyurethane foam blocks with rigid spacers in a 1:1
ratio by count to form a dual media fixed bed reactor [4], as illustrated in Figure 1. The two packings are placed in the reactor in a random configuration so that pockets of dead zones are not formed. Inclusion of the rigid spacers makes the fixed bed considerably less compressible, reducing flow channeling. More importantly, the rigid spacers provide an open structure around the polyurethane foam blocks, keeping them apart. Because the spacers have a minimum surface area and a maximum void space, the biomass concentration on the spacers is very low due to elutriation of excess biomass by hydraulic flow and aeration shear forces. Thus, microbial growth cannot plug the spacers, whose function is to maintain open spacing between the foam blocks. Therefore, clogging induced by excessive biomass accumulation is minimized in this unique dual media biofilm reactor, first developed by AlliedSignal (now Honeywell) and marketed under the trade name Immobilized Cell Bioreactor (ICB).

Even though the dual media biofilm reactor technology has been applied commercially to the treatment of various industrial effluents, process data available that reveal reactor performance are scant in the open literature. DeFilippi and Lupton [4] provided limited laboratory and full-scale data on COD removal efficiency and organic loading rate for a range of industrial wastewaters including textile, specialty chemicals, cosmetics and coal tar. Jou and Huang [8] reported results of a pilot test on oil refinery wastewater treatment while Hsien and Lin [7] demonstrated that effective treatment of a phenolic wastewater was possible using a laboratory-scale dual media biofilm reactor. The scope of the present study was to evaluate the effectiveness of the dual media biofilm reactor technology in treating two different types of industrially produced pesticide wastewaters and to characterize reactor performance in terms of COD and ammonia removal efficiencies.

### Table 1: Characteristics of the two media.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Polyurethane foam</th>
<th>Polypropylene Pall ring</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape</td>
<td>Cube</td>
<td>Cylinder</td>
</tr>
<tr>
<td>Dimensions (cm)</td>
<td>2.5 × 2.5 × 2.5</td>
<td>2.5 × 2.5</td>
</tr>
<tr>
<td>Void (%)</td>
<td>93</td>
<td>95</td>
</tr>
<tr>
<td>Surface area (m²/m³)</td>
<td>820</td>
<td>112</td>
</tr>
<tr>
<td>Pore size (pores/cm)</td>
<td>6 ± 2</td>
<td>—</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>58</td>
<td>395</td>
</tr>
</tbody>
</table>

2 Materials and methods

Two bench-top biofilm reactor systems comprising either three or four cylindrical columns made of Perspex, linked in series, were constructed for the present study. Each column (stage) was packed with an evenly distributed mixture of polyurethane foam blocks and rigid spacers in the form of polypropylene Pall rings. Media characteristics are given in Table 1. The total working volume of each reactor system was 4 L (1+1+2 L for the three-stage system and 1+1+1+1 L for the four-stage system).

Raw wastewater samples were collected from two different pesticide production sites located in Jiangsu province, China. The first type of wastewater, provided by a site that produces pyrethroids as its main pesticide products, was fed to the three-stage reactor. The second wastewater type, collected from an organophosphorus pesticide production site, was treated with the four-stage reactor. The initial biomass was collected from a municipal wastewater plant and acclimated in the biofilm reactors. Sludge was screened and inoculated into the reactors operated in batch mode to allow for biofilm development on the polyurethane foam under aerobic conditions. During the acclimation period, the influent COD and ammonia were increased step by step to original concentrations by decreasing the dilution ratio. This phase lasted for four weeks before the reactors were linked up and switched to a continuous flow mode.

The two reactor systems were operated at 20–25 °C, pH was maintained at 7.0–7.3 and dissolved oxygen (DO) was kept above 3 mg/L throughout the whole experimental period. The influent wastewater was fed to the base of the first stage using a peristaltic pump and allowed to flow upward through the fixed bed. Effluent from the top of the first stage flowed to the base of the next stage. Aeration was provided by air pumps connected to the base of the columns. Each stage was equipped with sampling ports that allowed liquid samples to be withdrawn. Sample analysis included COD, NH₃-N, PO₄-P, pH and DO, all according to national standard methods of China. In addition, aniline was assayed using a GC with a flame ionization detector.

3 Results and discussion

Although pesticides are by nature recalcitrant or biodegraded very slowly, using microorganisms in engineered
systems to detoxify wastewater emanating from pesticide manufacturing is a promising approach because of the low cost. The first type of pesticide wastewater evaluated in this study was collected from a site that produces pyrethroids as its main products, which are a group of synthetic insecticides similar to naturally occurring pyrethrins having insecticidal properties. In addition to pyrethroids, the site produces over 60 types of other pesticides and chemicals. The second type of pesticide wastewater tested was supplied by a production site whose major products are organophosphorus pesticides. Similar to the pyrethroid production site, this site is a multi-product operation producing a myriad of pesticides.

Both the flow and composition of the two wastewaters were highly variable, over both short term (days) and long term (months) due to the batchwise nature of the manufacturing operation. These unpredictable variations in wastewater characteristics created difficulties in monitoring the fate of a particular pesticide subjected to aerobic degradation in the biofilm reactor. Reactor performance was thus assessed in terms of COD and ammonia removal efficiencies.

3.1 Pyrethroid pesticide wastewater

The pyrethroid pesticide wastewater used in the bench-scale test was a mixed wastewater with undefined composition. The COD and NH$_3$-N concentrations of the feed samples ranged from 4000 to 4400 mg/L and from 135 to 200 mg/L, respectively. The three-stage biofilm reactor had a working volume of 4 L (1 L + 1 L + 2 L). All three stages of the reactor were sparged with air to facilitate aerobic degradation. Figure 2 depicts the removal efficiencies of COD at 48h overall hydraulic retention time (HRT) and 2.1 g COD/L-day average organic loading rate (OLR). It is evident that the effluents of all three stages fluctuated within a similar range over 60 days of operation, indicating that most of the influent COD was removed in the first stage. The COD reduction in Stage 1 was around 72–83%, with an average of 78% removal. Slight increments in COD removal were observed for Stages 2 and 3, achieving average removal efficiencies of 82 and 84%, respectively. Note that the HRT of Stage 3 (24 h) was twice that of Stages 1 or 2.

Since most of the COD had been removed in Stage 1, Stages 2 and 3 could promote nitrification by allowing slow-growing nitrifiers to thrive. Figure 3 illustrates temporal profiles of ammonia for each stage of the biofilm reactor. As can be observed in the figure, nitrification was not established with very little or no ammonia removal during the first 10 days of operation. After day 10, the effluent ammonia concentration of Stage 1 was noticeably higher than that of the influent, reaching as high as 340 mg/L. The high ammonia levels can be attributed to the release of ammonia from the degradation of nitrogen-containing organic compounds in Stage 1. Some of the pesticide products such as chlorfluazuron (C$_{20}$H$_{9}$Cl$_3$F$_5$N$_3$O$_3$), imidacloprid (C$_9$H$_{10}$ClN$_5$O$_2$), acetamiprid (C$_{10}$H$_{11}$ClN$_4$) and tribenuron-methyl (C$_{15}$H$_{17}$N$_5$O$_6$S) contain considerable amounts of nitrogen. From day 22, the ammonia concentration in the effluents of Stages 2 and 3 started to drop rapidly with most of the ammonia removed by the Stage 2 reactor. The effluent ammonia concentration of Stage 3 was less than 10 mg/L from day 22, achieving removal efficiency of the order of 97% (based on the influent ammonia concentration). It can be concluded that nitrification was well established in the biofilm reactor and no residual organic compounds in the pyrethroid pesticide wastewater exhibited inhibition effect on the nitrifiers within the biofilm reactor.

The high COD and ammonia removal efficiencies are likely due to the high concentration of active immobilized biomass within the polyurethane foam blocks. Also, the biofilm reactor benefited from the open space maintained by the rigid Pall rings which ensured good distribution of both
3.2 Organophosphorus pesticide wastewater

Many of the widely used organophosphorus pesticides such as diazinon, parathion and malathion are amenable to biodegradation [18]. The organophosphorus pesticide wastewater used in this study had the following characteristics: COD = 6400–7200 mg/L, NH3-N = 50–160 mg/L and PO4-P = 50–110 mg/L. According to the pesticide production site, the COD of raw pesticide wastewater can be as high as 20000 mg/L and the pH in the range 1–2. The composite feed samples evaluated in this study had been pretreated onsite to remove cyanide and diluted with other process water streams. The COD removal efficiencies of the four-stage biofilm reactor at 72 h overall HRT and 2.3 g COD/L·day average OLR are illustrated in Figure 4. It is evident that the biofilm reactor was able to establish a stable COD reduction throughout the test period with an average value of 77% removal. Stages 1 and 2 showed relatively major contributions to total COD removal; around 50% COD reduction occurred in Stage 1, with Stage 2 accounting for 22%, and minor contributions from Stages 3 and 4 (5%).

Since the HRT of each stage was 18 h, an HRT of 36 h was needed to remove 72% of the influent COD in the first two stages. By comparison, most of the COD reduction (78%) occurred in the first stage of the biofilm reactor treating pyrethroid pesticide wastewater at 12 h HRT. Since both reactors were subjected to similar OLRs, it can be surmised that the dual media biofilm reactor was less efficient in treating organophosphorus pesticide wastewater, presumably on account of its complex organic carbon content. To date there are very few reports of direct biological treatment of actual industrially produced organophosphorus pesticide wastewater. Lin [11] has reported the successful use of an aerobic suspended growth reactor in treating a real organophosphorus pesticide wastewater. However, high COD removal efficiency was obtained at a relatively long HRT of up to 30 days. In order to overcome the problems of toxicity and poor biodegradability, a real organophosphorus pesticide wastewater was first pre-treated with a Fenton-coagulation process before it was subjected to biological oxidation in a moving bed biofilm reactor [2].

Figure 5 depicts the ammonia levels in each stage of the biofilm reactor. During the entire test period, the ammonia levels in all stages were much higher than that of the influent, indicating the release of ammonia from the degradation of nitrogen-containing organic matter. Most of the pesticide products including the organophosphorus pesticides contain nitrogen. Significant production of ammonia was observed in Stages 1 and 2, and to a lesser extent, in Stage 3. Stage 4 did not exhibit any nitrification activity, as indicated by the high ammonia levels. The HRT of Stage 4 (18 h) was probably not long enough to promote nitrification.

Another factor that could have prevented nitrification from occurring in Stage 4 is the chemical inhibition. The activity of nitrifiers is susceptible to a number of organic and inorganic chemicals. This sensitive nature of the nitrifying bacteria explains why many industrial wastewater treatment plants fail to establish stable nitrification even though environmental conditions for nitrification such as pH, DO and temperature are properly maintained. For instance, aniline has been shown to be a nitrification inhibitor in biofilm systems [6,14]. Given that aniline is used as an intermediate in the production of pesticides, it is not surprising to find aniline in pesticide wastewaters as a result of the partial biodegradation of certain pesticides. Some of the effluent samples collected from Stage 4 were assayed for this...
industrially produced pyrethroid and organophosphorus pesticides. This study has investigated the aerobic treatment of organophosphorus pesticide wastewater by biofilm reactors combined with zero-valent iron precipitant. The COD removal efficiency of the biofilm reactor treating pyrethroid pesticide wastewater averaged out to 84% at 48 h HRT. The biofilm reactor also exhibited excellent ammonia removal efficiency in spite of the fact that the degradation of organic matter resulted in the release of significant amounts of ammonia. These results provide evidence that the dual media biofilm reactor facilitated efficient treatment of this pesticide wastewater. In contrast, the biofilm reactor treating organophosphorus pesticide wastewater was less efficient, reaching a lower COD removal efficiency of 77% at a longer HRT of 72 h and exhibiting no ammonia removal.

4 Conclusions

This study has investigated the aerobic treatment of industrially produced pyrethroid and organophosphorus pesticide wastewaters using two laboratory-scale dual media biofilm reactors operated at similar OLRs (2.1 and 2.3 g COD/L-day). The COD removal efficiency of the biofilm reactor treating pyrethroid pesticide wastewater averaged out to 84% at 48 h HRT. The biofilm reactor also exhibited excellent ammonia removal efficiency in spite of the fact that the degradation of organic matter resulted in the release of significant amounts of ammonia. These results provide evidence that the dual media biofilm reactor facilitated efficient treatment of this pesticide wastewater. In contrast, the biofilm reactor treating organophosphorus pesticide wastewater was less efficient, reaching a lower COD removal efficiency of 77% at a longer HRT of 72 h and exhibiting no ammonia removal.

References


