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NOVEL MBBR SYSTEMS BIOFILM CARRIERS AND PHYSICAL-CHEMICAL ANALYSIS

Ovidiu IORDACHE[1], Ioana Corina MOGA[2], Cornelia MITRAN[1, 3], Dana CIUTARU[1], Irina SANDULACHE[1], Lucia SECAREANU[1], Gabriel PETRESCU[2], Elena PERDUM[1]

[1]National R&D Institute for Textile and Leather (INCDTP), 16 Lucretiu Patrascanu Street, District 3, Bucharest, Romania
[2]DFR Systems L.L.C., 46 Drumul Taberei Street, District 6, Bucharest
[3]Politehnica University of Bucharest, 313 Splaiul Independentei, District 6, Bucharest

Corresponding author email: iordacheovidiu.g@gmail.com

Abstract

Moving Bed Biofilm Reactors systems (MBBRs) have lately emerged as highly effective tools for treatment of wastewaters originating from various industrial sectors. System performance within the MBBRs is highly dependent on the carriers used, regarding efficiency in wastewater treatment (BOD/COD removal, heavy metal content reduction, nitrification and denitrification processes, various recalcitrant compounds removal etc.). Novel carrier structures have been obtained (patents pending), based on a mix of polyethylene with inorganic and organic compounds. Morphology analyses were carried out by Scanning Electron Microscopy, for assessment of internal surface structure, which will serve as an immobilization substrate for future bio-functionalization experiments. Chromatographic profile was assessed by Headspace Gas Chromatography, in order to identify Volatile Organic Compounds from the developed structures. The carried out analyses will serve as a starting point for future augmentation of the carriers with microbial strains.

***Key words**: MBBRs, reactors, wastewater treatment.*

INTRODUCTION

Moving Bed Biofilm Reactors systems (MBBRs) technology utilizes free-moving biofilm carriers, which represents a future evolution of the activated sludge process that allows a greater pollutant removal degree in smaller systems (i.e., bioreactors) (Puigagut et al., 2007). The biofilm grows protected within small plastic carriers, which are carefully designed with high internal surface area. These biofilm carriers are suspended and mixed throughout the water phase. The wastewater treatment with bio-media consists in adding biofilm carriers (small cylindrical shaped polyethylene carrier elements with specific density) in aerated or anaerobic basins to support biofilm growth (Chao et al., 2015). MBBR technology is widely involved in advanced wastewater treatment solutions for the industrial and municipal markets. This solution is used for the removal of organic substances, nitrification and denitrification, BOD and COD reduction etc., in highly polluted effluents (Pulicharla et al., 2017). The wastewater treatment based on MBBR systems allows a self-regulating biofilm formation inside the polymeric structures, which is stable in extreme parameters conditions (treated water organic load), it is an easy to run process, without need of sludge backflow, in order to achieve a good treatment efficiency (Jing et al., 2009; Moga et al., 2011). Microbial biofilms have the advantages of allowing environmental changes and presence of toxic chemicals inside the treatment tank (through several cellular bioaccumulation and biosorption mechanisms of pollutants) (Babel et al., 2003; Miriazimi et al., 2015; Kratochvil & Volesky, 1998).

Key parameters that define efficient carriers inside an MBBR system take into account performance, stability in time, 3D structure, wear resistance, composition etc.

In this paper, a new generation of carriers has been tested, which consists of a mix of polyethylene with inorganic and organic compounds (patent pending). Physical-chemical analyses were carried out on the new generation of carriers: Scanning Electron Microscopy (SEM) for assessment of surface morphology; GC-Headspace analysis, for study of volatile compounds from the samples.

MATERIALS AND METHODS

HDPE carriers and SEM analysis

Four new HDPE based carriers were subjected to morphological analysis. The newly developed carriers are based on a mix consisting of HDPE and inorganic and organic compounds, in various ratios. Sample notations are as follows: 1F, 2F, 3F and 4F.

SEM analysis was performed on a Quanta 200, Fei (Netherlands) electron microscope, GSED detector, Low Vacuum mode, spot beam size of 4.0, 20 kV filament voltage, with image acquisition at 27.2 seconds. Samples were visualized without metallic coating, on both the surface of the structures, and the interior (internal spacers). Sample acquisition was carried out at magnification levels of 5000x and 1000x.

GC-Headspace analysis

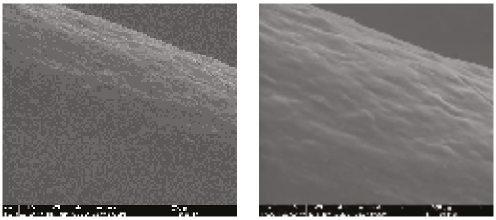
GC analysis was carried out on an Agilent Technologies 6890N GC with 7694E Headspace (Agilent Technologies) and 5973N MS detector. Samples were cut in small pieces, weighted to approximately same mass (1F = 0.9460 g; 2F = 0.9720 g; 3F = 0.9280 g; 4F = 9850 g), and placed in Headspace vials.

Headspace parameters were set as follows: vial temperature: 140°C; Loop temperature: 135°C; Transfer line temperature: 130°C; Stirring: Stop; Balance equilibration time: 120 min; Pressurization time: 2 min; Loop filling time: 3 min; Loop Balancing Time: 2 min. Following GC method was used: Capillary column: DB-35MS (J&W)®, length: 35 m, inner diameter 0.25 mm; Layer thickness: 0.25 µm; Injection system: splitless; Injector temperature: 300°C; Constant flow: 1.2 ml/min; Carrier gas: Helium; Temperature schedule: 50°C (1 min) at 290°C with 10°C/min, 290°C (10 min); Injection volume: 2.0 µl; Auxiliary: 300°C; MS detector: scan mode.; Scanning range: 50-450 amu.

RESULTS AND DISCUSSIONS

SEM analysis was used as a pre-screening tool in order to assess the surface morphology of the newly developed samples. The carriers will be further used, in future experiments, for bio-augmentation with various microbial strains, and knowledge about the surface morphology can prove useful, when selecting the strain (based on enzymatic activity and battery of specific enzymes). SEM images are showcased in Figures 1 to 4, for the four samples (1F, 2F, 3F and 4F), for the external and internal surface (500x and 1000x).

External surface (500x) External surface (1000x)



Internal surface (500x) Internal surface (1000x)

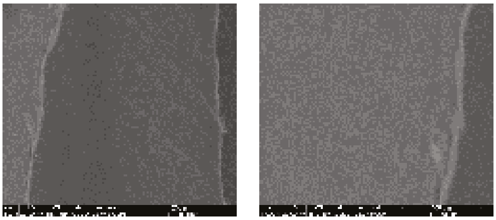
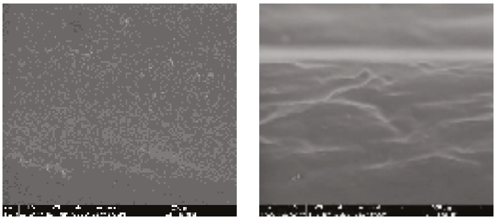


Figure 1. SEM analysis for 1F carrier

External surface (500x) Internal surface (1000x)



Internal surface (500x) Internal surface (1000x)

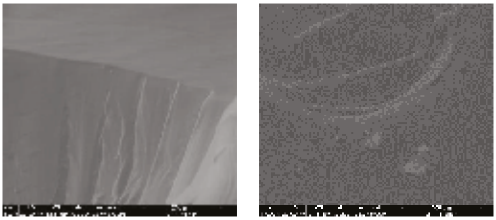
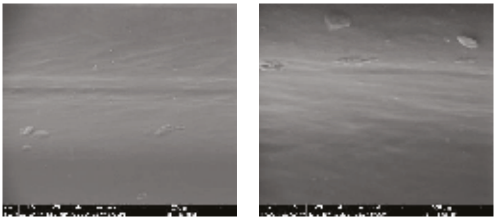


Figure 2. SEM analysis for 2F carrier

External surface (500x) External surface (1000x)



Internal surface (500x) Internal surface (1000x)

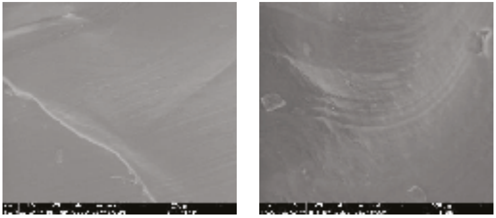
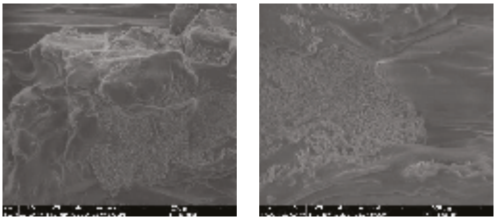


Figure 3. SEM analysis for 3F carrier

External surface (500x) External surface (1000x)



Internal surface (500x) Internal surface (1000x)

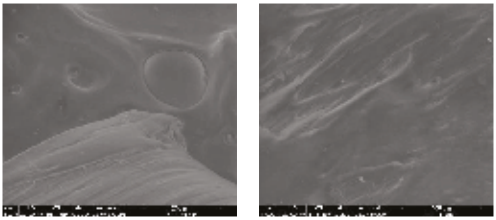


Figure 4. SEM analysis for 4F carrier

SEM analysis revealed different surface morphologies of the carriers, from sample to sample.

Therefore, it can be observed that surface rugosity increases from sample 1F to sample 4F, with sample 4F having the most rugose surface, while sample 1F has a plain-smooth looking surface.

Gas Chromatography analysis was carried out on each sample (Figures 5 to 8), in order to assess the main volatile compounds present in each sample. This can contribute to building a knowledge base that could prove useful to better understand the behaviour of the newly developed carriers in various conditions.

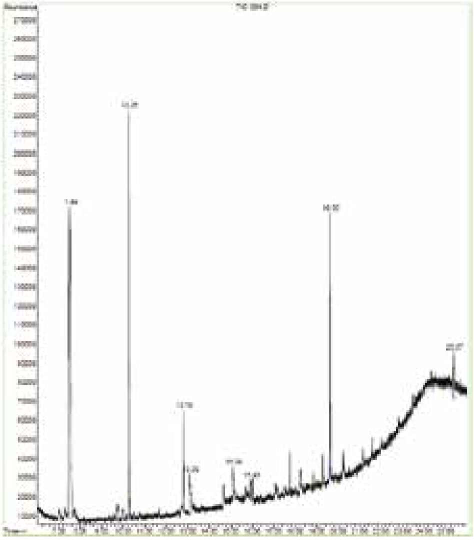


Figure 5. GC chromatogram for 1F carrier

Following compounds were assessed in 1F sample: 1-Decene; 1-Tetradecanol; Tetradecyl trichloro acetate; 2,6-Di-tert-butylphenol; Benzyl oleate; 2-tert-Butyl-4-(2-phenylpropan-2-yl) phenol; Ethyl stearate; p-Xylenolphthalein (Table 1).

Table 1. Sample 1F compounds

Rt.	CAS	Name	Area
7.488	112-41-4	1-Decene	715334
10.254	112-72-1	1-Tetradecanol	397588
12.788	74339-52-9	Tetradecyl trichloro acetate	86066
13.085	5875-45-6	2,6-Di-tert-butylphenol	97170
15.094	55130-16-0	benzyl oleate	56278
15.926	56187-92-9	2-tert-Butyl-4-(2-phenylpropan-2-yl) phenol	44334
19.617	111-61-5	Ethyl stearate	216783
25.372	50984-88-8	p-Xylenolphthalein	69848

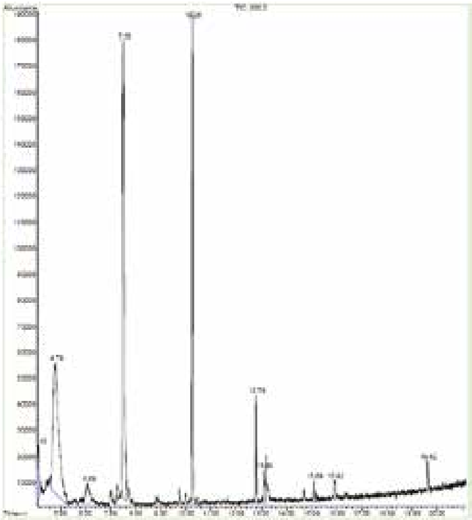


Figure 6. GC chromatogram for 2F carrier

Following compounds were assessed in 2F sample: 4,4′-Dichlorodiphenyl sulfone (DCDPS); 1-Decene; 2-Butyloctanol; 1-Tetradecanol; 1-Hexadecene; 2,6-Di-tert-butylphenol; 7-(Z)-Hexadecane; 2-tert-Butyl-4-(2-phenylpropan-2-yl) phenol; Ethyl stearate (Table 2).

Table 2. Sample 2F compounds

Rt.	CAS	Name	Area
4.118	80-07-9	4,4′-Dichlorodiphenyl sulfone (DCDPS)	96275
4.787	872-05-9	1-Decene	781144
6.089	3913-02-8	2-Butyloctanol	77097
7.497	112-41-4	1-Decene	763939
10.254	112-72-1	1-Tetradecanol	352165
12.788	629-73-2	1-Hexadecene	65223
13.085	5875-45-6	2,6-Di-tert-butylphenol	54442
15.089	35507-09-6	7-(Z)-HEXADECANE	31672
15.917	56187-92-9	2-tert-Butyl-4-(2-phenylpropan-2-yl) phenol	23068
19.622	111-61-5	Ethyl stearate	23643

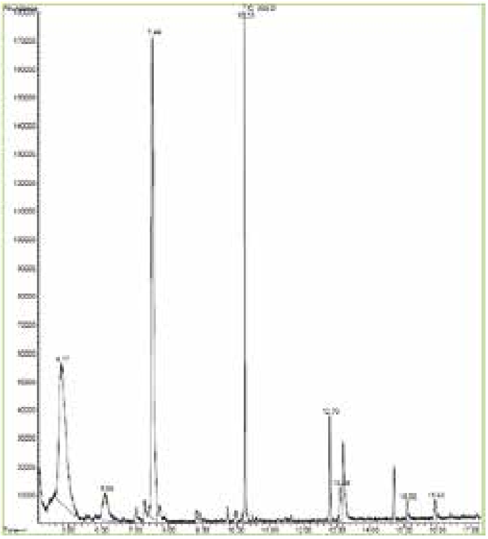


Figure 7. GC chromatogram for 3F carrier

Following compounds were assessed in 3F sample: 1-Decene; 2-Butyloctanol; 1-Tetradecanol; 1-Hexadecene; 2,6-Di-tert-butylphenol; Eicosane; 1,5-Diphenyl-1H-1,2,4-triazole-3(2H)-thione (Table 3).

Table 3. Sample 3F compounds

Rt.	CAS	Name	Area
4.769	872-05-9	1-Decene	717238
6.089	3913-02-8	2-Butyloctanol	112187
7.493	112-41-4	1-Decene	731741
10.254	112-72-1	1-Tetradecanol	333366
12.788	629-73-2	1-Hexadecene	60157
13.090	5875-45-6	2,6-Di-tert-butylphenol	49967
15.094	74685-33-9	Eicosane	23186
15.926	5055-74-3	1,5-Diphenyl-1H-1,2,4-triazole-3(2H)-thione	21285

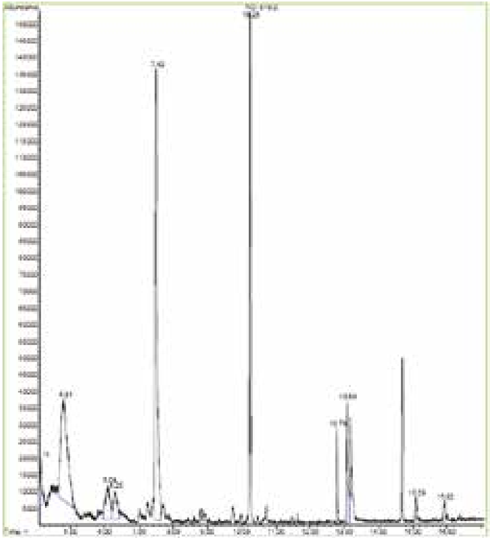


Figure 8. GC chromatogram for 4F carrier

Following compounds were assessed in 4F sample: 4,4′-Dichlorodiphenyl sulfone (DCDPS); 1-Decene; 2-Butyloctanol; 5-methyl furfural**;** 1-Tetradecene**;** 1-Hexadecene; 2,6-Di-tert-butylphenol; Eicosane; 1,5-Diphenyl-1H-1,2,4-triazole-3(2H)-thione (Table 4).

Table 4. Sample 4F compounds

Rt.	CAS	Name	Area
4.131	80-07-9	4,4′-Dichlorodiphenyl sulfone (DCDPS)	45225
4.806	872-05-9	1-Decene	405661
6.089	3913-02-8	2-Butyloctanol	96121
6.284	620-02-0	5-methyl furfural	63686
7.488	112-41-4	1-Decene	603158
10.249	1120-36-1	1-Tetradecene	275861
12.788	629-73-2	1-Hexadecene	49887
13.076	5875-45-6	2,6-Di-tert-butylphenol	118058
15.094	74685-33-9	Eicosane	18905
15.921	5055-74-3	1,5-Diphenyl-1H-1,2,4-triazole-3(2H)-thione	19402

Overlapped chromatograms of samples 1F, 2F, 3F and 4F are showcased in Figure 9.

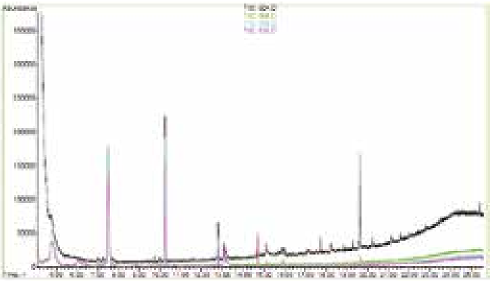


Figure 9. Overlapped chromatograms (sample 1F=804.D; sample 2F=806.D; sample 3F=808.D; sample 4F=810.D)

Polyethylene, whether high density (HDPE) or low density (LDPE) is essentially a very long hydrocarbon molecule. Pyrolysis of PE produces shorter hydrocarbons, mostly normal alkanes, alkenes and dienes, which may be analysed by gas chromatography.

4,4′-Dichlorodiphenyl sulfone (DCDPS) is an organic compound with the formula $(ClC_6H_4)_2SO_2$. Classified as a sulfone (Sime et Abrahams, 1960), this white solid is most commonly used as a precursor to polymers that are rigid and temperature-resistant such as PES or Udel™.

Besides many uses of 1-decene, it can be used in the manufacture of C11 plasticizer alcohols. 1-Decene and Eicosane was also found in samples of Polyethylene (Hermabessiere et al., 2018) and High-Density Polyethylene (Sarker et al., 2011).

Previous studies (Kato, 1967) showed that volatile compounds were produced through the radicals formed by the scission of glyosidic linkages of cellulose and oxidized cellulose. Chromatographic method for the identification of cellulose degradation compounds highlighted presence of acetaldehyde, furan, propionaldehyde, acrolein, acetone, diacetyl, furfural and 5-methyl furfural.

Other compounds that were analysed in the fur samples: 1-Tetradecene, is often found as a semi-volatile emission compound, in agricultural plastics (Linak et al., 1989); 2,6-Di-tert-butylphenol is an alkylated phenol, its derivatives being used industrially as stabilizers for hydrocarbon-based products (plastics included) (Fiege et al., 2002); 7-(Z)-Hexadecane and 7-(Z)-Hexadecene compounds have been often found in various resin films structures (Niimura and Miyakoshi, 2003); 2-tert-Butyl-4-(2-phenylpropan-2-yl)phenol is a compound with wide usage as an additive for plastics.

CONCLUSIONS

Within the current paper, four newly developed carriers based on a mix of HDPE and inorganic and organic compounds where morphologically characterized along with the assessment of their chromatographic profiles. Scanning Electron Microscopy allowed assessment of specific surface morphology which will prove useful in future experiments, in order to see modifications of the surfaces, after bioaugmentation of microbial strains (due to enzymatic activity). Chromatography analyses allowed identifycation of volatile compounds originating from the newly developed carriers, based on a mix of HDPE with organic and inorganic compounds. This allowed building up of knowledge base regarding carriers used in MBBR system for industrial wastewaters treatment.

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