OPERATIONAL EXPERIENCES WITH A NANOFIBRE BIOMASS CARRIER USED FOR THE TREATMENT OF TOXIC INDUSTRIAL WASTEWATERS

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Abstract

Biofilm processes are very often used for the treatment of low biodegradable or toxic contaminants. The main advantages of a biofilm biotechnology are a higher residence time and concentration of biomass in the bioreactor. Crucial requirements for any carrier are excellent colonization, the maximum specific surface area, optimal density and ease of production. Based on these crucial parameters the Technical University of Liberec developed new types of biomass carriers which are based on the use of different kinds of polymeric nanofibre materials. The key component is a yarn which consists of a carrier fibre supporting a layer of nanofibres with a diameter in the order of hundreds of nanometres. A priority of the nanofibre carriers, presented previously [1], is a large protected specific surface area which promotes the initial adhesion and rapid development of the biofilm. The aim of this contribution is to present long-term full-scale operational experiences with the first type of nanofibre carrier applied for the treatment of industrial wastewaters from production of chloramines and perchlorate bleach. The bioreactor with the nanofibre carrier is operated under real conditions in parallel with a conventional activated sludge system. A direct comparison of the efficiency of both the systems and an evaluation of their mechanical properties are presented in this contribution. The full-scale application of the nanofibre carrier confirmed its potential to stabilize the treatment process.

Keywords:

nanofibre biomass carrier, industrial wastewater, biofilm process, chloramines

1. INTRODUCTION

1.1. Biological treatment of toxic industrial wastewaters

The biodegradation of toxic xenobiotics is limited by the threshold level of maximum concentrations and the organic loading, which are specific for the given microbial consortium – wastewater system. Although it is possible to ascertain the threshold concentrations from the available references, modelling or even better semi operational testing is recommended to confirm the reliability of the biological process and verify the limit values of the main parameters.

The residence time of the biomass in the system is a key parameter for determining the how long the critical micro-organisms remain in the system [2]. In addition to providing its minimum values is necessary in specific cases to provide inoculation using a selectively prepared inoculum, which is physiologically adapted to the contamination present and the composition of the wastewater (bioaugmentation). The optimal solution in terms of the treatment rate appears to be inoculation using a biomass from plants with a similar character to the contamination and type of wastewater, or inoculation using groundwater with a long-term presence of the same contaminants. In addition to the type of contamination the minimum residence time is determined by the physical and chemical properties of the water e.g. high total salinity or low temperature, which in itself leads to a slowing down of the growth of the biomass and therefore the necessary increase in its residence time.

When it comes to finding the maximum load of the biological stage, it is always necessary to verify both the maximum permissible concentrations and the organic load of biomass over the long term. Therefore for concentration reasons, dilution with other water is often the only possible solution. The stability of the process is affected by the consistency of the added contamination and therefore balancing the quality of the wastewater with the content of toxic substances is essential for stable process efficiency. In cases where such wastewater is a decisive C source, the balancing of quality is a prerequisite for the stabilization of the balanced concentration of biomass in the system [2].

When designing the biological treatment technology it is very important to determine the efficiency of the process under all possible operational conditions (especially temperature effects during the year), not only the minimum generally reducing the activity of the microbial consortia but also the maximum, which, in addition to the composition of the wastewater, reduces the oxygenation capacity of the proposed aeration system and affects the economy of the operation.

The above-mentioned key parameters for biological treatment of toxic substances (biomass retention time and maximum concentrations of contaminants) predetermine the use of biofilm processes, which, besides increasing the concentration of biomass and maintaining slow growing microorganisms in the system, provide the advantage of increased resistance to the toxic effect of the contaminants.

1.2. Biofilm processes in industrial wastewater treatment, biomass carrier

Immobilization of biodegraders of a specific contamination in the form of a natural biofilm is a prerequisite not only for primarily slow-growing microorganisms but also in situations where the decisive microorganism grows slowly under specific conditions (type and concentration of substrate, salinity and temperature). Higher resistance of naturally immobilized microorganisms is associated with increased production of extracellular polymers, providing microorganisms capable of producing a natural biofilm with a natural diffusion barrier [3].

Immobilization of microorganisms in natural biofilm technology has been used since the beginning of the last century. Trickle-bed biofilters used for wastewater treatment have undergone massive expansion in the Czech Republic as well as the so-called English filters used in water supply for the slow filtration of raw water. Biofilters used in water treatment industries are mostly trickle-bed columns, whose major drawbacks included overgrown carriers, limitations in the supply of oxygen and generally lower efficiency compared with conventional activation processes [2]. These disadvantages are usually eliminated by using combined systems with a fixed biomass in a submerged biofilm as well as free biomass (in suspension). The first technologies used a fixed biomass carrier made from profiled plastic structures in the form of a biological honeycomb. These techniques do not eliminate the possibility of the filling becoming overgrown and also complicate maintenance of the structural parts of the bioreactors, particularly the aeration systems. For these reasons, modern biomass carriers are made from various parts on a fluidized bed or as removable segments. This contribution focuses on the long-term verification of such types of carriers using nanofibre materials.

The biomass carrier is a determining factor for the technology of wastewater treatment in biofilm reactors. Current trends have clearly reached the stage where carriers are being developed for different types of wastewater or wastewater systems - critical microbial consortium. The carrier material must be biochemically inert, chemically and physically stable, whilst at the same time it must be morphologically suitable and compatible with the surface structures of the produced biofilm. The density of the carrier should be comparable with that of the wastewater, even after an increase in biomass or coagulum. The aim is mainly to maximize the specific surface of the carrier and adjust its porosity according to the type of wastewater.

The biomass carrier is a key element of the technology in biofilm processes. The “roughness” of the surface of the carrier, which is characterized by its morphology, is a decisive property in terms of speed of biofilm formation [4]. Another essential feature is the hydrophobicity of the surface of the carrier and a complex characteristic is the specific surface. A nanofibre carrier has been developed at TUL which can be modified as produced taking into account the above-mentioned facts. Its main advantages are its surface morphology, the high specific surface area of the material, and considerable material freedom in terms of the choice of nanofibre surface. The basic form of the carrier is a yarn containing nanofibres, from which it is possible to produce 2D and 3D structures [1]. This contribution summarizes the operational experience gained during the 3rd and 4th year of operation of an industrial wastewater treatment plant with an installed nanofibre carrier pilot module.

2. MATERIALS AND METHODS

Microorganisms – Activated sludge from a municipal wastewater treatment plant (WWTP) in Bohumín was used as a primary inoculum for the start up of the Bochemie WWTP.

Determination of chemical oxygen demand (CoD) – The sum of all organic substances in the sample was determined via the dichromate method using single-purpose cuvette tests (Hach-Lange, Germany).

2.1. Bochemie Bohumín wastewater treatment plant

The biological part of the WWTP is designed for treating both technology as well as sewage wastewater from the plant operation. The dominant organic load comes from the final separation of the product from the mother liquor for 2 produced types of chloramines. The original chloramine B (sodium benzenesulfonchloramide) was later supplemented by its methyl derivative - chloramine T.

From a technological perspective, the WWTP is a conventional activated sludge system with fine bubble aeration and aerobic stabilization of excess sludge operated as a low loaded system with a tertiary treatment stage. The WWTP consists of two independent technological lines, which can be operated variably.

Due to the nature and composition of the wastewater, phosphorus is fed as a deficient macronutrient. Technological wastewater from the plant is pre-treated in the original neutralization station. Sedimentation of sludge produced during neutralization takes place in two lamellar settling tanks.

The aeration tanks each have a volume of 125 m^3 and are operated in parallel. At the end of 2010, an installation with a nanofibre biomass carrier, consisting of knitted fabric fixt to a frame made from polyester yarn coated with a nanofibre covering of polyurethane, was placed in the second aeration tank (AN2). The size of the carrier was limited to 130 m^2 by the production capacity at the time of installation. The activated sludge is subsequently deposited in secondary settling tanks with a volume of 65 m^3 (see Table 1). Most of the sludge is returned to the activation as return sludge. Part of the sludge is removed from the system as excess sludge depending on the load of the WWTP (the actual situation in production). The excess sludge is aerated in the excess sludge tank and after addition of a flocculent polymer is dewatered in a filter press where the sludge from the on-site neutralization station is also dewatered.

The treated water from the settling tanks is further treated on a micro-screen drum filter and discharged through a Parshall flume to the recipient. The average flow of wastewater is about 600 m^3 / day. Currently, sewage wastewater from the facilities used by approximately 50 employees in the amount of 4-5 m^3/d is routed to the WWTP.

Table 1 –Overview of the basic technical and technological parameters of the Bochemie WWTP.

Parameter	Value
Geometry of the activation tank [m]	5.6x5.6x4
Total volume of activation (2 tanks) [m3]	250 (2x125)
Wastewater flow [$m^3 \cdot d^{-1}$]	400-1050
Hydraulic retention time [h]	5.7–15
COD loading of the carrier [$g \cdot m^{-2} \cdot d^{-1}$]	192–288
Total surface of the carrier [m^2]	130

2.2. Nanofibre biomass carrier

Nanofibre carriers have the advantage of a large surface area, high porosity and small pore size. These characteristics allow for easier adhesion, which simplifies the first stage of the surface colonization. Another advantage is the possibility to choose the polymer type or to combine more materials with the aim of obtaining the appropriate density of final composite carrier [1].

The final yarn used for the first carrier prototype production was prepared from supporting fibres covered with polyurethane nanofibres. The nanofibre carrier is generally composed of three parts: a basic (supporting) fibre composed of polypropylene Prolenvir (660 dtex), and a coating composed of the polyurethane nanofibre Larithane (50 dtex, electrospinning method, diameter around 260 nm); both of which are twice-wrapped in a protective polyethylene fiber (167 dtex, for fixation). All of the nanofibres used in this study were produced by electrospinning on a Nanospider™ unit [5,6]. The resulting yarn can be further processed using common textile technology into a woven structure (planar) interlaced with an embedded weft (for use in a fixed bed; Fig. 1c). The final woven structure was fixed via special stainless frames, which allow subsequent tensioning. The specific surface of the nanofibre carrier installed in frames can reach more than 1000 m^2/m^3.

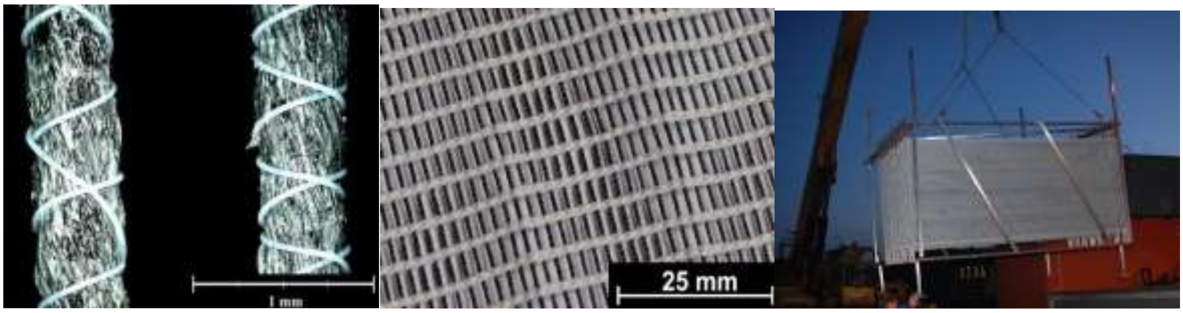

Fig. 1. a) A nanofibre thread with protective polyethylene fibres, b) woven plannar structure of nanofibre bound threads and c) final carrier module.

2.3. Monitoring of the WWTP and comparative study of CAS and hybrid system with a nanofibre carrier

Long-term monitoring of the WWTP is carried out usually 3-4 times per week. The monitored concentrations are mainly the organic and inorganic loads and their development on the outflow from the WWTP. After complete stabilization of the increase in biomass on the carrier in 2012 (steady-state value of biomass concentration on the carrier) both technological lines composed of an activation and final sedimentation tank were hydraulically and materially loaded identically. The biomass concentration in both of the systems was measured separately.

During 2013 and part of 2014, a comparative study of the two lines was performed by taking 24 hour samples from the two settling tanks. The values presented in the results are averages of a minimum of 3 such samples after each other (3-4x 24-hour samples within the monitoring campaign). The efficiency of COD removal was monitored in particular.

3. RESULTS

3.1. Loading of WWTP and monitoring of a biomass

The main source of contamination at the Bochemie WWTP is the production of chloramines, which is highly variable and determined by the actual production program. Both types of chloramines are produced in direct relation to sales. The production volume is medium to low due to the capacity for which the WWTP was designed. Given the imbalances in production, the result is a considerable inconsistency in the sludge conditions (erratic concentration of biomass) even after optimizing the balance of quality of water entering the installation by levelling the concentrated stream from the chloramine production. The variable concentration of biomass results in unbalanced efficiency, which initiated the need to verify the installation of the biomass carrier in order to partially stabilize the process. The Fig. 1 below documents the imbalanced biological load at the WWTP in relation to the production volume and the concentration of biomass in the system.

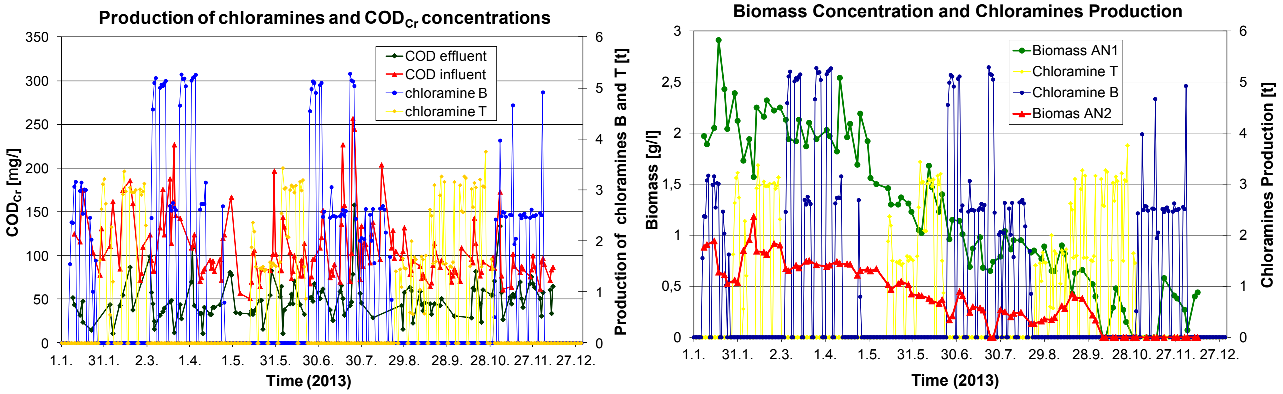

Fig. 2: Monitoring of the Bochemie WWTP

3.2. Parallel comparison of the operational lines of the WWTP with the nanofibre carrier

The monitoring campaign carried out several times during the monitored period clearly showed that the CoD removal efficiency is higher on the line with the installed biomass carrier. The differences generally increase at higher loads, i.e. at high volumes of production of chloramines.

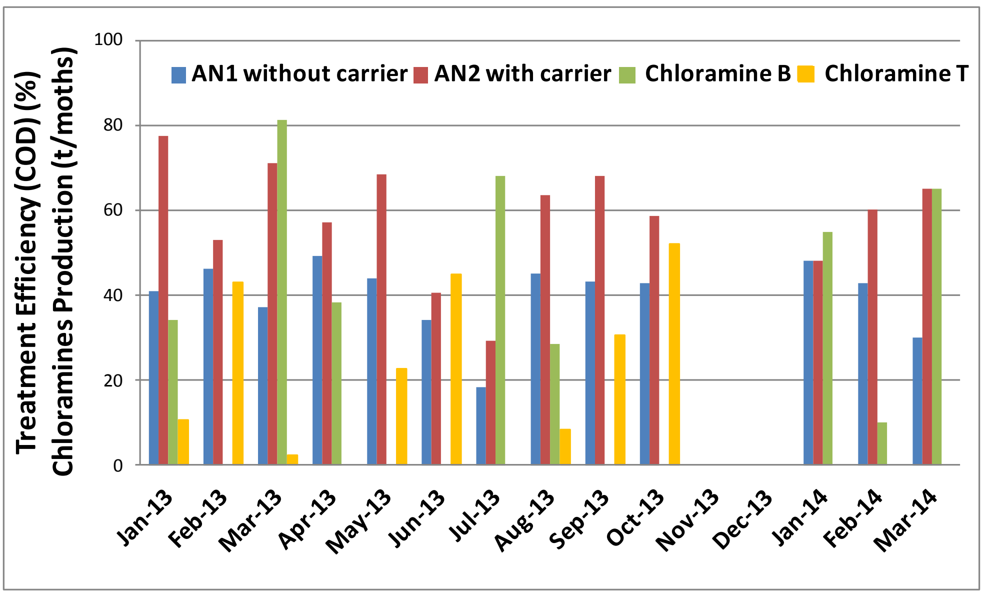

Fig. 3 Comparative study of both the conventional activated sludge system and the hybrid system with the nanofibre carrier

4. CONCLUSION

This contribution summarizes the long-term operational experience of an industrial wastewater treatment plant designed to remove toxic chloramines. The character of wastewater production corresponds to the production program, which is currently imbalanced. The imbalance is reflected in the biomass concentration and consequently deterioration in efficiency. This contribution summarizes a parallel comparison of activation lines with and without an installed nanofibre carrier.

The results of the comparison of the two parallel technological lines of the WWTP removing chloramines, where one was fitted with a nanofibre carrier, showed the following: The line with biomass carrier achieved higher removal efficiency of the supplied contamination. The activation line with the carrier operated as a hybrid system generally has a lower concentration of suspended biomass, which reduces the metabolic load on the settling tanks. There are clear differences in the treatment efficiency even with the limited size of the pilot installation (3x3x2m, a total carrier size of only 130 m^2) in the aeration tank enabling the volume of the installation of up to 4x4x3m. The differences are especially pronounced at higher concentrations and conversely less pronounced with the existing character of substance loading of the WWTP, where in several cases the inlet concentration is only slightly higher than the steadily achieved outlet concentration given by the nature of the supplied ballast water from the hydraulic protection and hydraulic efficiency of the settling tanks and the remaining dispersal biomass. There were no problems in the lifespan of the installed carrier during time of the the operational testing (4 years).

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