Scientific paper

Estimation of the Specific Surface Area for a Porous Carrier

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Dedicated to the memory of the late Prof. Dr. Valentin Koloini

Abstract

In biofilm systems, treatment performance is primarily dependent upon the available biofilm growth surface area in the reactor. Specific surface area is thus a parameter that allows for making comparisons between different carrier technologies used for wastewater treatment. In this study, we estimated the effective surface area for a spherical, porous polyvinyl alcohol (PVA) gel carrier (Kuraray) that has previously demonstrated effectiveness for retention of autotrophic and heterotrophic biomass. This was accomplished by applying the GPS-X modeling tool (Hydromantis) to a comparative analysis of two moving-bed biofilm reactor (MBBR) systems. One system consisted of a lab-scale reactor that was fed synthetic wastewater under autotrophic conditions where only the nitrification process was studied. The other was a pre-denitrification pilot-scale plant that was fed real, primary-settled wastewater. Calibration of an MBBR process model for both systems indicated an effective specific surface area for PVA gel of 2500 m^2/m^3, versus a specific surface area of 1000 m^2/m^3 when only the outer surface of the gel beads is considered. In addition, the maximum specific growth rates for autotrophs and heterotrophs were estimated to be 1.2/day and 6.0/day, respectively.

Keyword: Surface area, biocarrier; biofilm; MBBR; nitrification rate; PVA gel

1. Introduction

Based on wastewater treatment performances of moving-bed biofilm reactor (MBBR) systems utilizing biocarriers of variable size and shape, the authors demonstrated that similar treatment levels could be expected where the loading rates were compared on an equal footing with respect to the effective surface area of the biocarriers.[1,2] Surface-area loading rate was thus shown to be a valuable tool not only for design of MBBR unit processes but also for making fair comparisons between MBBR systems regardless of the type of biocarrier being used where the effective surface area for biomass attachment can be known.

Working with the spherical PVA-gel biocarrier, though, that relies predominately on the network of microscopic pores in the core of the gel beads for retention of active biomass, the authors were confronted with the dilemma of how to determine the effective surface area for biofilm growth.[3] They thus set out to make a comparison between a PVA-gel based MBBR unit process with that of another unit process containing a biocarrier for which the surface area characteristics are easily know by direct observation. Thus, employing the cylindrical Kaldnes K1 biocarrier (effective specific surface area, 500 m^2/m^3) in parallel testing, they were able to establish nearly equal relative maximal nitrification rates for the two units. However, considering that a lower volumetric filling of PVA gel (9.7%) versus that of K1 (37%) was used, the observed results could not be explained by considering only the measurable exterior specific surface area (1000 m^2/m^3) of the PVA-gel beads; rather, a considerably larger specific area was required (2500 m^2/m^3), inferring a significant contribution from the porous interior of the gel beads.

Parametric models such us ASM1 used in simulation software are mainly used for the design and optimization of wastewater treatment plants.[4] The most crucial

steep in the overall modeling process is the calibration.[5] This can be done from different approaches involving the knowledge and experience of the modeler. Some proposed a procedure for calibrating a general model from a process engineering perspective.[6] The most important elements included the determination of reactor hydraulics, characterization of wastewater and biomass as well calibration of model parameters.

The aim of the study was to estimate by calibration the effective specific surface area for PVA-gel beads under two differing testing conditions using the simulation software known as GPS-X. The testing modes consisted of a lab-scale reactor that was fed synthetic wastewater and operated solely under autotrophic conditions and a pilot-scale plant that was fed real municipal wastewater and thus operated simultaneously under heterotrophic and autotrophic conditions. Both tests were conducted under previous studies[3,8] and thus were not designed and operated for nor influenced by the purpose and goal of this study.

Based on the application of the GPS-X simulation tool to the experimental data the effective specific surface areas were estimated and evaluated in light of the limitations of the simulation methods used.

2. Materials and Methods

2. 1. Carrier

The PVA-gel carrier is slightly heavier than water (S.G., 1.025). The gel beads Figure 1 (a) consist of 4-mm diameter spheres that are hydrophilic in nature and have a very porous structure with only 10% solids and a continuum of passages 10 to 20 μm in diameter tunneling throughout each bead Figure 1 (b). A volume of 100 mL can hold approximately 2000 beads. Water displaced by the gel beads is 0.08 m^3/m^3 at a 9.6% volumetric filling. It is claimed that bacteria cultivated inside the core of the beads do not slough off and are protected from predation, thus being highly retained.[7] The gel beads are typically used at volumetric packing ratios of only 5% to 15% versus much higher ratios of 30% to 70% common to the Kaldnes K1 carrier. Loading rates are normally determined with respect to the settled-bed volume of the PVA-gel beads (or total reactor volume with consideration to filling ratio) instead of the surface area of the carrier because the biomass is cultivated and retained primarily inside the beads rather than on the surface.[8] In this paper the rates are with respect to the reactor volume.

2. 2. Lab-scale Test

The lab-scale reactor had a volume 3.54 L and was filled with 0.34 L (9.6 vol%) of the PVA-gel carrier (Figure 2). The gel beads had previously been enriched with heterotrophic and autotrophic biomass and were taken from an oxic reactor of a semi-industrial-scale (200 L) pilot plant used for nitrogen removal and fed for more than one year with wastewater following the primary mechanical stage of the Domzale-Kamnik, Slovenia, wastewater treatment plant. The reactor was continuously fed with synthetic wastewater containing only ammonium ($(NH_4)_2SO_4$), phosphate (KH_2PO_4) and growth minerals (Nitritox monitor, Growth Powder, Art. 704751; LAR Germany). The average concentrations in the synthetic wastewater were 85.6 ± 3.8 mg NH_4–N/L, 0.7 ± 0.1 mg PO_4–P/L, 8.2 ± 0.3 mg NO_x–N/L, 12.5 ± 1.5 mgCOD/L and some trace compounds. The nitrification process was automatically regulated to pH 7.5 ± 0.1 using a buffer solution (Na_2CO_3). With selective enrichment over six months, most of the heterotrophic organisms were considered washed out of the reactor, as was evident by changes in the appearance of the biofilm.

During the six months of selective feeding, nitrification activity was regularly checked and the ammonium loading was increased stepwise to maintain at least 1 mg-NH_4–N/L in the effluent. The reactor was operated at a temperature of 20 ± 1 °C and oxygen was maintained at

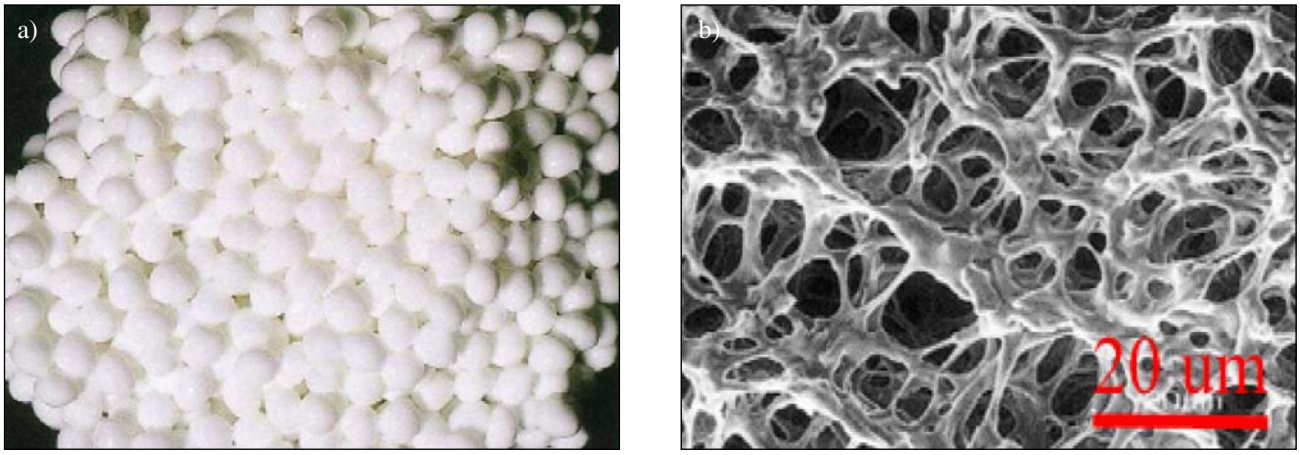


Figure 1: (a) Appearance of the PVA-gel carriers before use (Kuraray, Japan); (b) Surface of a PVA-gel bead showing the microscopic structure.[7]

8.0 ± 0.5 mg/L. The inner walls of the lab-scale reactors were cleaned weekly to reduce bacterial wall-growth effects. Influent and effluent samples were analyzed for ammonium, nitrate and nitrite nitrogen and Kjeldahl nitrogen according to ISO standards. The influent and effluent values were based on daily spot samples. At the end of the test, a mixer was used to remove biofilm from the carrier to analyze the biomass composition. The COD concentration of the biomass was 1.2 mgCOD/mgVSS and the nitrogen content 0.034 mgN/mgCOD.

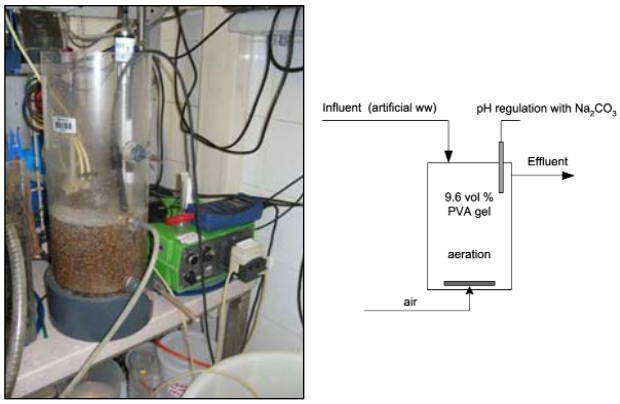
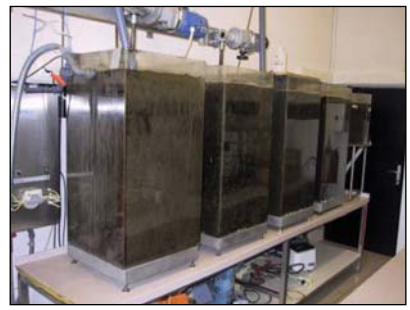


Figure 2: Photo and schematic diagram of the lab scale pilot plant.

2. 3. Pilot-scale Test

The semi-industrial-scale pilot plant consisted of two biological parts: the first being a nitrogen-removal process, consisting of pre-denitrification with recycle of nitrified liquor (Figure 3). This process included an anoxic reactor followed by an aerobic (oxic) reactor, both containing the PVA-gel biocarrier. Biological treatment activity was attributed to attached growth because suspended activated sludge was not returned to (or retained in) this process. Subsequently, a sludge elimination process was used for total-oxidation of excess organic solids (biomass). The experimental program included a series of seven runs conducted at various loading rates (dependent on hydraulic retention time (HRT) and influent composition), internal recycle levels and temperatures. All reactors used in this study were constructed of Plexiglas and had operational volumes of 200 L. The anoxic and oxic reactors of the nitrogen-removal process contained a 15% volume of PVA-gel beads, which were kept in suspension by mechanical mixing and retained in their respective zones by using slotted strainers. Detailed results were presented in a previous study.[8] In this paper we considered only the data of the nitrification and denitrification processes in the pilot plant and not the sludge elimination unit (Tox).

Wastewater after the mechanical stage of the Domžale-Kamnik wastewater treatment plant was fed to the system and recycled between units by using peristaltic pumps. Inflow parameters measured on-line consisted of TOC and total nitrogen (TN) (Shimadzu, Japan) and NH_4–N (WTW, Germany). Treatment performance was monitored by following total Kjeldahl nitrogen (TKN), NH_4–N, NO_2–N, NO_3–N, COD and BOD_5 as determined on spot samples. All analysis of spot samples were conducted in accordance with ISO methods. Samples for determination of soluble components were passed through Sartorius cellulose nitrate membrane filters prior to analysis.



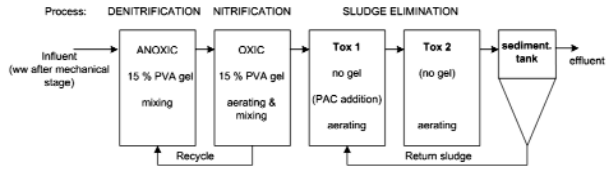


Figure 3: Photo and schematic diagram of the semi-industrial scale pilot plant.

2. 4. Mathematical Model

The specific surface area was estimated by using the GPS-X simulation software.[9] To estimate the surface area in the MBBR process, a hybrid-system model was used, which combines a standard plug-flow tank configuration with suspended growth biomass, and a biofilm model representing fixed-film growth on the carrier inserted into the tank. In the model, the reactor contents are represented with 6 layers, the first layer representing the bulk liquid, while the remaining five flat layers represent the biofilm formed on the carrier. The transfer of soluble state variables between each of these layers is by diffusion only (Fick's second law). Each layer of the biofilm is modeled as a CSTR with the same biological reactions as the suspended-growth biological reactor. In our case we used the Mantis model, which is similar to the well-known Activated Sludge Model No. 1 (ASM1)[4] with some minor modifications[9]. Attachment and detachment coefficients are used to provide for a means of transfer of particulate components between the biofilm surface and the liquid.

The default kinetic and stoichiometric GPS-X parameters were used in our study, except the maximal autotrophic and heterotrophic growth rates were adjusted to get the best fit with the experimental data. The range in

the literature for maximal growth rate for the autrotrophs is from 0.14/day to 1.12/day and for the heterotrops is from 1.3/day to 6/day. The calibration of the model was done by a manual procedure based on visual inspection of the simulated and measured results.

3. Results and Discussion

3. 1. Lab-scale Test

The wastewater used for the lab-scale test consisted of tap water supplemented only with ammonia nitrogen, thus a detailed characterization was not deemed necessary. In Figures 4 and 5, the best fit of the simulation results with the experimental data was shown to occur at a specific surface area of about 2500 m^2/m^3 with a maximal autotrophic growth rate of 1.2/day, which is higher than the model's default value of 0.75/day, though within the range of typically reported values. The specific surface area obtained by this method is in agreement with estimated area in our previous study by making a comparison with the well characterized Kaldnes K1 carrier having a known specific surface area.[3] With selective feeding of only ammonia nitrogen and no substances that could inhibit growth of nitrifying organisms, a maximum nitrification rate as high as 3.1 gNOx–N/m^2.day was obtained in the previous study.[3] Typically, nitrification rates with mixed cultures are observed only to reach about 1.5 gNOx –N/m^2.day (at 20 °C). Microbiological analyses (PCR 16SrDNA) have shown that biofilm cultures fed only with an ammonium substrate select for different species of nitrifying organisms than of those fed with municipal wastewater.[10,11] Although the influent contained only 12.5 mgCOD/L, some heterotrophic microorganisms would still be thought to be present. At the low influent COD concentration used here, though, there was no observable influence of heterotrophic activity in the simulation study. Simulation with influent COD concentration higher than 50 mg/L, though, did show an influence on nitrification performance coupled with a poorer correlation with the experimental data (results not shown).

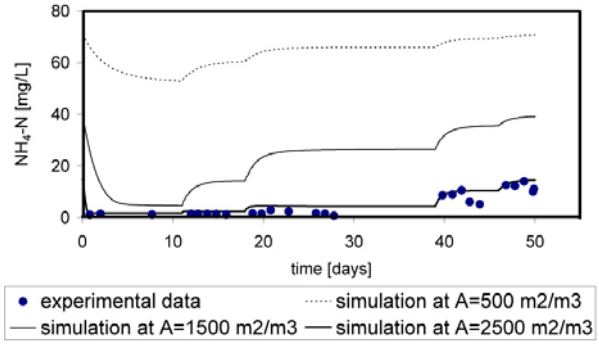


Figure 4: Correlation between experimental data for effluent NH_4–N and simulation curves at different specific surface areas.

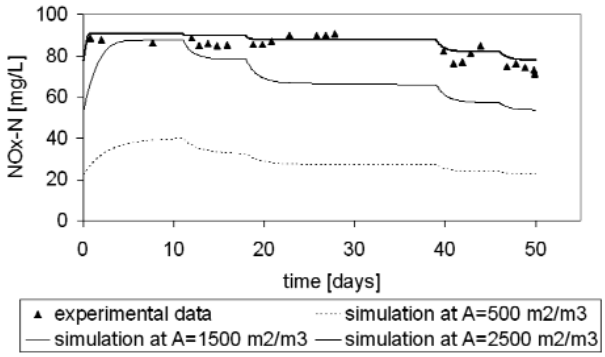
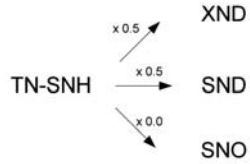


Figure 5: Correlation between experimental data for effluent NO_x–N and simulation curves at different specific surface areas.

The GPS-X simulation indicated that the biofilm thickness was 30 μm, the concentration of active autotrophic biomass was 48.2 mg COD/L (0.021 mgCOD/carrier) and heterotrophic biomass was 16.4 mg COD/L (0.007 mgCOD/carrier); thus the autotrophic biomass would appear to be 74.6 % of all active biomass in the biofilm.

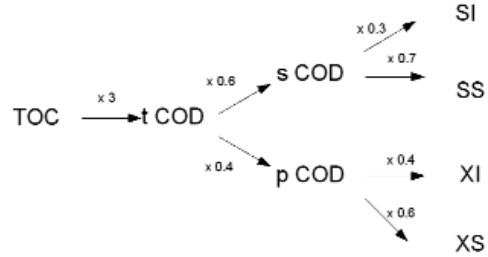
3. 2. Pilot-scale Test

The pilot plant was operated for more than one year under various testing conditions.[8] Influent levels of TOC, TN and ammonia were followed online and daily averages of the data were applied to the GPS-X model according to our prior studies.[12] For use in the GPS-X mathematical model, constant ratios between measured data (TOC, TN, NH_4–N) and model state variables (XND, SND, SNO, SS, SI, XS, XI) were maintained for the entire period. The ratios in Equations 1 and 2 are averaged factors from two weeks of detailed influent wastewater characterization and were calculated using the Hydromantis Influent advisor software. The measured parameters were total and soluble COD, BOD_5, BOD_{ul}, TN, NH_4–N, NOx–N, TSS and VSS.



(1)

The levels of particulate organic nitrogen (XND), soluble organic nitrogen (SND) and nitrate nitrogen (SNO) were calculated from the measured values of total nitrogen (TN) and ammonia nitrogen (SNH) as shown in Equations 1.



(2)

From the known TOC data, total COD (tCOD), soluble COD (sCOD) and particulate COD (pCOD) were calculated first and then the model state variables as soluble inert COD (SI), soluble biodegradable COD (SS), particulate inert COD (XI) and particulate biodegradable COD (XS) were determined based on known relationships as shown in Equations 2.

For this modeling study, data covering 326 consecutive days of operation in the pilot-scale test (Runs II through VIII) were used.[8] Time-series data for HRT, reactor temperature, influent TOC, influent TN, and influent NH_4–N are shown in Figure 6 and Figure 7.

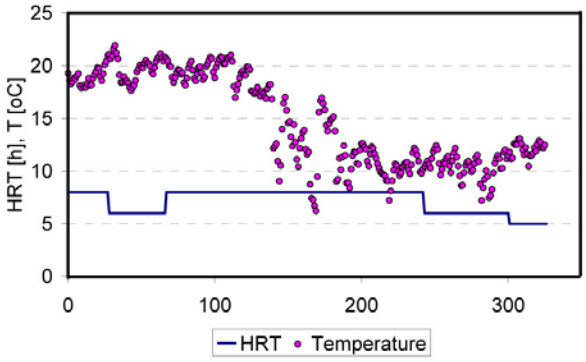


Figure 6: Time-series data for total HRT in the pilot plant and the temperature in the first reactor.

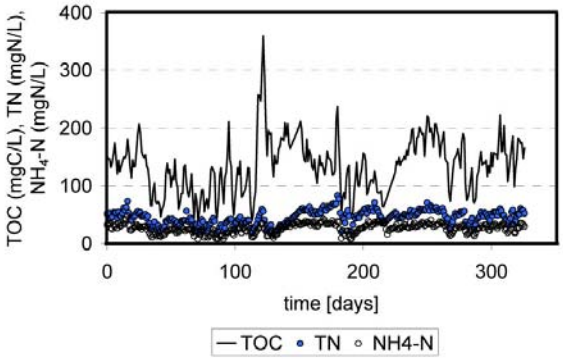


Figure 7: Time-series data for daily average values for influent TOC, TN and NH_4–N.

As shown in Figure 8 through 13, specific surface areas from 500 to 3000 m^2/m^3 were evaluated in an attempt to calibrate the model to the experimental data. For this purpose, simulation curves for ammonia nitrogen, nitrate nitrogen and COD in the pre-denitrification reactor and in the post-nitrification reactor were used. The overall best fit with the experimental data occurred at a specific surface area between 2000 and 2500 m^2/m^3, although on some days the correlation was very poor, for which various reasons are considered:

– Assuming a constant ratio between the measured influent parameters and the model variables may significantly miss the mark in some cases.
– The number of sampling events under some operational conditions may have been inadequate for accurate determinations.
– The possibility of inhibitory substances from local industries appearing in the wastewater used as influent for the pilot study may have occurred.
– With great variations in loading conditions at times, shock loads may have temporarily had inhibitory effects on treatment performance.
– For the GPS-X model, certain parameters in the biofilm model were assumed, leading to some degree of uncertainty in the simulation results.
– The model assumes the biofilm to be a flat surface; the actual conditions, though, in the porous matrix of the PVA gel could be quite contorted and in cases perhaps even non-biofilm like in nature. In this case, though, the surface of the PVA gel is spherical and the biofilm thickness appears to be about 300 μm; thus, some deviations can be expected.

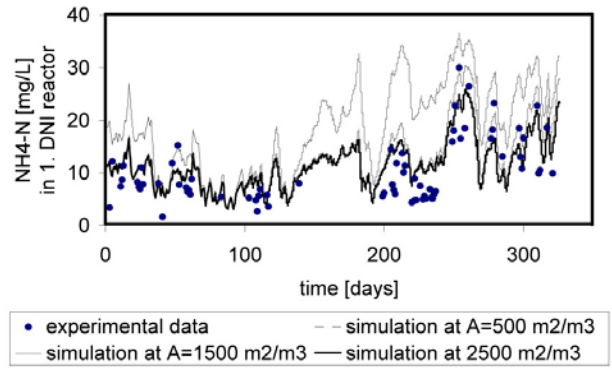


Figure 8: Simulation of ammonium at different specific surface areas in the anoxic reactor.

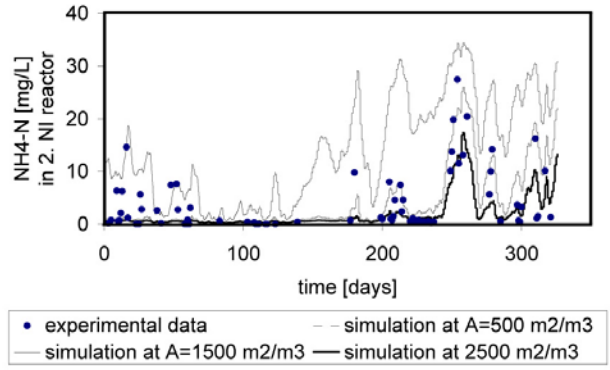


Figure 9: Simulation of ammonium at different specific surface areas in the oxic reactor.

Furthermore, some influence on the modeling accuracy might be due to the assumed heterotrophic growth rate. A change in the maximal heterotrophic growth rate from the default value of 3.2/day to 6.0 /day does offer an

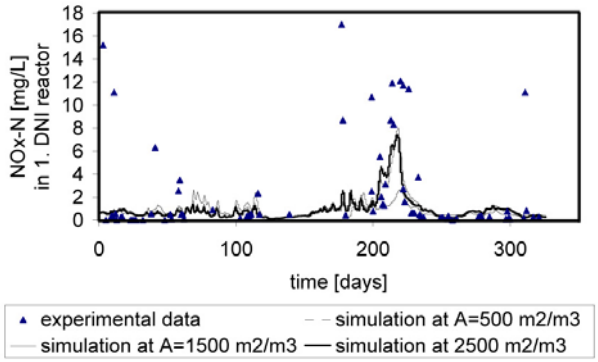


Figure 10: Simulation of nitrate at different specific surface areas in the anoxic reactor.

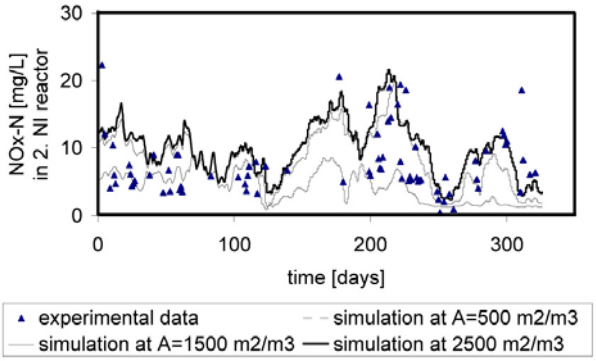


Figure 11: Simulation of nitrate at different specific surface areas in the oxic reactor.

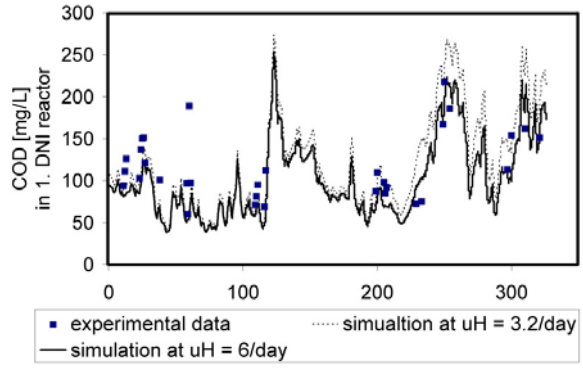


Figure 12: Simulation of filtered COD at different heterotrophic growth rates in the anoxic reactor.

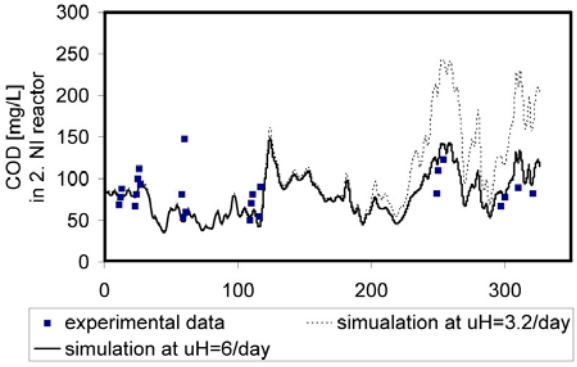


Figure 13: Simulation of filtered COD at different heterotrophic growth rates in the oxic reactor.

improved correlation between the simulation results and the experimental data (see Figures 12–13). For the autotrophic decay rate the default GPS-X value (0.04/day) was used.

The maximum simulated nitrification rate was 14.5 mgN/L.h (0.9 gN/m^2 day) at 16 ºC, versus 15 mgN/L.h at 15 °C in the experimental data.[8] Furthermore, the GPS-X simulation indicated that the biofilm thickness was 290 µm, the concentration of active autotrophic biomass in the second nitrification reactor was 213 mgCOD/L (0.07 mgCOD/carrier) and heterotrophic biomass was 1937 mgCOD/L (0.63 mgCOD/carrier); thus the autotrophic biomass would appear to be 10% of all active biomass in the biofilm.

Table 1: Comparison of different parameters under the two testing conditions

parameter	**unit**	**lab -scale nitrification reactor**	**pilot-scale nitrification reactor**
max. obtained nitrification rate 1.1 (20 °C)	mg N/m^2.d	3.1 (20 °C)	0.9 (15 °C)
best fit for the specific surface area	m^2/m^3	2500	2000–2500
bifilm thickness	µm	30	290
active autotrophic biomass:			
biofilm+suspended	mgCOD/L	48.2	213
biofilm	mgCOD/L	40.1	209
biofilm	mgCOD/carrier	0.021	0.07
active heterotrophic biomass:			
biofilm+suspended	mgCOD/L	16.4	1937
biofilm	mgCOD/L	13.8	1878
biofilm	mgCOD/carrier	0.007	0.63
autotrophic fraction in total biomass	%	75	10

3. 3. Comparison

In Table 1 the comparison between different parameters under two testing conditions are presented. From the table we can see that the maximum obtained nitrification rate and autotrophic fraction of the biomass is higer in lab-scale nitrification reactor fed only with artificial wastewater. The best fit for the specific surface area was in the same range for both the lab-scale and pilot-scale plants (2000–2500 m^2/m^3).

4. Conclusions

Commercially available simulators with process models capable of describing biofilm systems, can assist in the estimation of unknown factors such as the effective surface area of porous media. For the PVA-gel carrier, using a calibrated mathematical model, the effective specific surface area was shown to be 2500 m^2/m^3, which was in agreement with that obtained by other means in a previous study. In this study, though, the correlation between experimental data obtained using real wastewater was not always in good agreement with simulated results. As an avenue of further research, more understanding is needed on the use of the hybrid model function for simulation of the spherical biocarriers where the biofilm thickness is in excess of 100 μm.

5. References

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Povzetek

Učinkovitost procesa čiščenja odpadne vode s pritrjeno biomaso v obliki biofilma na nosilnih elementih temelji na celotni razpoložljivi površini nosilnega elementa v reaktorju. Specifična površina je tako parameter, ki omogoča primerjavo delovanja procesov čiščenja odpadne vode z uporabo različnih nosilnih elementov. V naši študiji smo določili aktivno specifično površino sferičnih poroznih nosilnih elementov iz polivinil alkohola (PVA gel) podjetja Kuraray (Japonska), katere predhodne študije so pokazale učinkovito naselitev tako heterotrofnih kot avtotrofnih mikroorganizmov. Določitev smo izvedli na osnovi kalibracije napovedi matematičnega modela v GPS-X (Hydromantis) orodju in empiričnih rezultatov procesa čiščenja v dveh različno vodenih pilotnih sistemih. Prvi sistem je bila pilotna naprava, kjer je potekal proces nitrifikacije z dotokom umetno pripravljene odpadne vode le na avtotrofnem nivoju. Drug sistem pa je bila pilotna naprava, kjer se je vršil proces denitrifikacije in nitrifikacije z dotokom odpadne vode po mehanski stopnji. Kalibracija obeh procesov je pokazala, da je najboljše ujemanje z merjenimi podatki pri aktivni specifični površini PVA gela 2500 m^2/m^3, maksimalni hitrost rasti avtotrofov 1,2/dan in heterotrofov 6,0/dan. Izračunana zunanja površina aktivnega PVA gela je znašala 1000 m^2/m^3.