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Thesis of Ph.D. dissertation

BIOLOGICAL TREATMENT OF INDUSTRIAL WASTEWATER INCLUDING SLOWLY BIODEGRADABLE OR TOXIC COMPOUNDS

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INTRODUCTION

Increasing importance of environmental protection and increasingly stringent requirements for the treated wastewater made it necessary to apply new technologies and processes. During the evolution of biotechnology it had been demonstrated that the bioreactor arrangement – and compartmentalization of its volume –in a wastewater treatment system has strong influence on the effectiveness of the whole system. It is especially important when the wastewater contains toxic or slowly biodegradable components.

GOALS

The goals of the experiments were to establish a cost-effective bioreactor reconfiguration that enables an enhanced pollutant removal of the wastewater originated from a chemical industrial plant. Since the kinetic behavior of microorganisms is affected by the environment and by the wastewater itself, lab-scale on site experiments were performed by using the existing wastewater in various reactor arrangements, and values of the chemical and kinetic parameters were measured.

EXPERIMENTAL METHODS

In setting up the lab-scale experiment Nitrokémia Rt.'s wastewater treatment plant was considered as a starting point. Three volume-proportional models were built up with different configurations, in order to be able to use the lab-scale results in the full-scale practice.

During the experiments we investigated the sludge settling and filtration properties, the chemical characteristics of treated wastewater, such a pH, COD (**C**hemical **O**xygen **D**emand), the concentration of nitrogen forms – nitrate, nitrite, ammonia – the concentration of orthophosphate ions and salt content. We also measured the reactor temperatures and dissolved oxygen concentrations. The characterization and evaluation of individual components were performed by GC-MS method. We paid special attention to comparing the properties (settleability and filtratability) of sludges originated from different systems.

In the **first experiment** three trains were used with reactors in parallel, in series, and a two-sludge system. Each of the systems contained a denitrification basin at the entrance of the reactor chain. It was followed by the aeration tanks and the settler. The influent was fed into the first denitrification basin. The experiment was run for 9 weeks.

In the **second experiment** four trains of bioreactors were operated for 11 weeks in order to optimize the most effective serial system. We used a parallel system as a reference, two serial and one two-sludge systems. The various arrangements resulted in different performance as it had been expected. The serially (1+1+3) connected bioreactor chain proved to be the best, regarding most of the investigated parameters. This one assured the most stable operation, the highest tolerance against disturbances, and the sludge originated from this system was easy to handle.

The **third experiment** was based on the experience aimed the optimization. We operated three various trains of bioreactors, a serially connected system (I.), a regular two-sludge system (II.) and the new, modified two-sludge system (III.), which has been patented (Pat. Num.: 212 001). This system incorporates the advantages of a conventional two-sludge system, without it's disadvantages, and allows the second step to have an effective nitrification rate, because it is protected against the high concentration of toxic or xenobiotic compounds. Consequently, the sensitive nitrifiers can be safely retained in the system, and the produced nitrate is denitrifiable in the first step. The denitrification basin placed at the entrance of the reactor chain allows an enhanced pH stabilization, therefore it is enough to set the pH value of the wastewater into the range of 4.5 – 5.5. System III. was very similar to system II. in the arrangement and volumes, but the treated wastewater was fed back into the first reactor, and we made it possible to feed 3-5% of influent into the second stage.

The experiment was run for 102 days, and the results demonstrated the advantages of the new process during the low and high loaded periods as well.

In the **fourth experiment** we worked out a new, attached growth biological treatment process. This process and equipment is patented under the Patent Number of 216 576. The investigations covered three systems. The simplest one was an aerobic reactor, the second one contained an anoxic and an aerobic reactor, and the third one had an anaerobic, anoxic and aerobic reactor in series. All the systems were operated as flow-through reactors, without recirculation.

The **fifth experiment** served to investigate the connected systems (activated sludge systems and post treatment reactors). We compared two variations of the modified two-sludge system coupled with the post-treatment unit. In the first arrangement the post-treatment unit was connected after the base system, in the second arrangement the attached-growth unit was submerged into the aeration tank of the second step. The third arrangement was the serial base system connected with the post-treatment unit. The HRT (***H***ydraulic ***R***etention ***T***ime) in the post-treatment units was 3 hours in each case. We measured the concentration of the individual chemical compounds, and investigated the toxicity of the raw and the treated water. The post-treatment units eliminated the color and toxicity of the treated water in a very effective way.

To operate continuous systems is often costly and time consuming, therefore in this work batch experiments were used to model continuous systems. We compared the variation of extant kinetic parameters in a CMAS (***C***ompletely ***M***ixed ***A***ctivated ***S***ludge) tank reactor, and in an SBR (***S***equencing ***B***atch ***R***eactor) at different loads. The experiments were performed at the Clemson University SC. USA, Department of Environmental Engineering and Science. The SBR was run for 5 month.

The CMAS reactors represented a parallelly connected biotreatment system, while the SBR modeled a serial system. The CMAS reactors were operated in steady state, (constant load, HRT and SRT [***S***ludge ***R***etention ***T***ime]). In order to follow the changes of biodegradation, we investigated the variation of extant kinetic parameters by respirometry, in both of the systems for two test-compounds. The results were compared to the values of extant kinetic parameters of an SBR which was operated with different loads. In the SBR the concentration gradient was established in time. To characterize the load, F/M ratio (Food/Microorganism) was used, which is the ratio of the organic materials COD fed pro day to the mass of biomass.

In the case of CMAS the biogenic compounds were fed into a selector placed preceding the reactor. The xenobiotic compounds (test-substrates i.e. the phenol and isophorone as well) were fed directly into the reactor with an F/M=4,5 day^{-1} ratio. Therefore there was no substrate gradient in this system for the xenobiotic compounds.

The SBR was fed simultaneously by the xenobiotic and biogenic feed. Therefore, when the F/M ratio was increased, the concentration gradient increased also for both of the substrates. In the SBR the load was varied within 2.25 and 18 day^{-1}. It was assumed that the increased test-substrate concentration gradient will evolve a selector-effect, i.e. enhance the growth of a biomass that has an increased biodegradation rate.

The HRT, the SRT, the reactor volume, the volumetric aeration flow, the pH, and the sludge recirculation ratio were the same in both of the systems at the beginning of the experiment. In order to change the load (F/M ratio), we modified the flowrate of the influent. After the shift of the load, the reactor was operated for 3 weeks (~3 SRT) to reach the steady-state stage.

The extant kinetic parameters of the biomass were determined by respirometry at each F/M ratio for both of the test-substrates in the SBR and in the CMAS systems respectively. The measured oxygen consumption rate was evaluated by a nonlinear curve fitting by a fourth order Runge-Kutta method. The resulted μ_{max} and K_S values were used to generate specific growth rate values as a function of substrate concentration, and the curves were averaged to estimate the extant kinetic parameter sets of that stage.

SUMMARY

It was verified that the substrate concentration gradient selects the microorganisms and that population gains advantage which have a higher biodegradation rate and/or higher inhibition tolerance capability. These findings explain why staged systems have benefits over parallelly connected ones in the elimination of xenobiotic compounds.

SCIENTIFIC RESULTS (THESIS)

[1.] In order to prepare the raw wastewater for biological treatment, a new neutralization method was developed. The substance of it is that one of the separated industrial wastewaters' pH is set to 12, which results in a well-sedimenting precipitate. After sedimentation the clear supernatant is added to the unneutralized wastewater. The mixing does not initiate further precipitation, and the pH is easily adjustable to the appropriate value.

We verified, that this way the total lime demand was less, the precipitate settled better, the prepared wastewater contained less salt and sulfate ions, than wastewater prepared in conventional way.

[2.] Significant differences were detected in the operation of the differently arranged systems, with the advantage of the serial arrangement in all investigated respects. This system resulted in the most stable operation, the highest tolerance against disturbances, the best effluent quality, and the best processable sludge structure. Since we did not use two of the four settlers of the existing wastewater treatment plant, they are free to be applied for further purposes. The investigations suggested that an optimal rearrangement of the aeration basins may set whole combined aerating-settling units free, which could be used for further utilization.

[3.] The results showed that the various serial reactor arrangement were different in their performance. The advantage of the system with 1+1+3 connection of the bioreactors proved to be the best in most of the aspects investigated, i.e. most stable operation, the highest tolerance against disturbances, the better effluent quality, and the best processable sludge.

[4.] Comparison of three different reactor arrangements, provided information about the effects on the quality of the effluent in case if one of the combined aerating-settling units were set free. The results showed that under normal operation, there where no significant difference performance of the 1+1+3 and 1+1+2 systems. It may be hypothesized that after a verifying full-scale study, one of the combined units could be used for post-treatment purposes.

The results suggest that the two-sludge system with 1+2+2 reactor connection would tolerate the disturbances much less. In case one of the reactors would break down in the first step, the risk of toxicity would increase, whereas an error of a unit in the second step might cause sludge settling problems.

[5.] In order to couple the advantages of the one-sludge and two-sludge systems and to overcome the disadvantages of the two-sludge system we compared different reactor arrangements in a lab-scale field experiment. This experiment resulted in the **patented, <u>modified two-sludge process</u>**. This arrangement keeps that advantages of the conventional two-step biological wastewater treatment process, i.e. in the second step the biomass can grow under low concentration of toxic organic compounds. According to this, sensitive nitrifiers may be retained safely in that step. At the same time this process decreases the risk of inhibition in the first step and allows to denitrify the nitrate produced in the second step. The denitrification basin placed at the entrance of the reactor chain will stabilize the pH due for of the denitrifiers' activity, therefore enough to set the pH value into the 4,5-5,5 range. The comparative 102-day field study verified the advantages of this activated sludge system both in low and in high load circumstances.

[6.] We stated that the effluent of the biological wastewater treatment process needs further treatment in order to meet the regulations.

During the experiments we developed a special system for post-treatment purposes, which contains bioreactors filled with an activated carbon containing textile as a support material for microbial growth. The new process was efficient both regarding COD elimination and stability. Especially good results were obtained with this system in the elimination of the effluent's ammonia content, and in the decolorization and clarification, which is a problem word-wide. Based on the advantages this process also gained patent protection.

[7.] The anoxic/aerobic and the anoxic/anaerobic/aerobic fixed film systems did not significantly confirm the higher costs (i.e. two or three times bigger reactor volumes, etc.); therefore the aerobic reactor was found to be sufficient for post-treatment purposes. This one has also the advantage that the produced nitrate is discharged into the reservoir and thereby inhibits the anaerobic activity relatable to bed smell.

[8.] In the field experiments the raw wastewater contained benzene, toluene, xilene, various chlorophenols, and herbicides, like AD-67 and acetochlor. The undiluted raw wastewater killed all the three (*Daphnia Magna, Scenedesmus obtusiusculus, Zebra Danio*) test-organisms. Through the activated sludge treatment this situation improved in all cases. The effluent originating from the reactor with the submerged material was still above the toxicity limit. Both the one-sludge and two-sludge systems connected with the post-treatment units satisfied the regulations. It can be stated, that the serially connected post-treatment units were effective to eliminate toxic compounds remaining after the activated sludge treatment.

[9.] Kinetic investigations showed that extant kinetic parameter sets of phenol biodegradation changed proportionally to the F/M ratio. It means higher specific growth rate and higher half-saturation coefficient. This caused a higher growth rate at higher substrate concentration. Simultaneously we observed, that at extreme low loading (F/M=2,25) in the SBR the measurable biodegradation rate was lower than that of the CMAS system, where in the selector the F/M ratio was set to 4.5. The consequence is that the change of the parameter set at lower F/M was also proportional to the phenol concentration gradient.

[10.] Extant kinetic parameter sets of isophorone showed, that the population in the CMAS system changed during the experiment. Preceding this change, the isophorone degradation run according to the Andrews kinetics in both types of reactors. The results of SBR and CMAS at F/M=4.5; 9 and 18 ratios referred to the fact that the increased load resulted in increased biodegradation capacity, but only the highest

(F/M=18) ratio provided higher capacity in the SBR than in the CMAS at higher substrate concentrations. All the three parameter sets of SBR contained higher K_I values than the CMAS, showing the higher tolerance against the substrate inhibition.

[11.] The extant kinetic parameter set evaluating at F/M=2,25 ratio, was performed after the microbial changing in the reactors. In these measurements both systems behavior were Monod-like. The CMAS system certified its competitive benefit over the SBR system, when the test-substrate concentration was higher than 0,005 mg/L. This was the opposite of our expectations based on the data published in the literature.

[12.] Based on the kinetic studies performed in the SBR and CMAS systems, it can be concluded that the elimination rate of the target substrates was affected by the concentration gradient of the biogenic substrates in these systems. This can be explained by ability of the biomass to degrade all or most of the biogenic components of the feed, (which represented the bulk of the organic fraction). The concentration gradient of the biogenic feed determined the physiological state of the phenol- and isophorone eliminating microorganisms, and thereby also influenced the degradation rate of these xenobiotic compounds.

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