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4 **Unwanted metals and hydrophobic contaminants in bioreactor effluents are associated**  
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6 **with the presence of humic substances**  
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4 **Abstract**  
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8 Biological treatment of landfill leachate is difficult due to the presence of complex compounds.  
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10 Here we treated an old landfill leachate using a membrane bioreactor under the following  
11 conditions 24 hours for hydraulic retention, 65 days of sludge retention and an average organic  
12 load rate of  $1.71 \pm 0.16$  g/L/day. We observed a high removal of ammonia, phosphorous and some  
13 metals. However, removal of organic carbon was incomplete. Specifically, despite a major  
14 removal of suspended solids, hydrophobic and volatile hydrophilic compounds; high  
15 concentration of fulvic acid and hydrophilic contaminants were found in the effluent. Overall we  
16 demonstrate that the presence humic substances in the effluent is associated with the detection of  
17 arsenic, copper and chromium and di(2-ethylhexyl) phthalate.  
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34 **Keywords:**  
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37 Landfill Leachate, Membrane Bioreactor, Dissolved Organic Carbon, Metals, Nitrification.  
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# 1 Introduction

Strict regulation on the effluent of wastewater, challenges the conventional landfill leachate treatment plants (Ahn *et al.* 2002; An *et al.* 2006), as their deficiency in removal of chemical oxygen demand (COD), ammonia and micro-pollutants were repeatedly reported (Kjeldsen *et al.* 2002). Landfill leachate contains high concentration of concerned micro and macro pollutants, comprising four distinctive categories: (1) recalcitrant COD, mainly humic substances, (2) ammonium ( $\text{NH}_4^+$ ), (3) micro-pollutants, such as plasticizer, polycyclic aromatic hydrocarbon, pharmaceutical products; and (4) heavy metals, such as lead and arsenic (Kjeldsen *et al.* 2002). Upflow anaerobic sludge blanket reactor and lagoons comprise 60% of total conventional treatment plants (Kjeldsen *et al.* 2002). Unlike conventional processes, membrane bioreactor process has (1) high performance on different flow rate, and concentration of contaminants (Alvarez-Vazquez *et al.* 2004; Ahmed & Lan 2012). Although biological processes showed reasonable performance on young and medium landfill leachate, by ageing the landfill, the biodegradable materials bind together to form more complex dissolved organic carbon with low biodegradability (Alvarez-Vazquez *et al.* 2004). Membrane bioreactor allowed development of nitrifying bacteria and heterotroph bacteria for degradation of ammonia and emerging contaminants (An *et al.* 2006; Ahmed & Lan 2012). Trace organic compounds are divided into different groups based on their charge and hydrophobicity. Di 2-ethyl hexyl phthalate (DEHP) is highly hydrophobic, negatively charged plasticizer (Zolfaghari *et al.* 2014). Fluoranthene is the positive charged, hydrophobic compound with log Kow of 4.5. Finally, carbamazepine is a hydrophilic pharmaceutical product with neutral charge.

In order to alter the current treatment plants for reaching the future regulations, investigation of each micro and macro-pollutants was required. In this study, after optimizing the operating

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conditions, fate of carbon, nitrogen, phosphorous and metals was separately investigated to find out the most problematic characteristic of landfill leachate.

## 2 Material and Methods

### 2.1 Sampling

The targeted landfill was located in Frampton district, around 60 kilometers south east of Quebec City, Québec, Canada. As the landfill is still under operation, production of landfill leachate was widely varied by seasonal changes. The landfill production was stopped during winter; hence, the sampling started at the beginning of summer. Samples were taken monthly from the entrance of storage tank and instantly stored at 4°C, before the experiments.

### 2.2 Membrane Bioreactor Pilot

The lab-scale aerobic membrane bioreactor used in this study consisted of a 5 liters aeration basin equipped with two air diffusers and a submerged ultrafiltration membrane (ZW1, Zenon Environmental Inc., Oakville, ON, Canada) with pore size of 45 nm and filtration surface area of 470 cm<sup>2</sup>. Landfill leachate was introduced into the aeration basin by pulsed peristaltic pump through 20 liter closed storage tank. Meanwhile the filtrate was taken by the similar pump controlled by transmembrane pressure. Physical fouling by sludge cake was removed through backwash; while, chemical treatment was used for removal of organic and inorganic matter stocked in the pores. Air flow was controlled for keeping the dissolved oxygen always more than 7 mg O<sub>2</sub>/L. The range of 18±2 °C and 7.5±0.3 was measured for the operating temperature and pH, respectively.

### 2.3 Analytical methods

Samples were taken twice per week from the inlet, aeration basin and outlet of the process and kept at 4°C, prior to the analysis. All the analytical methods were adopted from previous study (Zolfaghari *et al.* 2016). Determination of total organic carbon (TOC) and total nitrogen (N<sub>tot</sub>),

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4 total alkalinity, pH, electrical conductivity,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , COD,  $\text{BOD}_5$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , metals and  
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6 daphnia and *Vibrio Fischeri* toxicity was fully discussed in this study.  
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9 Prior metals analysis by inductively coupled plasma atomic emission spectroscopy, 20 ml of  
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11 neutral sample was digested by 3 and 2 mL of trace metal hydrogen peroxide and nitric acid for 2  
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13 hours in the temperature of 95 °C by Digiprep MS digester (SCP Science, Baie-d'Urfé, Quebec,  
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15 Canada). Extraction of humic and fulvic acid was taken from the protocol developed by van  
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17 Zomeren and Comans (2007). Acidification was required for extraction of humic acid, while  
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19 resin XAD 8 was used for the adsorption of fulvic acid. TOC analysis was used for desorbed  
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21 humic and fulvic acid by NaOH solution. It worth mentioning that suspended solid and  
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23 hydrophobic portion was analyzed by the difference in total carbon between raw leachate and  
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25 permeates of microfiltration and ultrafiltration, respectively.  
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31 For analysis of emerging contaminants, 200 mL of sample was mixed with 200 ml of  
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33 dichloromethane using liquid-liquid extraction method. N-pentadecane with concentration of 5  
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35 mg/L was added into the vial as an internal standard. The fragments 194, 101 and 149 m/z were  
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37 selected as the reference peak for DEHP, fluoranthene, and carbamazepine, respectively. The  
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39 GC/MS analysis was fully described in previous studies (Zolfaghari *et al.* 2016). It should be  
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41 noted that the concentration of DEHP, fluoranthene, and carbamazepine in raw leachate was  
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43 43.2±12, 0.2, 0.1 µg/L; therefore, fluoranthene and carbamazepine concentration was raised by  
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45 their complexation with methanol to reach 100 and 200 µg/L, respectively.  
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### 3 Results and Discussion

#### 3.1 Start-up and optimization

The pilot was inoculated by the sludge collected from aerated lagoons of the same landfill leachate biological treatment with the initial concentration of 6673 and 3851 mg/L of total solid and volatile solid, respectively. The reactor was fed by raw leachate from 1 June 2015 by hydraulic retention time and solid retention time of 2 and 200 days, respectively. During the course of 9.5 weeks (till 7 August 2015), organic load rate was gradually increased to 2.314 gCOD/L/day to develop the proper niche of microorganisms (Table 1). Sludge withdrawal rate was increased to control the fouling rate. Even though the sludge retention time was decrease below 35 days, the average fouling rate was 18 kPa/day. Therefore, the membrane flux rate would not be increased more than  $1.6 \times 10^{-6}$  m/s. Moreover, nitrification will be affected for the sludge retention time below 35 days. Monitoring the process performance during start-up showed domination of air stripping as the only removal pathway of nitrogen and alkalinity in the in first three stages. Nitrification started at the last stage after 50 days. Rapid biological nitrification share 98% of transformation of ammonia into nitrate. Phosphorus removal was not dependent on the operation conditions. On the contrary, removal of carbon was mainly by heterotroph bacteria and it depended on food/microorganism (F/M) ratio. Based on the carbon removal, fouling rate and nitrification, hydraulic retention time of 24 h and solid retention time of 65 days were selected as the optimum condition.

#### 3.2 Fate of carbon

During optimized condition, complete removal of biodegradable carbon was observed. BOD removal was up to 97%, due to the presence of 12.5 g/L of activated sludge. COD removal, on the other hand, fluctuated between 60 to 70% for retention time above 24 hours. Organic load

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4 rate more than 2 g COD/L/day, declined COD removal (Aloui *et al.* 2009), due to the toxicity of  
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6 complex organic carbon (Setiadi & Fairus 2003; Svojitka *et al.* 2009) and ammonia (Ahmed &  
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8 Lan 2012). Like COD, TOC removal was not exceeded 50%. Generally, the carbon pollution  
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10 could be divided into five major groups: (1) suspended solid, (2) hydrophobic organic carbon,  
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12 such as fatty acids, grease and phenolic hydrocarbon (Aloui *et al.* 2009), (3) humic acid, (4)  
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14 fulvic acid, and (5) hydrophilic acid (van Zomeren & Comans 2007). The passage of the first  
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16 group was blocked by the membrane, as no turbidity was detected in the outlet. Hydrophobic  
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18 fatty acid was also restrained by hydrophilic ultrafiltration. Removal of humic acid was around  
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20 60% due to the adsorption through activated sludge with amount of 70 mg/g<sub>sludge</sub> (Feng *et al.*  
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22 2008). Humic acid removal was depended on sludge production. Keeping high sludge retention  
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24 time, therefore, negatively affected its removal (Hasar *et al.* 2009). Membrane bioreactor  
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26 removed around 40% of hydrophilic acid, mainly volatile fatty acid, by biodegradation and air  
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28 stripping (Campagna *et al.* 2013). Finally, fulvic acid showed the removal of just 11%, as it  
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30 rarely interact with sludge. All in all, remaining humic and fulvic acid and hydrophobic portion  
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32 with molecular weight larger than 500 Dalton was considered the most problematic carbon  
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34 pollutant (Table 2). Hydrophobic, positive charged fluoranthene significantly adsorbed on  
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36 negative sites of the sludge. On the other hand, hydrophilic carbamazepine had weak interaction  
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38 with the sludge that resulted in the removal efficiency below 30%. The concentration around 50  
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40 µg DEHP/L was the result of complexion with organic carbon (Figure 1). The degradability of  
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42 organic carbon that adsorbed the emerging contaminants determined their bioavailibility (Bauer  
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44 *et al.* 1998). Therefore, DEHP removal was almost equal to the removal of organic carbon. All in  
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46 all, the deficiency of the sludge for adsorption or degradation of fulvic acid resulted in low  
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48 removal efficiency of color, total organic carbon and DEHP.  
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### 3.3 Fate of nitrogen and phosphorous

Transformation of toxic ammonia into inert nitrate resulted from the activity of nitrosomonas, nitrobacter and nitrospira bacteria (An *et al.* 2006; Wang *et al.* 2016). After start-up of nitrification after 56 days,  $N_{\text{tot}}$  removal decreased to only 2.7% and remained the same throughout the operation. Moreover, by developing nitrobacter, no nitrite was found in the effluent of aeration basin. Although heterotroph nitrifiers performance are free from organic load rate, increase nitrogen organic load could have negative effect on the activity of heterotroph bacteria (Ahmed & Lan 2012). Toxicity was significantly removed from landfill leachate as the concentration of ammonia was remained less than 5 mg/L.

The concentration of  $\text{PO}_4^{3-}$  fluctuated independently, since aerobic process could not remove phosphorous. As shown in [table 2](#), the average removal was 35% during optimization period, due to the assimilation by microorganisms (6 mg P/ g of sludge). Furthermore, organic phosphorous was mainly consisted of hydrophobic organic matters (Aloui *et al.* 2009) that remained in the aeration basin; therefore,  $P_{\text{tot}}$  removal efficiency remained more than 60%.

### 3.4 Fate of Metals

Due to the presence of weak carboxylic and amino acid groups, such as glycine in the bacterial cell membrane (Artola *et al.* 1997), three pKa with values of 4.8, 6.9, and 9.4 were reported for the sludge. Humic acid also has three pKa with value of 2.5, 6.1 and 8.8 (Wightman & Fein 2001). At the neutral pH, hence, the surface of sludge and humic acid had the negative site, which interacts with metal cations. Ternary interaction of metal-humic acid-sludge justified the adsorption of humic acid and metal by the sludge (Wang *et al.* 2003; Feng *et al.* 2008). Humic substances contains considerable portion of couple of metals in raw leachate ([Figure 1](#)). Beside adsorption, precipitation is another metal removal pathway. Calcium, manganese and iron are

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4 well-known to form insoluble hydroxide and sulfide precipitate (Cameron & Koch 1980). The  
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6 results showed that manganese and lead are mostly precipitated in the form of suspended solids  
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8 and colloid. By membrane retention their removal efficiency was more than 70% (Table 2).  
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10 Surprisingly, nickel and Cobalt weakly interacted with either sludge (Artola *et al.* 1997) or  
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12 humic acid, leading to negligible removal efficiencies. On the other hand, chromium, copper and  
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14 arsenic were mostly found in humic substances. Therefore, their removal was depended on  
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16 humic substances removal. Dissolved  $\text{Cu}^{2+}$ , however, made a strong complex with glycine in  
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18 sludge (Artola *et al.* 1997), resulting in 49% of removal efficiency. Similarly, iron, zinc and  
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20 aluminum partially interact with humic substances, and the remaining dissolved part was well  
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22 removed by the sludge. Three valence cations showed stronger interaction with sludge, increase  
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24 its adsorption (Mahmoudkhani *et al.* 2014). Finally zinc showed high interaction with both  
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26 humic substances and sludge, resulting in high removal efficiency. As humic acid removal  
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28 enhanced in lower solid retention time, the removal efficiency of arsenic, chromium, iron,  
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30 aluminum, zinc and copper, increased by higher sludge withdrawal uptake.  
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4 **4 Conclusion**  
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8 By monitoring the fate of different micro and macro-pollutants in landfill leachate treatment by  
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10 membrane bioreactor, it could be concluded that ammonia, biodegradable and hydrophobic  
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12 organic carbon, suspended solid, alkalinity and toxicity were significantly removed by the  
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14 membrane bioreactor (up to 90%). Humic acid, phosphorous, and free hydrophobic emerging  
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16 contaminates had removal efficiencies up to 60%, due to adsorption by high concentration of  
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18 activated sludge (12.5 g/L); however, fulvic acid and hydrophilic organic compound with higher  
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20 molecular weight comprised the main source of total organic carbon in the effluent. Residual  
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22 concentration of hydrophobic emerging contaminates, as well as metals such as, iron, arsenic,  
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24 lead, copper and cobalt were connected to the presence of humic substances. Therefore, the  
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26 removal in the post-treatment processes should be the first priority.  
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Figure 1

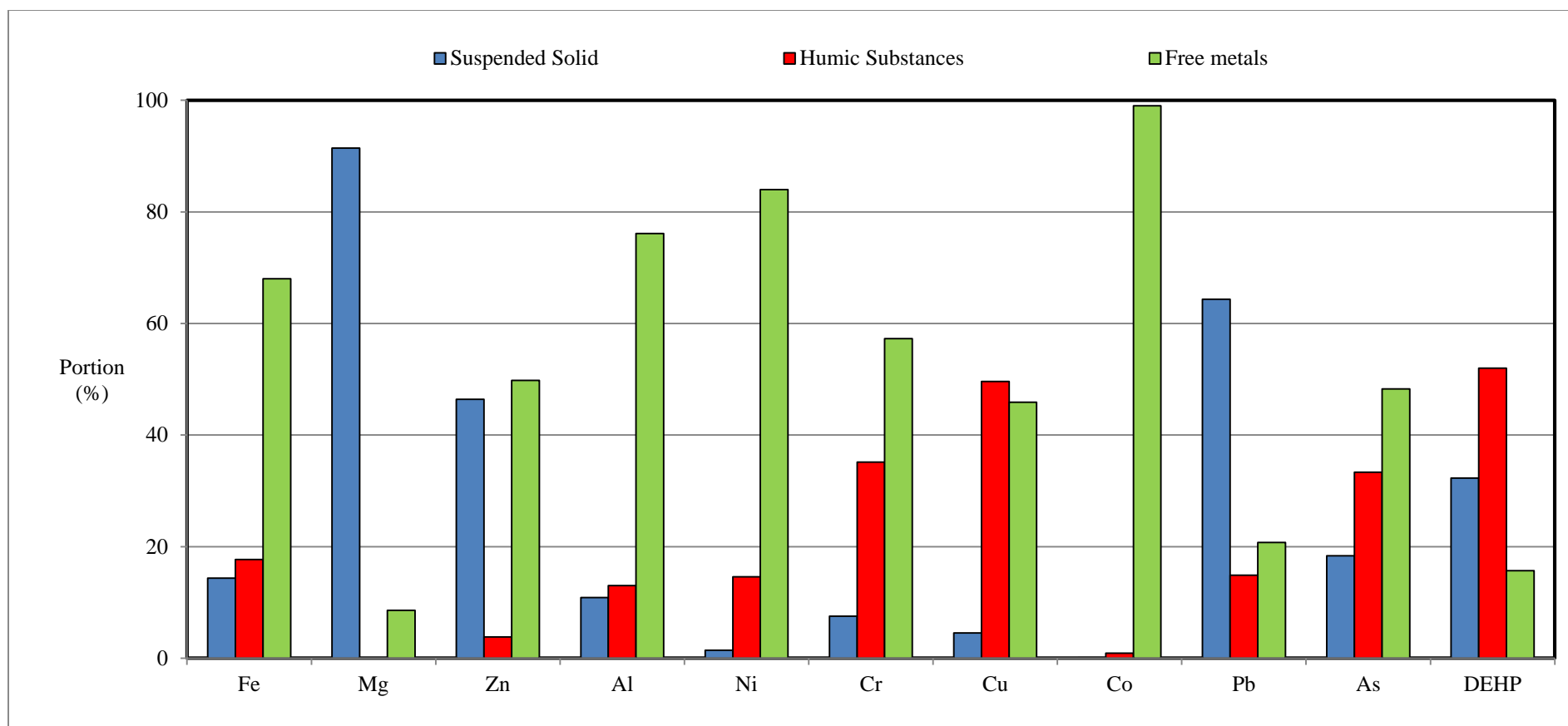


Figure 1. Portion of metals and Di (2-ethylhexyl) phthalate in suspended solid, humic substances and dissolved part in raw landfill leachate. Note that the portion associated with suspended solid was retained by the membrane, and contaminants in free form could interact with the sludge. Yet, contaminants with highest portion in humic substances are problematic.

Table 1. Operating conditions of membrane bioreactor during start-up period (average  $\pm$  standard deviation). Note that organic load rate was gradually increased to develop the desirable concentration of sludge inside aeration basin. The solid retention time was later measured based on the volume of sludge withdrawal during the period for controlling membrane fouling (COD = chemical oxygen demand, TVS = total volatile solid).

Parameter	unit	Stage			
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Operation period	day	20	14	14	14
Hydraulic Retention Time	h	44	32	24	18
Sludge retention time	day	200	160	50	35
Total Solid	g/L	9.131 $\pm$ 2.131	11.255 $\pm$ 1.019	15.815 $\pm$ 2.314	14.423 $\pm$ 2.212
Volatile Solid		6.432 $\pm$ 1.412	6.996 $\pm$ 0.871	8.847 $\pm$ 1.012	7.58 $\pm$ 1.134
Turbidity	NTU	309 $\pm$ 52	304 $\pm$ 48	422 $\pm$ 75	339 $\pm$ 61
Electrical Connectivity	ms/cm <sup>2</sup>	6.47 $\pm$ 0.61	6.54 $\pm$ 0.74	6.47 $\pm$ 0.39	6.85 $\pm$ 0.12
Organic Load Rate	g COD/L/day	0.953 $\pm$ 0.271	1.3 $\pm$ 0.282	1.562 $\pm$ 0.312	2.104 $\pm$ 0.121
Food/ microorganism ratio	g COD/g TVS/day	0.203 $\pm$ 0.081	0.174 $\pm$ 0.073	0.17 $\pm$ 0.061	0.286 $\pm$ 0.049
Membrane flux rate	$\times 10^{-6}$ m/s	0.67	0.92	1.23	1.64

Table 2. Average performance of membrane bioreactor in the optimum operating condition (organic load rate=1.71±0.16 g/L/day, food/microorganism ratio= 0.26±0.07 gCOD/g sludge/day, membrane flux of 9.2-12.3 ×10<sup>-5</sup> m/s, 12.5±1 g total solid/L and 6.2±0.6 g total volatile solid/L).

Parameter	Unit	Inlet	Outlet	Removal
Chemical oxygen demand	mg O <sub>2</sub> /L	1933±216	926±121	51±6.6
Biological oxygen demand		242	5.3	97.8
Total organic carbon	mg C/L	410±24	241±22	41.2±5.8
Humic acid		52	22	57.7
Fulvic acid		156	138	11.5
Suspended solid		27	ND	100
Hydrophobic portion		61	ND	100
Hydrophilic portion		124±14	75±21	39.2±9.8
Di 2-ethyl hexyl phthalate	μg/L	43.2±12	17.7±22	59.0±24.3
Spiked fluoranthene		98±5	6.7±7.2	96.5±2.4
Spiked carbamazepine		201±31	133±38	29±20.5
Ammonia		555±106	4.4±1.4	99±0.6
Nitrate		0.5±0.6	563±117	
Total nitrogen		613±115	596±122	2.7±2.1
Phosphate		2.7±0.7	1.6±0.7	36.1±30.2
Total phosphorous		5±0.6	1.7±0.5	66.2±20.5
Total alkalinity		4391±754	560±139	87±3
Toxicity(Daphnia)		Uta	15	1.2
Vibrio fischeri	53		2.8	94.7
Color	TCU	1621±284	1580±273	2.5±0.5
Electrical conductivity	ms/cm	10.3±1.3	8.8±1.4	15.6±6.9
Turbidity	NTU	564±88	ND	100.0
Iron	μg/L	18200±8830	2050±620	81.8±10.9
Magnesium		7800±2400	590±210	91.4±6.9
Zinc		730±130	310±94	72.2±18.9
Aluminum		680±89	202±34	68.7±7.4
Nickel		340±141	325±70	4.6±3.1



Chromium	250±17	204±30	24±10
Copper	224±53	115±73	48.5±7.6
Cobalt	76±14	75±14	0.5±0.2
Lead	72±29	19±13	73.9±11.2
Arsenic	58±18	44±14	23.3±1.1

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Quebec, November 17<sup>th</sup>, 2016

Dear Dr. *Eric Lichtfouse*

Chief Editor

Environmental Chemistry Letters

Please find enclosed a copy of the revised manuscript entitled « *Fate of Macro and Micro-Pollutants during Landfill Leachate Treatment Using Membrane Bioreactor* » (Ms. Ref. No.: ECLE-D-16-00168). The manuscript has been revised according to your comments.

Thank you very much for your kind collaboration.

Best regards.

Patrick DROGUI, Ph.D.

Professor, INRS-ETE

# CHECKLIST FOR THE EDITORIAL BOARD

## Environmental Chemistry Letters

Reference No: ECLE-D-16-00168

Title: *Fate of Macro and Micro-Pollutants during Landfill Leachate Treatment Using Membrane Bioreactor*

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### Response to chief editor

- *Title: delete and write a title showing the major result, advance, benefit or discovery (versus current knowledge): see titles of published articles in ECL. See also comments below.*

**Answer:** the title was changed into “Effect of Carbon Fate in Deficiency of Membrane Bioreactor Performance for Macro and Micro-pollutants Removal” that showed the major results of this study versus current knowledge.

- **Abstract: delete and apply ECL instructions: THIS IS WHAT IS WRITTEN ON THE PDF AVAILABLE ON ECL WEBSITE :**

#### Abstract

In less than 250 words, the abstract is structured in three parts: the first part abstracts the Introduction section, it thus gives the background, the global and specific issues, and the hypothesis (about 3-4 sentences). The second part abstracts the Experimental section, it thus gives a brief overview of the experiments (about 2-3 sentences). The third part abstracts the Results and discussion section, it thus gives: the 1-2 major results using precise trends and data, then the interpretation of those results, then the claimed novelty of those results versus current knowledge, then the basic or applied benefits of those results. Novelty claims should be made in an affirmative way, using for instance “Here we show that ...”, “Here we demonstrate that ...” or “This is the first...”.

**THEREFORE, IF I DO NOT SEE THE EXPLANATION OF THE LIMITS OF KNOWLEDGE AT THE END OF THE FIRST PART; IF RESULTS ARE NOT SUPPORTED BY DATA/NUMBERS IN THE THIRD PART, AND IF THERE IS NO EXPLANATION OF THE NOVELTY OF THE MAIN RESULT VERSUS CURRENT KNOWLEDGE AT THE END OF THE THIRD PART, I WILL DEFINITELY REJECT THE ARTICLE.**

**- F/M COD and VS must be explained at first appearance (abstract).**

**Answer:** Abstract was changed accordingly.

In the end of first part, the authors mentioned that “In this study, after optimizing the operating conditions, fate of carbon, nitrogen, phosphorous and metals was separately investigated to find out the most problematic characteristic of landfill leachate.”, Although there have been couple of studies on this field; to the best of our knowledge, no studies was performed to thoroughly investigated the fate of all macro and micro-pollutants to showed the deficiency in the performance of MBR

In the end of third part 3.2, the authors showed the limit of knowledge in this field, and the connection with taken result in the following statement: “All in all, the deficiency of the sludge for adsorption or degradation of fulvic acid resulted in low removal efficiency of color, total organic carbon and DEHP.”

The same statement applied in the end of part 3.4: “As humic acid removal enhanced in lower solid retention time, the removal efficiency of arsenic, chromium, iron, aluminum, zinc and copper, increased by higher sludge withdrawal uptake.”

Finally, the characterization of DEHP and metal brought in figure 1, and comparing with removal efficiency in table 2, proof our statement.

**- Figure captions must contain 3-4 sentences to describe the results show, and to explain their interpretation, significance and novelty/difference.**

**- ALL abbreviations appearing in figures, tables and captions must be explained at the end of the corresponding captions.**

**Answer:** the figure 1 was removed and figure 2-a was assimilated into the table 2 to remove the unnecessary information. The results in the figures were briefly discussed. Furthermore all abbreviation was explained.

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