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MERITVE IN MODELIRANJE PROCESNIH VPLIVOV SUBSTRATOV IN FILTER MEDIJEV NA ČISTILNIH NAPRAVAH S PRITRJENO BIOMASO MEASUREMENT AND MODELLING OF PROCESS IMPACTS OF SUBSTRATES AND FILTER MEDIA TO THE OPERATION OF WASTEWATER TREATMENT PLANTS WITH FIXED BIOMASS

Darko DREV, Jože PANJAN

Substrati in filter mediji se vgrajujejo v čistilne naprave na različne načine, pri čemer imajo lahko bistven vpliv na učinek čiščenja. Postopke čiščenja lahko samo intenzivirajo ali pa so glavni nosilci čiščenja. Do sedaj so se pri projektiranju čistilnih naprav redko izkoriščali specialni učinki čiščenja, ki jih lahko dosežemo s substrati in filter mediji. Običajno je bil razlog v premajhnem poznavanju teh materialov ter dragi membranski filtraciji. Najbolj zanimive so tehnološke rešitve, pri katerih se izkoristi biološke postopke čiščenja v kombinaciji z različnimi substrati in filter mediji. Na to kažejo tudi izsledki preiskav, ki so podani v tem članku. Pri precejalnikih in rastlinskih čistilnih napravah lahko na primer z ustreznimi substrati odstranimo iz odpadne vode na relativno enostaven način fosfor in težke kovine. Ugotovili smo, da določene vrste substratov omogočajo bistveno ugodnejše pogoje za razvoj bakterijske združbe kot druge. Če se v proces čiščenja vključi še membranski filter, se lahko učinkovitost čiščenja pri enaki velikosti čistilne naprave bistveno izboljša. Na ta način lahko iz odpadne vode na relativno enostaven način odstranimo tudi viruse, bakterije in težke kovine.

Ključne besede: meritve biomase, modeliranje, čistilne naprave, hranila, CO₂, pritrjena biomasa, aktivnost mikroorganizmov, rastlinske čistilne naprave

Substrates and filter media are built in wastewater treatment plants in various ways, and can have a high impact on their operation effect. As such, they can either only intensify the treatment processes, or they can act as a main treatment carrier. The specific treatment effects, which can be achieved by substrates or filter media application, were until now rarely exploited in the wastewater treatment plants design. The usual reason for this was insufficient knowledge about these materials as well as the high costs of membrane filtration technology. Especially interesting are those technological solutions that use the biological treatment processes in a combination with various substrates and filter media. This can be also seen from the research results provided in this paper. The relatively easy removal of phosphorus and heavy metals from the wastewater, via suitable substrates, can, for example, take place in the percolators and constructed wetlands. It was found that some substrate types provide much more suitable conditions for the development of bacterial communities than others. If the membrane filter is included into the treatment process, then the treatment efficiency of the wastewater treatment plant can be significantly improved, although its size remains the same. Using these techniques, relatively easy removal of viruses, bacteria, and some heavy metals can also be achieved.

Key words: measurement of biomass, modelling, wastewater treatment plant, substrate, CO₂, fixed biomass, microbial mass activity, constructed wetlands

1. UVOD

Pri čistilnih napravah sodelujejo različni mehanizmi čiščenja, kot so fizikalni, kemijski in biokemijski procesi čiščenja (Gray, 1999).

1. INTRODUCTION

Wastewater treatment plants include different treatment mechanisms, such as physical, chemical treatment processes and

Točno razvrščanje posameznih procesov čiščenja, še posebej pri komunalnih odpadnih vodah, v eno izmed navedenih skupin je težavno, saj so praviloma pri vsakem procesu prisotni vsi trije mehanizmi.

Filtracija vode obsega več vrst fizikalnih in kemijskih separacijskih procesov, ki iz vode odstranjujejo nečistoče (Schweitzer, 1988). Nečistoče so lahko v obliki delcev ali raztopljenih snovi. Pri fizikalnih procesih filtracije ločimo več vrst mehanizmov zadrževanja delcev. S konvencionalno filtracijo se na filter mediju zadržujejo tisti delci, ki so večji od velikosti por. Če gre za zelo fine delce, koloide ali celo raztopljene snovi, govorimo o membranski filtraciji. Pri membranskih filter medijih se včasih učinek filtracije dodatno poveča z električnim poljem. Takrat govorimo o dializnih membranah.

Pri drugi pomembni skupini filter medijev se odstranjujejo nečistoče na podlagi adsorpcijske sposobnosti filter medijev. Zaradi privlačenja delcev na površino filter medija zadržuje filter delce, ki so manjši od velikosti por. Pri adsorpciji se vežejo nečistoče na površino filter medija na podlagi molekularnih privlačnih sil (aktivno oglje, diatomejska zemlja itd.).

Tretjo skupino predstavljajo filter mediji, ki kemijsko vežejo nečistoče iz vode. Najpomembnejši predstavniki tovrstnih filter medijev so ionski izmenjevalci.

Membranska filtracija se kot samostojni postopek čiščenja uporablja v glavnem le za specifične tehnološke odpadne vode (oljne emulzije, prisotnost kovin itd.). V kombinaciji z biološkim postopkom čiščenja pa se lahko uporabljajo membrane za: vpihovanje zraka v aeracijski bazen, zgoščevanje biomase v aeracijskem bazenu, odstranjevanje vode iz blata kot biofilter, za sterilizacijo itd. (Heinrichmeier, 2008). V preteklosti je bila glavna ovira za uporabo membranskih filtrov v kombinaciji z biološkim postopkom čiščenja hitra zamašitev membran. S sistemom sprotnega odstranjevanja pogache na membranskem filter mediju so ta problem zadovoljivo razrešili (Gründer, 2000).

Substrati se lahko v proces biokemijske razgradnje nečistoč aktivno vključijo kot

biochemical treatment processes (Gray, 1999). The exact categorisation of treatment processes into only one of the categories given above is difficult, especially in the case of municipal wastewater treatment, since all three mechanisms are regularly present in each process.

The water filtration includes several types of physical and chemical separation processes, which remove pollutants from the water (Schweitzer, 1988). The pollutants can be in the form of particles or dissolved matter. The physical filtration processes include several types of particle retention mechanisms. Using the conventional filtration, the particles larger than the size of the pores are retained on the filter media. The membrane filtration is applied in case of very fine particles, colloid particles or in case of dissolved matter. The filtration effect sometimes increases in the membrane filter media due to the electrical field. In such case dialysis membranes are used.

Another important category is the filter media that remove the pollutants via their adsorption capability. Since the filter media surface attracts the particles, the filter retains also those particles that are smaller than the size of the pores. During the adsorption process the pollutants bind on the filter media surface through the attractive forces between molecules (activated carbon, diatomaceous earth etc.).

The third category is represented by filter media that chemically bind water pollutants. These filter media are best represented by ion exchangers.

Membrane filtration is applied as an independent treatment process mainly in specific technological wastewater treatment (oil emulsions, if heavy metals are present etc.). Membranes can be used in a combination with the biological treatment process for: air injection into the aeration tank, sludge thickening in the aeration tank, as a bio-filter, for sterilisation etc. (Heinrichmeier, 2008). The fast clogging of the membranes used to be the main obstacle for the application of membrane filters in the combination with the biological treatment process. This problem, however, has been adequately solved by introducing the simultaneous cake removal (Gründer, 2000).

Substrates can be actively involved in the

substance, ki kemijsko vežejo določene snovi iz procesa ali ki jih v proces oddajo. Kemijsko aktivne substrate lahko razdelimo v dve glavni skupini:

- substrati, ki sodelujejo v procesu čiščenja z ionsko izmenjavo,
- substrati, ki sodelujejo v procesu čiščenja s kemijskimi reakcijami.

Za precejalnike in rastlinske čistilne naprave so primerni predvsem naravni anorganski ionski izmenjevalci, saj so bistveno cenejši od sintetičnih organskih ionskih izmenjevalcev.

Med anorganske ionske izmenjevalce štejemo različne naravne glinene materiale, ki imajo sposobnost ionske izmenjeve ter sintetične anorganske materiale (Degrémont, 2007).

Kot naravna ionska izmenjevalca sta najbolj poznana bentonit in zeolit. Naravni materiali, ki se uporabljajo kot ionski izmenjevalci, imajo običajno amorfnu strukturo, medtem ko imajo sintetični mikrokristalinično strukturo.

Čiščenje vode se pri tovrstnih materialih ne vrši zgolj z ionsko izmenjavo, temveč tudi s fizikalnim vezanjem (adsorpcijo). Zeoliti imajo zaradi sposobnosti vezanja ionov in molekul bistveno večjo čistilno sposobnost od bentonitov. Tako se na primer vežejo ioni težkih kovin (Pb, Cd, Zn, Cr, Ni, Hg itd.), NH_4^+ , H_2S , Cl_2 itd. Tudi aktivne gline in bentoniti imajo sposobnost vezanja različnih ionov, vendar so te lastnosti običajno nekoliko slabše izražene kot pri zeolilih.

Razne vrste materialov (substratov), na katerih je pritrjena biomasa, lahko reagirajo s posameznimi polutanti v odpadni vodi ali pa tudi ne. Polimerni nosilni materiali v precejjalnikih so praviloma kemijsko odporni na vse nečistoče v odpadnih vodah. Pri rečnemrodu, sloju kamnov, žlindri, različnih vrstah peskov ter podobnih materialih pa lahko prihaja do kemičnih reakcij med delci substrata in posameznimi snovmi v odpadni vodi. Reakcije potekajo praviloma med anorganskimi polutanti (fosfati, sulfati, nitrati, nitriti, halogenidi itd.) in ustreznimi anorganskimi snovmi v substratu. Če se kot substrat uporablja nestabilen organski material, kot na primer šota, razne umetne

process of biochemical pollutant decomposition as substances that either chemically bind a certain matter from the process, or they emit it into the process. The chemically active substrates can be divided into two main categories:

- Substrates used in the treatment process through ion exchange,
- Substrates used in the treatment process through chemical reactions.

Natural inorganic ion exchangers, which are essentially less expensive than synthetic organic ion exchangers, are especially suitable for percolators and constructed wetlands.

Different natural clay materials with ion exchange capability and synthetic inorganic materials belong to the group of inorganic ion exchangers (Degrémont, 2007).

Best known natural ion exchangers are bentonite and zeolite. The natural materials, which are used as ion exchangers, usually have amorphous structure, while the synthetic ones have microcrystalline structure. These materials do not clean the water only via ion exchange, but also via physical bonding (adsorption). Zeolites have much higher cleaning capability than bentonites, which is due to their capability of ion and molecule bonding. For example, heavy metal ions are bound in this way: (Pb, Cd, Zn, Cr, Ni, Hg etc.); NH_4^+ , H_2S , Cl_2 etc. Active clays and bentonites also have the capability to bind different ions; however, these characteristics are usually less expressed as in the case of zeolites.

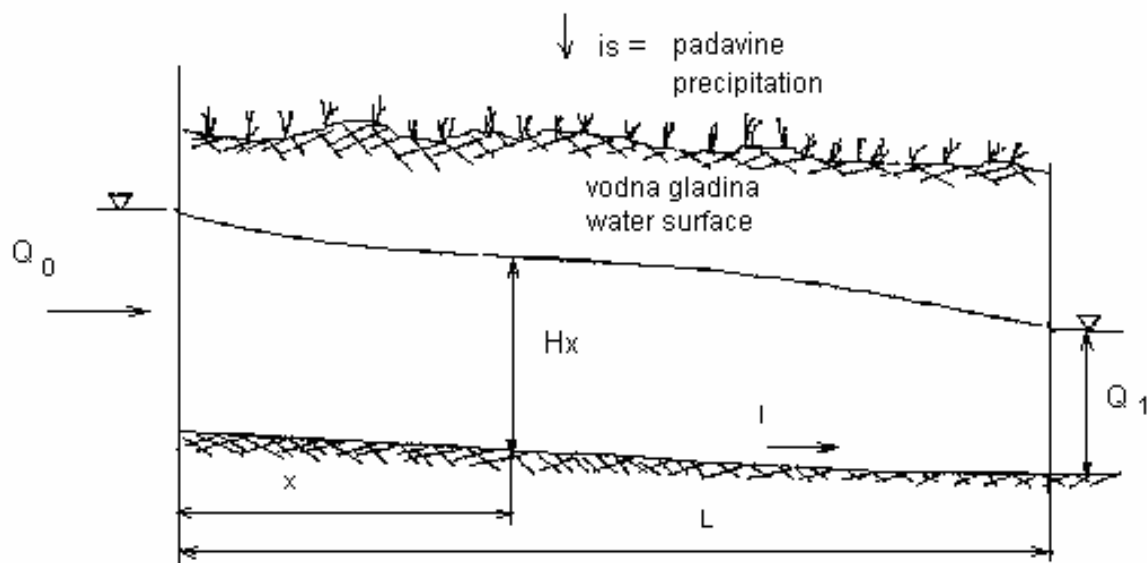
Various types of materials (substrates), on which the biomass is attached, can either react with certain pollutants in the wastewater, or not. Polymer supporting materials in the percolators are as a rule chemically resistant to all pollutants in wastewaters. However, chemical reactions between substrate particles and particular substances in the wastewater can occur in the case of river gravel, stone layer, scoria, various types of sand and similar materials. Reactions between inorganic pollutants (phosphates, sulphates, nitrates, nitrites, halogenides etc.) and inorganic materials in the substrate regularly take place. If unstable organic material is used as a substrate, such as peat, various artificial soils, or other similar material, then chemical reactions between organic pollutants and

zemlje ali kaj podobnega, lahko pride tudi do kemijskih reakcij med organskimi polutanti in substratom (huminske kisline, mlečna kislina, tenzidi, itd.). Možnih reakcij je več, odvisno od vrste odpadne vode in vrste substrata. V rečnemrodu so lahko na primer sestavine na bazi apnenca. Med apnencem in fosfati lahko poteče reakcija, s katero se fosfor veže iz odpadne vode na substrat. Tako pri precejšnjih in rastlinskih čistilnih napravah, ki imajo substrat na bazi apnenca ali podobnih mineralov, izločanje fosforja pogosto ne predstavlja večjih težav.

Pri rastlinski čistilni napravi s pritrjenim rastlinjem je pretok odvisen od velikosti in števila vmesnih prostorov med delci substrata, odpadne vode in dolžine poti (Plugge, 2001). Ko se na delcih substrata razvije bakterijska združba, se vmesni prostori med delci substrata še nekoliko zmanjšajo. Plavajoča bakterijska združba (dispergirana biomasa) lahko prav tako zmanjša hitrost pretoka. Pri rastlinski čistilni napravi je plavajoče bakterijske združbe manj kot 10 %, zato govorimo o čistilni napravi s pritrjeno biomaso. V času rasti imajo velik vpliv na pretok in koncentracije snovi tudi rastline, ki pa jih v tej preiskavi nismo proučevali. Slika 1 nam shematsko ponazarja tok vode v rastlinski čistilni napravi.

substrate can also occur (humic acids, lactic acid, tensides etc.). There are many possible reactions; the type of the reaction depends on the type of wastewater and the substrate. For example, river gravel components can be based on limestone. The reaction, which can take place between the limestone and phosphates, can make the phosphorus from the wastewater to bond on the substrate. Therefore, the phosphorus separation is unproblematic in the percolators and constructed wetlands, where the substrate is based on the limestone or on similar materials.

In constructed wetlands with fixed vegetation the flow depends on the size and number of spaces between the substrate particles, on the wastewater, and on the distance (Plugge, 2001). In addition, the spaces between the substrate particles become smaller, after the bacterial community develops on the substrate particles. The floating bacterial community (dispersed biomass) can also reduce the velocity of the flow. Constructed wetlands have less than 10% of bacterial communities; therefore they belong to the wastewater treatment plants with attached biomass. During the growing period the flow is also strongly influenced by plants; these, however, are not included in this investigation. A schematic representation of the flow in a constructed wetland is provided in Figure 1.



Slika 1. Shematski prikaz pretoka v rastlinski čistilni napravi v naravi.
Figure 1. Schematic representation of flow in a constructed wetland in the nature.

Pri rastlinskih čistilnih napravah ima substrat velik vpliv na pretočne količine in sposobnost čiščenja, kar je razvidno iz naslednje Darcyjeve enačbe (Börner, 1992):

In constructed wetlands the substrate has a strong impact on the flow rate and treatment efficiency, which can be seen from the following Darcy equation (Börner, 1992):

$$v_f = \frac{Q}{F} = -k_f \frac{d\Psi}{ds} \quad (1)$$

kjer je:

v_f hitrost filtracije [m/s]
 Q pretok vode [m³/s]
 k_f koeficient pretoka [m/s]
 $d\Psi/ds$ potencialni padec [-]
 F pretočni presek [m²]
 s pot vode [m]

where:

v_f filtration velocity [m/s]
 Q flow rate [m³/s]
 k_f hydraulic conductivity [m/s]
 $d\Psi/ds$ potential decline [-]
 F flow section [m²]
 s flow distance [m]

Pri rastlinski čistilni napravi se glavni procesi biokemijske razgradnje vršijo na substratu, na katerem je pritrjena bakterijska združba (EPA, 2000). Ta del je v bistvu polno zapolnjen precejalnik, pri katerem odpadna voda teče, za razliko od večine ostalih precejalnikov, v horizontalni smeri. Bakterijska združba bi brez prisotnosti rastlin bistveno slabše razgrajevala nečistoče, saj rastline vršijo dovajanje kisika in odvajajo nastalo biomaso.

The main biochemical decomposition processes, in constructed wetlands, take place on the substrate, which has the bacterial community attached (EPA, 2000). This part actually acts as a completely filled percolator, in which the wastewater flow is horizontal, in contrast to the majority of other percolators. The decomposition of pollutants due to the bacterial community would be much lower without the presence of plants, since the plants bring in the oxygen, and they take away the biomass formed.

Za precejalnike veljajo vsi osnovni mehanizmi biokemijske in kemijske razgradnje ter fizikalni postopki čiščenja (Panjan, 2006). V odvisnosti od vrste precejalnika so lahko določeni procesi čiščenja prevladujoči. Če govorimo o čiščenju (filtraciji), običajno mislimo na vse tri procese čiščenja.

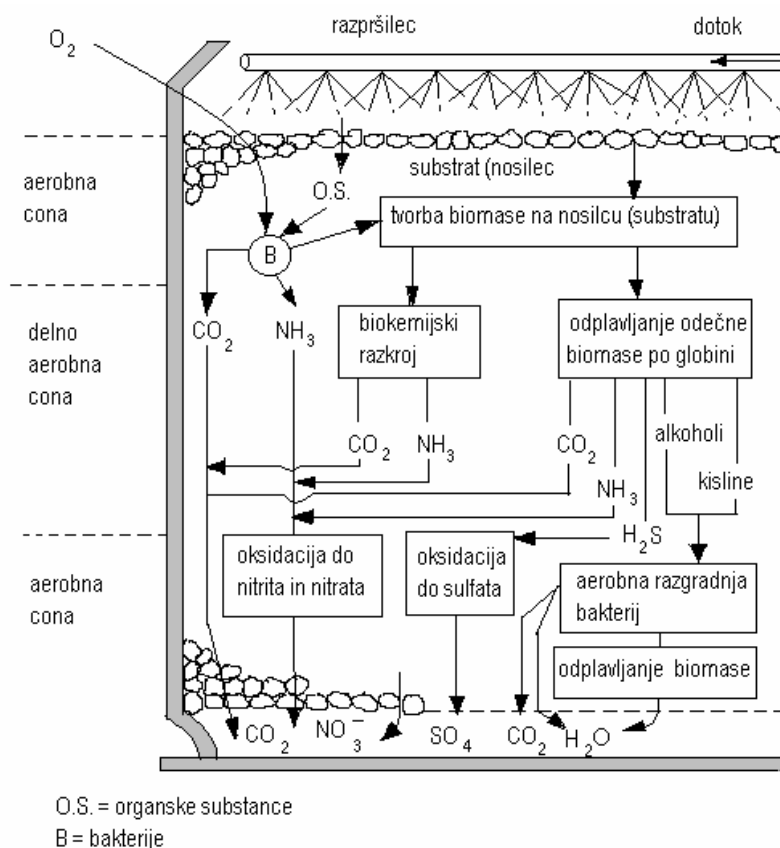
All basic biochemical and chemical decomposition mechanisms as well as physical treatment mechanisms can take place in the percolators (Panjan, 2006). Depending on the type of the percolator, certain treatment processes may dominate. When the term treatment (filtration) is used, it usually means all three treatment processes.

Pri naših preiskavah smo pogosto ugotavljali prevladujoče fizikalne in kemijske procese čiščenja na substratih, saj preiskave niso trajale tako dolgo, da bi se uspeli v zadostni meri razviti vsi mikroorganizmi in s tem povezani procesi biokemijske razgradnje.

In our research we often investigated the dominating physical and chemical processes of treatment on the substrates, since the duration of the investigations was not long enough for sufficient development of all microorganisms and, in connection with this, not enough for the biochemical decomposition processes.

Precejalniki so lahko polno zapolnjeni z vodo, tako kot je to primer z rastlinsko čistilno napravo s pritrjenim rastlinjem, ali pa se vrši pršenje odpadne vode na vrhu kolone s pritrjeno biomaso. Na sliki 2 je prikazan precejalnik, pri katerem se vrši razprševanje odpadne vode na vrhu kolone. Odpadna voda obliva substrat, na katerem je pritrjena biomasa.

The percolators can be either fully filled with water, such as in constructed wetlands with fixed vegetation, or the sprinkling of the wastewater can take place on the top of the treatment plant. The percolator where the sprinkling of wastewater takes place on the top of the treatment plant is presented in Figure 2. The wastewater passes all over the substrate with the biomass attached.



Slika 2. Biokemijski procesi razgradnje pri precejalniki s postopkom razprševanja.

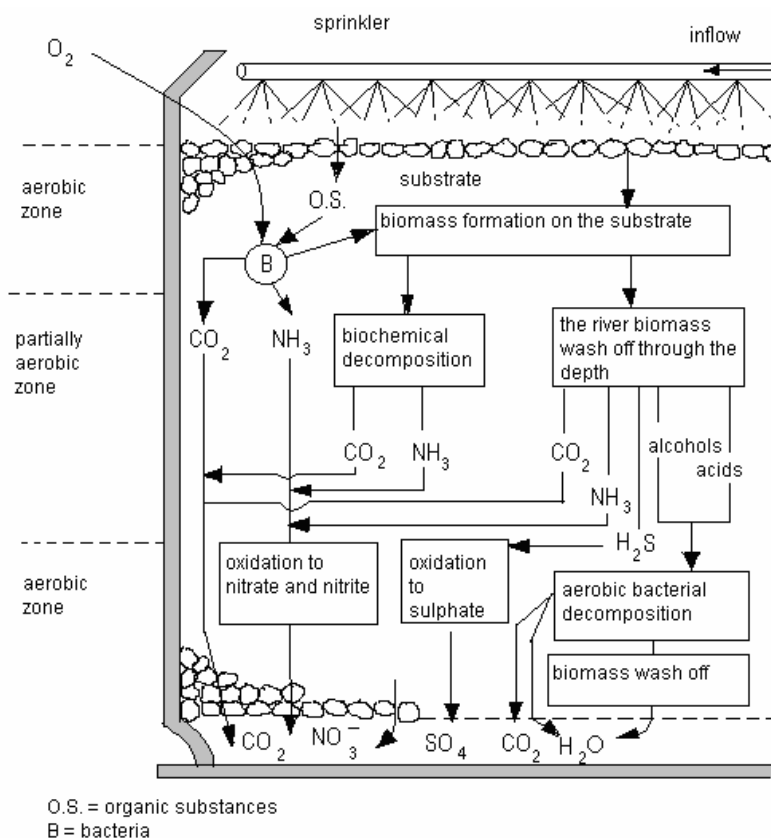


Figure 2. Biochemical decomposition processes in the percolator using the sprinkling procedure.

V tej shemi je substrat nevtralen, saj služi izključno za pritrditev bakterijske združbe. Naše preiskave pa so bile usmerjene v glavnem na specialne substrat, ki se aktivno vključujejo v proces čiščenja. Največ preiskav smo izvedli pod pogoji, ko je bil substrat potopljen v odpadni vodi.

2. MATEMATIČNO MODELIRANJE PROCESOV FILTRACIJE IN PRIRASTA BIOMASE

Glavni nosilci biokemijskih procesov čiščenja so bakterije (Gray, 1999). Kemijski procesi čiščenja pri precejalnikih in rastlinskih čistilnih napravah pa so odvisni tudi od substratov in raznih dodatkov. Kot fizikalne procese pa štejemo: prenos mase, prenos toplote, sedimentacijo, filtracijo itd. Za matematično modeliranje procesov smo preskusili več računalniških programov, in sicer: MATHCAD, SUPER PRO DESIGNER, GLEAMS – TC, MICROSOFT EXCEL in MATLAB.

Po pregledu programov smo se odločili za uporabo dveh programov, in sicer: MATLAB za izdelavo zahtevnega modela z možnostjo simulacij in DELPHI 2.0 za program s točno določenimi zahtevami. Komercialni računalniški SUPER PRO DESIGNER smo prav tako preskusili in ugotovili, da lahko služi le za celovitejšo obravnavo tehnoloških procesov čiščenja. Pripravljeni meniji v tem programu pa niso dovolj specifični za naše potrebe.

Osnovne zahteve, ki smo jih upoštevali pri izdelavi lastnih programov:

- delo v okolju WINDOWS,
- možnost upoštevanja različnih vplivov,
- možnost vnašanja različnih vhodnih parametrov,
- možnost prikazovanja različnih parametrov,
- možnost različnih simulacij in
- možnost nadgradnje programa.

Osnovni mehanizmi delovanja čistilne naprave, ki jih obdelujemo s tem programom, so:

1. Osnovni mehanizem biokemijske razgradnje nečistoč. Rast mikroorganizmov velja po Monodu (Spitz & Moreno, 1996):

The substrate in the figure is neutral and is used only for the fixation of the bacterial community. However, our investigations were oriented towards special substrates, which are actively involved in the treatment process. The majority of studies were done under the conditions, where the substrate was plunged into the wastewater.

2. MATHEMATICAL MODELLING OF FILTRATION PROCESSES AND BIOMASS INCREASE

Bacteria are the main carriers of the biochemical treatment processes (Gray, 1999). However, in percolators and constructed wetlands the chemical treatment processes are also dependant on the substrates and various supplements. The following processes are considered as physical processes: mass transfer, heat transfer, sedimentation, filtration etc. Several computer programs were tested for the mathematical modelling of processes: MATHCAD, SUPER PRO DESIGNER, GLEAMS – TC, MICROSOFT EXCEL and MATLAB.

After a close review we decided to use two programs: MATLAB for the development of a complex model using simulations, and DELPHI 2.0 as a program covering our exact requirements. We also tested the commercially available SUPER PRO DESIGNER and decided that it could be used only in more comprehensive analyses of technological treatment processes. For our requirements, the program menus are not specific enough. When developing our own programs the main requirements taken into account were:

- work in the WINDOWS environment,
- consideration of different impacts,
- inclusion of different input parameters,
- representation of different parameters,
- various simulations, and
- possibility of program upgrades.

The main wastewater treatment plant operating mechanisms to be analysed with this program are:

1. The main mechanism of biochemical pollutant decomposition. According to Monod, the growth of microorganisms is (Spitz & Moreno, 1996):

$$\frac{d[X]}{dt} = -Y \frac{d[C]}{dt} \quad (2)$$

$$Y = \frac{X - X_0}{C_0 - C} = \frac{\text{nastala biomasa (g)}}{\text{porabljena biorazgradljiva snov (g)}} = \frac{\text{formed biomass (g)}}{\text{used biodegradable matter (g)}} \quad (3)$$

2. Filtracija kot podaljšana longitudinalna disperzija (Panjan, 1998). Za take primere velja naslednja disperzijsko-difuzijska enačba:

2. Filtration as a prolonged longitudinal dispersion (Panjan, 1998). For such examples the following dispersion-diffusion equation is used:

$$D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \quad (4)$$

Rešitev te enačbe se glasi pri začetnih pogojih $t = 0$, $C = C_0$ in robnih pogojih $C_{(0,t)} = C_0 \cdot e^{-\gamma \cdot t}$ in $C_{(\infty,t)} = 0$ takole:

The solution to this equation under starting conditions $t = 0$, $C = C_0$ and limiting conditions $C_{(0,t)} = C_0 \cdot e^{-\gamma \cdot t}$ and $C_{(\infty,t)} = 0$, is the following:

$$C(x,t) = \frac{1}{2} C_0 e^{\gamma x} \left(e^{\frac{x(v-\xi)}{2D}} \operatorname{erfc} \frac{x-t\xi}{2\sqrt{Dt}} + e^{\frac{x(V+\xi)}{2D}} \operatorname{erfc} \frac{x-t\xi}{2\sqrt{Dt}} \right) \quad (5)$$

$$\xi = \frac{x+V+t}{L} \quad (6)$$

kjer je:

D	longitudinalni (vzdolžni) disperzijski koeficient - v našem primeru konstanten [m^2/min]
C	koncentracija raztopine v tekočini [mg/l]
V	povprečna hitrost toka [m/min]
x	koordinata, vzporedna s tokom tekočine [m]
t	čas [min]
γ	gostota toka tekočine [m^3/s]

where:

D	longitudinal dispersion coefficient – in our case it is constant [m^2/min]
C	concentration of the solution in the liquid [mg/l]
V	mean flow velocity [m/min]
x	co-ordinate parallel to the flow of the liquid [m]
t	time [min]
γ	liquid flow density [m^3/s]

Slika 3 prikazuje shemo za matematični model, izdelan s programom MATLAB, ki upošteva filtracijo kot podaljšano longitudinalno disperzijo za enačbo (5).

Figure 3 shows the design of the mathematical model developed using MATLAB, which considers the filtration as prolonged longitudinal dispersion in equation (5).

3. EKSPERIMENTALNI DEL

3. EXPERIMENTAL PART

Pri poizkusih smo kot najpomembnejše meritve, poleg klasičnih parametrov temperature, pH-vrednosti, KPK, BPK5, dušikovih in fosforjevih spojin, merili tudi

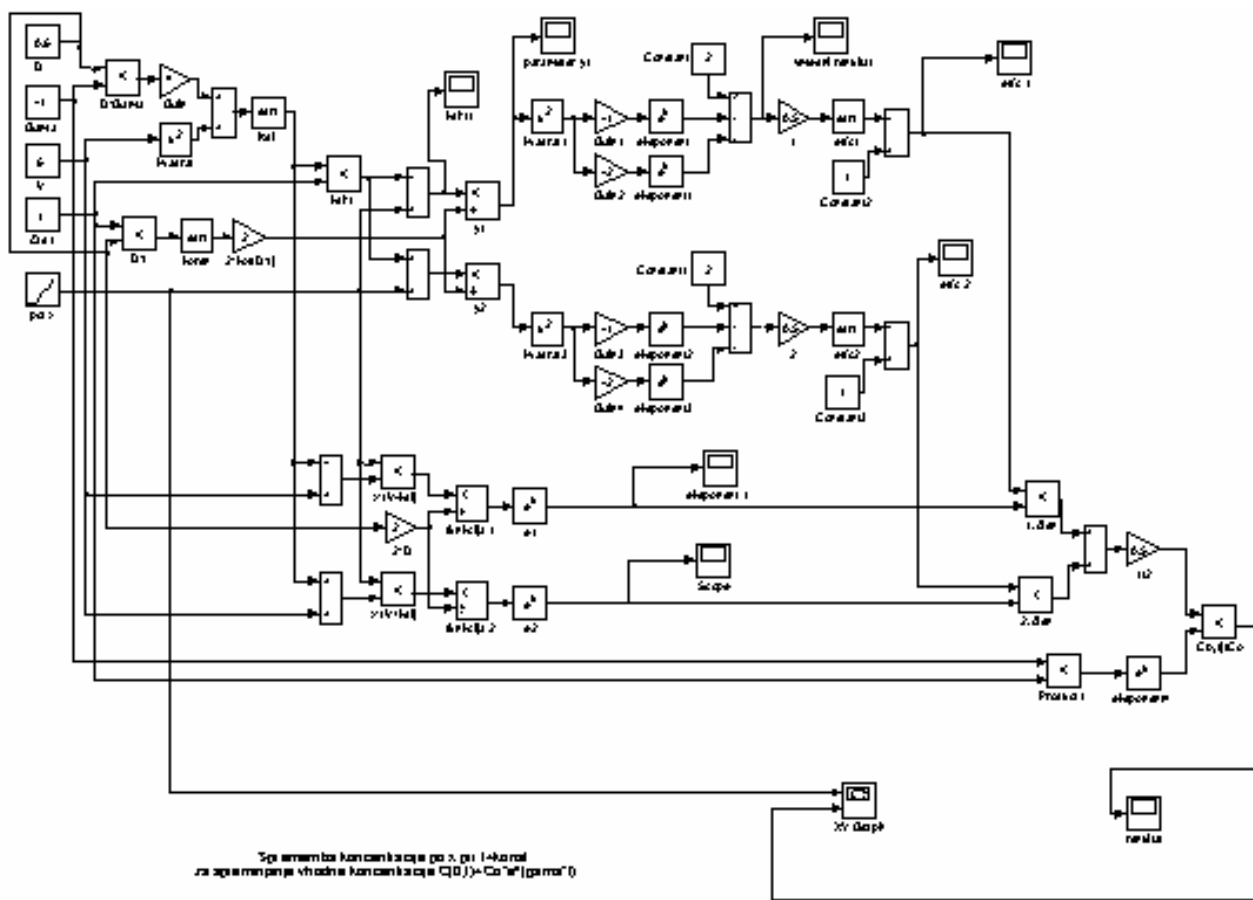
Next to the standard parameters (temperature, pH, COD and nitrogen compounds), measurements of biomass increase, carbon dioxide and biomass activity

prirast biomase, nastanek ogljikovega dioksida in aktivnosti biomase. Na sliki 5 je prikazana pilotna naprava, na kateri smo meritve opravili. V prekatke smo dajali substrate (rečni prod, zeolit, keramiko, steklo, šoto, vermikulit itd.) in odpadno vodo spuščali preko naprave na različne načine.

V velikih komorah P1, P2 in P3 smo imeli rečni prod, v komore 1, 2, 3 in 4 pa smo dodajali specialne substrate. Pred dodajanjem specialnih substratov smo spuščali prek čistilne naprave samo greznično odpadno vodo, da se je na pesku kot substratu formirala ustrezna bakterijska združba. Nato smo dodajali specialne substrate. Aktivnost mikrobne biomase smo merili z metodo pretvorbe INT (jodo-nitro-tetrazolijevega klorida) v formazan.

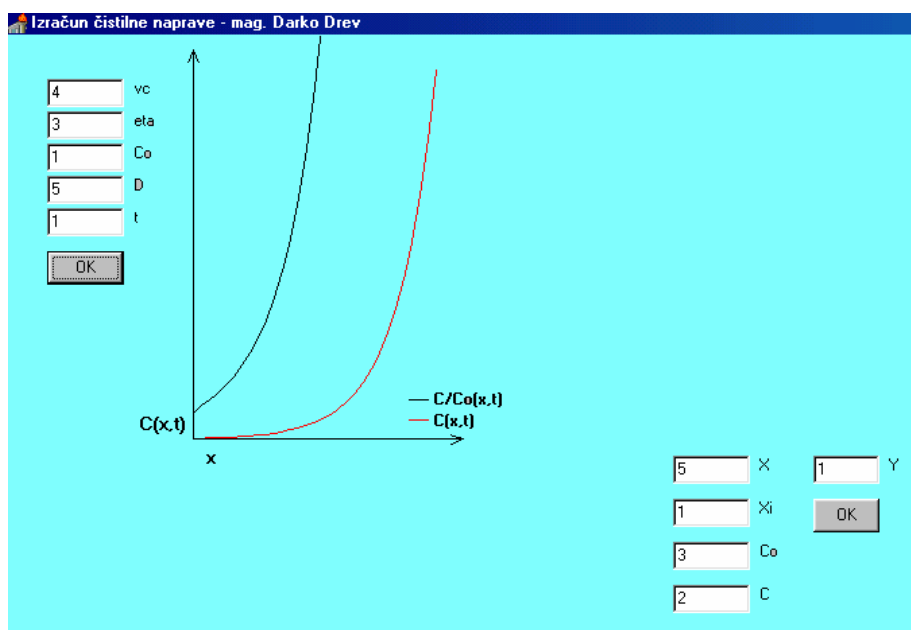
were performed in the experiments. The pilot plant, on which the measurements were done, is presented in Figure 5. The substrates were introduced into the chambers (river gravel, zeolite, ceramics, glass, peat, vermiculite etc.), while the sewage was passed through the device in different ways.

Large chambers P1, P2 and P3 were introduced with river gravel, and chambers 1, 2, 3 and 4 were introduced with special substrates. Before the addition of special substrates, drain sewage was passed through the water treatment plant so that the bacterial community formed on the sand (as substrate). Then we added special substrates. The activity of the microbe biomass was measured using the conversion of INT (iodo-nitro-tetrazolium chloride) in the formazan.



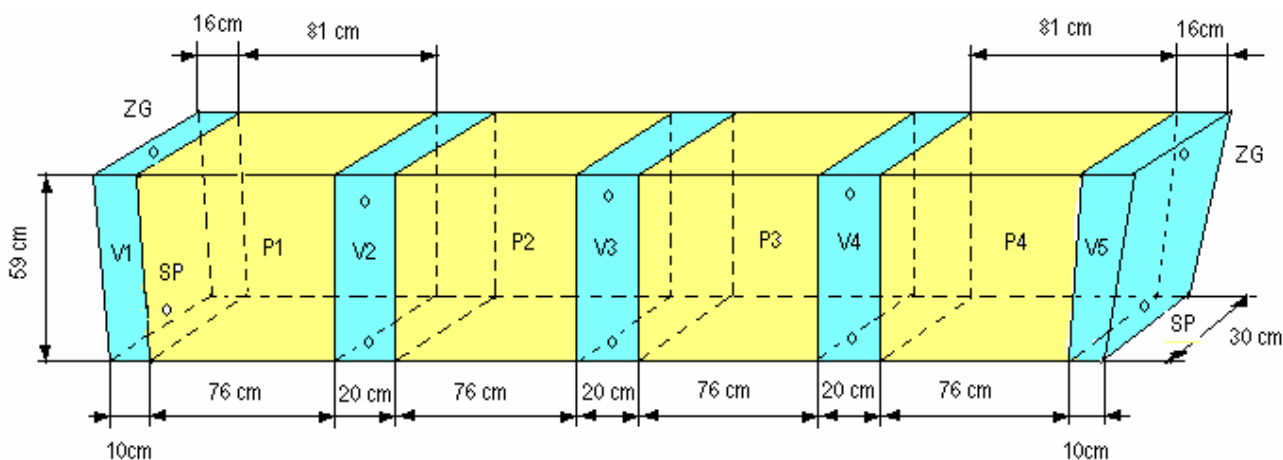
Slika 3. Matematični model, izdelan s programom MATLAB, ki upošteva filtracijo kot podaljšano longitudinalno disperzijo za enačbo (5).

Figure 3. Mathematical model developed using the MATLAB program, which considers filtration as prolonged longitudinal dispersion for equation (5).



Slika 4. Prikaz uporabe lastnega programa za izračune in izris krivulj razgradnje nečistoč z upoštevanjem enačb (2) in (3).

Figure 4. Application of our own program for computing and curve drawing, following equations (2) and (3).



Slika 5. Shema pilotne naprave.

Figure 5. Pilot plant scheme.

3.1 MERJENJE BIOMASE V PREKATIH ČISTILNE GREDE, NAPOLNJENE Z REČNIM PRODROM IN ZEOLITOM

Prekati P1, P2, P3 in P4 so bili napolnjeni z rečnim prodrom. Prekati V2, V3 in V4 so bili napolnjeni z zeolitom. Zeolit smo v te prekate spustili v vrečah iz plastične mreže. Postopek merjenja biomase je potekal tako, da smo po določenih časovnih terminih odvzeli vzorce s substratom in jih žarili.

3.1 BIOMASS MEASUREMENT IN THE TREATMENT POND CHAMBERS FILLED WITH RIVER GRAVEL AND ZEOLITE

The chambers P1, P2, P3 and P4 were filled with river gravel. The chambers V2, V3 and V4 were filled with zeolite. Bags made of plastic net and filled with the zeolite were put into these treatment pond chambers. In the biomass measurement process the samples containing the substrate were first sampled in certain time intervals, and ashed afterwards.

$$\frac{\text{biomasa}}{\text{substrat}} = \frac{\text{biomass}}{\text{substrate}} = \frac{A - B}{C - S} [\text{mg/g}] \quad (7)$$

kjer je:

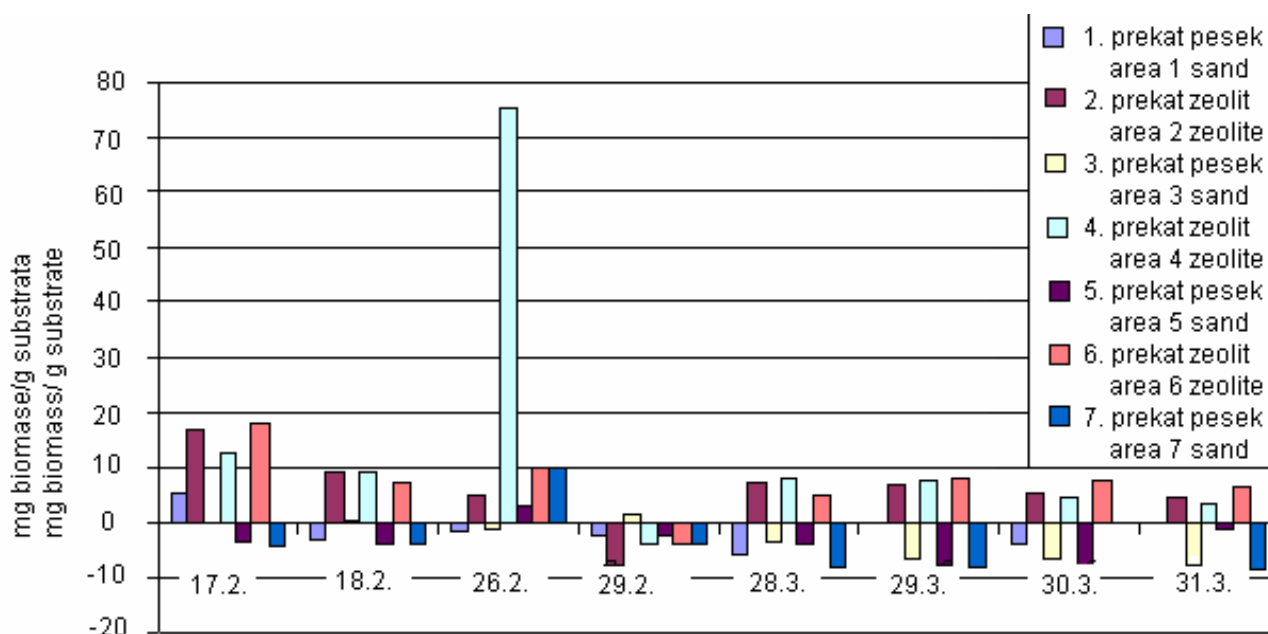
- A teža biomase pri 110 °C [mg]
- B teža biomase pri 550 °C [mg]
- C teža substrata [g]
- S substrat kot slepi preskus [g]

Iz grafikona na sliki 6 je razvidno, da se je na različnih substratih, pod različnimi pogoji, razvila različna količina biomase. Odvečna biomasa odpada iz substrata, zato se v določenih časovnih intervalih pojavljajo tudi negativni prirastki biomase.

where:

- A biomass weight at 110 °C [mg]
- B biomass weight at 550 °C [mg]
- C substrate weight [g]
- S reference substrate [g]

The graph on Figure 6 shows how different biomass amounts developed on different substrates and under different conditions. Since the surplus biomass falls off from the substrate, the negative increase of biomass also occurs in certain time intervals.



Slika 6. Prikaz vsebnosti biomase na substratu v [mg/g].

Figure 6. Amount of biomass on the substrate [mg/g].

3.2 MERJENJE KOLIČINE OGLJIKOVEGA DIOKSIDA V POSAMEZNIH PREKATIH MODELA ČISTILNE GREDE, NAPOLNJENE S SUBSTRATOMA REČNI PROD IN ZEOLIT

Količino ogljikovega dioksida smo merili z dvema metodama (Cooper, 2004): z metodo neposrednega merjenja smo določili raztopljeni kisik v 100 ml vode iz posameznega prekata modela. Dodali smo 1 do 3 kaplje fenolftaleinskega indikatorja in titrali z 0,1 N NaOH do pojava rdečkaste barve. Vsebnost CO₂ v odpadni vodi smo

3.2 MEASUREMENTS OF CARBON DIOXIDE AMOUNT IN CERTAIN AREAS OF THE TREATMENT POND MODEL FILLED WITH RIVER GRAVEL AND ZEOLITE SUBSTRATES

The amount of carbon dioxide was measured using two methods (Cooper, 2004): using the method of direct measurement we determined the amount of dissolved oxygen in 100 ml of water from the particular chamber of the model. We added 1 to 3 drops of phenolphthalein indicator, and titration with 0.1 N NaOH was performed until the appearance of red colour. The content of CO₂

določili po naslednji formuli: ml pri titraciji x 44 = mg / l ogljikovega dioksida.

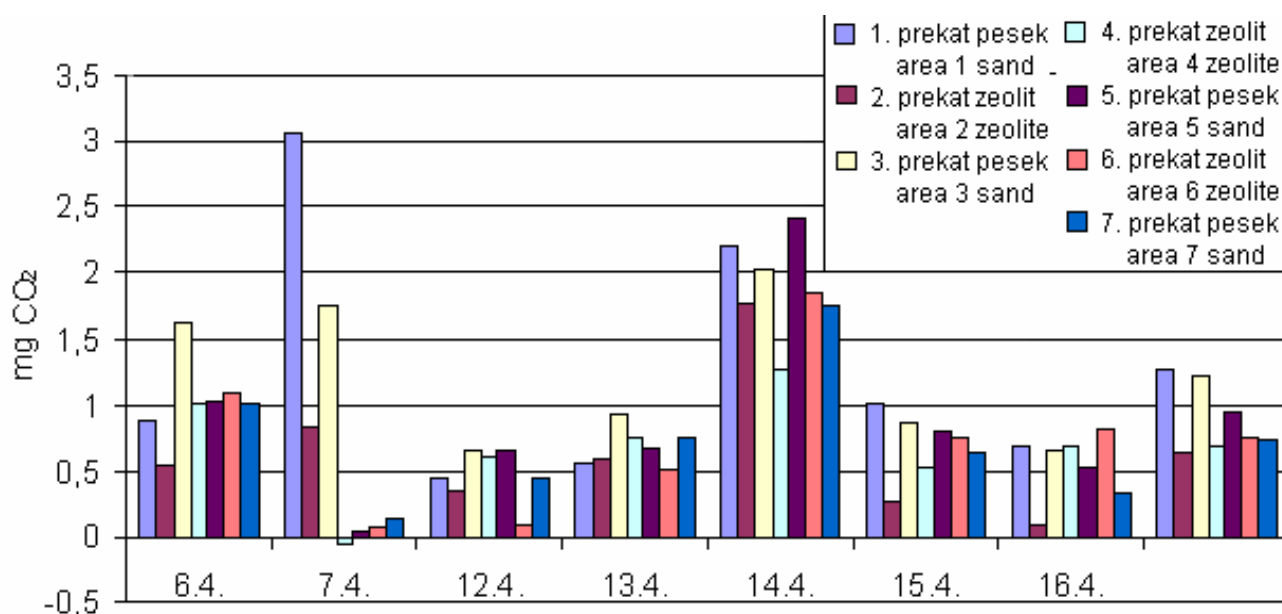
Pri metodi z barijevim hidroksidom smo določali količino ujetega CO₂, ki se ujame v plastenko nad sedimentom v 24 urah. Plastenko s približno 1,5 l smo odrezali v spodnjem delu in jo pogreznili v sediment, tako da je bil rob pod vodno gladino. Skozi zamašek smo namestili cev, skozi katero smo po 24 urah z akvarijsko črpalko izčrpali nabrane pline skozi posodo z raztopino Ba Cl₂. Posamezne posode smo nato prepihali z dušikom in titrirali z 0,05 N HCl, tako da smo najprej določili fenolftaleinski preskok od rdeče v brezbarvno, nato pa preskok metil oranžnega indikatorja (MO) od zelenkaste barve v čebulno barvo. Količino sproščenega oziroma v plastenko ujetega CO₂ v 24 urah smo izračunali po naslednji formuli: titracija (MO) v ml x 0,05 x 44 = mg CO₂.

Iz grafikona slike 7 je razvidno, da so bili procesi biokemijske razgradnje odpadne vode različni pri različnih substratih. Pri tem so imeli velik vpliv na te procese tudi drugi pogoji (različni precati).

in the wastewater was determined according to the equation: ml used in titration x 44 = mg/l of carbon dioxide.

Secondly, using the barium hydroxide method we determined the amount of CO₂ captured in the plastic bottle under the sediment, during the period of 24 hours. The bottom part of the approximately 1.5 l plastic bottle was cut and pushed into the sediment, in a way that the brim was under the water surface. A pipe was fixed through the plug, through which we pumped out the accumulated gasses during the period of 24 hours, using an aquarium pump. The gasses were pumped through the vessel containing BaCl₂ solution. The separate vessels were then flushed out with nitrogen and titrated with 0.05 N HCl. The titration was done in a way that we first determined the phenolphthalein change of colour from red to colourlessness, and then the methyl orange (MO) indicator colour change from green to onion colour. The amount of the evolved CO₂, or better the amount of CO₂ caught during the period of 24 hours, was calculated using the equation: titration (MO) in ml x 0.05 x 44 = mg CO₂.

The graph on Figure 7 shows that the biochemical wastewater decomposition processes were different in the case of different substrates. In addition, other conditions (different chambers) also had a strong impact on these processes.



Slika 7. Količina sproščenega CO₂ v modelu z BaCl₂.

Figure 7. Amount of evolved CO₂ in certain areas of the treatment pond model using BaCl₂.

3.3 MERJENJE AKTIVNOSTI MIKROBNE MASE PRI RAZLIČNIH SUBSTRATIH IN RAZLIČNIH OBREMENTVAH V POSAMEZNIH PREKATIH MODELA ČISTILNE GREDE

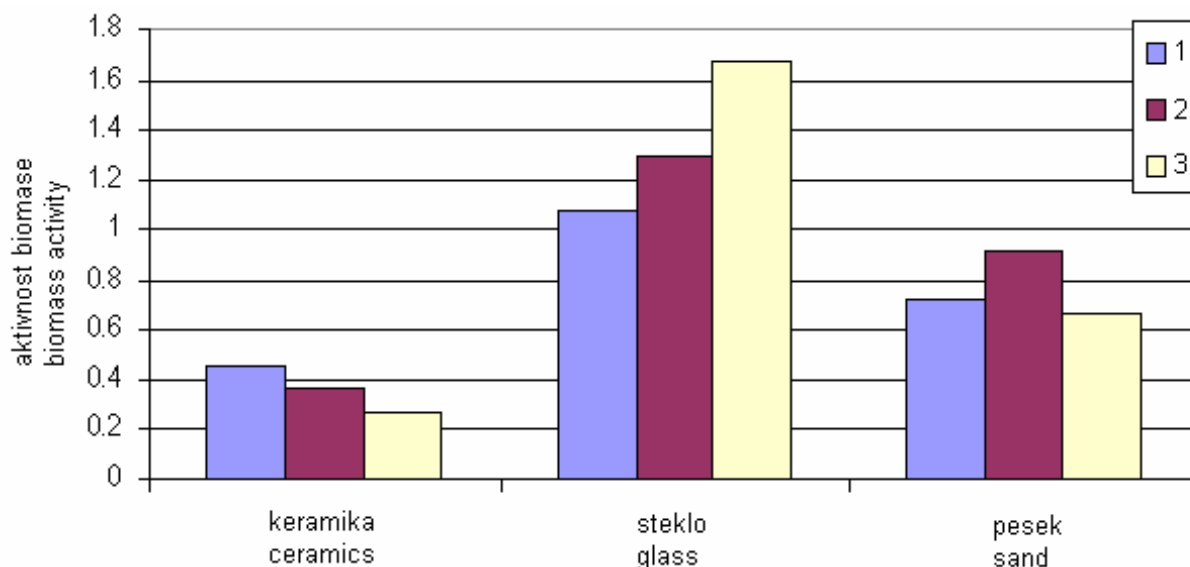
V prekate, v katerih se je nahajal pesek, smo namestili plastično cev s premerom 10 cm, ki je bila v predelu, ki je bil zakopan v pesek, perforirana. Na cev smo namestili plastenko s preluknjanim zamaškom, v katerega smo vstavili cevko, ki je vodila do stekleničke z barijevim hidroksidom ($\text{Ba}(\text{OH})_2$). Ves sistem je bil zatesnjen z lepilom. V prekate, ki so se nahajali za prekati, napolnjenimi s peskom, v katerih je bila le tekočina, smo potopili plastične vrečke, napolnjene s peskom in ostalimi substrati: steklene kroglice; drobljena keramika; šota; tufko, zmešan s peskom v razmerju 1 : 1; aktivno oglje, zmešano s peskom v razmerju 1 : 1, in agrogel, zmešan s peskom v razmerju 1 : 100. Vsak preskus z določeno odpadno vodo je trajal en teden. Na koncu dovajanja greznične vode smo odvzeli prvi vzorec, na koncu dodajanja hranilne juhe pa drugi vzorec.

V naslednjem poskusu smo kot glavno hranilno snov uporabili 1 % sladkorno raztopino, vzorčenje pa je bilo izvedeno tako v začetku (greznična voda) kot po koncu dodajanja sladkorja. Produkcijo ogljikovega dioksida smo merili v 24-urnih intervalih v treh prekatih, napolnjenih s peskom, z metodo z barijevim hidroksidom. Količino sproščenega oziroma v plastenko ujetega CO_2 in oborjenega z barijevim hidroksidom smo določili tako, da smo vzorce titrirali z 0,05 M HCl. Slika 8 prikazuje aktivnost mikrobne biomase, ki uporablja acetat kot vir energije za različne substrate, ki so bili obešeni v vrečkah za vsakim prekatom s peskom, slika 9 pa prikazuje aktivnost mikrobne biomase v $1.10^{-9} \text{ O}_2 \text{ ml}/(\text{g}\cdot\text{h})$ v treh prekatih, v katerih je hranivo sladkor.

3.3 MEASUREMENTS OF MICROBIAL MASS ACTIVITY AT DIFFERENT SUBSTRATES AND DIFFERENT LOADINGS OF INDIVIDUAL AREAS OF THE TREATMENT POND MODEL

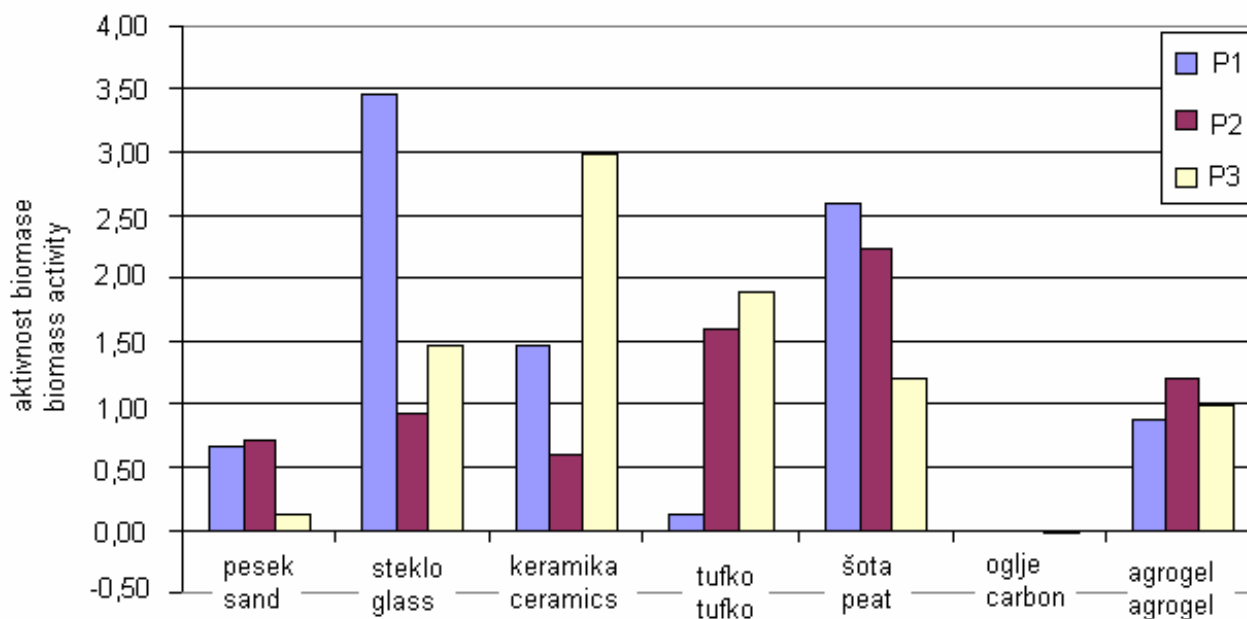
The chambers introduced with sand were fitted with a plastic pipe with a diameter of 10 cm. The part of the pipe buried into the sand was perforated. A plastic bottle with a drilled plug was fixed on the pipe. We fixed a smaller pipe into the plug, which was connected with the vessel containing barium hydroxide ($\text{Ba}(\text{OH})_2$). The system was tightened with glue. Into the other areas containing only water, which were located behind the areas containing sand, the plastic bags filled with sand and other substrates were dipped: small glass balls; crushed ceramics; peat; tufko (material based on zeolite) mixed with sand in the ratio 1 : 1; active carbon mixed with sand in the ratio 1 : 1; and agrogel (material based on synthetic polymers) mixed with sand in the ratio 1 : 100. The duration of each experiment with particular wastewater was one week. At the end of the application of the municipal wastewater the first sample was taken, and at the end of adding nutrient broth the second one was taken.

The main nutritive substance used in the next experiment was 1% sugar solution. The sampling was done in the beginning (municipal wastewater) as well as after the addition of sugar. In three areas filled with sand the carbon dioxide production was measured after 24-hour intervals, using the barium hydroxide method. The amount of evolved CO_2 , or actually, the amount of CO_2 caught in the plastic bottle, and precipitated using barium hydroxide, was determined with titration of the samples using 0.05 M HCl. Figure 8 shows the activity of microbial biomass, which uses acetate as energy source, in $1.10^{-9} \text{ O}_2 \text{ ml}/(\text{g}\cdot\text{h})$, for different substrates that were hung in the bags behind each area containing sand, while Figure 9 shows the activity of microbial biomass in $1.10^{-9} \text{ O}_2 \text{ ml}/(\text{g}\cdot\text{h})$ in areas where sugar was used as nutrient.



Slika 8. Aktivnost mikrobne biomase, ki uporablja acetat kot vir energije v $1 \cdot 10^{-9} \text{ O}_2 \text{ ml}/(\text{g} \cdot \text{h})$, za različne substrate.

Figure 8. Activity of microbial biomass, using acetate as energy source, in $1 \cdot 10^{-9} \text{ O}_2 \text{ ml}/(\text{g} \cdot \text{h})$, on different substrates.



Slika 9. Aktivnost mikrobne biomase v $1 \cdot 10^{-9} \text{ O}_2 \text{ ml}/(\text{g} \cdot \text{h})$ v treh prekatih, v katerih je hranivo sladkor.

Figure 9. Activity of microbial biomass in $1 \cdot 10^{-9} \text{ O}_2 \text{ ml}/(\text{g} \cdot \text{h})$ in three areas, where sugar is used as nutrient.

Raziskave so pokazale, da se na posameznih substratih razvije bistveno več bakterijske združbe kot na drugih (preglednica 1). Ekspandirano steklo se je pokazalo kot najbolj ugodna podlaga za razvoj mikroorganizmov. Tudi rečni prod in porozna keramika sta dala dobre rezultate.

The studies have shown that the bacterial community developed considerably more on certain substrates than on others (Table 1). Expanded glass proved to be the most suitable substrate for microorganism development. River gravel and porous ceramics also yielded good results.

Preglednica 1. Razvrstitve največje do najmanjše aktivnosti biomase na posameznem substratu glede na aktivnost v vseh prekatih.

Table 1. The categorisation, from highest to lowest, of biomass activity on individual substrates, according to the activities in all areas.

substrat – <i>Substrate</i>	1. mesto <i>1st place</i>	2. mesto <i>2nd place</i>	3. mesto <i>3rd place</i>	4. mesto <i>4th place</i>	5. mesto <i>5th place</i>	6. mesto <i>6th place</i>	7. mesto <i>7th place</i>
steklo – <i>Glass</i>	3 x	2 x		1 x			
pesek – <i>Sand</i>		1 x		3 x	2 x		
tufko – <i>Tufko</i>		2 x	3 x			1 x	
agrogel – <i>Agrogel</i>		1 x	1 x	2 x	2 x		
keramika – <i>Ceramics</i>	2 x		1 x		2 x	1 x	
šota – <i>Peat</i>	1 x	1 x		1 x		3 x	
ogljje – <i>Active carbon</i>							6 x

4. RAZPRAVA

Izbira substrata ima lahko velik vpliv na učinek čiščenja na čistilnih napravah s pritrjeno biomaso in v rastlinskih čistilnih napravah. Aktivnost mikrobne biomase je namreč pogojena z izbiro substrata. Vseh vplivov substratov za sedaj še ni možno točno kvantificirati, saj ne poznamo vseh mehanizmov delovanja posameznega materiala na procese biokemijske razgradnje na substratu zgrajene biomase. Danes se že raziskujejo tudi nekatere lastnosti t. i. “informiranih” substratov s spominom (iz keramičnih in steklenih materialov), ki dodatno pospešujejo procese biokemijske razgradnje (Panjan, 2006). Poleg eksperimentalnih meritev smo razvili še osnovne matematične modele, ki jih lahko po potrebi nadgrajujemo. Za opis procesa filtracije, kot procesa čiščenja na biofiltru, smo uporabili model s podaljšano longitudinalno disperzijo s programom Matlab. Ta že v osnovi zajema procese biokemijske razgradnje in fizikalnega čiščenja. Pri takšnem modelu je pomembno samo to, kaj v čistilno napravo priteče in kaj odteče. Z drugimi besedami, ni pomembno kateri procesi sodelujejo pri čiščenju.

Če postopku čiščenja naknadno dodamo še membranski filter, lahko iz vode na enostaven in direkten način odstranimo še večje količine organskih nečistoč. Na ta način lahko še

4. DISCUSSION

In the wastewater treatment plants with biomass attached to the substrate, the choice of the substrate has a strong impact on the effectiveness of the treatment plant. The microbial biomass activity depends on the substrate type. It is currently not possible to quantify all substrate impacts, since all of the operating mechanisms on the biochemical decomposition processes of the particular material are not known. The so-called “informed” substrates with memory, which additionally speed up the biochemical decomposition processes, are a separate topic (Panjan, 2006). It is possible to build such “information” into ceramic and glass materials. We have developed main mathematical models, which can be upgraded if necessary. The analysis of the biofilter treatment processes as a prolonged longitudinal dispersion using Matlab program. This in its basis includes all processes of biochemical decomposition and physical treatment. In such model the only thing important is what flows in and out from the treatment plant. Or, in other words, it is not important which mechanism is responsible for the treatment.

If a membrane filter is additionally included in the treatment process, the large amount of suspended organic pollutants can be easily and directly separated from the treatment process. This can increase the further treatment

dotatno izboljšamo učinkovitost čiščenja ob nespremenjeni velikosti čistilne naprave.

effectiveness, although the size of treatment plant remains the same.

5. ZAKLJUČKI

S poizkusi smo dokazali, da nam določene vrste substratov omogočajo bistveno ugodnejše pogoje za razvoj bakterijske združbe kot druge, kar je lahko prav tako pomemben parameter pri projektiranju čistilne naprave. Ugotovili smo, da sta se najintenzivneje razvijala mikrobna biomasa na ekspaniranem steklu in na keramičnem substratu. Tudi rečni prod je dal ugodne rezultate. Steklo in keramika se po kemični sestavi bistveno ne razlikujeta, zato ju lahko uvrstimo v širšo skupino anorganskih substratov. Mnenja smo, da je možno razviti takšen stekleni ali keramični material, ki bo zagotavljal še ugodnejše pogoje za razvoj mikrobne biomase.

V praksi se kot nosilci mikrobne biomase največ uporabljajo polimerni materiali (PE, PP, itd.). To so kemijsko in fizikalno inertni materiali do mikrobne biomase in nečistoč v vodi, zato ne pospešujejo biokemijskih procesov razgradnje. Običajno imajo tudi bistveno manjšo površino, kot jo lahko dobimo s poroznimi keramičnimi materiali ali z ekspaniranim steklom. Z izdelanimi matematičnimi modeli smo simulirali osnovne procese filtracije in prirasta biomase.

5. CONCLUSIONS

The experiments have shown that certain substrate types can provide much more suitable conditions for the development of bacterial community than others. This can be an important parameter in wastewater treatment plant design. It was established that the microbial biomass development was most intensive on expanded glass, followed by ceramic substrate. The river gravel also gave good results. According to their chemical composition, glass and ceramics do not differ considerably. Therefore, they can be categorised into the broader category of inorganic substrates. Our opinion is that it is possible to develop such glass or ceramic material that would guarantee even more suitable conditions for the microbial biomass development.

In practice, mainly polymer materials (PE, PP etc.) are used as a support for the microbial biomass. These materials are chemically and physically inert to the microbial biomass and to pollutants in the water. Therefore, they do not speed up the biochemical decomposition processes. Usually they have much smaller surfaces than porous ceramics or expanded glass. With the mathematical models developed, we simulated the basic processes of filtration and biomass increase.

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