

## The Effect of Organic Loading on Propylene Glycol Removal Using Fixed Bed Activated Sludge Hybrid Reactor

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Propylene glycol is discharged to the surface and underground waters and vicinity soils via industrial wastewater effluents, posing many health and environmental risks. The main goal of this study was to remove propylene glycol from synthetic wastewater in a fixed bed activated sludge reactor. To observe the effects of organic loading on bioreactor performance, the organic loading was increased by two sequencing stages: first by hydraulic retention time (HRT) depletion and second via propylene glycol concentration increase. Propylene glycol removal efficiency in HRTs of 8, 6, 4 and 2 h was 95.86, 95.12, 93.96 and 79.08 % respectively. A constant HRT of 6 h was selected for the second stage; propylene glycol concentrations of 500, 1000, 1500, 2000 and 2500 mg L<sup>-1</sup> were used. The removal efficiency for these concentrations was 95.12, 95.95, 88.54, 75.95 and 35.69 % respectively. Thus, the integrated fixed bed activated sludge reactor is an efficient, viable and promising technology for treating wastewaters containing propylene glycol.

*Key words:*

Propylene glycol, fixed bed, activated sludge, hybrid reactor, biodegradation

### Introduction

Propylene glycol is a chemical substance widely used as anti-freeze agent and also in the manufacture of polymers, paint, varnishes and other products as well as pharmacological industries, cosmetics, chemical and food processing industries.<sup>1,2,3</sup> Exposure to propylene glycol may lead to dermal effects such as erythema, dermal irritation, dermal edema and systemic effects such as blood disturbance, kidney effects and body mass variation outside the standard range.<sup>4</sup> LD<sub>50</sub> values for propylene glycol is >20 g kg<sup>-1</sup> body mass for rats.<sup>5</sup>

Following its release into the environment, propylene glycol ultimately reaches underground waters and contaminates them. Also, in surface waters, it can consume available dissolved oxygen (DO) of aqueous plants and animals and create undesired conditions in natural ecosystems. A considerable amount of propylene glycol is released to earth and contaminates soils near the discharge point.<sup>6,7</sup> The capacity to use propylene glycol as a carbon and energy source is widespread among aerobic and anaerobic microorganisms.<sup>8</sup> Under oxic conditions, several pure and mixed cultures of different bacterial groups have been proven capable of

degrading propylene glycol. Studies on metabolic pathways showed that propylene glycol degradation proceeds via lactaldehyde and pyruvate. Pyruvate is further metabolized to acetyl-CoA, which is oxidized to CO<sub>2</sub> by the tricarboxylic acid cycle. This information suggests that microbial degradation of propylene glycol under oxic conditions occurs without the accumulation of toxic and/or persistent organic intermediates.<sup>9,10</sup>

Different studies on propylene glycol removal via aerobic biological processes have been conducted. Biodegradation of propylene glycol as a sole carbon source in an aerobic biological process was studied by Joanna *et al.* (2003).<sup>11</sup> The results showed that propylene glycol as the source of carbon was biodegraded to ketenes and aldehydes.<sup>11</sup> Propylene glycol biological oxidation is studied in a continuous flow activated sludge process in aerobic conditions. It was revealed that propylene glycol was inherently biodegradable.<sup>5</sup> Aerobic or anaerobic processes are used for organic matter and propylene glycol removal individually. For example, Eiroa *et al.* (2005)<sup>12</sup> studied the ability of an activated sludge unit for organic loading of 0.01–1.40 g COD L d<sup>-1</sup>. Organic matter removal efficiency was 99.5 %.<sup>12</sup> In another study, Amor *et al.* (2005)<sup>13</sup> investigated the aerobic biodegradation of organic loading rate of 30 to 2700 mg COD L d<sup>-1</sup> in a suspended growth process.<sup>13</sup>

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Many attempts have been made to modify the conventional activated sludge process. For instance, the placing of integrated fixed or fluidized bed in aeration tanks, in order to enhance process efficiency is widely experienced in different investigations.<sup>14,15</sup> Some of the advantages of hybrid systems include: high concentration of biomass, potential of using low cost beds, treating greater flows or more efficiency in the same flow compared to the suspended growth processes, effective treatment of low concentration wastewaters, ability to treat organic compound with low degradation rate, resistance to the hydraulic and organic shocks, lower energy and space requirements, microorganisms growth with low yield and secondary effluent with better quality.<sup>16,17</sup> Considering the results of previous studies regarding propylene glycol biodegradation and the different methods of organic pollutants removal, the fixed bed activated sludge hybrid reactor for propylene glycol removal was examined in this experiment. The main objective of this study is to determine the effects of organic loading variations on propylene glycol removal in a fixed bed activated sludge hybrid bioreactor.

## Material and methods

### Fixed bed activated sludge lab scale reactor

A cubic Plexiglas reactor with total volume of 16 L (12 L for aeration tank and 4 L for settling tank) was used in this study with effective volume of 9 L (liquid volume + volume of pickings) for biological reactions. The settling tank, with total volume of 4 L, was separated from the aeration tank by a vertical wall. At the lower end of the separator wall, a distance of 0.5 cm was provided for continu-

ous recycling of sludge from the settling tank to the aeration tank via vacuum force of aeration. Twenty-two percent of the aeration tank was filled with a packing having specific surface area of  $650 \text{ m}^2 \text{ m}^{-3}$ , placed in two boxes that had a distance of 4 cm from the side walls. The characteristics of carriers are shown in Table 1. The reactor was aerated with an aerator pump with an injection capacity of  $14 \text{ L}_{\text{air}} \text{ min}^{-1}$ . Required air was adjusted proportionally to influent organic loading in the range of  $2.5 - 12.5 \text{ L}_{\text{air}} \text{ min}^{-1}$ . The aeration tank was mixed with diffused air. Synthetic influent wastewater was fed by a dosing pump with capacity of  $20 \text{ L h}^{-1}$ . The pilot was operated at room temperature ( $20-25 \text{ }^\circ\text{C}$ ). A schematic diagram of the lab scale hybrid reactor is shown in Fig. 1.

Table 1 – Characteristics of carriers

Parameter	Characteristics
Name	Be-cell 2000
Material	Polystyrene
Area of 1 media	$18 \text{ cm}^2$
Number of media in $1 \text{ m}^3$	361000
Specific area	$650 \text{ m}^2 \text{ m}^{-3}$
Mass of $1 \text{ m}^3$	140 kg
Porosity	87 %
Color	White
Density	$1030 \text{ kg m}^{-3}$

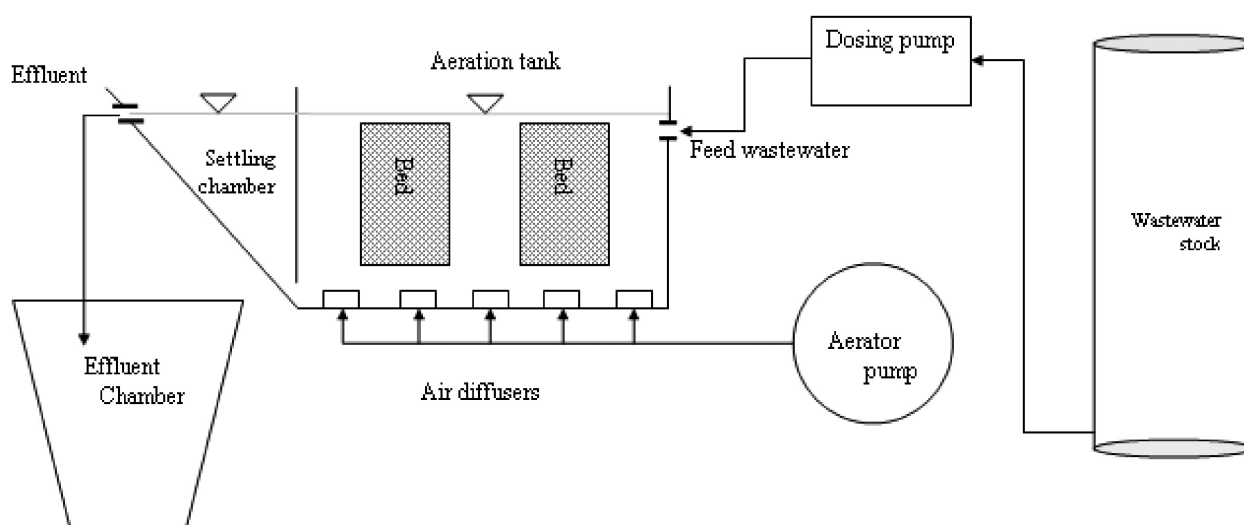


Fig. 1 – Schematic diagram of a lab-scale fixed-bed activated sludge hybrid reactor

## Inoculums

For use as inoculums, sludge was taken from the return sludge line of a full-scale municipal wastewater treatment plant in Tehran. The sludge was thoroughly aerated for two days, and the chemical oxygen demand (COD), volatile suspended solids (VSS) and pH of sludge were measured at room temperature.

## Synthetic wastewater

For startup, the reactor was fed with synthetic wastewater prepared with glucose and propylene glycols as carbon sources, while the mineral medium included  $\text{NH}_4\text{Cl}$ ,  $\text{KH}_2\text{PO}_4$  (as nitrogen and phosphorus sources),  $\text{Na}_2\text{CO}_3$  (for pH adjustment) and trace elements. Synthetic wastewater composition is presented in Table 2. The amounts of synthetic wastewater constituents were adjusted according to C : N : P ratio of 100 : 5 : 1 for optimum bacterial growth and metabolism.<sup>18,19</sup>

Table 2 – Composition of synthetic wastewater at the beginning of experiments<sup>a</sup>

Constituent	Amount
$\text{C}_3\text{H}_8\text{O}_2^{\text{b}}$ /mg L <sup>-1</sup>	112
$\text{C}_6\text{H}_{12}\text{O}_6^{\text{c}}$ /mg L <sup>-1</sup>	744
$\text{NH}_4\text{Cl}$ /mg L <sup>-1</sup>	28
$\text{KH}_2\text{PO}_4$ /mg L <sup>-1</sup>	5.6
$\text{Na}_2\text{CO}_3$ /mg L <sup>-1</sup>	0.8
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ /mg L <sup>-1</sup>	13.6
$\text{ZnCl}_2$ /mg L <sup>-1</sup>	0.16
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ /mg L <sup>-1</sup>	0.138
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ /mg L <sup>-1</sup>	0.032
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ /mg L <sup>-1</sup>	6.66
$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ /mg L <sup>-1</sup>	0.055

<sup>a</sup>Amounts for total COD of 500 mg L<sup>-1</sup>

<sup>b</sup>Purity of  $\text{C}_3\text{H}_8\text{O}_2$  = 75 %

<sup>c</sup>Purity of  $\text{C}_6\text{H}_{12}\text{O}_6$  = 60 %

Table 3 – Variations of carbon source in the synthetic wastewater for adaptation and reproduction of microorganisms for propylene glycol biodegradation<sup>a</sup>

Carbon source	Day of operation									
	1 <sup>st</sup>	8 <sup>th</sup>	13 <sup>th</sup>	16 <sup>th</sup>	18 <sup>th</sup>	20 <sup>th</sup>	23 <sup>rd</sup>	28 <sup>th</sup>	31 <sup>st</sup>	34 <sup>th</sup>
$\text{C}_6\text{H}_{12}\text{O}_6$ /mg L <sup>-1</sup>	744	662	578	496	412	330	247	165	82	0
$\text{C}_3\text{H}_8\text{O}_2$ /mg L <sup>-1</sup>	112	224	336	448	560	672	784	896	1008	1120

<sup>a</sup>Amounts for total COD of 500 mg L<sup>-1</sup>

## Reactor startup and biomass adaptation

The reactor was first operated in batch mode for approximately 6 weeks and DO was adjusted to 3–4 mg L<sup>-1</sup>. The COD at the beginning of the experiments was adjusted to 500 mg L<sup>-1</sup>, including glucose with a COD of 450 mg L<sup>-1</sup> and propylene glycol with a COD of 50 mg L<sup>-1</sup>. After 24 h of aeration, the aerators were switched off and the sludge was allowed to settle. Then 1 L of the supernatant was withdrawn and replaced with new synthetic wastewater. The concentration of influent glucose was reduced slowly during one month while the concentration of propylene glycol was increased. Acceptable COD removal improvement was the criteria of glucose depletion. Variations of glucose to propylene glycol are shown in Table 3.

## Experimental procedure

After obtaining consistent results in batch mode operation, the flow was made continuous. Organic load was increased in two sequencing stages, first through HRT depletion and then in the second stage, by the increase in propylene glycol concentration in constant HRT of 6 h. In all experiments, DO was decreased to less than 1 mg L<sup>-1</sup> when the organic load was increased. Therefore, the aeration flow rate was increased from 2.5 to 12.5 L min<sup>-1</sup> through experiments, proportional to the organic loading.

Steady state conditions in this study were defined as conditions in which the effluent characteristics did not vary significantly during 7 to 10 days of continuous operation. All of the experimental data taken under steady state conditions are expressed in terms of arithmetic averages obtained from at least three replicates.

## Loading in constant propylene glycol concentration and different HRT

The reactor in the first stage was operated at four hydraulic retention times of 8, 6, 4 and 2 h and constant influent COD of 500 mg L<sup>-1</sup>. The effluent COD, propylene glycol concentration, VSS, DO, temperature, and pH were monitored until steady state conditions were achieved. Achieving steady state conditions in each run took approximately 2 to 3 weeks.

### Loading in different propylene glycol concentrations and constant HRT

In the second stage, the reactor was operated at constant HRT of 6 h and COD concentrations of 500, 1000, 1500, 2000 and 2500 mg L<sup>-1</sup>. The parameters mentioned earlier were also monitored until steady state conditions at this stage were observed.

Table 4 – Operational conditions in different runs for continuous flow experiments

Stage	Run	HRT/h	Flow rate/L h <sup>-1</sup>	COD/mg L <sup>-1</sup>	OLR/kg COD m <sup>3</sup> d <sup>-1</sup>
Stage 1	1	8	1.125	500	1.5
	2	6	1.5	500	2
	3	4	2.25	500	3
	4	2	4.5	500	6
Stage 2	5	6	1.5	500	2
	6	6	1.5	1000	4
	7	6	1.5	1500	6
	8	6	1.5	2000	8
	9	6	1.5	2500	10

### Analytical methods

COD, DO and suspended VSS were measured according to standard methods.<sup>20</sup> The pH value was monitored frequently by a pH meter by Hach Company and was adjusted with sodium bicarbonate if necessary. A Cecil HPLC containing C<sub>18</sub> column was used for the measurement of propylene glycol. In this study, propylene glycol was analyzed according to Joanna.<sup>11</sup> The attached biomass was determined by the gravimetric method. The biofilm mass was determined using 100 media elements that were sampled randomly from the fixed bed bioreactor. The media elements were separated from the wastewater and oven-dried at 103 °C until constant mass. The dried samples were weighed in order to determine the total mass ( $m_{total}$ ) composed of media element mass ( $m_{media}$ ) and the attached biomass. The biomass was then washed off, the clean media elements were weighed, and the amount of biofilm solids attached to the 100 media elements was calculated using eq. (1). The amount of biomass in the reactor could then be determined since the total number of carrier elements in the reactor with filing grade of 22 % was 813.<sup>21</sup>

$$BS_{100} = m_{total} - m_{media} \quad (1)$$

### Results and discussion

In the batch mode experiments, the entire influent carbon source was supplied with propylene glycol after the 33<sup>rd</sup> day of operation. On the 41<sup>st</sup> day of operation, the effluent COD and propylene glycol concentrations decreased to less than 20 (Std ± 1) and 15 (Std ± 1) mg L<sup>-1</sup> steadily. This was an indication of microbial action/degradation for propylene glycol (Fig. 2). The amounts of suspended VSS concentration and sludge volume index (SVI) in steady state conditions for batch mode operation were 2136 mg L<sup>-1</sup> and 96 mL g<sup>-1</sup> respectively. After 31 days, steady state conditions appeared.

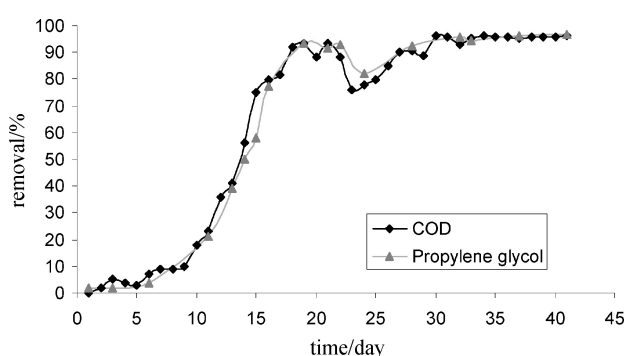


Fig. 2 – COD and propylene glycol removal efficiency variations in batch mode operation and influent COD concentration of 500 mg L<sup>-1</sup>

### Loading effects due to HRT variations

According to HRT variations from 8 to 2 h, organic loading was increased from 1.125 to 4.5 kg COD m<sup>-3</sup> d<sup>-1</sup>. The amounts of COD and propylene glycol removal efficiency in HRTs of 8, 6, 4 and 2 h are shown in Fig. 3. Steady state conditions appeared after 12–16 days in these runs. The average COD removal in HRTs of 8, 6, 4 and 2 h was 95.86 % (Std ± 0.57), 95.12 % (Std ± 0.52), 93.96 % (Std ± 1.13) and 79.08 % (Std ± 1.13), respectively. The propylene glycol removal in the same operational and steady state conditions was 98.66 % (Std ± 1.96), 98.38 % (Std ± 1.44), 96.82 % (Std ± 1.73) and 84.32 % (Std ± 1.86), respectively. Reactor efficiency for COD removal until the HRT of 4 h was more than 93 % and COD effluent concentration was less than 35 mg L<sup>-1</sup>. These values are within the range of wastewater discharge standards to the receiving waters. However, in the HRT of 2 h, reactor efficiency decreased suddenly and reached less than 80 %. Therefore, the effluent concentration of COD and propylene glycol were 104 and 78.4 mg L<sup>-1</sup> respectively which cannot meet acceptable standards for discharge to receiving waters (COD value of 100 mg L<sup>-1</sup> for industrial effluents).<sup>22,23</sup>



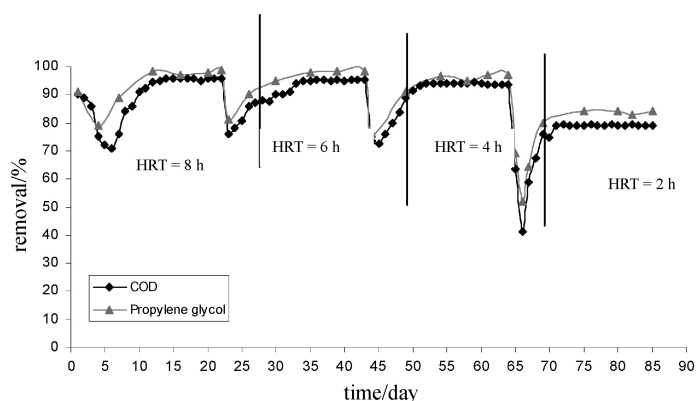


Fig. 3 – COD and propylene glycol removal efficiency variations in HRTs of 8, 6, 4 and 2 h, and influent COD concentration of  $500 \text{ mg L}^{-1}$

Other operational parameters including suspended VSS, SVI and DO for the first stage of experiments are shown in Table 5. The best SVI was observed in the 2<sup>nd</sup> run with HRT of 6 h providing SVI of  $117.2 \text{ mL g}^{-1}$ . DO concentrations were more than  $3 \text{ mg L}^{-1}$  in all runs. As indicated, the suspended VSS values decreased from  $2099 \text{ mg L}^{-1}$  to  $1896 \text{ mg L}^{-1}$  proportional to the HRT depletion. Apparently, despite achieving steady state conditions in each run, the high flow rate of wastewater has led to the excess washout suspended VSS from aeration tank.

Table 5 – Average of operational parameters in varying HRT and constant influent PPG in steady state conditions

Run	VSS/ $\text{mg L}^{-1}$	DO/ $\text{mg L}^{-1}$	SVI*/ $\text{mg L}^{-1}$	pH
1	2099	3.2	133.8	7.2
2	2093	3.6	117.2	7.1
3	1983	4.06	160.6	7.3
4	1896	3.15	179.4	7.2

\*Suspended VSS

At the first stage, it was observed that removal efficiency was decreased in each stage and after a few days steady state conditions were observed. HRT is one of the most important operational factors of biological systems that provides sufficient contact time between biomass and substrate and inhibits excess wash out of mixed liquor suspended solids (MLSS). According to the results obtained from the first stage of this study, it can be concluded that the average of suspended VSS in the aeration tank decreased from  $2099 \text{ mg L}^{-1}$  to  $1896 \text{ mg L}^{-1}$  proportional to HRT variations from 8 to 2 h. Because of excess washout of VSS, the microbial action of microorganisms which consume

propylene glycol as their carbon source has been decreased. A change in the structure of reactor in order to retain the VSS in the aeration tank is suggested for further studies. On the other hand, some propylene glycol was discharged without having undergone aerobic biodegradation due to the insufficient contact time with biomass as a result of short HRT. Therefore, at a constant concentration of influent propylene glycol, HRT was defined as a key operational parameter in the first stage of the study.

The results showed that the reactor was able to remove more than 84 % of influent propylene glycol at the substrate concentration of  $500 \text{ mg L}^{-1}$ , even in HRT of 2 h. Such a short HRT is an economical advantage. Compared to the conventional systems, this integrated system is able to treat more wastewater flow rates with the same efficiency in a shorter time.

#### Loading effects due to influent concentration variations

The maximum COD removal efficiency in the first stage corresponded to 8 and 6 HRTs, providing removal values of 95.86 % and 95.2 % respectively. A statistical analysis of *t*-test with a *P* value of 0.05 was carried out, which showed that the removal efficiency difference is not statistically significant. Furthermore, greater organic loading was possible in HRT of 6 h and other operational parameters such as SVI were more acceptable, compared to the HRT of 8 h. Average amounts of suspended VSS, SVI and DO in steady state conditions in HRT of 6 h were equal to  $2093 \text{ mg L}^{-1}$ ,  $117.2 \text{ mL g}^{-1}$  and  $3.6 \text{ mg L}^{-1}$  respectively. Considering all the points mentioned above, an HRT of 6 h was selected as optimum HRT for evaluating the effects of organic loading increase due to concentration variations.

As illustrated in Fig. 4, at this stage, the substrate concentration is the key parameter because removal efficiency decreases in proportion to the

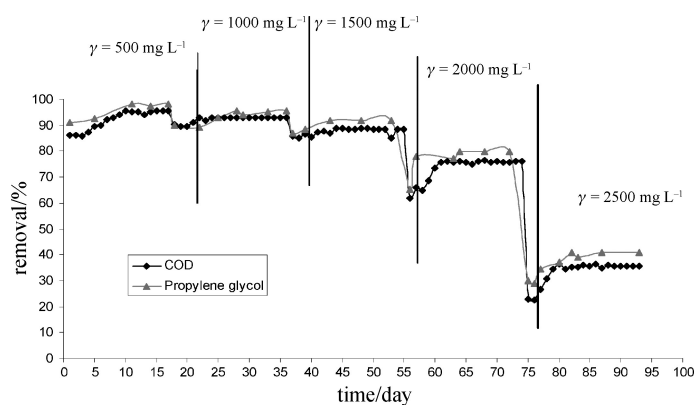


Fig. 4 – COD and propylene glycol removal efficiency in concentrations of  $500 - 2500 \text{ mg L}^{-1}$  and HRT of 6 h

increase in influent concentration. Removal efficiency in the selected influent COD concentrations of 500, 1000, 1500, 2000 and 2500 mg L<sup>-1</sup> were 95.39 % (Std ± 1.46), 92.95 % (Std ± 1.87), 88.54 % (Std ± 1.66), 75.95 % (Std ± 1.59) and 35.69 % (Std ± 1.91) respectively. Propylene glycol removal efficiency in the same conditions was 98.31 % (Std ± 1.22), 95.51 % (Std ± 1.68), 91.73 % (Std ± 1.75), 79.95 % (Std ± 1.37) and 40.84 % (Std ± 2.63), respectively. Table 6 presents the average VSS, SVI, DO and pH in steady state conditions (in constant 6-h HRT) for the second stage of the experiment.

Table 6 – Average of operational parameters in constant HRT and different influent PG in steady state conditions

Run	VSS/mg L <sup>-1</sup>	DO/mg L <sup>-1</sup>	SVI*/mg L <sup>-1</sup>	pH
5	2115	3.37	116.5	7.4
6	2269	3.26	125.1	7.2
7	2289	3.84	121.3	7.2
8	2287	3.08	157	7.3
9	2171	2.9	281	7.3

\*Suspended VSS

The best SVI value of 116.5 mL g<sup>-1</sup> was observed in the 5<sup>th</sup> run. Also, the highest and the lowest suspended VSS of 2289 and 2115 mg L<sup>-1</sup> were observed in the 7<sup>th</sup> and 5<sup>th</sup> runs respectively. In the second stage and at higher influent concentrations, removal efficiency decreased gradually and reached 35.69 % and 40.84 % for COD and propylene glycol, respectively, at an influent concentration of 2500 mg L<sup>-1</sup>. This led to effluent COD of 1607 mg L<sup>-1</sup> which was not acceptable and the bioreactor upset. The removal efficiency of hybrid reactor was more than 88 % and 91 % for COD and propylene glycol respectively, with a substrate concentration of 1500 mg L<sup>-1</sup> and HRT of 6 h (run 7). The COD and propylene glycol effluent concentrations were 180 and 135 mg L<sup>-1</sup>. Therefore, the removal efficiency is considerable and in terms of COD, effluent discharge standards for reuse in agriculture are met.<sup>22</sup>

The operational parameters of the reactor were investigated in order to determine the main reason of reactor disturbance. Results showed that DO concentration dropped to less than 1 mg L<sup>-1</sup> immediately after each increment of organic loading in each run. Therefore, it was necessary to provide supplement aeration. Despite the increase of aeration rate, reactor efficiency did not improve in COD concentrations beyond 1500 mg L<sup>-1</sup>. Propylene glycol can act as a toxic compound for microorganisms

in high concentrations. Joanna *et al.*<sup>11</sup> (2003) found that propylene glycol loses its metabolic functions at extremely high concentrations and acts as a toxic compound which threatens microorganism survival.<sup>11</sup> It seems that this effect has occurred in COD concentrations of more than 1500 mg L<sup>-1</sup> in this study. Therefore, when effective operational parameters such as temperature, DO, substrate, P and N concentrations were justified at optimum values, the only inhibitory factor of the microorganism's metabolism was the high concentration of influent propylene glycol. An extremely high concentration of influent substrate has adverse effects on enzymes and metabolic functions.<sup>24</sup>

The results of organic loading removal efficiency for different HRTs and substrate concentrations, based on COD are presented in Fig. 5. According to the variations of HRT and propylene glycol concentration, the same organic loading of 6 kg COD m<sup>-3</sup> d<sup>-1</sup> was applied to the reactor in the 4<sup>th</sup> and 7<sup>th</sup> runs. The important point was the higher efficiency in concentration of 1500 mg L<sup>-1</sup> and HRT of 6 h (run = 7, Point B in Fig. 5), compared to the concentration of 500 mg L<sup>-1</sup> and HRT of 2 h (run = 4, Point A in Fig. 5). While the COD and propylene glycol concentration were three times greater, the observed efficiency was approximately 9 % and 7 % higher respectively, which indicates the more important effects of HRT than influent concentration in the same organic loading rate.

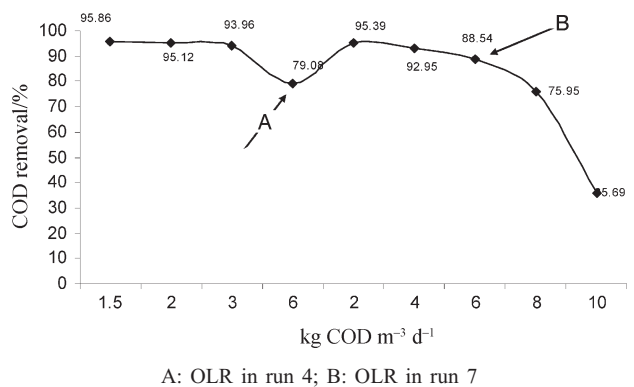


Fig. 5 – COD removal efficiency in different organic loadings of 1.5 – 10 kg COD m<sup>-3</sup> d<sup>-1</sup>

Wen *et al.* (1998)<sup>25</sup> studied the removal of propylene glycol by a biological fluidized bed. Under the steady-state conditions tested, the biological fluidized bed reactors are capable of achieving good TOC removal (>96 %) at empty bed HRTs as short as 1.7 h and at TOC loadings as high as 0.88 g L<sup>-1</sup> d<sup>-1</sup>.<sup>25</sup> Hamuda *et al.* (1998)<sup>26</sup> reported using an aerobic submerged attach growth pilot scale reactor to determine organic load removal from domestic wastewater. The value of COD removal effi-

ciency at loading rate of  $3 \text{ kg COD m}^{-3} \text{ d}^{-1}$  was 83 % which is less than in this study.<sup>26</sup> Jianlong *et al.* (2000)<sup>27</sup> used a hybrid attached and suspended growth bioreactor for municipal wastewater treatment. More than 80 % of COD was removed at loading rates up to  $3.5 \text{ kg COD m}^{-3} \text{ d}^{-1}$ .<sup>27</sup> The COD removal at organic loadings of  $3 \text{ kg COD m}^{-3} \text{ d}^{-1}$  was 92 % in the presented work which is more than in similar studies. Borghei *et al.* (2008)<sup>28</sup> investigated the kinetics of organic matter removal in fixed-bed aerobic biological reactor for sugar manufacturing wastewater. Different HRTs (24 to 12 h) and organic loadings ( $0.75$  to  $4.5 \text{ kg COD m}^{-3} \text{ d}^{-1}$ ) were experimented. The observed COD removal in different conditions was 89.8 to 94.7 %, confirming the data obtained in this study.<sup>28</sup>

Therefore, fixed bed activated sludge hybrid reactor is a very suitable process for treatment of high strength industrial wastewaters containing organic matter/propylene glycol as much as  $6 \text{ kg COD m}^{-3} \text{ d}^{-1}$ , because the removal rates obtained at these loads were near 88 % in this study.

As the operation proceeded, the time required for achieving steady state conditions were shortened in sequencing runs. For example, steady state conditions in the 6<sup>th</sup> run were observed after 15 days, but in the 7<sup>th</sup> run after day 7.

### Biofilm mass

Fig. 6 shows the overall trend in biofilm mass along with organic loading. Results show that biofilm mass has direct positive correlation factor of + 0.83 with organic loading. The biofilm mass on packing increased until the influent COD concentrations of  $1500 \text{ mg L}^{-1}$  (approximately day 100 of operation). This did not vary significantly in higher organic loadings where sometimes a slight loss in mass was observed (run 8 and 9).

The biofilm mass developed on beds is an important factor in the operation of attached growth processes and hybrid bioreactors. The least biofilm mass of  $2.089 \text{ g m}^{-2}$  was observed at a COD

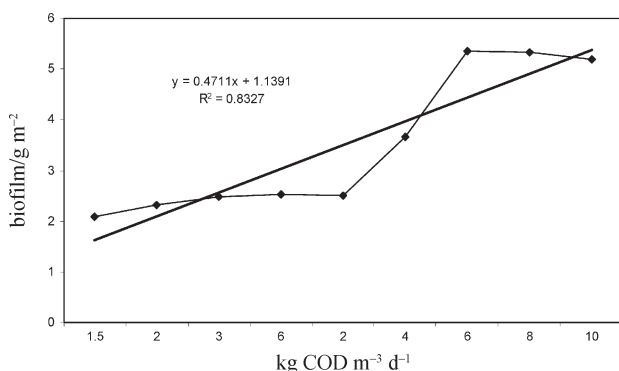


Fig. 6 – Biofilm mass in different organic loadings of  $1.5$  –  $10 \text{ kg COD m}^{-3} \text{ d}^{-1}$

concentration of  $500$  (1<sup>st</sup> run) while the greatest  $5.352 \text{ g m}^{-2}$  was observed at the COD concentration of  $1500 \text{ mg L}^{-1}$  (6<sup>th</sup> run). Providing more substrate and DO may have led to more metabolism and growth of biofilm. Otherwise, substrate and DO concentrations decrease in the inner layers of biofilm as the biofilm thickness develops.<sup>19</sup> The decrease in biofilm mass on packing in higher organic loadings of  $8$  (8<sup>th</sup> run) and  $10$  (9<sup>th</sup> run)  $\text{kg COD m}^{-3} \text{ d}^{-1}$ , may be attributed to the lack of sufficient DO and substrate in inner layers and dominance of anaerobic conditions in the film, which leads to the gradual sloughing of biofilm.

### Conclusion

An integrated fixed bed aerobic bioreactor with filling grade of 22 % was operated in two stages; first with varying HRT and constant COD of  $500 \text{ mg L}^{-1}$  and second with constant HRT of 6 h and varying COD concentrations of  $500$  to  $2500 \text{ mg L}^{-1}$  (organic loadings of  $1.25$  to  $10 \text{ kg COD m}^{-3} \text{ d}^{-1}$ ). Results show that depletion of HRT directly reduces the propylene glycol removal efficiency, but more than 88 % of COD removal is obtained at a COD concentration of  $1500 \text{ mg L}^{-1}$  and HRT of 6 h. Generally, more than 90 % removal efficiency was observed for organic loading of  $4 \text{ kg COD m}^{-3} \text{ d}^{-1}$  (run = 6). The results also showed that biofilm mass was directly affected by substrate concentration with a correlation factor of 0.83. The most biofilm mass of  $5.352 \text{ g m}^{-2}$  was achieved in the 7<sup>th</sup> run with COD concentration of  $1500 \text{ mg L}^{-1}$  and HRT of 6 h.

According to the results obtained from this work, it can be concluded that the integrated fixed bed activated sludge reactor is an efficient, viable and promising technology for treating wastewaters containing propylene glycol in full scale applications.

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### Abbreviations and Symbols

- COD – Chemical Oxygen Demand/ $\text{mg L}^{-1}$
- DO – Dissolved Oxygen/ $\text{mg L}^{-1}$
- HRT – Hydraulic Retention Time/h
- MLSS – Mixed Liquor Suspended Solids/ $\text{mg L}^{-1}$
- SVI – Sludge Volume Index/ $\text{mL g}^{-1}$
- VSS – Volatile Suspended Solids/ $\text{mg L}^{-1}$
- PPG – Propylene glycol/ $\text{mg L}^{-1}$

## References

1. Karl, K., Jatinder, B., Antonia, M., *Reproductive Toxicology* **77** (2006) 485.
2. Klotzbucher, T., Kappler, A., Kristina, L., Straub, K. L., Haderlein, B., *Journal of Geothermics* **36** (2007) 348.
3. Staples, C. A., Davis, J. W., *Chemosphere* **49** (2002) 61.
4. Zgola-Greskowiak, A. (a), Greskowiak, T., Zembrzuska, J., Magdalena, F., Rafal, F., Kozik, T., Luskaszewski, Z., *Chemosphere* **67** (2007) 928.
5. Zgola-Greskowiak, A. (b), Greskowiak, T., Zembrzuska, J., Magdalena, F., Rafal, F., Luskaszewski, Z., *Biodegradation* **19** (2007) 365.
6. Bielefeldt, A. R. T., Illangasekare, T., Uttecht, M., Laplante, R., *Water Research* **36** (2002) 1707.
7. Jaesche, P., Totsche, K. U., Kogel-Knabner, I., *Journal of Contaminant Hydrology* **85** (2006) 271.
8. Veltman, S., Schoenberg, T., *Biodegradation* **9** (2004) 113.
9. Andrea, C., Salvatore, D., Roberto, S., Emo, C., *Journal of Environmental Polymer Degradation* **6** (1998) 121.
10. Xiaoping, H., Akira, F., Xin, L., Kazuhide, K., Fusako, K., *Applied Microbial Biotechnology* **73** (2007) 1407.
11. Rychlowska, J., Zgola, A., Grzeskowiak, T., Luskaszewski, Z., *Journal of Chromatography* **1021** (2003) 11.
12. Eiroa, M., Kennes, C., Veiga, M., *Bioresource Technology* **96** (2005) 1914.
13. Amor, L., Eiroa, M., Kennes, C., Veiga, M., *Water Research* **39** (2005) 2915.
14. Yen-Hui, L., *Applied Mathematical Modeling* **32** (2008) 2360.
15. Bajaj, M., Gallert, C., Winter, J., *Bioresource Technology* **99** (2008) 8376.
16. Cresson, R., Escudie, R., Steyer, J., Delgenes, J., Bernet, N., *Water Research* **42** (2008) 792.
17. Xin, Z., Yanming, W., Zhengfang, Y., *Process Biochemistry* **41** (2006) 1475.
18. Bitton, G., *Wastewater Microbiology*. 3<sup>rd</sup> Edition. John Wiley & Sons, Inc. Publication, New Jersey, 2005, pp 211–307.
19. Tchobanoglous, G., Burton, F., David Stensel, H., *Wastewater Engineering Treatment and Reuse*, 4<sup>th</sup> Edition, Mc Graw-Hill Inc., New York, 2003, pp 565–601.
20. APHA, *Standard Methods for the Examination of Water & Wastewater*. 21<sup>st</sup> Edition. American Public Health Association. New York, 2005.
21. Plattes, M., Henry, E., Schosseler, P., Weidenhaupt, A., *Biochemical Engineering Journal* **32** (2006) 61.
22. Environmental Protection Agency (EPA), USA, *EPA Economic Analysis of Final Effluent Limitations Guidelines and Standards for the Landfills Point Source Category*, 2005.
23. Environmental Protection Department (EPD), Hong Kong Special Administrative Region (HKSAR), *Technical Memorandum Standards for Effluents Discharged into Drainage and Sewerage Systems, Inland and Coastal Water*, 2005.
24. Agnieszka, Z. (c), Tomasz, G., Joanna, Z., Zenon, L., *Chemosphere* **64** (2006) 803.
25. Wen, K., Lepore, J., Zandi, I., *Water Research* **38** (1998) 145.
26. Hamuda, M., Al. Gusain, I., *Water Science and Technology* **38** (1998) 213.
27. Jianlong, W., Hancheng, S., Yi, Q., *Process Biochemistry* **36** (2000) 297.
28. Borghei, S., Sharbatmaleki, M., Pourrezaie, P., Borghei, G., *Bioresource Technology* **99** (2008) 1118.