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Removal of aniline, cyanides and diphenylguanidine from industrial wastewater using a full-scale moving bed biofilm reactor

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ABSTRACT

Treatment of industrial wastewaters is usually difficult due to large variations in their composition, high organic matter content and presence of poorly biodegradable compounds. This paper describes operational experience with the first full-scale application of a moving bed biofilm reactor (MBBR) in the Czech Republic. The MBBR treats industrial wastewater from the Lučební závody Draslovka a.s. (Kolín) chemical plant in the Czech Republic, and particularly that from production of diphenylguanidine. The wastewater is characterised by a high content of cyanides and aniline, very high salinity, diphenylguanidine and phenylurea residues, and considerable fluctuations in concentrations as well as temperature during the year.

Long-term (5-years) MBBR operation has demonstrated that, following initial stabilisation and implementation of additional pretreatment, the system is capable of treating such hardly biodegradable industrial wastewater with high removal efficiency, with mean cyanide removal efficiency ranging from 75% to 99%. Aniline removal efficiency also reached more than 85%, while diphenylguanidine, phenylurea and N,N-diphenylurea removal was almost quantitative.

1. Introduction

Aniline and particularly cyanides are very hazardous compounds to humans as well as the environment. Cyanides, in some forms, are a very powerful and fast acting toxin causing rapid breathing and serious neurological problems already at short-term exposure [1]. Aniline shows general ability to inhibit enzyme activity and U.S. Environmental Protection Agency considers aniline to be a probable human carcinogen [2].

Occurrence of cyanides in the environment is mainly due to the human activities since cyanides are extensively used mainly in metal finishing and mining industry. Aniline is predominantly used in a number of industrial processes and applications, e.g. such as a chemical intermediate for the dyes, pigments, agricultural, polymer, pharmaceuticals, and rubber accelerator [3,4].

Aniline and cyanides are well soluble in water, therefore they represent serious risk for possible water pollution and wastewaters containing cyanides and aniline must be properly treated before their discharge to the water bodies. The moving bed biofilm reactor (MBBR) might be a possible treatment option of wastewater concomitantly containing cyanides and aniline.

The MBBR principle was developed in Norway and firstly introduced about 30-years ago [5,6]. The MBBR displays all the advantages of a standard biofilm reactor while simultaneously handling high particle loads [7]; as such, it represents a promising alternative to conventional activated sludge wastewater treatment technology. MBBRs have a number of advantages over conventional activated sludge technology, including a reduced footprint and higher plant capacity due to higher biomass concentration, ease of existing plant upgrade, increase in solids retention time, and high removal performance under extreme loading conditions [8]. Higher solids retention time prevents the wash-out of slow-growing microorganisms including nitrifying bacteria from the system. The main advantage of MBBR, however, is its ability to accumulate suspended and biofilm biomass in the same reactor and at the same time [9], allowing a significantly higher density of biomass in the system. A further increase in biomass concentration can be achieved by increasing the number of biomass carriers [10].

Abbreviations: COD, chemical oxygen demand; MBBR, moving bed biofilm reactor; SS, suspended solids; CN, total concentration of cyanides; DPG, diphenylguanidine; HRT, hydraulic retention time; MLSS, mixed liquor suspended solids.

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Table 1
Characteristics of incoming industrial wastewater observed during 5-years of MBBR operation. Average annual concentrations (minimum and maximum in parentheses) are in mg L^{-1} (salinity in g L^{-1}).

Parameter	Aniline	CN	COD	NH_4-N	SS	Salinity
1st year (2008; trial operation)	600 (78; 1720)	110 (1.6; 850)	2870 (40; 6600)	152 (19.4; 580)	51 (15; 130)	28.4 (16.5; 44.1)
2nd year (2009)	900 (76; 4970)	15.8 (0.8; 540)	3200 (60; 11,220)	154 (44.0; 321)	120 (50; 600)	27.5 (7.4; 41.5)
3rd year (2010)	1120 (8.0; 3350)	7.7 (0.8; 115)	3160 (700; 8340)	189 (43.8; 651)	87 (45; 150)	37.7 (31.0; 43.8)
4th year (2011)	1470 (390; 4130)	6.3 (1.1; 63)	3950 (1300; 9660)	240 (37.4; 430)	430 (160; 750)	39.6 (14.2; 49.7)
5th year (2012)	1166 (220; 3572)	13.7 (1.5; 156)	4015 (1820; 10,340)	224 (54; 932)	343 (190; 496)	39.1 (26.7; 49.5)

MBBRs fulfil all necessary requirements for developing specialised biomass [11] and enable to increase the biodiversity of the biomass. MBBRs have been shown to be more efficient and stable for toxic compounds and nutrient removal, even when concentrations, loading and pH values fluctuate significantly [8,12]. Furthermore, stable nitrification under low temperatures [13–15] and fast adaptation of biomass activity to toxic compounds can be achieved. MBBR technology, therefore, is particularly applicable for special applications where the removal of difficult biodegradable pollutants and detoxification of hazardous contaminants, such as e.g. volatile aromatic hydrocarbons, chlorinated solvents, phenolics and chlorinated aromatics or pesticides is required [16–18]. Moreover, some toxic compounds in influent can cause changes in activated sludge morphology when fed into a conventional wastewater treatment plant, leading to non-flocculating and non-settling fragments. In an MBBR, non-flocculating fragments, filamentous bacteria and biological foams are significantly suppressed compared to conventional activated sludge systems [19]. Furthermore, biomass is not easily washed out of the reactor through process disturbance [11].

Widespread application of MBBR is, however, limited by higher initial costs (primarily through high acquisition costs for biomass carriers), and higher air supply needed for aerobic processes and homogenisation. In addition, sufficient raw wastewater pretreatment needs to be installed in front of the MBBR due to the possibility of biomass carriers clogging. On the other hand, particularly in the case of large-scale and industrial wastewater treatment plants, MBBR represents a cheaper option for treatment of industrial wastewaters than other processes, e.g. adsorption [20], oxidation [21], or membrane processes [22,23].

During the past decade, MBBRs and biofilm-based processes have been successfully used to treat a range of industrial and municipal wastewaters [16,24–26]. However, there has been no study to date dealing with the removal of aniline, cyanides and diphenylguanidine (a substance used in the tire production) from industrial wastewater. This paper reports on operating experience obtained during five years operation of the first full-scale application of MBBR technology in the Czech Republic. The MBBR was used to treat industrial wastewater resulting from the production of diphenylguanidine (DPG).

2. Material and methods

2.1. Wastewater composition

The wastewater contains high concentrations of aniline, cyanides, DPG, phenylurea residues and other accompanying organics, and has very high salinity (Table 1). In addition, temperature in MBRR fluctuated considerably throughout the year ranging from 10 to almost 40 °C due to a high HRT.

2.2. Preparation of bacterial inoculum

Pre-selection of bacterial strains was performed at Institute of Chemical Technology Prague; *Rhodococcus erythropolis* CCM 2595 being chosen as most suitable. Bacterial strains of the genus *Rhodococcus* have a proven ability to catabolise a wide range of compounds and metabolise harmful environmental pollutants such as cyanides, aniline, DPG and phenylurea. In addition, they have a good biofilm-forming ability and have a high resistance to extreme conditions (e.g. salinity 2–3% and temperatures of 10–38 °C).

Table 2
Overview of basic technical and technological characteristics of the MBBR.

Characteristic	Value
Diameter and depth of tanks (m)	8 × 5.9
Total volume (m^3)	520 (2 × 260)
Amount of wastewater (m^3 d^{-1})	50 – 130
Hydraulic retention time (d)	4.1 – 10.4
COD loading (g m^{-2} d^{-1})	2.2 – 11.2
Aniline loading (g m^{-2} d^{-1})	0.59 – 3.3
Total volume of carriers (m^3)	130
Maximal specific protected surface of carrier (m^2 m^{-3})	500

Resistance to the main pollutants found in wastewaters from the Lučební závody Draslovka a.s. plant was confirmed; however, the concentrations of main pollutants in actual wastewater were higher than those during the pre-selection tests. For this reason, a process of adaptation was undertaken. This resulted in a strain that not only displayed the required level of resistance but also showed a capacity to profusely grow on the AnoxKaldnes™ K3 biomass carriers. This strain was subsequently used as the inoculum for the MBBR. The inoculum was grown in a 10 m^3 tank at the production plant where the adaptation process continued via a step-wise increase in addition of aniline, solutions of potassium cyanide and sodium chloride. Phosphoric acid was used to neutralise the suspension and as phosphorus source.

2.3. Setup and operation of the MBBR

Prior to design of the full-scale MBBR, numerous long-term laboratory and pilot-scale experiments were carried out using raw industrial wastewater and AnoxKaldnes™ K3 biomass carriers in order to assess the optimal setup for the MBBR. The basic technical and technological characteristics of the final setup are displayed in Table 2. A graphical scheme of wastewater treatment plant is shown in Fig. 1; an absorption column was implemented into the vacuum pump stream originating from the whole DPG production (including chlorcyane production) in September 2008.

The MBBR is designed to treat a maximum of 170 m^3 d^{-1} of wastewater, though average wastewater flows range from ca. 50–130 m^3 d^{-1}. Prior to entering the MBBR, wastewater stream from the chlorcyane synthesis containing high concentration of cyanides and chlorcyane is pre-treated through steam stripping and through a two-step neutralisation based on controlled mixing of separate streams. Steam stripping has a high removal efficiency for cyanides (up to 98%) and chlorcyane (up to 100%), significantly improving overall water quality to the extent that biological treatment can proceed. The cyanides and chlorcyane extracted are recycled into the production process. Pre-treated stream is collected in a small equalisation tank. Two further reservoirs are used for quality stabilisation of wastewaters from DPG separation and from vacuum pumps. The three streams are mixed in the first step