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IMPROVEMENT OF BIOFILM CARRIERS FOR THE TREATMENT OF AUTOMOTIVE INDUSTRY WASTEWATER

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The efficient biological treatment of the wastewater of the automotive industry is difficult, mainly because of the low biological oxygen demand/chemical oxygen demand (BOD/COD) ratio. Moreover, wastewater of the automobile industry contains heavy metals and other chemical substances that may have toxic effects. Biofilm and hybrid technologies could be optimal solutions for the treatment of such heavily biodegradable wastewater streams. This paper presents the experimental results of the examination of modified biofilm carriers developed for the treatment of the wastewater of the automotive industry. Three modified biofilm carriers were examined: a high-density polyetyilene (HDPE), an HDPE modified with 50% carbon nanotube (CNT) content, and an HDPE modified with 75% CNT content. They were compared to a patented biofilm carrier having similar morphological properties (control). The examination consisted of two parts: (1) studying the colonisation of biofilm on each carrier, and (2) studying the biological COD removal efficiency of biofilm reactors filled with the four different biofilm carriers in 25% volumetric ratio each with an influent industrial emulsion sewage. The obtained results demonstrated that neither the rate of biofilm colonisation, nor the COD removal efficiency show any significant difference comparing the four biofilm carriers. The colonisation of biofilm was appropriate on each carrier and this ensured proper efficiency of COD removal in each biofilm reactor. Based on the results, it can be stated that the suggested advantageous characteristics of CNTs do not appear as it is mixed in the plastic raw material during the production of biofilm carriers. The absence of the significant difference observed between the examined carriers suggests that the production of biofilm carriers from recycled plastic could carry financial advantages compared to the control carrier. Further experiments could specify differences by various hydraulic loads or toxic effects.

Keywords: automotive industry wastewater, biofilm carrier, CNT, COD removal, emulsion sewage

Introduction

During biological wastewater treatment processes, bacteria utilize various forms of C, N and P present in wastewater [1]. The biological treatment processes can be characterized according to the presence of the microbiological forms. The microbes are aggregated into flocks in the activated sludge (AS) processes or fixed on the surface of biofilm carriers (biofilm technologies). The processes, where both flocks and biofilm carriers are present are called hybrid systems. The history of conventional activated sludge treatment dates back to hundreds of years. In the past fifty years, several experiments have been made with biofilm or hybrid technologies due to the advantages these technologies hold compared to the conventional AS systems [2]. The main points of it are the better achievable nutrient removal, the possibility of higher applied specific nutrient load, and the reduced sensitivity of the biofilm towards the toxic compounds of wastewater [2].

The efficient biological treatment of the wastewater of the automotive industry is difficult, mainly because of the low biological oxygen demand/chemical oxygen demand (BOD/COD) ratio. Moreover, wastewater of the automobile industry contains heavy metals and other chemical substances that may have toxic effects [3]. The advantages of biofilm or hybrid technolgies, therefore, can be exploited in the treatment of automotive industry astewater.

This paper presents the experimental results of the examination of modified biofilm carriers developed for the treatment of the wastewater of the automotive industry.

Methods

According to several studies, the relatively fast colonisation of biofilm has been observed on the surface of activated carbon [4–7] compared to the conventional plastic carriers. The examined biofim carriers in this study have been modified with the addition of carbon nanotubes (CNT) to the plastic raw material during the production of carriers. The raw plastic was high-density polyetyilene (HDPE).

Three biofilm carriers have been produced and examined:

1. 100% HDPE
2. HDPE modified with 50% CNT
3. HDPE modified with 75% CNT.

These three biofilm carriers have been compared to a patented biofilm carrier [8] having similar morphological properties (control).

The first part of the examination was mainly morphological: some properties of the three modified carriers have been investigated and compared to the control one.

In the second part of the experiment, biofilm carriers have been examined during biological wastewater treatment. This part of the experiment consisted of two stages:

1. studying the colonisation of biofilm on each carrier,
2. studying the biological COD removal efficiency of biofilm reactors, filled with the four different biofilm carriers, in 25% volumetric ratio each, with an influent industrial emulsion sewage.

First, the colonisation of the biofilm on the carriers was carried out in four Sequencing Batch Reactors reactors (SBR) of the same kind, having a useful volume of 4 litres, with 25% carrier filling ratio. The reactors were inoculated with municipal sewage sludge and were fed with municipal sewage. The biological wastewater treatment took place within aerobic conditions (since the focus of the experiment was solely COD removal). After 3 weeks of operation, the Mixed Liquid Suspended Solid (MLSS) concentration was reduced to 0.5 g/l to allow faster colonisation of the biofilm. The colonisation of the biofilm took about 6 weeks. After the first 6 weeks of operation, the amount of colonised biofilm on the carriers was determined in every 3 weeks by a method developed in the Institute of Environmental Engineering, University of Pannonia, Veszprém.

After the visible colonisation of the biofilm on the carriers, the feedstock of the reactors was changed to an emulsion sewage. The focus of the experiment was the examination of COD removal in the reactors. The applied reactor configuration can be seen in *Figure 1*.

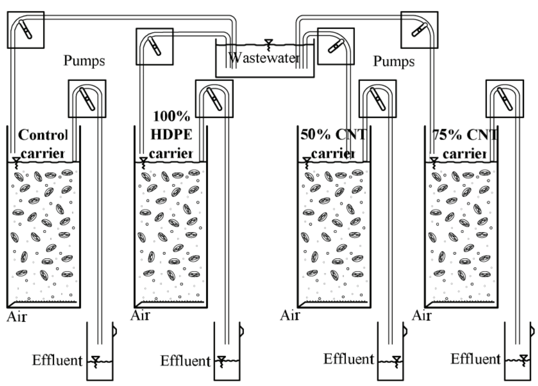

Figure 1: 4 parallel reactors

The inlet of the reactors can be characterized with the following parameters: COD_{total} 1000–1700 mg/l; $COD_{filtered}$ 800–1600 mg/l; BOD_5/COD ratio 0.4–0.5; NH_4-N 15–25 mg/l; orto-P 5–160 mg/l. The hydraulic retention time in the reactors was 4 days in the first 8 weeks, after that it was reduced to 3 days until the end of the experiment. The MLSS concentration was controlled between 0.5–1.5 g/l.

Results and discussion

Morphological examinations showed that the weight of the modified biofilm carriers is about 30% more than the weight of the control carrier, independent of the amount of CNT added. It resulted in a different bulk density of the modified biofilm carriers, but no difference has been observed in hydrodynamics compared to the control carrier. The modified biofilm carriers showed more roughness on their surface compared to the control carrier, and some dimensions of the modified carriers also differed slightly from the control carrier.

Biofilm colonisation has been examined on the biofilm carriers after it became visible (after about the first 6 weeks of operation). The results of the determination of the amount of biofilm colonised on the carriers is depicted in *Figure 2*. The figure shows the biofilm concentration in g/l, which is an excess MLSS concentration in the reactors, calculated from the measured amount of biofilm per carrier and the filling ratio. According to *Fig. 2* no significant difference can be observed either between the three moified carriers, or compared them to the control carrier.

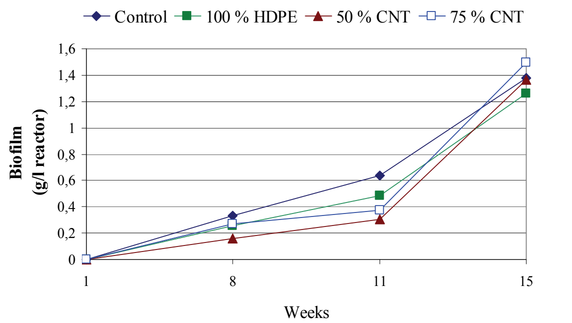

Figure 2: The results of the determination of the amount of biofilm

In the last experimental period, the biological COD removal was studied in the 4 reactors, filled in 25% with the 4 different biofilm carriers. Results are shown in *Figures 3–6*. Continuous vertical lines show the change in the influent wastewater, while broken lines show the date of excess sludge removal from the reactors.

According to *Fig. 3–6*, no significant difference can be seen either between the COD removal of the reactors filled with the modified biofilm carriers, or compared them to the reactor filled with the control carrier. The effluent from each reactor contained 130–140 mg/l COD_{total} (100–110 mg/l $COD_{filtered}$). The difference between COD_{total} and $COD_{filtered}$ is indicated by the difficulty of decantation in the SBR reactors. The examined four biofilm carriers flow up to the surface during sedimentation, and some sludge is removed this way during decantation. The excess sludge removal caused a slight increase in the effluent COD each time in each reactor (broken vertical lines in *Fig. 3–6*). The reason is the sudden increase in the specific organic load of the sludge remaining in the reactors when excess sludge is removed.

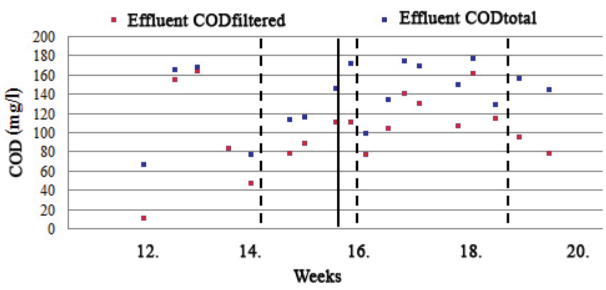

Figure 3: COD removal in the control reactor

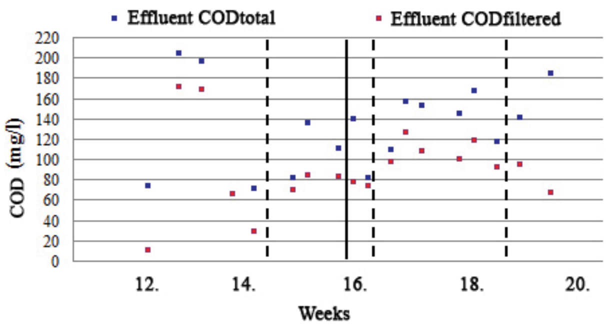

Figure 4: COD removal in the 100% HDPE reactor

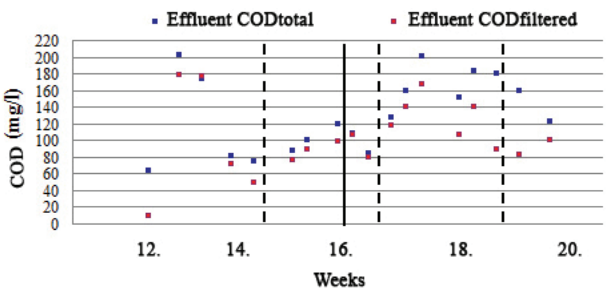

Figure 5: COD removal in the 50% CNT reactor

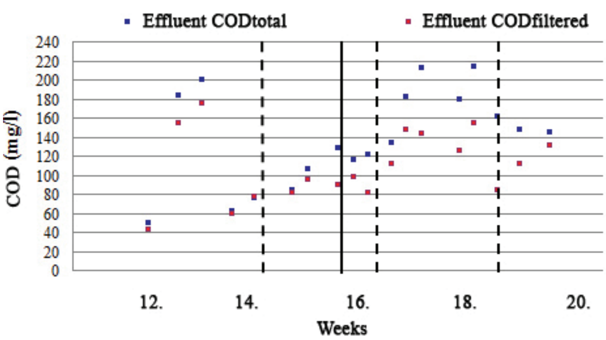

Figure 6: COD removal in the 75% CNT reactor

Conclusions

The obtained results demonstrated that neither the rate of biofilm colonisation, nor the COD removal efficiency show any significant difference either comparing the three modified biofilm carriers, or comparing them to the control carrier. The colonisation of biofilm was appropriate on each carrier and this ensured proper efficiency of COD removal in each biofilm reactor. Based on the results, it can be stated that the suggested advantegous characteristics of carbon nanotubes do not reveal as it is mixed in the plastic raw material of the biofilm carriers. The absence of the significant difference observed between the examined carriers suggests that the production of biofilm carriers from recycled plastic could have financial advantages compared to the control carrier. Further experiments could specify differences by various hydraulic loads or toxic effects.

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