Polish Journal of Environmental Studies Vol. 13, No. 5 (2004), 573-577

Removal of Organic Compounds from Municipal Wastewater by Immobilized Biomass

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Received: 25 July 2003
Accepted: 13 October 2003

Abstract

Two porous ceramic carriers (internal active surface 0.04 m^2 for carrier I and 0.2 m^2 for carrier II) with immobilized activated sludge were the stationary filling of the reactors. Municipal wastewater was treated at hydraulic retention time (HRT) from 70 to 15 min. The efficiency of organic compounds removal from wastewater changed for reactor I from 85.2 to 93.8%, for reactor II from 62.9 to 87.1%. The contribution of oxidation, biomass synthesis, denitrification and intracellular storage in organic compounds removal depended on the type of carrier and on hydraulic retention time (HRT). Over 20% of organic loading in influent to reactors I and II was used for cellular oxidation. Only for reactor I at HRT 30 and 15 min higher participation of nitrate respiration than oxygen was one observed. From 6.1 to 14.5% of loading in influent was removed as a result of sludge yield. For reactor I the high contribution of intracellular storage in organic compounds removal from wastewater was observed.

Keywords: biomass immobilization, porous ceramic carriers, municipal wastewater, organic compounds removal by oxidation, denitrification, sludge yield and internal storage

Introduction

Organic compounds from wastewater can be oxidized by microorganisms for energy production, incorporated into new cellular components or stored as glycogen, poly-β-hydroxybutyrate (PHB), or other storage compounds [1]. If there are oxidized nitrogen forms in wastewater, organic compounds are also used for their reduction.

In reactors with immobilized biomass, sludge yield is limited [2]. Canales et al. [3] showed that maintaining high biomass concentration and long SRT in the reactor limited sludge production. According to Gander et al. [4] and Chiemchaisri and Yamamoto [5] the higher biomass concentration, the lower Food/Microorganisms (F/M) ratio. For this reason, wastewater can be treated with reduced sludge production. Jefferson et al. [6] and Witzig et al. [7] proved that bacteria present in the highly concentrated biomass of the membrane reactor used the energy supplied for their maintenance metabolism and were not in a physiological state characteristic for growth. Only if energy is supplied in excess bacteria are able to grow.

Under aeration conditions the synthesis and accumulation of readily biodegradable storage compounds are observed [8, 9]. Jones et al. [1] proved that storage compounds can be used for denitrification under starvation conditions. The possible role of PHB as a carbon and energy source in denitrification was examined by incubation of *Paracoccus denitrificans* cells in medium without an external carbon donor and with nitrate [8]. PHB-rich cells were obtained by preincubating the cells under anaerobic conditions for 12 h in the presence of acetate. Under these conditions, a decrease in the PHB content of the cells coincided with a release of acetate into the medium and a decrease in nitrate.

In this work the contribution of cellular oxidation, denitrification, biomass synthesis and intracellular storage in organic compounds removal from municipal

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Table 1. Characteristics of porous carriers.

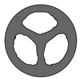
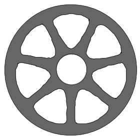
Carrier	Cross-section	External diameter [mm]	Length [mm]	Internal surface [m^2]	Total volume [dm^3]
I		10	1200	0.04	0.094
II		25	1178	0.20	0.578

Table 2. Chemical characteristics of wastewater.

	Unit	Mean value
COD	[mg COD/dm^3]	337.6
COD soluble	[mg COD/dm^3]	118.0
Volatile acids	[mg CH_3COOH/dm^3]	85.4
Kjeldahl nitrogen	[mg TKN/dm^3]	47.4
Ammonium nitrogen	[mg N-NH_4/dm^3]	27.0
Total suspended solids	[mg TSS/dm^3]	236.4

wastewater by immobilized biomass were determined depending on hydraulic retention time and internal structure of the carriers.

Experimental Procedures

Characteristics of Carriers

Activated sludge was immobilized in two porous ceramic cylinder-shaped carriers. The carriers differ in internal structure, number of internal channels, the size of internal surface and total volume (Table 1). Pore diameter amounts to 4-6 µm, material porosity 35-40%. The carriers are both made from aluminium oxide (Al_2O_3), titanium oxide (TiO_2) and zirconium oxide (ZrO_2).

Colonization Procedure

The activated sludge derived from the sequencing batch reactor was the source of inoculum. It was thickened to a concentration of about 23 g TSS/dm^3. The immobilization was made by circulating the activated sludge in the reactors for 24 h. Initial carrier loading amounted to 24.5 g TSS/dm^3 (carrier I) and 18.2 g TSS/dm^3 (carrier II).

Characteristics of Reactor

Each carrier with immobilized biomass was the stationary filling of the reactor. Carrier I was placed in reactor I, carrier II – in reactor II. The bioreactors worked under aerobic conditions. It was supplied about 50 dm^3/h of air to reactor I and about 120 dm^3/h to reactor II in order to maintain oxygen concentration of 2 mg O_2/dm^3. The experiment was carried out at a temperature of 20°C. The scheme of reactor and the description of wastewater flow have been published earlier [10].

Characteristics of Wastewater

Municipal wastewater taken directly from a sink basin was used in research. Average content of organic compounds, nitrogen compounds and total suspended solids is presented in Tab. 2.

Organization of Experiment

The studies were carried out at hydraulic retention times (HRT) of 70, 60, 30 and 15 min for reactor I. For reactor II at HRT 15 min nitrification was not obtained, so the results only for HRT 70, 60 and 30 min were analyzed. In Table 3 there are volumetric loading rates (VLR) and surface loading rates (SLR) for both carriers.

For reactor I at HRT of 60 min and for reactor II at HRT of 70, 60 and 30 min a changeable internal circulation (q_i) was used: 20, 40 and 60 dm^3/h. In the remaining series the circulation was stable and amounted to 40 dm^3/h.

Analytical Methods

Wastewater was assayed for the concentration of organic compounds (expressed as COD and COD soluble), volatile acids, Kjeldahl nitrogen, ammonium nitrogen and total suspended solids according to Polish Standards.

The respirometric activity of immobilized biomass was measured using the OxiTop method. Surplus sludge from effluent was analyzed. In order to determine substrate respiration, sample of biomass, raw wastewater and thiourea as a nitrification inhibitor were put in measuring vessels. The organic loading rate was stable and amounted to 0.25 g COD/g TSS·d (similarly to used by Van Benthum et al. [11]).

The presence of organic compounds stored (PHB) in immobilized activated sludge was determined in samples of surplus sludge according to Jenkins et al. [12].

Table 3. Scheme of research.

Reactor		I				II		
HRT	[min]	70	60	30	15	70	60	30
SLR	[g COD/m²·d]	15.3	18.8	48.8	114.6	15.6	16.8	47.9
VLR	[g COD/dm³·d]	6.5	8.0	20.8	48.8	5.4	5.8	16.6

Calculation Methods

Sludge yield (Y) was calculated with the equation (1). It was assumed that total excessive biomass was washed out of the reactor and all TSS from influent were solubilized and hence were not included in the calculation of sludge yield [13]:

$$Y = \frac{TSS_1 - TSS_0}{COD_i - COD_e},\ gTSS/gCOD \qquad (1)$$

TSS_1 - total suspended solids in effluent at time t_{n+1} [mg TSS/dm³]
TSS_0 - total suspended solids in effluent at time t_n [mg TSS/dm³]
COD_i - organic compounds in influent [mg COD/dm³]
COD_e - organic compounds in effluent [mg COD/dm³]

The loadings of organic compounds removed as a result of biomass synthesis, cellular oxidation, denitrification and intracellular storage were estimated as follows:

- organic loading used for biomass synthesis [g/d]

$$Q_{syn} = \left(\frac{Y \cdot (COD_i - COD_e) \cdot q}{1000}\right) \cdot 0.8 \qquad (2)$$

Y - sludge yield [g TSS/g COD]
COD_i - organic compounds in influent [mg COD/dm³]
COD_e - organic compounds in effluent [mg COD/dm³]
q - flow rate of wastewater [dm³/d]
0.8 - COD concentration, corresponding with 1 g TSS [g COD/g TSS]

- organic loading oxidized in cellular respiration [g/d]

$$Q_{ox} = \frac{L_0 \cdot q}{1000} - Q_{syn} \qquad (3)$$

L_0 - total concentration of oxygen used for oxidation of organic compounds from wastewater determined by respirometric measurements [mg O_2/dm³]
q - flow rate of wastewater [dm³/d]
Q_{syn} - organic loading used for biomass synthesis [g/d]

- organic loading used for denitrification [g/d]

$$Q_{den} = \frac{C_{Nred} \cdot 2.6 \cdot q}{1000} \qquad (4)$$

C_{Nred} - concentration of nitrogen removed in denitrification [mg TKN/dm³]
2.6 - amount of organic compounds used for reduction of 1 mg of oxidized nitrogen [14] [mg COD/mg]
q - flow rate of wastewater [dm³/d]

- loading of organic compounds stored intracellularly [g/d]

$$Q_{acc} = Q_{in} - Q_{eff} - Q_{ox} - Q_{syn} - Q_{den} \qquad (5)$$

Q_{in} - organic loading in influent [g/d]
Q_{eff} - organic loading in effluent [g/d]
Q_{ox} - organic loading oxidized in cellular respiration [g/d]
Q_{syn} - organic loading used for biomass synthesis [g/d]
Q_{den} - organic loading used for denitrification [g/d]

Results and Discussion

Internal active surface of the three-channelled carrier I amounted to 0.04 m², whereas of the eight-channelled carrier II – 0.2 m². Volumetric loading rate (VLR) of the carrier in reactor I was from 6.5 to 48.8 kg COD/m³·d, of the carrier in reactor II from 5.4 to 16.6 kg COD/m³·d (Table 3). An increase in active surface of the carrier to 0.2 m² did not improve the efficiency of organic compounds removal. The effectiveness of the removal of organic compounds (expressed as COD) amounted to, for reactor I, from 85.2% at HRT 60 min to 93.8% at HRT 15 min, for reactor II from 62.9% at HRT 30 min to 87.1% at HRT 60 min. Thus, the efficiency of organic compounds removal was determined by carrier structure used for immobilization of activated sludge. It was estimated that internal channels accounted for about 50% of total volume of carrier I and about 44% of total volume of carrier II. During COD removal by biomass immobilized in porous carriers the carrier porosity and open structure allowing bioflocculation in the environment of low shearing stress are of great significance. According to Matsumura et al. [15] the proper balance between active surface of a carrier and open space is very important, because it influences the rate of mass transport.

Our own research shows that the contribution of elementary processes in organic compounds removal by immobilized activated sludge depends on HRT and carrier structure.

Organic loading in influent to reactor I (Q_{in}) was from 0.6 g/d at HRT 70 min to 4.6 g/d at HRT 15 min, to reactor II from 3.0 g/d at HRT 70 min to 7.9 g/d at HRT 30 min.

For reactor I organic loading removed by cellular oxidation (Q_{ox}) accounted for about 21% Q_{in} at HRT 70 and 60 min (Fig. 1). For reactor II the participation of Q_{ox} was slightly higher than for reactor I, decreased with the shortening of HRT and was from 26.6% Q_{in} at HRT 70 min to 21.6 % Q_{in} at HRT 30 min. Van Niel et al. [16], during respirometric measurements of *Thiosphaera pantotropha* incubated in medium with acetate, proved that 29% of acetate was oxidized. The shortening of HRT in reactor I to 30 and 15 min limited oxidation. The contribution of oxidation in organic compounds removal accounted for 4.1 and 2.8% Q_{in}, respectively. At HRT 30 and 15 min in reactor I the anoxic zones could have occurred in internal layers of immobilized biomass, which caused a lowering of the participation of oxygen respiration in organic compounds removal. Simultaneously, an increase in COD used for the reduction of oxidized nitrogen (Q_{den}) was observed. Only at HRT 30 and 15 min the contribution of nitrate respiration dominated oxygen respiration and amounted to about 23.6 and 11.3% Q_{in}, respectively. Under remaining operating conditions organic compounds used for denitrification was lower than for cellular oxidation and accounted for about 20% Q_{in}.

The lowest values of organic loading in effluent (Q_{eff}) were observed for reactor I at HRT 15 min (6.1% Q_{in}) and for reactor II at HRT 60 min (12.8% Q_{in}).

For both reactors, organic loading used for biomass synthesis (Q_{syn}) was low and decreased with a shortening of HRT. For reactor I it was from about 11% Q_{in} at HRT 70 and 60 min to about 6.4% Q_{in} at HRT 30 and 15 min. For reactor II Q_{syn} was from 14.5% Q_{in} at HRT 70 min to 6.7% Q_{in} at HRT 30 min. The forming of anoxic zones in internal layers of biomass at high loading could have been one of the reasons for lowering sludge yield by shortening HRT. An aerobic yield is higher than the corresponding anoxic yield [17].

In our earlier research the sludge yield (Y) in reactors with immobilized biomass was calculated at the level of 0.066-0.175 g TSS/g COD (unpublished data). Choo and Stensel [18], during operation at 1400-day calculated SRT, observed the average biomass yield of approximately 0.03 g MLVSS/g COD. In the membrane bioreactor, Cicek et al. [19] obtained sludge production of 0.29 g TSS/g COD.

In conventional systems of activated sludge it is assumed that 2/3 of organic compounds in influent is used for sludge yield. Our research showed that in reactors with immobilized biomass the contribution of biomass synthesis in organic compounds removal was lower. Dionisi et al. [20] proved that under stress conditions, for example in reactors with high biomass concentrations, substrate removal mechanisms can be different. Microorganisms are able to store organic compounds and, subsequently, reuse them for growth. Intracellular storage requires less physiological adaptation than growth. In our research it was assumed that organic compounds not used for cellular oxidation, biomass synthesis and denitrification are stored. Microscope analysis of immobilized activated sludge confirmed the presence of stored substance in the form of poly-ß-hydroxybutyrate (PHB) in cells. For reactor I the contribution of organic compounds accumulated (Q_{acc}) was from 31.8% Q_{in} at HRT 60 min to 73.7% Q_{in} at HRT 15 min. For reactor II the participation of Q_{acc} was lower than for reactor I and was from 16.1% Q_{in} at HRT 70 min to 31.2% Q_{in} at HRT 60 min. Van Niel et al. [16], incubating *Thiosphaera pantotropha* in medium with acetate, claimed that 14% of acetate was used for biomass synthesis and 57% for accumulation as PHB.

For reactor II at HRT 60 min with the change of internal circulation (q_i) from 20 to 60 dm^3/h the amount of PHB in biomass increased from 3.9 to 27.9% TSS. The sludge yield (Y) decreased by 20.8% (Fig. 2). At HRT 30 min and the change of q_i a decrease in Y by 36.8% occurred simultaneously with an increase in the amount of PHB in biomass from 16.2 to 23.8% TSS. Investigations by Beun et al. [21] showed that during accumulation of

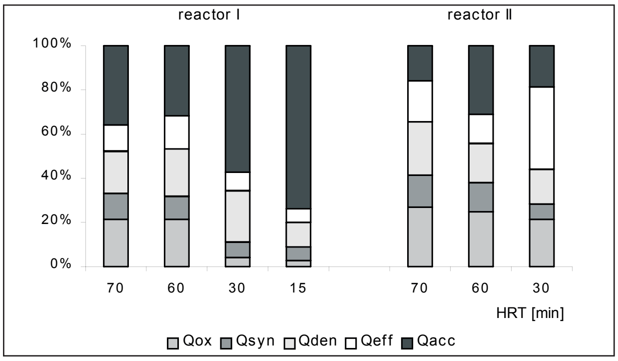


Fig. 1 Contribution of unit processes in organic compounds removal for reactors I and II (at stable internal circulation of 40 dm^3/h).

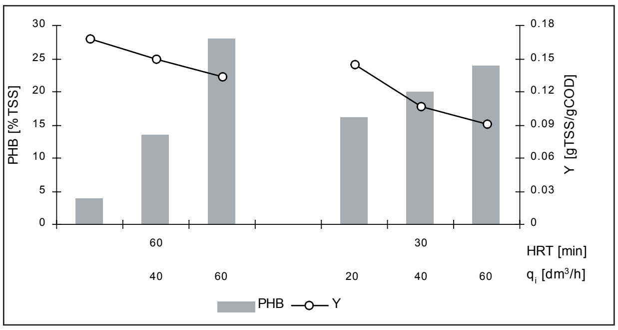


Fig. 2 Dependence between PHB amount in immobilized biomass and sludge yield (Y) in reactor II.

PHB, sludge yield decreased by 4-10%. Van Aalst-van Leeuwen et al. [22], on the basis of the research of *Paracoccus pantotrophus,* claimed that PHB accumulation leads to a decrease in sludge yield by 6%.

Conclusions

1. The efficiency of organic compounds removal from municipal wastewater by immobilized biomass did not depend on the active surface of the carriers. Internal structure of the carriers, i.e. the participation of internal channels in total volume, had an impact on wastewater treatment efficiency.
2. Organic loading used for cellular oxidation accounted for 21.2-26.6% of total loading in influent. Only in reactor I, the shortening of HRT to 30 and 15 min caused the domination of organic compounds used for nitrate respiration.
3. In reactors of high concentration of biomass the amount of the organic compounds used for biomass synthesis was low and equalled from 6.1 to 14.5% of total loading in influent.
4. The contribution of loading of organic compounds accumulated in immobilized biomass was the highest for three-channelled reactor I and at HRT 15 min reached a maximal value – 73.7% of total loading in influent.

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