

5. Scientific Results

Abstract

Under a joint US-Hungarian R&D project financed by the NATO Science for Peace Programme an innovative zeolite modification method and a wastewater treatment technology based on the application of zeolite modified with cation active polyelectrolyte (CAP) were developed between 1999 and 2002 [Kalló et. al., 2000].

In the frame of the R&D work the physical-chemical properties of Hungarian zeolitic rocks were determined, the rock of best quality were pretreated and modified with CAPs of different type and molecular weight. In order to determine the chemical composition and the stability of CAP modified zeolite (CAPMZ), as well as predict its effects on the biological treatment of wastewaters, total organic carbon (TOC), Fourier transform infrared (FTIR) spectroscopic measurements, as well as laboratory and pilot-scale biological degradability tests were carried out.

The data of TOC and FTIR measurements showed that using the patented zeolite modification method 1-3 mg CAP could chemically be attached to the surface of 1 g natural zeolite of 100 µm grain size. The stability test of CAPMZ showed that 92 % of the CAP-zeolites bonds remained stable at even pH 9 after 3 days. The laboratory tests showed that CAPMZ suspended in wastewater decreased the reaction order and increased the reaction rate of the biological oxidation of organic matters by 20 – 30%.

The pilot- and industrial-scale experiments, in harmony with the laboratory ones, employing CAPMZ resulted in significantly better effluent water quality, and verified that CAPMZ additive was capable to reduce the operational costs of wastewater treatment plants (WWTP) and increase their capacity expressed in chemical oxygen demand (20-50%), ammonical-nitrogen removal (40-60%), phosphorous removal (15-25%) and suspended solids removal (30-40%). The best results belonged to the zeolitic rock of powder size (grain size < 100 µm) modified with the acidic solution of a Polyacrylamine type CAP, the molecular weight of which was 50,000.

Keywords

Zeolite, wastewater, biological wastewater treatment, biological degradability, analysis

Introduction

The most often used wastewater treatment (WWT) method is the aerobic biological one, in which the organic and inorganic pollutants are decomposed and converted to gases and cell tissue by bacteria in the presence of oxygen. The culture of bacteria forms a living, so called activated sludge. The capacity and the loadability of WWTPs considerably depend on the activity and settling characteristics of the activated sludge. These sludge parameters however, can be improved with the addition of zeolite particles into the raw wastewater.

Zeolite particles are excellent carriers of bacteria and substrates. Since both oxygen and the adsorbed substrates are accessible in high concentrations for bacteria immobilized on the zeolite particles, the decomposition rate of organic compounds becomes higher. Since the specific gravity of bacteria flocs containing zeolite is higher than that of usual flocs, the settling rate of the waste sludge is higher [Kiss et. al., 1984, 1988; Kalló, 1995].

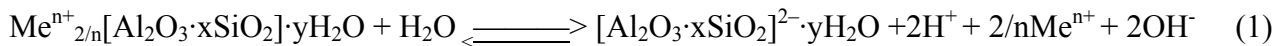
Application of a natural zeolite, in spite of the advantageous effects, has a significant drawback. The zeolite additive becomes effective only after 5 - 7 days. This can be explained by the slow or inhibited biopolymer production of bacteria, since bacteria attach to the zeolite particles through their biopolymer chains.

In this project, a novel zeolite modification method and a wastewater treatment technology (WWTT) have been developed in order to accelerate and improve the zeolite - bacteria interaction, as well as increase the loadability of WWTPs, improve the quality of treated water and decrease the investment and operation costs of WWTPs.

Theory

The zeolite modification process and the beneficial effects of CAPMZ can be explained by the followings:

- Natural zeolites dissociate in aqueous media due to their ion exchange properties resulting in free negative lattice charges on their surface (see Reaction equation 1). Positively charged ions and particles in the aqueous phase begin to compete for the negatively charged sites of the zeolite lattice.



where Me: Na, K, Mg, Ca
 x:> 2 (depend on zeolite type)
 y: 1-8 (depend on zeolite type)

- The surface charge of bacteria is also negative in aqueous phase. It is well-known that particles of same charge repulse each other, therefore the adsorption of bacteria on the zeolite surface is hindered. The fact that the zeolite-bacterium bond is formed can be attributed to the extracellular polymers (ECP) produced by the bacteria, since the ECP molecules support positive charges and can bridge the bacteria and the zeolite surface. However, the biopolymer production is a slow process, which is inhibited by toxic effects.
- If positively charged cationic polymers are bonded to the zeolite particles having negative surface charges, the CAP molecules are able to bind the bacterium flocs to themselves and to bind to the zeolite in a prompt reaction by their remaining free positively charged groups. This means that the slow and uncertain ECP production of bacteria is not allowed to control the fixation of bacteria on zeolite.
- The CAP molecules attached to zeolites particles change the sorption characteristics of zeolite, because its cation exchange capacity are partly converted to anion exchange capacity, i.e., CAPMZ can adsorb not only cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Hg^{2+} , Cd^{4+} , Pb^{4+} , Cr^{6+} , $\text{NH}_4\text{-N}$, other organic and inorganic cations), but anions (Cl^- , Br^- , I^- , NO_3^- , PO_4^{3-} , other organic and inorganic anions), as well.

The CAPMZs patented earlier are the physical mixture of zeolite, CAPs and other materials (Gerhard, 1990; Heinzl and Papp, 1994; Nagan and Island, 2001). The zeolite-CAP mixture however, is not stable enough in aqueous media As a consequence of the weak physical absorption, CAP molecules easily remobilise from the zeolite surface. It means that the lifetime of the zeolite-CAP product is short in aqueous phase, therefore only the aqueous suspension of zeolite and CAP are present in aqueous suspension. Consequently there is no joint zeolite-CAP effect (Kalló et. al., 2000).

Experimental

The R&D programme was implemented in seven steps. These and the applied analytical, as well as experimental methods were as follows:

1. Investigation and selection of natural zeolites
 The physical-chemical properties of Hungarian zeolites (mineral composition, zeolite content, cation exchange capacity, Si/Al ratio) were determined, and based on the properties two zeolites containing clinoptilolite at least in 50% were selected.
2. Pre-treatment of zeolites selected

- *Mechanical treatment*
The zeolite bearing rocks were ground and the sieve fractions < 100 μm was selected.
- *Conversion to H^+ -form at room temperature*
10 g of mechanically treated zeolite was suspended in 200 ml of 0.5 normal HCl solution. The suspension was intensively stirred for 1 hour, thereafter decanted and the solid phase was washed with ion-free water until the pH of the liquid phase increased up to 6. (This is called: Acidic I treatment.)
- *Specific surface increasing and conversion to H^+ -form*
10 g of mechanically treated zeolite was suspended in 200 ml of 0.5 normal HCl solution. The suspension was heated and refluxed at the temperature of boiling point for 1 hour. Thereafter the suspension was decanted and the solid phase was washed with ion-free water until the pH of the liquid phase increased up to 6. (This is called: Acidic II treatment.)
- *Conversion to NH_4^+ -form*
10 g of mechanically treated zeolite was suspended in 200 ml of aqueous solution of 0.5 normal NH_4Cl at room temperature. The suspension was intensively stirred for 1 hour, thereafter decanted and the solid phase was washed with ion-free water until the $\text{NH}_4\text{-N}$ concentration of the liquid phase became < 0.05 mg/L. (This is called: NH_4Cl treatment.)

3. Modification of the pre-treated zeolites

The pre-treated zeolites were treated with CAP products commercially available on the market. The basic characteristics of the applied CAPs containing quaternary ammonium or amino groups were as follows:

- a. Polyacrylamine (Poly-2-hydroxypropyl-N,N-dimethyl ammonium chloride), molecular weight 10,000, 50,000, 250,000 (Cytec, Inc., USA, trade-marks: C567, C573, C581)
- b. Polydiallyl dimethyl ammonium chloride (Poly-DADMAC), molecular weight 500,000 (Cytec, Inc., USA, trade-mark: C591)
- c. Polyacrylamide, molecular weight 1,000,000 (Cytec, Inc., USA, trade-mark: C610)

Variables of zeolite modification experiments were the followings:

- Type of zeolite (grained and powdered Zeotrade and Geoproduct-BBC clinoptilolite)
- Type of zeolite pre-treatment (Acidic I, Acidic II and NH_4Cl treatment)
- Type and molecular weight of CAP
- CAP/zeolite ratio* [total ion exchange capacity (IEC), surface lattice IEC, surface lattice IEC/2, surface lattice IEC/3, surface lattice IEC/4]

*Calculation of the CAP/zeolite ratio was based upon the IEC of zeolite and the equivalent weight of CAP molecules. It was considered that CAPs could not connected to the inner lattice points of zeolites (size problem), i.e., only the surface charge was reachable for CAPs, which is practically 10 - 15 % of the total IEC.

The process of modification was as follows: 10 g of pre-treated zeolite was suspended in 50 ml of tap water. In parallel experiments 4.00 g, 0.40 g, 0.20 g, 0.13 g or 0.10 g of aqueous solution of CAP of 50 % were given to the suspension at room temperature. After one hour intensive mixing the suspension was settled, decanted and washed with organic carbon (OC)-free water.

4. Quantitative and qualitative characterization of CAP-zeolite bond-strength

- *Determination of the chemically bound CAP content of zeolites modified*

Quantity of the chemically bound CAP content of CAPMZs was determined in the form of organic carbon by TOC measurements. CAPMZs were washed through with TOC-free water to remove the mechanically adhered CAP molecules. Thereafter the TOC of the “unwashable” CAP content of CAPMZs was determined.

CAPMZ treatment was as follows: 1g of CAPMZ was suspended in 1 litre of TOC-free water. After 1-hour intensive mixing, the suspension was settled and decanted. The above treatment of washing was repeated 5 times. Before TOC measurement the CAPMZ was dried at room temperature.

- *Bond strength examination*

The type and strength of bond between zeolite and CAP were examined by Fourier transform IR spectroscopy.

Description of the experiment is as follows: 10 g of CAPMZ was suspended in 10 ml of paraffin oil. The IR spectrum of the suspension was determined in the 4000 – 500 cm^{-1} wave number range, applying 4 cm^{-1} optical resolution.

- *Stability test of the zeolite-CAP bond*

Examinations on CAPMZ stability were as follows: 130g of CAPMZ containing 2.6 $\text{mg}^{\text{“unwashable”TOC}}/\text{g}_{\text{zeolite}}$ was suspended in 1 litre of TOC-free water. The suspension was intensively stirred and TOC concentration in the aqueous phase, directly proportional with the quantity of remobilized CAP content, was measured as a function of pH (pH: 4.5, pH: 7.1, pH: 9.1) and time (0.5 - 72 hour).

5. Laboratory experiments

- In order to determine which modification technology and CAP result in best effluent quality, biological degradability and sludge settling tests were done in a batch reactor of 2 L. The activated sludge concentration of a synthetic wastewater samples were adjusted to 3 g/L. In parallel experiments CAPMZs of different type were added to the wastewater - activated sludge (AS) mixtures in 100 $\text{mg}_{\text{CAPMZ}}/\text{g}_{\text{AS}}$ concentration, then the samples were aerated. After 3-, 6- and 9-hour aeration COD, $\text{NH}_4\text{-N}$, Kjeldahl-N and $\text{NO}_3\text{-N}$ analyses were done, as well as the suspended solid concentration and the sludge volume index (SVI) were determined.
- The interaction between CAPMZ and AS was examined with light microscope. Microscopic pictures were taken from zeolite-activated sludge-wastewater and CAPMZ-activated sludge-wastewater systems in five minutes following the zeolite and CAPMZ addition. The sludge and the zeolite/CAPMZ concentrations were 3 $\text{g}_{\text{AS}}/\text{L}_{\text{wastewater}}$ and 120 $\text{mg}_{\text{CAPMZ}}/\text{g}_{\text{AS}}$ in both cases.
- In order to determine the effect of CAPMZ on carbonaceous biochemical oxygen demand (CBOD) and nitrogenous biochemical oxygen demand (NBOD), oxygen requirement of a communal wastewater was tested in the presence of CAPMZ. The control samples did not contain CAPMZ. During the CBOD measurements, nitrification was suppressed with a nitrification inhibitor that was added both to the CAPMZ containing and the control samples. Measurements were accomplished according to the Standard Methods (19995). DO concentration of the samples were measured with an oxygen membrane electrode) after 1-, 2-, 4-, 5-, 6-, 8- and 10-day incubation. Wastewater sample was taken at the WWTP of Szob. The $\text{NH}_4\text{-N}$ concentration of the wastewater was 11.5 mg/L, the applied CAPMZ concentration was 50 mg/L.

- In order to determine the effect of CAPMZ on the reaction rate and order of biological oxidation, the mixture of a wastewater sample and AS originating from the WWTP of Dunakeszi was aerated in a batch reactor of 50 L. The AS concentration in the sample was 3 g/L. In parallel experiments CAPMZ was added to the wastewater-activated sludge mixture in 0.1 g_{CAPMZ}/g_{AS} concentration. The COD, BOD₅ and NH₄-N concentration in the control and CAPMZ samples were determined after 0-, 0.5-, 2.5-, 5-, 10-, 13-, 16.5-, 20-, 24- and 30-hour aeration.
- In order to examine the relationship between the applied CAPMZ concentration and the effects of CAPMZ on the effluent water quality and sludge settling properties, continuous laboratory experiment were carried out with and without CAPMZ.

An innovative respirometer was developed for modelling the operation of biological WWTPs consisting of an aeration tank and a secondary clarifier. The respirometer operation was based on conducting oxygen in a closed system at constant pressure through the wastewater examined. Oxygen consumed by the biological system was continuously measured, so that an oxygen flow equivalent to that consumed was electrochemically generated. Carbon dioxide produced by the biological system was bound in an alkaline gas washer. The parameters of experiments (flow rate, hydraulic detention time, biological loading, sludge concentration, sludge age, recirculation rate, excess sludge removal) set on the respirometer were calculated on the basis of the operational data of the WWTP of Szob.

Description of continuous laboratory experiment is as follows: 2,000 ml wastewater containing 6 g AS and 600 mg CAPMZ (10% CAPMZ related to the sludge content) was poured into the biological reactor of respirometer. The reactor was continuously aerated and fed with raw wastewater containing CAPMZ in 50 mg/L concentration. The feeding rate of the raw wastewater and the rate of recirculation was set to 4,000 ml/day (12-hour detention time) and 100%, respectively. After the starting-up period of 24-hour, the sludge removal was set to 1 g/day, and the oxygen consumption of the biological system, the quality parameters of effluent water were determined, as well as the sludge sedimentation was examined. The experiments were carried out with different CAPMZ concentrations and without CAPMZ. The other applied CAPMZ concentrations were as follows: 2% (120 mg_{CAPMZ} + 10 mg_{CAPMZ}/L), 3% (180 mg_{CAPMZ} + 15 mg_{CAPMZ}/L), 5% (300 mg_{CAPMZ} + 25 mg_{CAPMZ}/L), 8% (480mg_{CAPMZ} + 40 mg_{CAPMZ}/L), 12% (720mg_{CAPMZ} + 60 mg_{CAPMZ}/L)

For the better understanding of experimental parameters it should be mentioned that the purpose of continuous CAPMZ supply (mg/L) of the biological reactor was to ensure the constant CAPMZ concentration during the experiment, i.e., to make up the CAPMZ removed with the surplus sludge from the reactors.

6. Pilot- and industrial-scale experiments

The WWTP using CAPMZ (trade name: ZeoRap[®]) were installed and set to work at twelve Hungarian WWTPs. This report introduces the WWTP of Szob and the experiments accomplished at the WWTP of Szob.

WWTP of Szob

The WWTP is located in the southern part of Szob city, on the east bank of the Danube. The process flow diagram and the main technical data of the WWTP are shown on Figure 1 and summarized in Table 1. The WWTP had two individual cleaning lines during the experiments. The “ZeoRap line” applied the ZeoRap[®] technology, while the other one served as a control line. To evaluate the effects of ZeoRap[®], water and sludge quality data of the ZeoRap line were compared to data of the control line. Calculation of the

CAPMZ (ZeoRap[®]) demand of a 3-month experimental operation is shown in Table 2. (The total duration of the experiments was 10 months.)

The influents of the WWTP frequently causes water and sludge quality problems primarily during the fruit processing season in the fall. During this period the effluent COD generally exceeds the standard value (75 mg/l) and the SVI is usually higher than 100 ml/g indicating poor settling.

The experiments started on March 30, 2001 and were completed on January 14, 2002. The applied ZeoRap[®] concentration was between 5 % and 10 % (percentile values are expressed in $\text{g}_{\text{ZeoRap}}/\text{g}_{\text{AS}} \times 100$ units).

Wastewater and sludge samples were taken twice a week. Daily average water samples were collected from the influent and from the effluent of ZeoRap and control lines. Sludge samples were taken from both aeration tanks and recirculation systems. (The sampling places are shown on Figure 1.)

Water samples were analyzed for pH, COD, filtered COD (COD_f), BOD_5 , TOC, $\text{NH}_4\text{-N}$, Kjeldahl-N, $\text{NO}_3\text{-N}$, total-P and suspended solids (SS). The quality parameters of sludge analysis were the followings: (1) sludge concentration and sedimentation in the aeration tank, (2) sludge concentration and sedimentation in the recirculation system, (3) excess sludge concentration and organic content, (4) daily quantity of excess sludge.

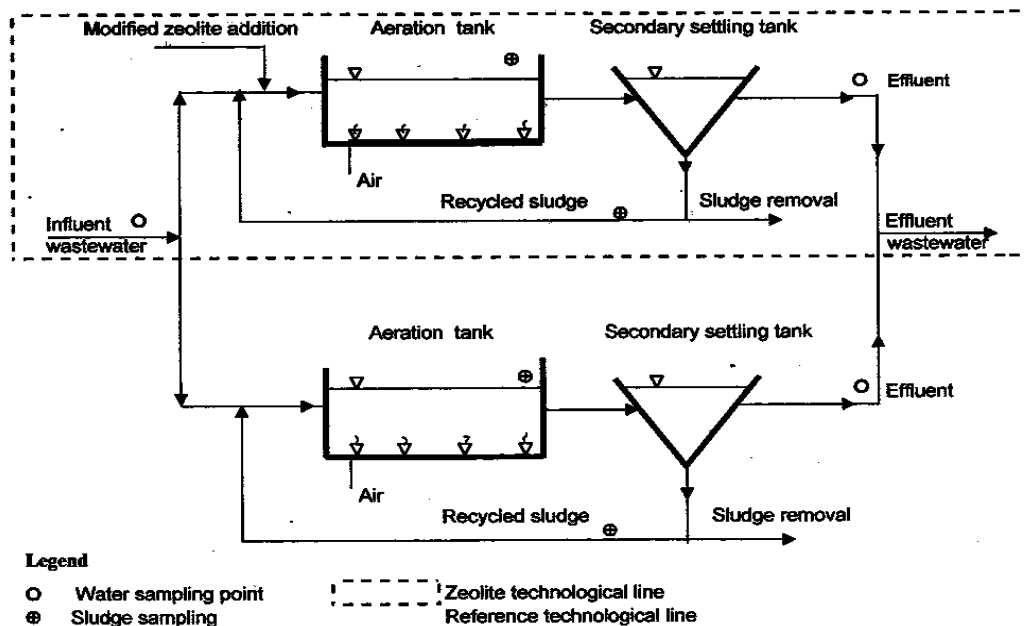


Figure 1: Process Flow Diagram of the WWTP of Szob

Table 1: Technical Data for the WWTP of Szob

Character of influent wastewater:	Domestic and food industrial (fruit processing)
Total hydraulic capacity of WWTP:	1,000 m ³ /day
Volumetric capacity of ZeoRap technological line:	500 m ³ /day
Volumetric capacity of control technological line:	500 m ³ /day
Technical specifications of both technological lines:	
• Volume of aeration tank:	470 m ³
• Dry sludge concentration in the aeration tank:	~ 4.3 kg/m ³
• Dry-sludge quantity in the aeration tank (G_A):	~ 2,021 kg

• Volume of secondary clarifier:	235 m ³
• Dry sludge concentration in the secondary clarifier:	~10,6 kg/m ³
• Dry-sludge quantity in the secondary clarifier (G _S):	2,491 kg

Table 2: Calculation of ZeoRap Demand of a 3-month Experimental Operation at Szob

ZeoRap demand to increase the CAPMZ content of the AS up to 5%: (G _A) + (G _S):= ~ 2,021 kg + ~ 2,491 kg = ~ 4,512 kg	225 kg
ZeoRap demand to keep 5% CAPMZ concentration	7 kg/day
Daily ZeoRap removal with the excess sludge = 140kg sludge removal x 5%	210 kg/month
ZeoRap demand to increase the CAPMZ content of the AS from 5% to 8 %:	135 kg
ZeoRap demand to keep 8% CAPMZ concentration	11.2 kg/day
Daily ZeoRap removal with the excess sludge = 140kg sludge removal x 8%	336kg/month
ZeoRap demand to increase the CAPMZ content of the AS from 8% to 10%:	90 kg
ZeoRap demand to keep 10% CAPMZ concentration:	14 kg/day
Daily ZeoRap removal with the excess sludge = 140kg sludge removal x 10%	420 kg/month
Total ZeoRap demand = (225kg + 210 kg + 135 kg + 336 kg + 90 kg + 420 kg)	1,416 kg.

7. Manufacturing of modified zeolites

A semi-industrial equipment for producing CAPMZ was developed.

Results and Discussion

a. Selection and Investigation of Natural Zeolites

Natural zeolites occur throughout Hungary in volcanic origin regions. Zeolites are thus found near Dunabogdány in the Velence Mountain, in the Balaton highlands, in the Eastern Mecsek Mountains and in the Zemplén Mountains in large quantities. Analcime, chabazite and stilbite as crystals of mm size are found in vesicles of basalts in Dunabogdány (Csódi hill), 30 km north of Budapest [Koch 1871; Schafarik 1884].

Extended mineralogical, physical, chemical and genetic investigations of these occurrences were summarized recently [Tóth et. al., 1999]. Similar traces of analcime, chabazite, dachiardite, epistilbite, heulandite and stilbite appear in the volcanic rocks of Visegrád mountains and Southern Börzsöny mountains, i.e., within ten kilometers of the Csódi Hill. In spite of attractive habits of these natural zeolite occurrences, the amounts are negligible and cannot be taken into account for large-scale applications.

In the Velence mountains (Nadap) (50 km southwest of Budapest) gmelinite, stilbite, epistilbite and laumontite are found mainly as inclusions; in the Highland of northern shore of Balaton (Haláp, Gulács) some heulandite, scolecite, mesolite, thomsonite inclusions could be identified [Pécsi-Donáth, 1984].

Sediments containing clinoptilolite and mordenite comprise essentially larger quantities. In the Eastern Mecsek mountain (Morágy Hill) (South Hungary). Miocene rhyolite and dacite tuffs were zeolitized by weathering resulting in formations of clinoptilolite and subordinate amount mordenite [Hamor, 1978; Ravasz-Baranyi, 1973].

In some cases chabazite overgrowths on clinoptilolite were observed. Due to low concentrations and mostly deep location of relatively thin layers, these zeolite occurrences are of subordinate importance for production [Puzder and Badinszky, 1962 and 1963]. Smectite (clay mineral) and clinoptilolite (zeolite mineral) occur together due to geochemical reasons, the applicability of their mixture was, therefore, suggested [Máthé et. al., 1997].

Sedimentary zeolites, but in essentially larger amounts and higher concentrations near to the surface were discovered in the Bükk and Zemplén Mountains (Northeast Hungary). Nemez and Varjú (1962 and 1963) reported first clinoptilolite occurrences in Tokaj mountain where volcanic tuffs

were hydrothermally transformed to zeolite. Later mordenite containing layers were also discovered similarly near to the surface in the same region [Papp et. al., 1975].

Detailed investigations were carried out with clinoptilolite (from Rátka) and mordenite (from Bodrogkeresztúr) [Pécsi-Donáth and Nagy, 1988]. The largest layers of sedimentary zeolites (clinoptilolite and mordenite) cover several ten square kilometers of different thickness and composition in Zemplén Mountain.

The rocks of the highest zeolite content are quarried in the area of three villages, Mád, Rátka, and Bodrogkeresztúr, about 10 km east of the famous wine production center Tokaj. Clinoptilolite is mined mainly in the district of the first two villages, while mordenite rich tuffs near to Bodrogkeresztúr.

Occurrences of zeolite containing rocks in Hungary are shown in Figure 2.

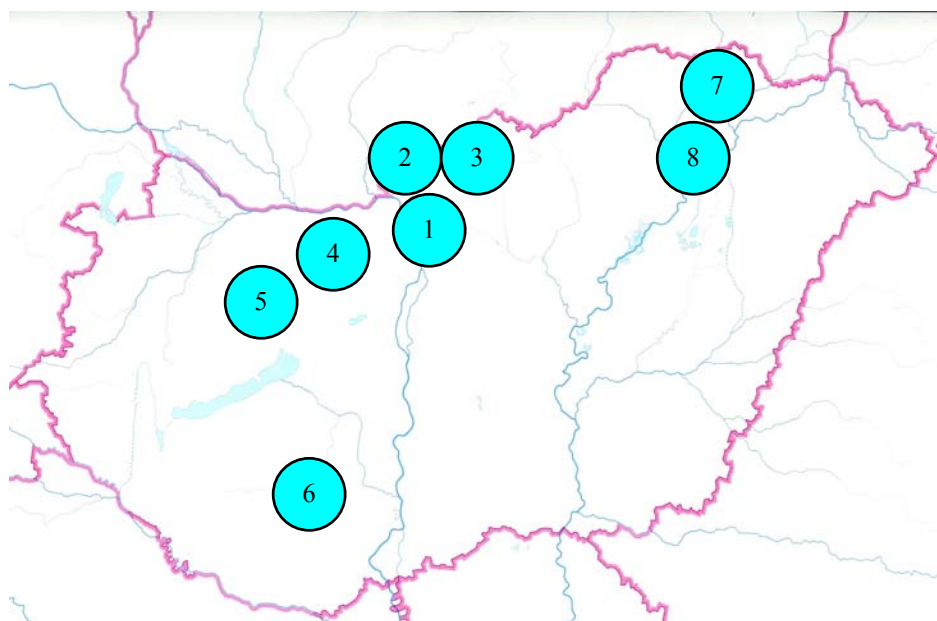


Figure 2
Map of Hungarian Zeolite Occurrences

1. Csódi hill
2. Visegrád mountains
3. Börzsöny mountains
4. Velence mountains
5. Balaton highland
6. Mecsek mountain
7. Zemplén mountains
8. Tokaj mountain

Characteristic data of typical clinoptilolite and mordenite containing rocks (or more precisely: rhyolite tuffs) in this area are given in Table 3. The overall chemical composition relates to the rock, similarly the ignition loss, which corresponds to the water content. The IEC was determined by exhaustive exchange for NH_4^+ carried out in 2 M solution of NH_4NO_3 for 4x4 hours under refluxing. Each time 400 ml fresh solution was added to 100 g powdered rock. During heating up to 700 °C NH_3 desorbed from the ion exchanged sample containing the zeolite in NH_4 -form. The amount of described ammonia was determined and related to 1 g rock providing the IEC in meq/g_{rock}.

Zeolite contents were calculated from CO_2 adsorption at room temperature on deammoniated, i.e., heat treated samples, when the dehydrated zeolites are present in H-form. Under such conditions CO_2 adsorption takes place exclusively in zeolitic pores and the adsorption on the external surface of embedded zeolite crystals influenced by their size is negligible as well as the adsorption on other mineral constituents like quartz, cristobalite, montmorillonite, volcanic glass, etc. (see Table 5). The adsorption capacity ($a_{0,\text{ref}}$) of pure clinoptilolite is 2.88 mmol/g, that of pure mordenite 3.43 mmol/g. Zeolite contents are equal to $a_0/a_{0,\text{ref}}$ ratio.

Clinoptilolite containing rock from Rátka was crushed and the composition of 0.5 - 2 μm clinoptilolite crystals embedded in the rock was determined by Energy Dispersive X-ray microanalysis (EDAX) in Scanning Electron Microscope (SEM). Similarly mordenite containing rock from Mád-Harcsa was analyzed. The embedded mordenite needles are of 0.5 \times 5 μm average size. The composition of zeolite phases is summarized in Table 4.

These values correspond to the IEC found for pure zeolites, i.e., 2.2 and 2.3 meq/g_{Na-zeolite} for clinoptilolite and mordenite, respectively (see later). It should be remarked that clinoptilolite phase

does not contain either sodium or magnesium whereas in mordenite magnesium is absent.

Two companies are mining in the considered zeolite fields. (1) Zeotrade, Ltd., which produces yearly several thousand tons clinoptilolite and mordenite containing rocks of different grain size. The other company (2) Geoproduct, Ltd. quarries clinoptilolite containing rocks in Rátka (marked BBC), Mád-Suba (MSC) and mordenite in Bodrogkeresztúr (MHZ). The actually accessible fractions < 100 µm required in ZeoRap technology were investigated in detail.

X-Ray powder Diffraction (XRD) patterns were recorded for five samples: Zeotrade clinoptilolite, Zeotrade mordenite., Geoproduct BBC-clinoptilolite, MSC-clinoptilolite, and MHZ-mordenite.

The crystalline constituents of the quarried products were semi-quantitatively determined. The excess missing is amorphous volcanic glass as not crystallized parent material, which could obviously not be detected by XRD. The mineralogical composition of product samples as determined with XRD are listed in Table 5.

Thermal analysis of NH_4^+ exchanged samples was performed. The samples were heated with a rate of 10 °C/min up to 1,000 °C and the curve of weight loss (TG), its derivative (DTG) and heat effects reflected by DTA curve were determined. Endothermic peaks were observed on DTA curves at 170-200 °C due to the fastest loss of physically adsorbed water the desorption of which continued till 500 °C. The weight loss till 500 °C (Δw_{500} in Table 6) corresponds to the total amount of physically adsorbed water. Upon heating between 500 and 1000 °C a monotonous weight loss (decrease of TG curve) is attributed to the deammoniation and dehydroxylation, i.e., the removal of (acidic) OH-groups generated by evolution of ammonia (Δw_{1000} in Table 6). For Zeotrade mordenite an exothermic peak appeared at 300 °C the origin of which may be burning of organic impurities or nitrate decomposition. The corresponding weight loss was considerable; Δw_{500} in this case is much greater than the value owing to the water content.

Δw_{500} was related to the water content (w_z) of pure Na-clinoptilolite, 15.8 wt %, or to that of pure Na-mord, 12.3 wt % (Table 6). The calculated values involve, however, the water adsorption capacity not only of zeolite, but also of other constituents, too.

NH_4^+ IECs were determined as described before and related to that of pure zeolites (IEC_{ref}): 2.2 meq/g for pure clinoptilolite produced by Hector (USA), and 2.3 meq/g for pure mordenite product of Norton Co., (USA), in order to follow the zeolite content of samples or to supply IEC in equivalent zeolite amount. The zeolite contents are overestimated in this way, too, since other aluminosilicates present in the rock may also be responsible for IEC.

The adsorbed amount of CO_2 at saturation of zeolite pores (a_0) was determined as shown before. Values of a_0 were related to that of pure clinoptilolite, 2.88 mmol/g, and to that of mordenite 3.43 mmol/g. The zeolite contents determined in this way are the most reliable.

The results of investigation of zeolites produced in large scale in Hungary can be summarized as follows:

- The clinoptilolite content of the products of Zeotrade and Geoproduct companies are 50-60 wt %; other compositional characteristics seem also suitable. Any of them can be applied in wastewater treatment
- Zeotrade mordenite is of acceptable quality, too, however an exothermic decomposing component makes the application questionable.
- MSC clinoptilolite and MHZ mordenite of Geoproduct are of poor quality
- Zeotrade, clin and the Geoproduct, BBC-clin should be used for further experiments

Table 3: Composition of Some Typical Clinoptilolite and Mordenite Containing Rocks from Hungary

Sample		Oxide composition (wt %)									Ignition loss	Ion exchange capacity	Zeolite content
Type	Origin	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	TiO ₂	MnO	wt %	meq/g	wt %
Clin	Mád, Suba	74.38	11.88	1.24	0.48	1.68	1.11	1.12	0.31	-	6.00	0.65	25
Clin	Sátoraljaújhely	74.81	9.13	1.63	0.87	2.03	0.10	2.53	0.10	-	7.37	1.07	57
Clin	Mád, Suba II	71.56	12.14	1.17	0.78	2.45	1.55	1.75	0.31	-	6.85	1.19	56
Clin	Mád, Rátka	72.41	10.42	1.21	0.25	2.18	0.90	3.23	0.10	0.40	8.90	2.03	69
Mord	Bodrogkeresztúr	77.83	9.76	0.77	0.92	3.80	0.40	1.75	0.10	0.43	4.26	0.72	36
Mord	Bodrogkeresztúr	72.86	11.01	0.98	1.35	5.45	0.15	1.69	0.11	-	5.93	0.74	36
Mord	Újhuta	68.07	14.75	1.20	1.50	1.65	0.52	2.02	0.08	0.32	8.80	1.16	52
Mord	Mád, Harcsa	71.16	10.75	0.85	1.27	2.66	0.28	1.85	0.08	0.26	10.84	1.34	61

Legend: Clin: clinoptilolite Mord: mordenite

Table 4: Atomic Ratios (M/Al) in Clinoptilolite and Mordenite Embedded in Zeolitic Rock

Element	Clinoptilolite phase	Mordenite phase
Si	6.10	5.34
Al	1.00	1.00
Fe	0.07	0.08
Na	0.00	0.33
K	0.30	0.11
Mg	0.00	0.00
Ca	0.40	0.28

Table 5: Content of Crystalline Components in Zeolitic Rocks Produced in Large-scale

Sample	Crystalline component, wt %					
	Clin	Mord	Montmorillonite	Smectite	α-Cristobalite	Quartz
Zeotrade, clin	50	2-5	< 10	-	-	-
Zeotrade, mord	2-5	40	15	≈ 10	-	-
Geoproduct, BBC-clin	60-70	-	10-15	5-10	-	-
Geoproduct, MSC-clin	20	< 5	≈ 5	-	≈ 10	-
Geoproduct, MHZ-mord	1-2	< 20	≈ 10	≈ 20	≈ 10	-

Legend: Clin: clinoptilolite Mord: mordenite

Table 6: Main Characteristics of Zeolite Samples of Large-scale Production

Sample	$\Delta w_{500}^{(a)}$ %	$\Delta w_{1000}^{(b)}$ %	IEC meq/g	$a_o^{(c)}$ mmol/g	Zeolite content, %		
					$\Delta w_{500}/w_z$	IEC/IEC _{ref}	$a_o/a_{o,ref}$
Zeotrade, clin	8.5	10.0	1.47	1.38	54	67	48
Zeotrade, mord	12.6	14.9	1.15	1.47	-	50	43
Geoproduct, BBC-clin	10.0	11.8	1.45	1.63	63	66	57
Geoproduct, MSC-clin	9.6	12.1	0.60	0.61	61	27	21
Geoproduct, MHZ-mord	5.5	21.7	0.80	0.76	45	35	22

Legend: Clin: clinoptilolite • Mord: mordenite • IEC: Ion exchange capacity • ^(a): loss of weight up to 500 °C

^(b): loss of weight up to 1000 °C • ^(c): saturation adsorption capacity of H-forms for CO₂; H-forms are produced by deammoniation of ammonium exchanged samples

b. Quantitative and Qualitative Characterization of CAP-zeolite Bond-strength

Determination of the Chemically Bound CAP Content of Zeolite Modified

The TOC data of natural and pre-treated Geoproduct BBC clinoptilolite modified with Polyacrylamine (molecular weight: 50.000) are summarized in Table 7 and illustrated on Figure 3.

Table 7: Effect of Zeolite Pre-treatment on Strongly Attached CAP Content of Modified Zeolite

Type of zeolite and treatment with CAP	“Unwashable” TOC content of CAPMZ (mg _{TOC} /g _{zeolite})					
	2.18	2.20	2.30	2.34	2.40	2.40
Natural zeolite (background TOC)	2.18	2.20	2.30	2.34	2.40	2.40
Natural zeolite + CAP (Mixture)	1.85	2.17	2.10	2.19	2.11	2.11
H-form zeolite + CAP (Acidic I treatment)	1.85	4.09	4.49	4.60	4.68	4.70
H-zeolite (increased specific surface) + CAP (Acidic II treatment)	1.55	2.97	3.76	4.08	4.18	4.23
NH ₄ -zeolite + CAP (NH ₄ -Cl treatment)	1.67	3.79	4.35	4.45	4.56	4.56
CAP/zeolite ratio during modification (mg _{CAP solution} /g _{zeolite})	0	10	20	40	200	400

The data show that

- CAP molecules could not strongly be attached to the natural zeolite (There was no “unwashable” TOC-increase on the zeolite, moreover the natural zeolite partly lost its background TOC content due to washing.),
- if the zeolite was in H- or NH₄-form the “unwashable” TOC-increase ranged between 1.9 and 2.9 mg_{TOC}/g_{zeolite}, i.e., max. 2.9 mg CAP could chemically be immobilized on the surface of 1 g natural zeolite of 100 μm grain size,
- the modification of zeolite pre-treated with cold HCl resulted in CAPMZ of highest CAP content (This CAPMZ was used for further experiments),
- acidic I (high temperature) treatment decreasing the IEC of natural zeolite resulted in poorer quality CAPMZ,
- the optimal CAP/zeolite ratio of modification was 20 mg_{CAP solution}/g_{zeolite}.

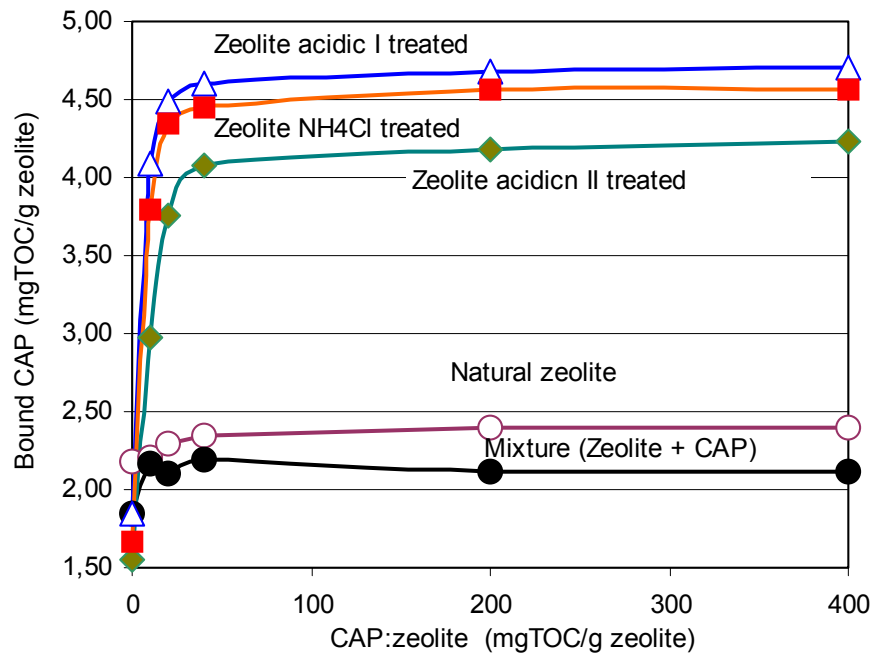


Figure 3: CAP Content of Modified Zeolite as Function of Zeolite Pre-treatment and CAP-Zeolite Ratio Applied during Modification

Bond-strength Examination

The IR spectrums of a natural zeolite and CAPMZs, regardless of their CAP content, showed fairly similar picture. To identify the hidden adsorption bands, the second derivative of the IR spectrums were plotted and evaluated.

The characteristic adsorption bands and the second derivative of the IR spectrums in the 1180 – 950 cm^{-1} wave number range, in the case of a Hungarian natural zeolite and three different CAPMZs, are shown in Table 8 and Figure 4. The data show that CAP molecules changed the asymmetric vibrations caused by the Al-O-Si and Si-O-Si bonds among tetrahedrons of zeolite, i.e., the interaction between zeolite particles and CAP molecules should be stronger than a physical adsorption.

Table 8: Adsorption Bands of Natural and Modified Zeolites

Sample	Adsorption bands		
	3700-3200 cm^{-1}	1 st group	2 nd group
Natural zeolite	3740, 3637, 3555, 3406, 3220	1210, 1155, 1137 (doublet)	1075, 1026, 1008 (doublet)
CAPMZ 10 $\text{mg}_{\text{CAP}}/\text{g}_{\text{zeolite}}$	3740, 3637, 3555, 3400, 3196	1212, 1155, 792, 725, 600	1073, 1054, 1034 (triplet)
CAPMZ 20 $\text{mg}_{\text{CAP}}/\text{g}_{\text{zeolite}}$	3636, 3555, 3400, 3200	1210, 1153, 789, 720, 598	1076, 1032 (doublet)
CAPMZ 40 $\text{mg}_{\text{CAP}}/\text{g}_{\text{zeolite}}$	3638, 3554, 3400, 3200	1212, 1157, 789, 723, 598	1086, 1069, 1031, 969

Stability Test of Zeolite-CAP Bond

The TOC data of stability tests are summarized in Table 9 and Figure 5. Taking into consideration that the total remobilisation of the all quantity of CAP attached to zeolite would increase the TOC concentration of filtered samples up to 338 mg/L , it can be stated that more than 90 % of the CAP-zeolite bonds remained stable at even pH 9 after 3 days. Since the pH of communal wastewaters is always below 9, the zeolite-CAP connection can be considered stable in the process of biological wastewater treatment.

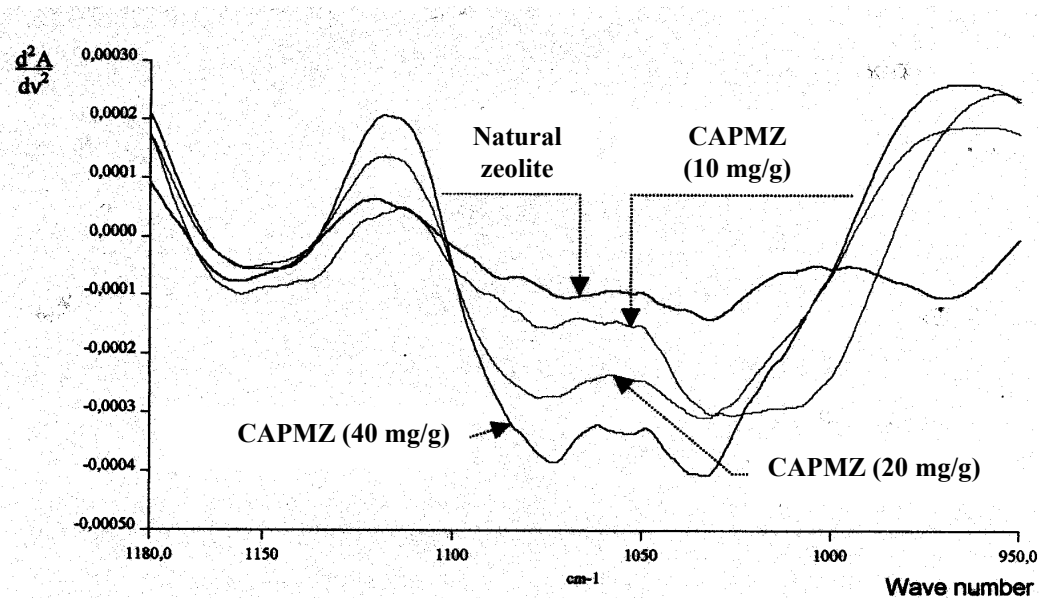


Figure 4: Second Derivatives of the Absorbency of Natural and Modified Zeolites as a Function of Wave Number

Time of treatment (hour)	TOC concentration in the aqueous phase (washed out CAP)		
	pH=4.5	pH=7.1	pH=9.1
0.5	1.1	1.1	1.8
1.0	1.5	1.6	2.5
3.0	4.6	6.3	10.0
5.0	7.5	9.2	14.2
8.0	9.2	13.4	15.9
24.0	10.7	15.9	18.8
48.0	13.6	16.0	23.2
72.0	14.5	18.8	25.9

Note: 13 g CAPMZ suspended in 1 L water

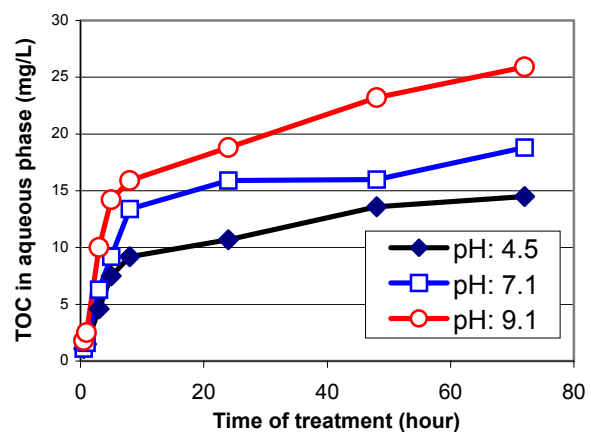


Table 9: Immobilization of CAP Molecules from CAPMZ as Function of Time and pH

Figure 5:

c. Laboratory Experiments

Batch Reactor Tests

Some typical analytical data of batch tests on biological degradability are summarized in Tables 10 and 11. Data of Table 10 show that (1) application of CAPMZ, regardless of its kind, resulted in better effluent quality, (2) the best water quality parameters belonged to the zeolite pre-treated with cold HCl and modified with polyamine of 50,000 molecular weight. Data of Table 11 show that the application of CAPMZ significantly superior both the traditional and Zeofloc technologies in respect of all measured water and sludge quality parameters.

Table 10: Discontinuous Biological Degradability Experiments Using Different type of Modified Geoprodukt, BBC-clinoptilolite

Zeolite pre-treatment	CAP		COD in the treated wastewater (mg/L)				Nitrogen content of the treated wastewater (mg/L)					
	Product labelling	Mol. weight	Time of treatment (hour)				Time of treatment (hour)					
			0	3	6	9	0			6		
							NH ₄ -N	Kjeldahl -N	NO ₃ -N	NH ₄ -N	Kjeldahl -N	NO ₃ -N
NH ₄ Cl	<i>No zeolite addition</i>		282	185	142	123	41.6	52.4	0.6	34.2	42.5	6.8
	<i>CAP-free zeolite addition</i>		282	168	127	114	41.9	52.8	0.6	28.3	33.8	12.6
	C567 Polyamine	10,000	287	161	121	113	42.0	52.9	0.6	25.6	30.1	12.8
	C573 Polyamine	50,000	291	156	115	109	42.1	52.8	0.6	21.3	24.5	13.8
	C581 Polyamine	250,000	288	180	135	120	41.2	51.8	0.6	25.0	31.2	14.5
	C587 Poly-DADMAC	200,000	284	170	140	125	41.1	52.0	0.6	26.3	32.4	13.0
	C591 Poly-DADMAC	500,000	290	165	142	123	42.0	52.8	0.6	25.9	32.4	13.8
	C610 Polyamide	1,000,000	285	179	131	120	42.5	52.3	0.6	27.6	38.0	14.3
Cold HCl (Acidic I)	<i>No zeolite addition</i>		480	310	162	133	38.6	49.5	1.0	33.6	42.4	5.0
	<i>CAP-free zeolite addition</i>		480	280	151	109	38.6	49.5	1.0	23.1	29.4	17.8
	C567 Polyamine	10,000	491	265	130	20.6	38.6	49.5	1.0	20.6	26.2	19.2
	C573 Polyamine	50,000	487	251	101	18.5	38.6	49.5	1.0	18.5	22.9	21.1
	C581 Polyamine	250,000	489	300	118	19.3	38.6	49.5	1.0	19.3	25.2	15.0
	C587 Poly-DADMAC	200,000	490	260	112	20.5	38.6	49.5	1.0	20.5	27.6	18.5
	C591 Poly-DADMAC	500,000	480	270	145	25.0	38.6	49.5	1.0	25.0	29.8	17.6
	C610 Polyamide	1,000,000	488	280	132	23.6	38.6	49.5	1.0	23.6	30.0	16.4
Hot HCl (Acidic II)	<i>No zeolite addition</i>		480	310	162	133	38.6	49.5	1.0	33.6	42.4	5.0
	<i>CAP-free zeolite addition</i>		480	286	147	112	38.6	49.5	1.0	25.3	31.0	17.2
	C567 Polyamine	10,000	492	260	145	22.3	38.6	49.5	1.0	22.3	28.9	18.5
	C573 Polyamine	50,000	488	260	135	20.4	38.6	49.5	1.0	20.4	25.8	18.7
	C581 Polyamine	250,000	487	285	121	20.2	38.6	49.5	1.0	20.2	26.0	15.3
	C587 Poly-DADMAC	200,000	484	279	124	21.0	38.6	49.5	1.0	21.0	27.2	19.7
	C591 Poly-DADMAC	500,000	483	283	139	24.7	38.6	49.5	1.0	24.7	30.4	17.2
	C610 Polyamide	1,000,000	490	277	140	25.2	38.6	49.5	1.0	25.2	31.9	15.9

Parameters of the experiments:

Zeolite grain size: <110 μm (60%: <60 μm, 30%: >60μm <100 μm, 10%: >100 μm <110μm)

Zeolite concentration: 100 mg_{CAPMZ}/g_{AS}

Concentration of activated sludge: 3.0 g_{AS}/L_{wastewater}

Table 11: Biological Degradability Experiments Using Natural Zeolite and CAPMZ

Wastewater sample	Added zeolite	COD mg/L	BOD ₅ mg/L	NH ₄ -N mg/L	NO ₂ -N mg/L	NO ₃ -N mg/L	Kjeldahl-N mg/L	Suspended solids mg/L	SVI ml/g
Influent		551	210	28.6	0.1	0.3	39.0	510	-
Effluent	-	75	18	20.0	2.3	6.5	27.5	80	134
	Natural zeolite	75	18	20.0	2.3	6.5	27.5	50	98
	CAPMZ	50	12	15.2	1.5	8.2	21.6	32	83

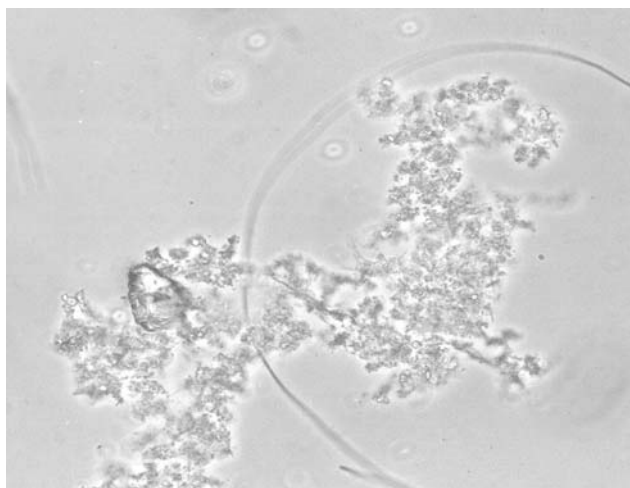
Parameters of the experiment:

Type of zeolite:	Geoprodukt, BBC-clinoptilolite pre-treated with cold HCl, modified with polyamine 50,000 molecular weight
Volume of the biological reactor:	2,000 ml
Residence time in the biological reactor:	12 hour
Concentration of activated sludge in the wastewater:	3.0 g _{AS} /L _{wastewater}
CAPMZ concentration in the activated sludge:	60 mg _{CAPMZ} /g _{AS}
Beginning of sampling:	24 hour, after experiment starts
Sludge removal rate (after the starting-up period):	1g/day
CAPMZ concentration in the influent wastewater:	30 mg _{CAPMZ} /L _{wastewater}

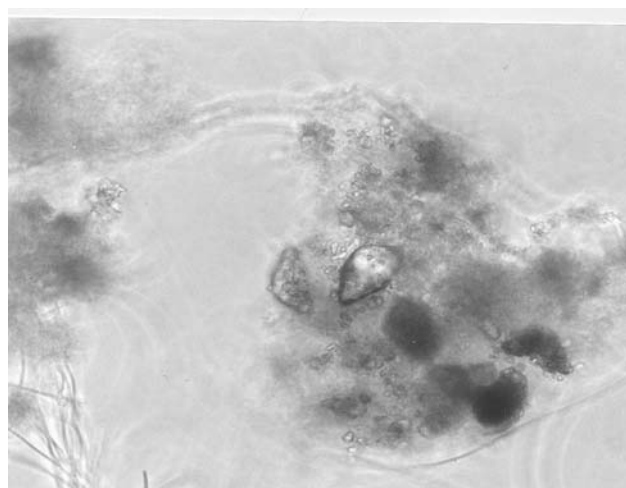
Microscopic Examination of "Zeolite-CAPMZ-Activated Sludge-Wastewater" System

Results of microscopic tests are shown on Pictures 1 and 2, which were taken from two "activated sludge-wastewater" systems. The only difference between the two systems was that the first one (1st picture) contained natural zeolites and the second one (2nd picture) zeolite modified with CAP. The dark areas on the second picture were caused by the increased thickness of bacteria flocs on the zeolite surface, i.e., the increased bacteria concentration on the zeolite surface.

The microscopic experiments proved that the time demand of the bacteria layer development on zeolite surface reduced to a few minutes on the effect of modification (pictures were taken immediately after zeolite and CAPMZ addition). It means that the basic drawback of the Zeofloc technology, i.e., slow adsorption of bacteria on the zeolite surface (5 - 7 days) was eliminated.



Picture 1: Natural Zeolite-Activated Sludge-Wastewater System



Picture 2: Modified Zeolite-Activated Sludge-Wastewater System

Effect of CAPMZ on Biological Oxygen Demand

The data of standard CBOD and NBOD measurements are summarized in Table 12. The CBOD and NBOD data, as well as the differences between CAPMZ and control data are illustrated as a function of incubation time on Figures 6 – 9. It can be seen that CAPMZ increased the wastewater oxygen consumption. The highest percentile differences (82 – 30 %) between the CBODs of CAPMZ and control samples could be observed at shorter incubation times (less than 4 day). This was because CAPMZ rapidly absorbed bacteria, organic matters and $\text{NH}_4\text{-N}$ resulting in higher concentration on its surface than the bulk concentration in the aqueous phase. In the case of NBOD differences between the CAPMZ and control samples were increasing with time (more than 100 % after 8 day). It can be explained by (1) the catalytic effects of CAPMZ mentioned above and (2) the experience that nitrification practically starts only on the 2nd – 3rd day of incubation.

Table 12: Data of Standard Biochemical Oxygen Demand Measurements

Incubation time (day)	BOD (mg/L)		CBOD (mg/L)		NBOD (mg/L)	
	CAPMZ	Control	CAPMZ	Control	CAPMZ	Control
0	0	0	0	0	0	0
1	80	44	77	42	3	2
2	134	79	127	75	7	4
4	167	121	151	115	16	6
5	179	137	157	129	22	8
6	192	151	163	140	29	12
8	205	160	166	145	39	15
10	215	171	171	151	44	20

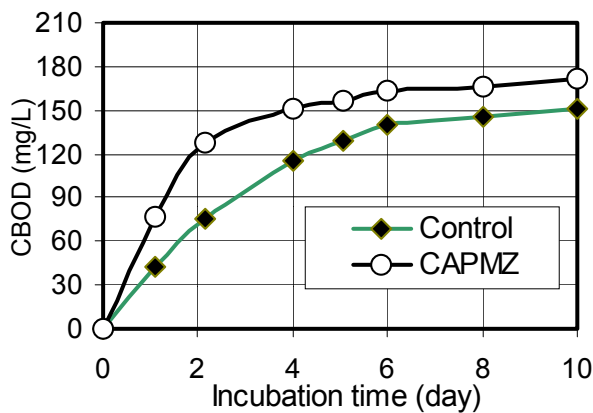


Figure 6: CBOD of Wastewater as a Function of Incubation Time

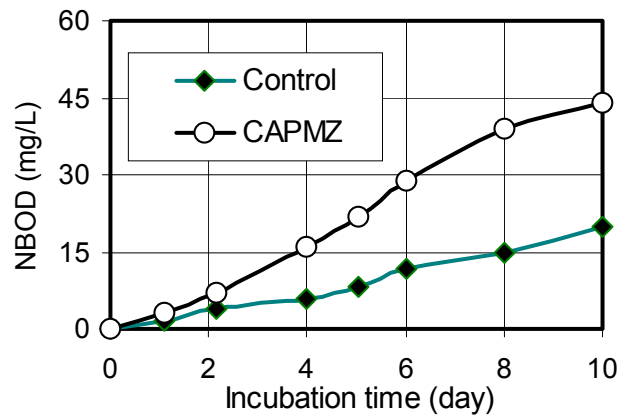


Figure 7: NBOD of Wastewater as a Function of Incubation Time

The ultimate carbonaceous BODs (UCBOD) were determined by the graphical method of Fujimoto (Fujimoto, 1961). As Figures 10 and 11 show an arithmetic plot of BOD_{t+1} versus BOD_t was prepared and on the same plot a line with a slope of 1 was drawn. The value at the intersection of the two lines corresponds to the UCBOD.

The difference between UCBOD values ($\text{UBOD}_{\text{CAPMZ}}$: 169 mg/L, $\text{UBOD}_{\text{Control}}$: 163 mg/L) were small indicating that CAPMZ accelerated only the aerobic decomposition of organic matters, but did not increase the amount of the biodegradable constituents of wastewater.

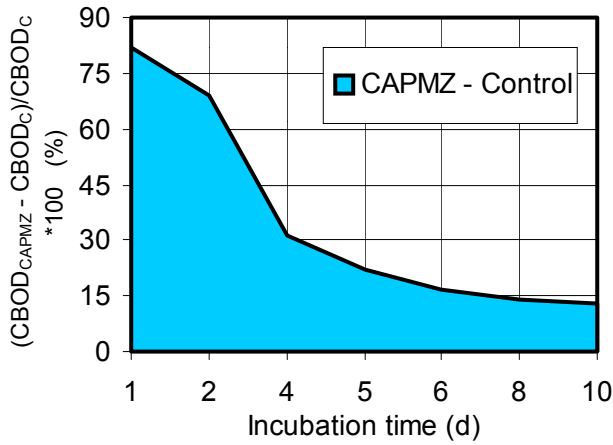


Figure 8 : Differences between CBODs Measured in Control and CAPMZ Samples as a Function of Incubation Time

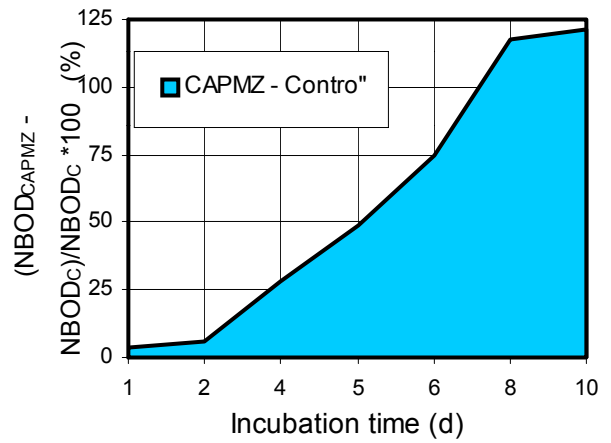


Figure 9: Differences between NBODs Measured in Control and CAPMZ Samples as a Function of Incubation Time

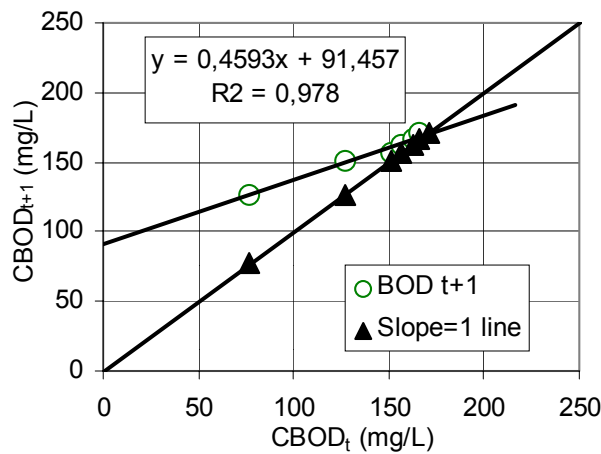


Figure 10: Determination of Ultimate CBOD in the Presence of CAPMZ

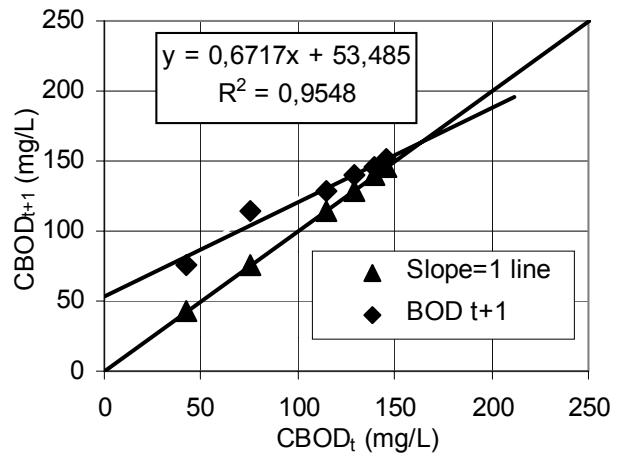


Figure 11: Determination of Ultimate CBOD for the Control Wastewater Sample

Assuming a first-order reaction, the rate of CBOD oxidation can be described as

$$CBOD_t = UCBOD(e^{-kt}) \quad (2)$$

where

$CBOD_t$ = remaining CBOD (mg/L) of the wastewater after incubation of time t (day)

$UCBOD$ = total or ultimate carbonaceous BOD (mg/L)

t = time (day)

k = first-order reaction rate constant at time t (d^{-1})

The k values at 1, 2 and 5 days are as follows:

$$k_{CAPMZ}: 0.786 d^{-1} (BOI_1), \quad 0.143 d^{-1} (BOI_2), \quad 0,015 d^{-1} (BOI_5)$$

$$k_{control}: 1.349 d^{-1} (BOI_1), \quad 0.388 d^{-1} (BOI_2), \quad 0,047 d^{-1} (BOI_5)$$

The reaction rate constant was always lower in the presence of CAPMZ. The explanation is the following: Although CAPMZ accelerated the biological oxidation of organic matters, the $UBOD/BOD_t$ ratio decreased at every incubation time. It is probably because, the CBOD oxidation can not be described with the Equation 2 generally applied. The oxidation as it will be seen in the next chapter did not followed a first-order reaction.

Effect of CAPMZ on Reaction Order and Rate

The effect of CAPMZ on reaction order and reaction rate was calculated from the analytical data of biological degradability tests accomplished in a batch reactor of 50 L. The data summarized in Table 13 show that CAPMZ considerably decreased the concentration of all the three parameters at every aeration time, i.e., increased the decomposition rate of COD, BOD₅ and increased the nitrification rate.

Table 13: Biochemical Oxidation of a Wastewater Originating from the WWTP of Dunakeszi

Aeration time (h)	COD (mg/L)		BOD ₅ (mg/L)		NH ₄ -N (mg/L)	
	Control	CAPMZ	Control	CAPMZ	Control	CAPMZ
0,0	968	968	311	311	68,0	68,0
0,5	710	610	262	240	65,0	60,4
1,5	530	455	240	207	56,0	51,9
2,5	258	214	189	154	46,0	41,1
5,0	147	118	122	87	37,0	25,7
10,0	98	75	82	48	24,0	14,9
13,0	77	57	65	51	18,0	9,9
16,5	70	43	48	29	12,0	5,8
20,0	51	36	42	31	8,1	4,4
24,0	50	38	42	32	4,9	4,1
30,0	49	34	42	39	3,9	2,9

From the data of Table 13 the reaction order for every parameter was calculated as

$$n = \frac{\log(-dC_{t1} / dt_1) - \log(-dC_{t2} / dt_2)}{\log C_{t1} - \log C_{t2}} \quad (3)$$

where

n: reaction order

C_{t1}, C_{t2}: concentration of a constituent at t₁ and t₂ times

Using the data obtained at hour 1.5 and 16.5

$$\frac{dC_{t1}}{dt_1} = \frac{C_{t1+1} - C_{t1-1}}{2.0}, \quad \frac{dC_{t2}}{dt_2} = \frac{C_{t2+1} - C_{t2-1}}{7.0} \quad (4)$$

In the case of COD for control data

$$\frac{dC_{t1}}{dt_1} = \frac{258 - 710}{2.0}, \quad \frac{dC_{t1}}{dt_1} = \frac{51 - 77}{7.0} \quad (5)$$

The reaction rate coefficient was calculated as

$$k = \left(\frac{1}{C_t} - \frac{1}{C_0} \right) / t \quad (6)$$

where

k: reaction rate coefficient (hour⁻¹)

C₀, C_t: concentration of a constituent (mg/L) at time 0 and t (h)

t: aeration time (h)

Reaction order and reaction rate coefficient data are summarized in Table 14. It can be seen that on the effect of CAPMZ the reaction order decreased, the reaction rate increased. It means that, CAPMZ (1) virtually increased the concentration of reactants during the oxidation of organic compounds and ammonical nitrogen, (2) accelerated the process of biochemical oxidation.

Table 14: Reaction Order and Reaction Rate Coefficient Values for Control and CAPMZ Samples

Parameter	COD		BOD ₅		NH ₄ -N	
	Control	CAPMZ	Control	CAPMZ	Control	CAPMZ
Reaction order	2.03	1.78	1.50	1.38	1.24	1.14
Reaction rate coef. (d ⁻¹)	0.0006	0.0008	0.0006	0.0011	0.0021	0.0031

Continuous laboratory experiments

The objectives of these experiments were to determine the optimal CAPMZ concentration to be applied to wastewater treatment. Wastewaters of twelve WWTPs were tested. The analytical data of the tests on a wastewater sample originating from the WWTP of Szob are shown in Table 15 and Figure 12, 13. The data show that the beneficial effects of CAPMZ increased with the CAPMZ concentration between 2 and 10%. At lower concentrations (< 2%) the sludge and effluent quality improvement was negligible, while above 10% practically no further beneficial effects could be achieved. (The percentile values mean the CAPMZ content of the activated sludge in g_{CAPMZ}/g_{AS} x 100 unit.)

Table 15: Results of Continuous Biological Degradability Tests on the Wastewater of WWTP of Szob

Wastewater sample	CAPMZ applied	COD mg/L	NH ₄ -N mg/L	Kjeldahl - N mg/L	NO ₃ -N mg/L	Total-P mg/L	SVI ml/g
Influent		1310	16.5	29.1	0.1	8.3	-
Effluent	0%	95	2.4	3.5	15.8	7.6	110
	2%	90	1.8	3.1	16.2	7.3	106
	3%	83	1.5	2.5	18.5	6.8	97
	5%	73	1.1	2.1	19.6	5.9	86
	8%	65	0.6	1.3	20.4	5.2	79
	10%	60	0.4	1.0	21.7	4.9	75
	12%	58	0.3	0.9	22.1	4.8	72

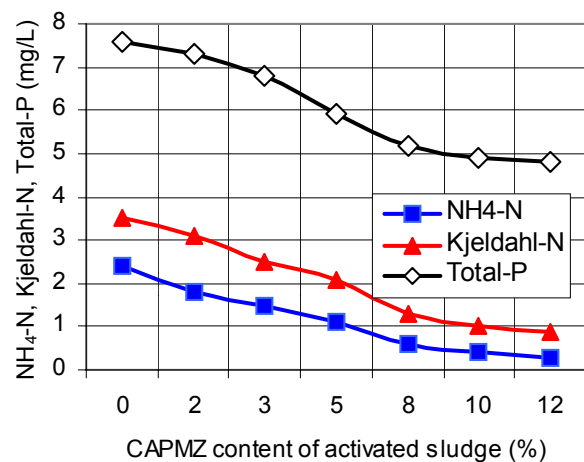
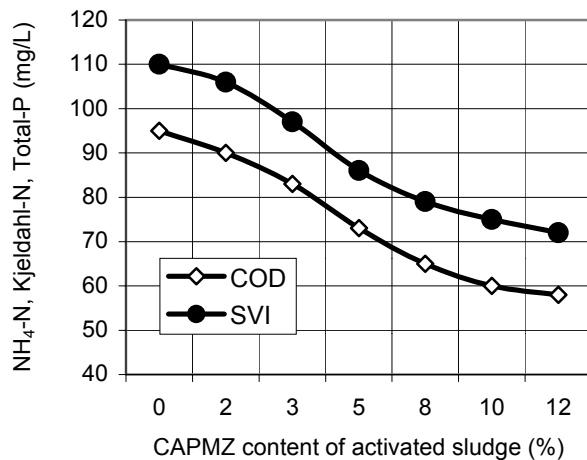


Figure 12: Sludge Settling and Effluent COD as a Function of CAPMZ Content

Figure 13: Effluent NH₄-N, Kjeldahl-N and Total-P as a Function of CAPMZ Content

c. Pilot- and Industrial-scale Experiments

The analytical data of experiments are summarized in Tables A and B. These tables can be found in the Technical Annex of this chapter. The COD and typical BOD₅ data are illustrated on Figures 14 – 16, too. The structure of activated sludges originating from the aeration basins are shown on Photos 3 and 4. The oxygen uptake rate (OUR) values measured in the water samples taken from the aeration basins are shown in Table 16.

Nitrate and pH are not involved in the evaluation, because (1) CAPMZ does not have any effect on the effluent pH, (2) the NO₃ content of effluent water was generally less than 1 mg/L.

Based on the hydraulic and organic loads, as well as the applied CAPMZ (trade name: ZeoRap[®]) concentration the experimental period was divided into three periods. These were as follows:

- 30 March 2001 to 18 June 2001 Low load, 7 kg_{ZeoRap}/day (5 %) operation
- 21 June 2001 to 26 Sept. 2001 Medium load 11 kg_{ZeoRap}/day (8 %) operation
- 1 Oct. 2001 to 14 January 2002 High load 14 kg_{ZeoRap}/day (10 %) operation

The average values of organic and hydraulic loads in the different periods were as follows:

- Period of low load: 257 kgCOD/day, 496 m³/day
- Period of medium load: 419 kgCOD/day, 712 m³/day
- Period of high load: 685 kgCOD/day, 836 m³/day

Water quality data and, on the example of COD and BOD₅, Figures 14 – 16 show that both cleaning lines operated satisfactorily during the low load season. In medium and high load seasons, however the effluent water quality frequently exceeded the related standard values (75 mg/L for COD and 25 mg/L for BOD₅) and was extremely poor in many cases in the control line. Differences between the effluent quality of control and ZeoRap lines were most significant in the high load period.

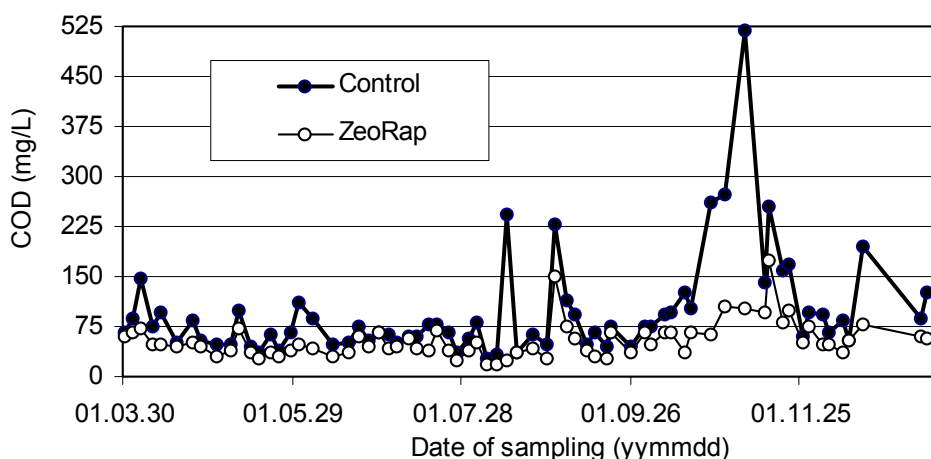


Figure 14: COD Values Measured in the Effluents of the Control and ZeoRap lines of the WWTP of Szob

The SVI measured in the ZeoRap line was usually less than the critical value of 100 ml/g in low and medium load seasons. SVI increased in both lines in high season, and differences between the two cleaning lines were the largest in this season.

The SS values, in harmony with SVI (improved sludge settling properties), were lower in the effluent of ZeoRap line. The lower SS concentrations generally resulted in a decrease in COD. Differences, however between the COD values of filtered samples of the two cleaning lines showed that CAPMZ decreased the COD of treated water by accelerating the biochemical oxidation, too. The lower BOD₅ values measured in the ZeoRap line also supports the above statement.

On the effect of increased biological activity, the OUR values were bigger by 18-27% in the ZeoRap line (see Table 16).

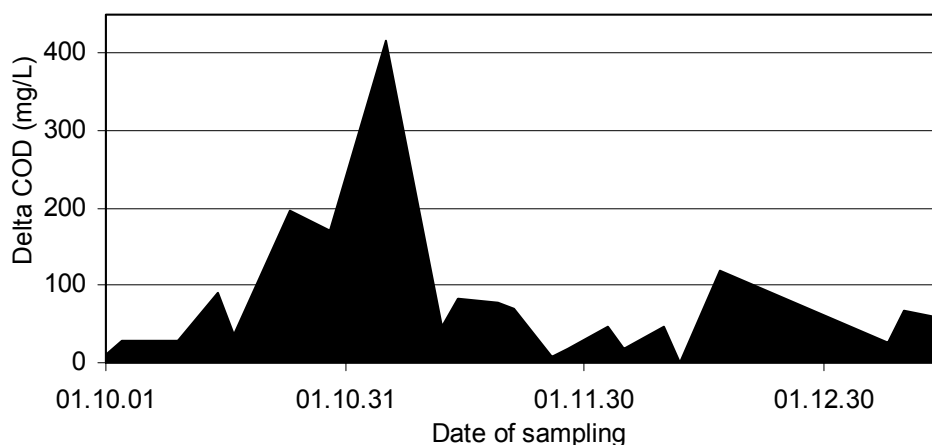


Figure 15: Differences between COD Values Measured in the Effluents of the Control and ZeoRap lines of the WWTP of Szob

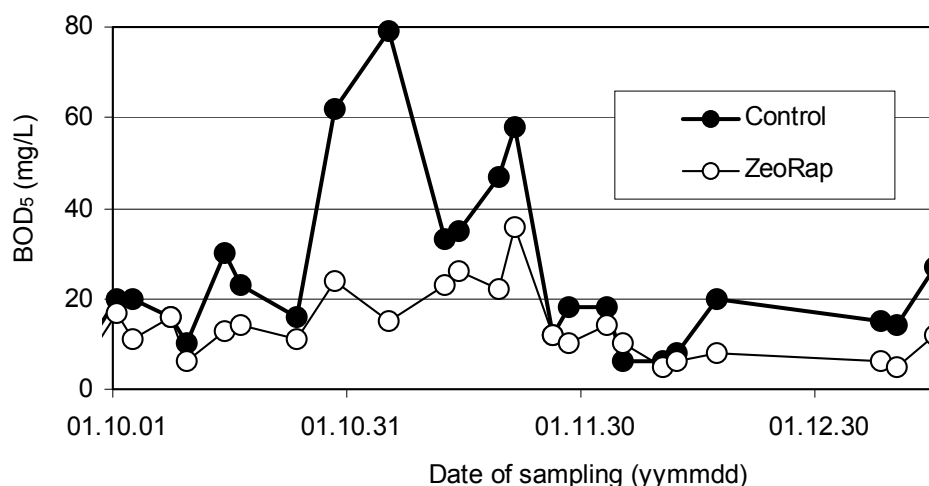


Figure 16: BOD₅ Values Measured in the Effluents of the Control and ZeoRap lines of the WWTP of Szob

Table 16: Oxygen Uptake Rate of Water Samples Originating from the Aeration Basins of the WWTP of Szob

Date of sampling	09 April 2001		02 August 2001		01 October 2001	
	Control	CAPMZ	Control	CAPMZ	Control	CAPMZ
OUR (g _{oxygen} /kg _{sludge} hour)	15,2	18,0	16,5	19,6	18,0	22,0
OUR expressed in the percent of the OUR measured in the control line (%)	100	122	100	119	100	122
OUR expressed in the percent of the OUR measured in the control line on 9 April 2001 (%)	100	118	109	129	118	145

The relationships between water quality parameters measured in the effluents of the two cleaning lines are shown on Figures 17 - 22. It can be seen that there was logarithmic relationship in the case

of COD, BOD₅ and SS, while linear relationship was found for TOC, NH₄-N and Total-P. ZeoRap significantly improved the effluent water quality. For example in the case of COD, when the concentration in the control effluent was 150 mg/L, the ZeoRap line still could ensure adequate water quality (75 mg/L). The control effluent water quality at which the effluent of ZeoRap line still meet the standard values for the other parameters were as follows: 56 mgBOD₅/L (standard: 25 mg/l), 22 mgTOC/L (no standard), 6.8 mgNH₄-N/L (standard: 5.0 mg/L), 2.3 mgTotal-P/L (standard: 2.0 mg/L), 200 mgSS/L (standard: 100 mg/L.)

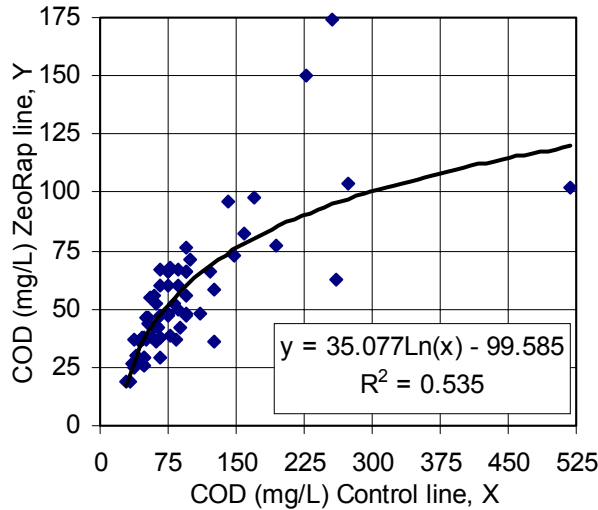


Figure 17: Relationship between Effluent COD Values Measured in the Control and ZeoRap Lines of the WWTP of Szob

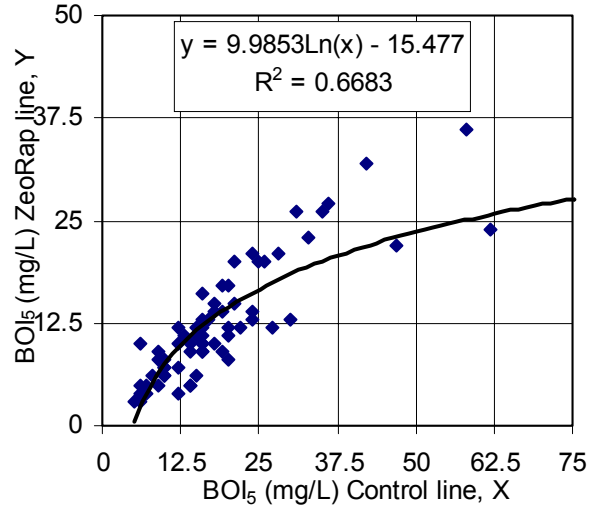


Figure 18: Relationship between Effluent BOD₅ Values Measured in the Control and ZeoRap Lines of the WWTP of Szob

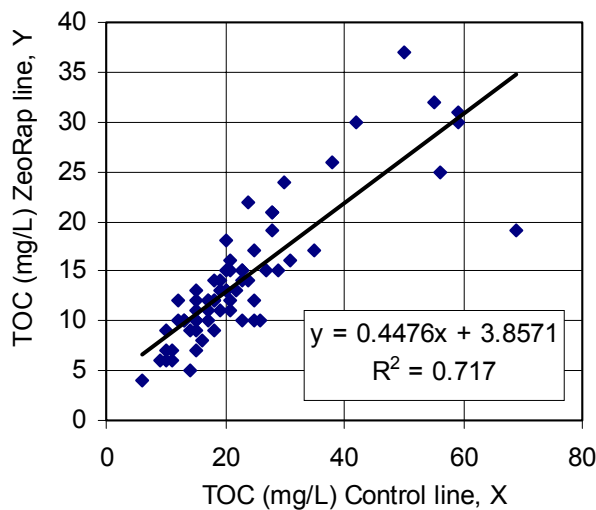


Figure 19: Relationship between Effluent TOC Values Measured in the Control and ZeoRap Lines of the WWTP of Szob

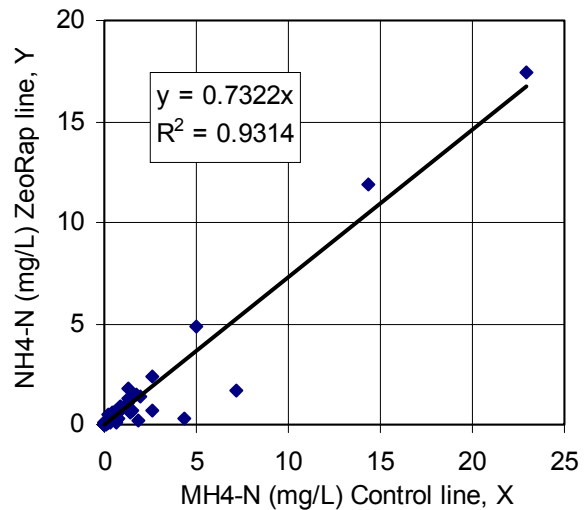


Figure 20: Relationship between Effluent NH₄-N Values Measured in the Control and ZeoRap Lines of the WWTP of Szob

The excess-decomposed COD in the ZeoRap line as a function of ZeoRap concentration employed is illustrated on Figure 23. Figure shows that differences between the decomposed COD of the two lines increased rapidly with the ZeoRap concentration. While the ZeoRap concentration was increased from 5% to 10%, differences between the decomposed COD increased from 2,4 kg/day to 29,3 kg/day. Because, at 10% ZeoRap concentration the daily ZeoRap demand was 14 kg, the value specific COD removal was 2.1 kg_{COD}/kg_{ZeoRap}. The specific values of pollutants' removal for the other water quality parameters were as follows:

- COD_f: 0.7 kg_{CODf}/kg_{ZeoRap}
- BOD₅: 0.3 kg_{BOD5}/kg_{ZeoRap}
- NH₄-N: 0,8 kg_{NH4-N}/kg_{ZeoRap}
- Total-N: 0,3 kg_{Total-N}/kg_{ZeoRap}
- Total-P: 0.3 kg_{Total-P}/kg_{ZeoRap}
- Suspended solids: 2.3 kg_{SS}/kg_{ZeoRap}

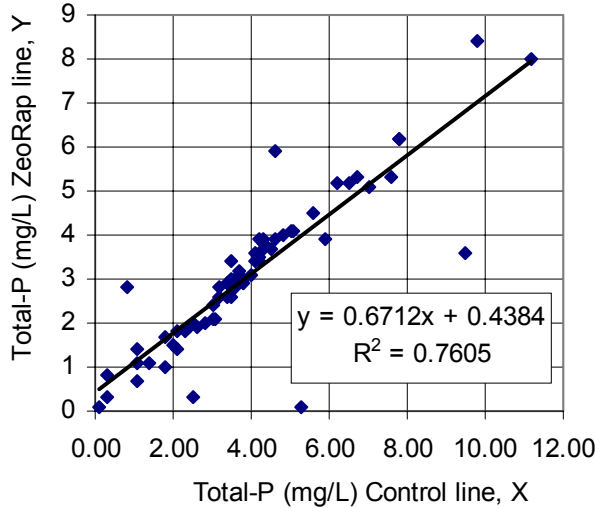


Figure 21: Relationship between Effluent Total Phosphorous Values Measured in the Control and ZeoRap Lines at Szob

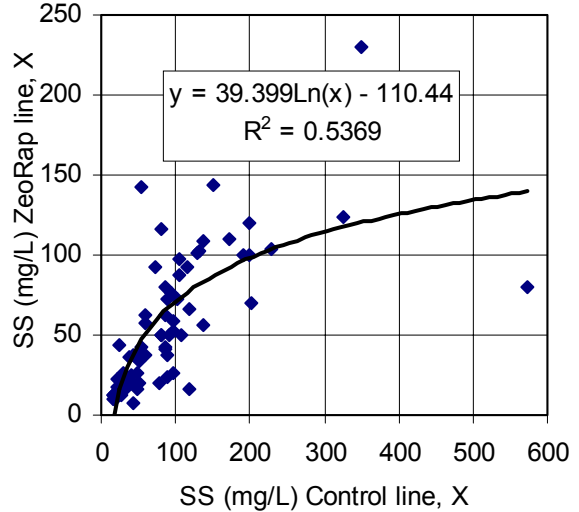


Figure 22: Relationship between Effluent Suspended Solid Values Measured in the Control and ZeoRap Lines at Szob

A logarithmic relationship was found between SVI improvement and ZeoRap concentration (see Figure 24). It means that the increase of ZeoRap concentration had no such a significant effect on SVI than on water quality parameters. Decrease in SVI values changed from 16% to 22% while the ZeoRap concentration was increased from 5% to 10%.

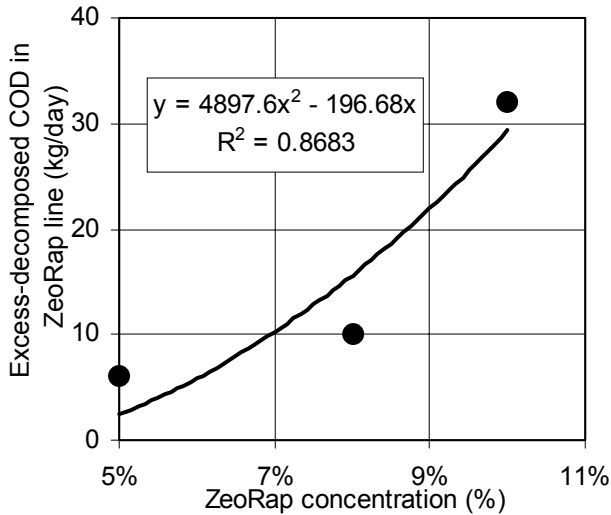


Figure 23: Differences between Decomposed COD of Control and ZeoRap Lines versus Applied ZeoRap Concentration

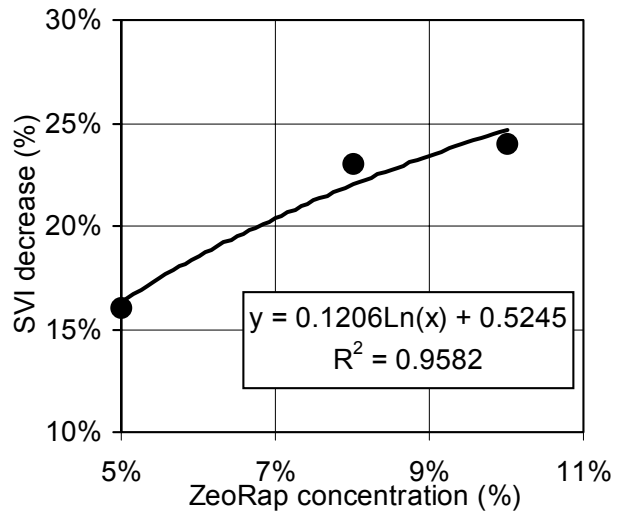


Figure 24: Effect of Applied ZeoRap Concentration on SVI Improvement

The microscopic images taken from recycled sludges showed that the sludge originating from the ZeoRap line had a thicker structure (See Photo 3 and 4), which resulted in better settling properties and more effective dewatering.

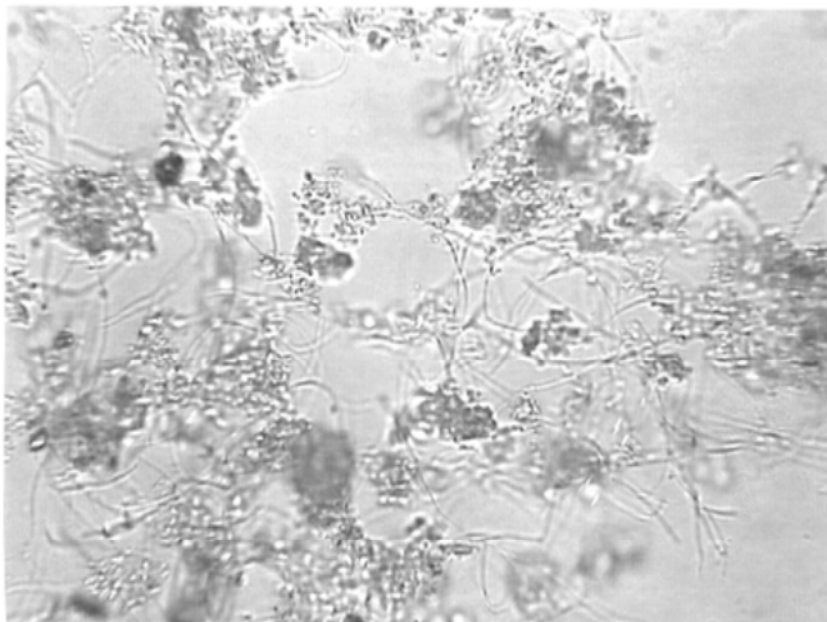


Photo 3: Microscopic Image of Recycled Sludge Originating from the Control Line of Szob

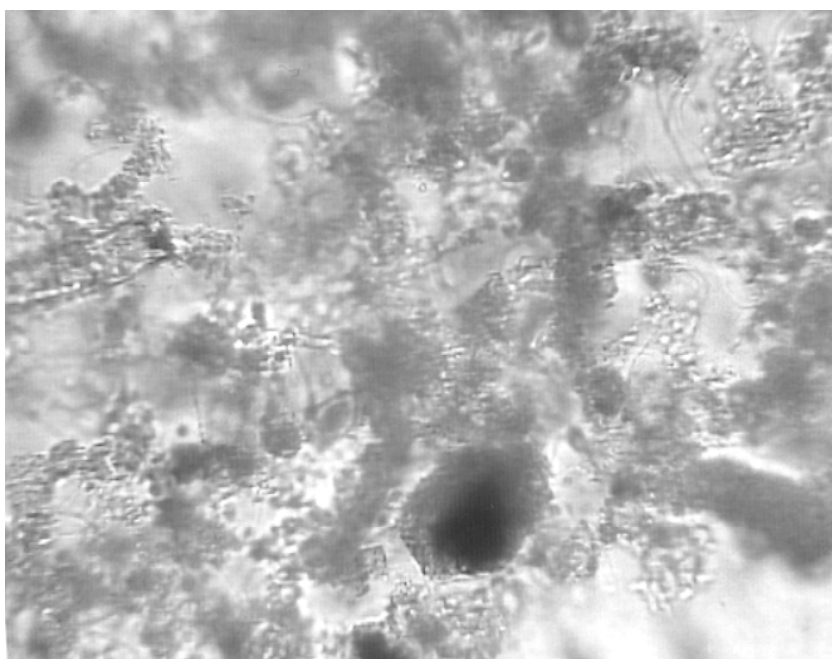


Photo 4: Microscopic Image of Recycled Sludge Originating from the ZeoRap Line of Szob

Determination of Optimal ZeoRap Concentration and Cost Benefit Analysis of ZeoRap

The data of water and sludge quality measurements of industrial-scale experiments showed that the beneficial effects of ZeoRap technology increased with the CAPMZ (hereafter the trade name of CAPMZ, ZeoRap is used) concentration. It means that, with respect to water and sludge quality, larger ZeoRap concentration yielded more favourable results. The increase of ZeoRap, however is limited by its price and the other additional costs of ZeoRap WWTT. Therefore, a determination of optimal ZeoRap concentration requires a cost to benefit analysis.

Cost Elements of ZeoRap at Szob

- ZeoRap including transportation: 0.272 EUR/kg

- Storage and supply of ZeoRap: 0.002 EUR/kg
- ZeoRap feeder: 2 000.000 EUR

All of the additional costs of ZeoRap operating full WWTP (both cleaning lines) by the ZeoRap method and accounting for the amortization of the ZeoRap feeder by ten years yield the following:

„2x7 kg _{ZeoRap} /day” operation	ZeoRap (450 kg + 5 110 kg):	1512.32 EUR
	Storage and supply of ZeoRap:	11.12 EUR
	ZeoRap feeder	200,00 EUR
	Total	1 723.44 EUR
„2x11 kg _{ZeoRap} /day ” operation	ZeoRap (720 kg + 8 030kg):	2 380.00 EUR
	Storage and supply of ZeoRap:	17,50 EUR
	ZeoRap feeder	200.00 EUR
	Total	2 577.50 EUR
„2x14 kg _{ZeoRap} /day ” operation	ZeoRap (900 kg + 10 220 kg):	3 024.64 EUR
	Storage and supply of ZeoRap:	22.24 EUR
	ZeoRap feeder	200.00 EUR
	Total	3 246.88 EUR

Economic Efficiency of ZeoRap at Szob

a. Environmental penalty Saving

A new and more stringent effluent water penalty system was introduced in Hungary on January 1, 2005. Standard values for COD, BOD₅, NH₄-N, Total-N, Total-phosphorous and suspended solids, according to the new regulation (9/2002. (III.22.) KöM-KöViM decree) are summarized in Table 17.

Based on the data of hydraulic load and water quality analysis, the differences between the annual quantity of pollutants discharged above the standard concentration from the control and ZeoRap lines were calculated. These quantities and the relating penalties are summarized in Table 18 and Figure 25. It can be seen that the penalty savings considerably increases with the ZeoRap concentration. For example while ZeoRap concentration changed from 8 to 10 %, penalty saving increased by 400 %.

Table 17: Standard Values and Fines for Effluent Water in the Category of „Other Protected Area” According to the 9/2002. (III.22.) KöM-KöViM Decree

Parameter	Standard value* (mg/L)	Penalty (EUR/kg _{pollutant} **)
COD	75	0.56
BOD ₅	25	2.10
NH ₄ -N	5	2.80
Total-N	15	2,80
Total phosphorous	2	22.40
Suspended solids	100	0.56

*Remark: * In the case of WWTPs established before January 1, 2003 standard values are introduced gradually over the next 15 years. During this period, the actual values of standards are determined by the local environmental inspectorate in every year. (Standards for the transient period is still unknown, therefore the economic evaluation is based on the data of this table.)*

*** Quantity of pollutant discharged above the standard concentration by WWTP*

Table 18: Differences of Annual Quantity of Pollutants Discharged Above Standard Concentration from Control and ZeoRap lines at Szob Using Various ZeoRap Quantities, and the Related Financial Penalties

ZeoRap usage	7 kg _{ZeoRap} /day		11 kg _{ZeoRap} /day		14 kg _{ZeoRap} /day	
	Δ quantity of pollutant (kg)	Penalty (EUR)	Δ quantity of pollutant (kg)	Penalty (EUR)	Δ quantity of pollutant (kg)	Penalty (EUR)
COD	907,0	508	1550,1	868	9532,2	5 338
BOD ₅	54,8	115	71,7	151	882,7	1 854
NH ₄ -N	9,1	26	0,0	0	140,0	392
Total-N	0,0	0	0,0	0	0,0	0
Total phosphorous	74,8	1 676	74,4	1 666	123,3	2 761
Suspended solids	573,1	321	2056,0	508	7494,2	4 197
Penalty saving (EUR)		2 530		3 042		12 688
Penalty saving if both lines are operated by ZeoRap (EUR)		5 061		6 085		25 377

Remark: Of the COD and BOD₅, in accordance with the 9/2002. (III.22.) KöM-KöViM decree, only COD was taken into account as a penalty factor.

b. Cost saving in sludge treatment

The surplus sludge is thickened at the WWTP and then transported to a waste dumping area. The cost of transportation and deposition is 4 EUR/m³ thickened sludge. Considering that the quantity of ZeoRap containing thickened sludge is smaller in volume by 5 - 12 % than that of traditional thickened sludge, the total treatment cost (thickening, transportation, deposition), in spite of the higher dry matter content, is lower in the case of ZeoRap containing sludge. The yearly quantity and treatment cost of the control and ZeoRap containing sludges are summarized in Table 19.

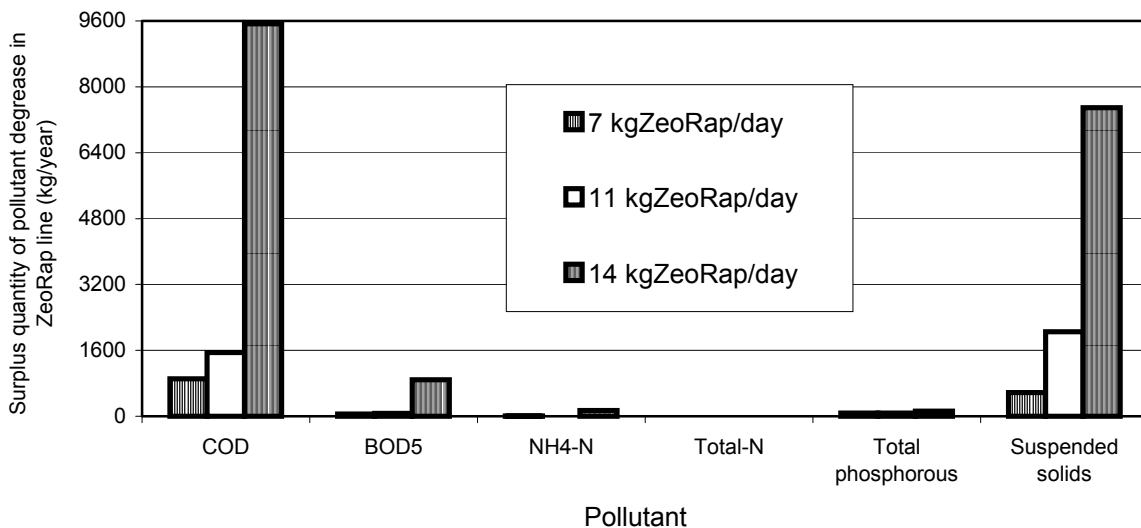


Figure 25: Differences between the Annual Quantities of Pollutants Discharged Above the Standard Concentration from the Control and the ZeoRap Cleaning Lines of Szob

Summary of Benefits to Costs of ZeoRap

The economic advantage of ZeoRap WWTT as a function of applied ZeoRap concentration is as follows:

Operation of 2x7 kg _{ZeoRap} /day, (5%)	Penalty-saving:	5 061 EUR/year
	Cost-saving in sludge treatment:	1 752 EUR/ year
	Additional costs:	-1 723 EUR/ year
	Cost advantage:	5 090 EUR/year
Operation of 2x11 kg _{ZeoRap} /day, (8%)	Penalty-saVing:	6 085 EUR/ year
	Cost-saving in sludge treatment:	2 920 EUR/year
	Additional costs:	-2 578 EUR/year
	Cost advantage:	6 427 EUR/ year
Operation of 2x14 kg _{ZeoRap} /day, (10%)	Penalty-saving:	25 377 EUR/year
	Cost-saving in sludge treatment:	4 672 EUR/year
	Additional costs:	-3 247 EUR/year
	Cost advantage:	26 802 EUR/year

Table 19: Annual Quantity and Treatment Cost of Surplus Sludge at Szob

Name of cleaning line	Control line	ZeoRap line		
Quantity of ZeoRap	-	7 kg _{ZeoRap} /day	11 kg _{ZeoRap} /day	14 kg _{ZeoRap} /day
	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>
Quantity of thickened sludge (m ³ /year)	5 110	4 891	4 745	4 526
Cost of sludge treatment (EUR/year)	24 440	19 654	18 980	18 104
Differences between treatment costs (<i>1-2, 1-3, 1-4</i>) (EUR/year)		876	1 460	2 336
Differences between treatment costs if both lines are operated by ZeoRap (EUR/year)		1 752	2 920	4 672

Data show that the efficiency of ZeoRap benefits increase significantly with the concentration. The optimal ZeoRap concentration and the economic efficiency of ZeoRap, however, primarily depend on the standard values, that will be determined for the Szob WWTP in the future. That is to say that the optimal concentration will depend upon application of the environmental penalty. The relationship between the economy of ZeoRap and environmental penalty is shown in Figure 26. If the WWTP, due to the high individual standards values remains penalty-free in the future, the optimal ZeoRap concentration will be 5% (2x14 kg_{ZeoRap}/day).

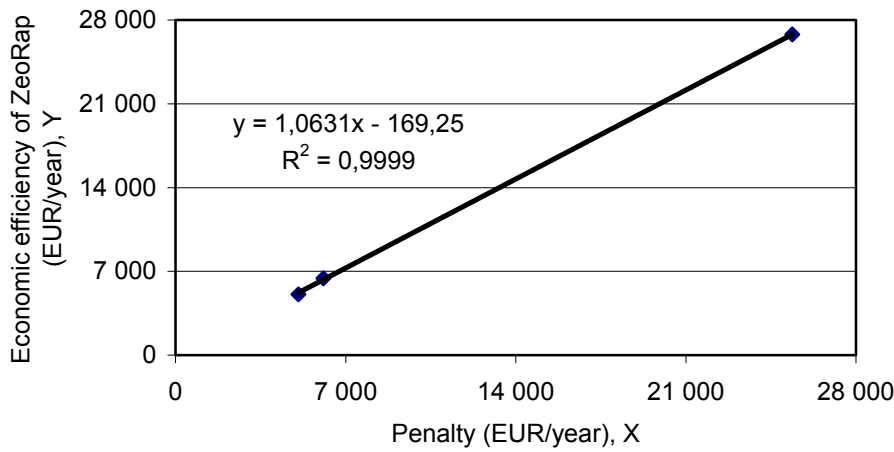


Figure 26: Economy of ZeoRap vs. Environmental Penalty

d. Development of an Innovative Equipment for the Production of Large Quantities of ZeoRap

In order to ensure the CAPMZ demand of pilot- and industrial-scale experiments, a semi-industrial device for zeolite modification was developed. Figure 27 and Photo 5. show the construction of the Gravitational Zeolite Dust Modification Equipment with a capacity of 150 kgZeoRap/hour. The operation of this device is as follows:

- (1) A zeolite feeder transports pre-treated zeolite from a container into a buffer tank.
- (2) From the buffer tank, the zeolite dust streams, gravitationally, first onto a vibration-plate and then falls into the modification chamber.
- (3) An air pump pushes the modification solution into two air sprayers mounted in the modification chamber.
- (4) The vaporized modifying solution then mixes with a thin layer of zeolite dust falling into the chamber.
- (5) The treated zeolite leaves, gravitationally, the chamber and enters the sacking unit.

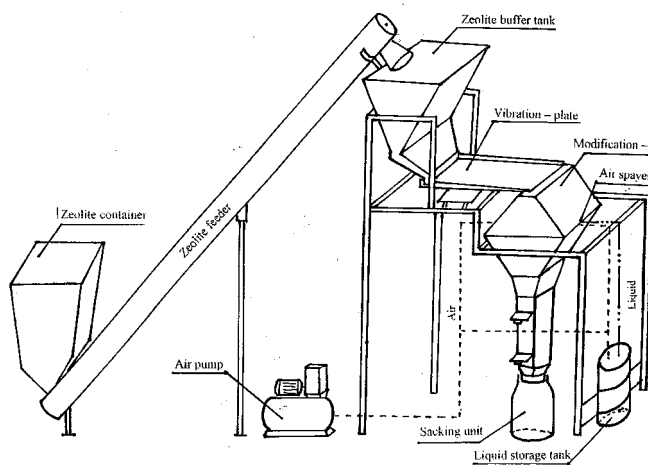


Fig 27: Construction of Gravitational Zeolite Dust Modifying Equipment



Photo 5: Gravitational Zeolite Dust Modifying Equipment

e. Model for Assessing the Improvement of the Biological Degradability of Wastewaters and that for the Changes in Treatment Cost, upon the Application of ZeoRap

A mathematical model concerning biological WWTPs called ZeoRapMod was made in order to enable the WWTPs' technical managers and operators to (1) predict the water and sludge quality improvements upon the application of ZeoRap[®] technology, (2) determine the optimal ZeoRap dosage rate and (3) assess the cost-benefit affects of the ZeoRap[®] technology on wastewater treatment.

The model-software was developed on the basis of the data of pilot- and industrial-scale experiments. The data analysis was focussed on the determination of the improvement of the pollutant removal efficiency of the treatment system upon the dosage of ZeoRap. This was done by writing mass balances of the form of differential equations for either on the entire system or its partial units. In doing so the removal rate of the system or part of it was represented by a single lumped reaction rate coefficient K_{rem} . (This parameter is called “the model coefficient” on the screens of the software). Therefore, the model developed is not a process model or design tool for treatment systems, but it is a mass balance model, which defines the relation between the pollutant concentrations of the influent and the effluent of the system. We tried to identify the relationship between the rate coefficient K_{rem} and the ZeoRap[®] dosage rate. Further on, this relationship was transformed into one, which specifies the relation between the improvement of the pollutant removal efficiency (that of the model coefficient) [%] and the ZeoRap dosage rate [%, $kg_{ZeoRap}/100*kg_{AS}$]. A similar relationship was identified between the SVI and the ZeoRap dosage rate, as well as the SVI improvement as a function of ZeoRap dosage was also determined.

The software also offers a cost-benefit analysis for the selection of the appropriate (optimum) ZeoRap concentration. The data needed for this are to be entered by the user, using the respective menu item and include (1) the environmental penalty values of the relevant (effluent) standard, (2) the respective limit values of the standard for the location of the given WWTP, (3) the costs of the ZeoRap technology (investment cost and the unit price of ZeoRap). If the user does not specify the penalty rates and standard limit values, then the programme uses the respective Hungarian standard [Joint decree of KöM-KöViM No. 9/2002. (III.22)].

The detailed description and users guide of ZeoRapMod model, as well as a CD containing the model can be found in Technical Annex 2 of this chapter.

Conclusions

Based on the results of batch-scale experiments it can be stated that the

- creation of chemical connection between zeolite particles and CAP molecules makes necessary the pre-treatment of natural zeolite,
- chemically bound CAP content of CAPMZ has an important role in the development of the beneficial effects of CAPMZ in the process of biological wastewater treatment,
- chemical bonds between zeolite and CAP are stable enough to resist the effects of remobilisation in the course of biological wastewater treatment,
- batch-scale tests are suitable to predict the expected beneficial effects of CAPMZ on effluent water and sludge quality.

The pilot- and industrial-scale experiments verified the results of laboratory tests. The application of ZeoRap

- increased the decomposition rate of organic compounds expressed in COD,
- increased the nitrification and denitrification rate,
- increased the rate of phosphorous removal,
- increased the rate of suspended solids removal,
- increased the sludge settling rate expressed in SVI,
- reduced the impact of industrial shock-loads on effluent quality

The advantages claimed for the ZeoRap WWTT are as follows:

- Increased treatment capacity
- Greater process stability
- Enhanced sludge settle ability
- Reduced investment and operation costs

Further Research Possibilities

The CAPMZ, that is natural zeolite modified with CAP, has high specific surface and special ion exchange properties. While natural zeolite can adsorb only cations, CAPMZ due to conversion of negative surface charges into positive has anion exchange capacity, as well, and can adsorb (1) polar and non-polar organic compounds, (2) viruses and bacteria, (3) toxic and non-toxic metals, (4) radio-isotopes from water. The differences between surface characteristics and ion exchange properties of natural zeolite and CAPMZ are illustrated on Figures 28 and 29.

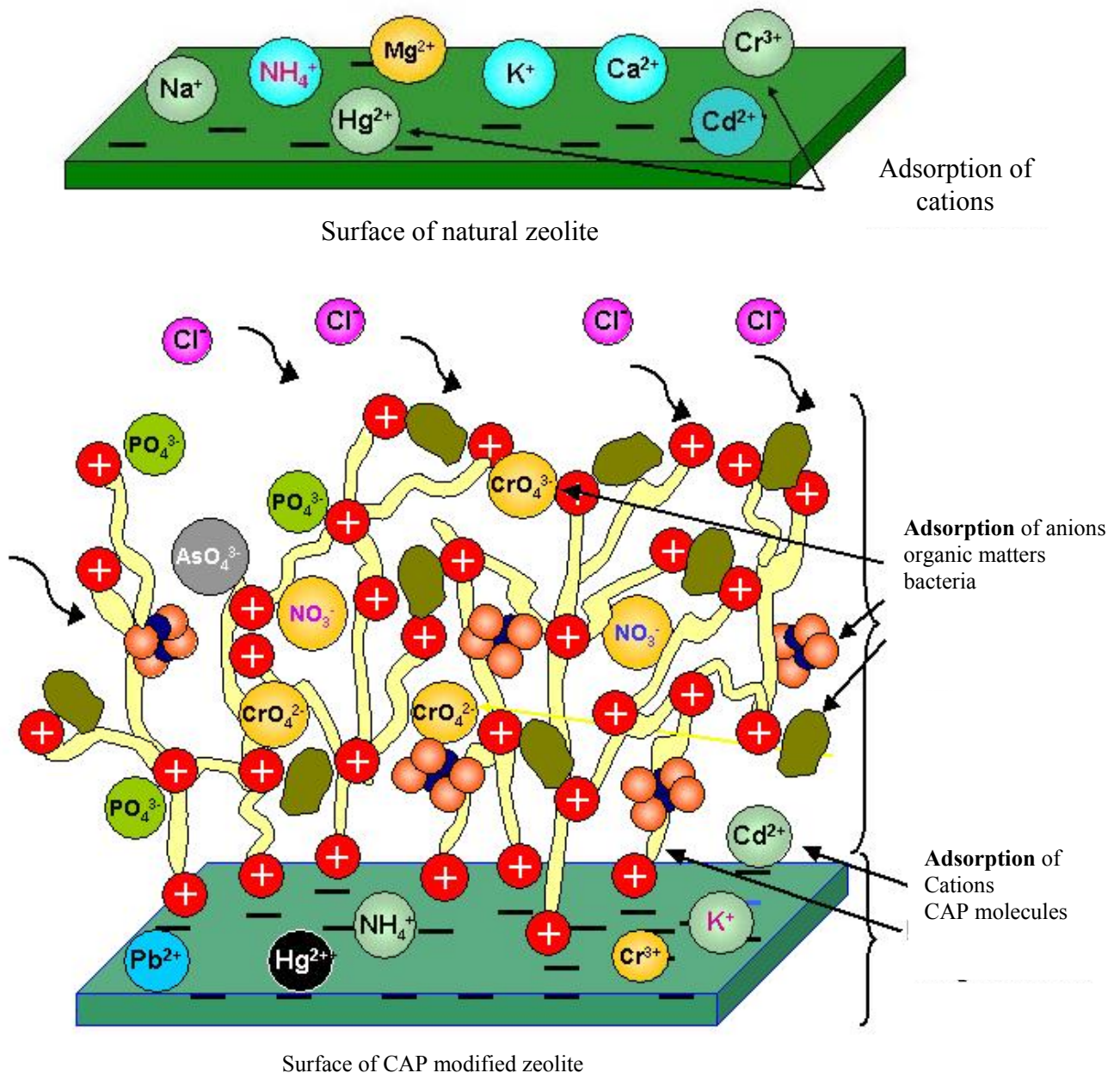


Figure 28: Surface and Adsorption Properties of Natural and CAP Modified Zeolite

The excellent sorption properties of CAPMZ make possible its application as filtering material to (1) wastewater treatment; in moving or fix bad biological reactors of suspended growth systems, (2) surface water and air purification. Naturally, these applications need grainy CAPMZ (grain size: 2 – 5 mm).

The application circumstances of CAPMZs of different grain size to wastewater treatment are being examined, and an industrial-scale equipment for producing CAPMZ is being developed in the frame of a new R&D project supported by the National Bureau for Research and Development in Hungary .

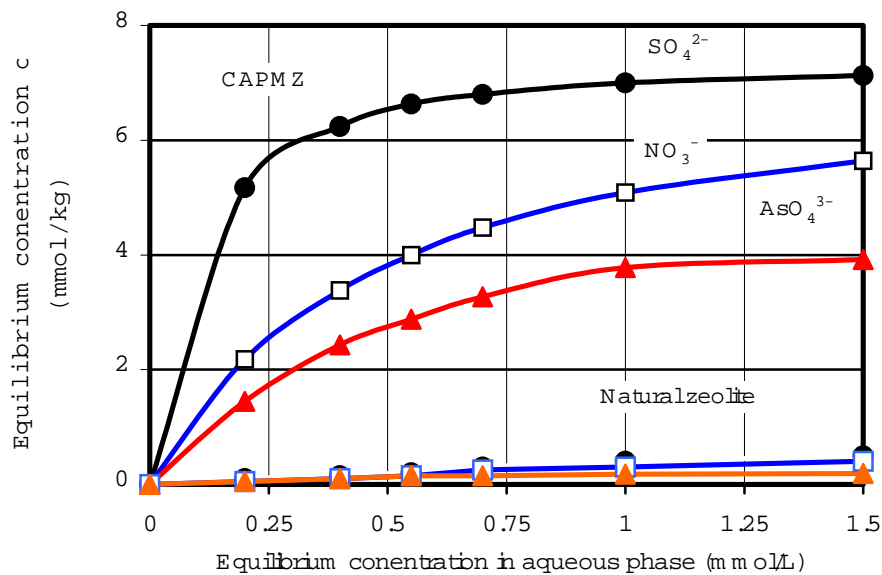


Figure 29: Adsorption of Anions on Natural and CAP Modified Zeolite

Acknowledgments

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Technical Annexes

Technical Annex 1: Water Quantity and Quality Data of Experiments Accomplished at the WWTP of Szob

Table A: Water Quantity and Quality Data of Experiments Accomplished at the WWTP of Szob

Sam- pling date	Wastewater (m ³ /d)		pH	COD	COD _f	BOD ₅	TOC	NH ₄ -N	Org-N	NO ₃ -N	Total-P	Susp. solids
	Quantity*	Type										
2001. 03. 30.	200	Infl.	6.6	1355	880	865	765	30.0	32.1	0.1	5.1	260
		Efl. Z	7.2	60	41	12	15	1.3	1.4	6.6	2.8	36
		Efl. C.	7.3	66	49	16	21	1.3	1.9	5.6	3.2	38
2001. 04. 02.	270	Infl.	6.5	667	456	199	212	32.0	25.4	0.1	9.2	400
		Efl. Z	7.1	67	45	20	22	2.4	1.3	2.8	3.4	100
		Efl. C.	7.0	87	55	21	24	2.6	1.7	5.8	3.5	200
2001. 04. 05.	260	Infl.	6.0	786	543	250	285	24.8	19.6	0.1	6.8	200
		Efl. Z	7.1	73	55	27	30	0.9	0.4	2.8	2.9	50
		Efl. C.	7.0	147	72	36	42	0.9	0.5	2.9	3.4	80
2001. 04. 09.	210	Infl.	6.0	1407	1179	338	425	45.0	32.3	0.1	10.6	255
		Efl. Z	6.8	48	40	21	19	0.7	0.2	3.5	8.4	19
		Efl. C.	6.8	76	56	28	28	0.8	0.4	3.7	9.8	31
2001. 04. 12.	230	Infl.	5.1	1293	922	345	438	20.0	15.4	0.1	10.1	230
		Efl. Z	6.8	48	33	12	14	1.0	0.3	6.9	3.1	50
		Efl. C.	6.8	95	57	22	23	1.2	0.5	5.0	4.0	80
2001. 04. 18.	195	Infl.	5.8	877	343	302	358	83.0	29.4	0.1	10.0	800
		Efl. Z	6.9	46	14	5	7	0.7	0.1	1.5	3.9	14
		Efl. C.	6.9	51	20	14	15	0.9	0.1	1.2	5.9	20
2001 04. 23.	295	Infl.	6.6	496	245	159	185	40.2	7.5	0.1	9.5	200
		Efl. Z	7.0	50	23	9	11	1.5	0.4	15.2	5.3	17
		Efl. C.	6.9	85	41	14	17	1.7	0.5	19.8	7.6	22
2001. 04. 26.	240	Infl.	5.8	811	523	254	287	20.6	12.2	0.1	6.3	200
		Efl. Z	6.8	45	36	14	20	1.0	0.6	6.1	1.1	13
		Efl. C.	6.8	54	45	16	27	0.7	1.1	11.7	2.9	17
2001 .05. 02.	280	Infl.	6.1	1131	450	328	368	22.7	14.6	0.1	14	200
		Efl. Z	7.3	29	24	5	7	1.8	0.4	23.1	6.2	13
		Efl. C.	7.3	48	28	9	11	1.3	1.2	15.4	7.8	17
2001. 05. 07.	210	Infl.	4.6	1741	662	502	543	28.4	8.3	0.1	11.0	578
		Efl. Z	7.2	38	30	21	12	0.50	0.6	11.5	6.2	13
		Efl. C.	7.1	47	41	24	18	0.5	0.6	15.8	7.8	15
2001. .05. 10.	300	Infl.	6.1	889	675	219	247	27.0	11.4	1.0	11.3	202
		Efl. Z	7.2	71	24	17	16	0.5	1.1	2.5	3.4	41
		Efl. C.	7.2	99	24	19	21	0.6	1.2	3.4	4.2	85
2001. 05. 14.	260	Infl.	6.4	744	317	189	234	24.9	3.0	1.0	16.8	359
		Efl. Z	7.5	36	15	10	14	0.2	0.2	5.4	3.7	13
		Efl. C.	7.6	45	20	12	18	0.2	0.5	6.5	4.5	27
2001. 05. 17.	220	Infl.	6.5	1597	944	501	583	21.7	2.5	0.1	9.2	120
		Efl. Z	7.3	27	20	11	11	0.9	0.1	6.5	2.6	22
		Efl. C.	7.3	36	23	13	15	0.9	0.1	1.5	3.4	22
2001. 05. 21.	370	Infl.	6.6	392	249	73	95	43.3	6.5	0.1	10.1	144
		Efl. Z	7.4	36	27	13	12	0.6	0.9	15.6	0.3	8
		Efl. C.	7.4	62	45	16	18	0.4	1.5	18.4	0.3	42

Sam- pling date	Wastewater (m ³ /d)		pH	COD	COD _f	BOD ₅	TOC	NH ₄ -N	Org-N	NO ₃ -N	Total-P	Susp. solids
	Quantity*	Type										
2001. 05. 24.	310	Infl.	6.7	540	380	172	195	49.	10.8	0.1	7.6	234
		Efl. Z	7.3	30	25	4	6	0.7	0.1	0.1	3.4	76
		Efl. C.	7.3	40	35	7	10	0.6	0.1	0.1	4.1	94
2001. 05. 28.	200	Infl.	4.7	1613	1229	381	459	25.0	10.70	0.1	8.4	686
		Efl. Z	7.4	38	29	9	10	11.9	0.1	0.2	1.4	66
		Efl. C.	7.4	67	51	9	13	14.4	0.2	1.4	2.1	118
2001. 05. 31.	290	Infl.	6.2	922	518	444	398	32.0	10.0	1.0	6.5	190
		Efl. Z	7.2	48	38	20	21	0.50	0.1	8.5	1.9	12
		Efl. C.	7.2	110	48	25	28	0.5	0.3	14.6	2.6	22
2001. 06. 05.	200	Infl.	6.0	1624	807	555	610	41.0	12.1	2.5	10.5	500
		Efl. Z	7.1	42	28	12	14	0.6	0.2	10.1	5.2	10
		Efl. C.	7.1	88	69	20	24	0.6	1.4	14.8	6.5	17
2001. 06. 12.	200	Efl.	5.4	1513	1242	375	384	31.0	6.5	1.7	6.2	476
		Efl. Z	7.5	29	20	7	9	0.6	0.4	2.8	0.8	88
		Efl. C.	7.4	49	39	12	15	0.5	0.5	1.0	0.3	104
2001. 06. 18.	220	Infl.	5.8	1612	585	268	328	17.5	16.0	0.1	8.1	960
		Efl. Z	7.4	37	14	15	15	4.9	0.1	0.3	1.1	23
		Efl. C.	7.5	50	30	21	23	5.0	0.1	1.5	1.1	37
2001. 06. 21.	275	Infl.	6.4	787	358	150	172	30.0	8.8	1.0	5.6	205
		Efl. Z	7.5	60	15	26	24	1.4	0.3	2.3	1.1	10
		Efl. C.	7.5	75	24	31	30	2.0	0.3	4.0	1.4	18
2001. 06. 25.	265	Infl.	6.3	878	496	121	146	30.0	9.7	2.5	6.3	507
		Efl. Z	7.5	46	28	15	12	1.1	0.3	0.1	2.0	97
		Efl. C.	7.5	54	31	18	17	1.3	0.7	0.9	2.8	106
2001. 06. 28.	295	Infl.	6.4	2994	2585	1210	1058	450	50.8	0.1	8.0	860
		Efl. Z	7.5	67	50	14	17	0.8	0.6	1.5	2.8	26
		Efl. C.	7.5	67	65	24	25	0.9	0.9	2.0	0.8	30
2001. 07. 02.	310	Efl.	6.3	694	485	249	315	30.0	6.5	0.1	7.8	405
		Efl. Z	7.5	43	24	10		0.7	0.3	19.9	3.9	59
		Efl. C.	7.4	62	43	16		2.6	0.7	18.4	4.2	98
2001. 07. 05.	350	Infl.	4.7	1900	1499	378	456	13.4	12.1	1.0	8.1	1582
		Efl. Z	7.4	44	23	7	10	0.6	0.7	5.8	3.0	38
		Efl. C.	7.4	52	47	10	15	0.6	1.6	6.9	3.6	48
2001. 07. 09.	340	Infl.	6.7	724	371	178	210	16.7	2.6	0.1	8.2	538
		Efl. Z	7.3	56	28	9	10	0.2	0.7	15.8	2.9	42
		Efl. C.	7.4	60	28	16	15	0.3	1.2	21.1	3.8	86
2001. 07. 12.	320	Efl.	6.6	1837	1276	531	549	22.9	18.5	0.1	6.9	1928
		Efl. Z	6.7	42	9	7	10	0.05	0.3	0.1	2.8	109
		Efl. C.	6.7	60	14	10	13	0.05	0.5	1.7	3.5	136
2001. 07. 16.	340	Infl.	6.9	957	860	208	238	2.6	9.9	0.1	7.8	594
		Efl. Z	7.0	39	20	3	4	0.5	0.4	6.9	2.1	110
		Efl. C.	7.0	78	39	5	6	0.2	0.7	10.8	3.1	172
2001. 07. 19.	280	Infl.	6.7	2892	1954	361	415	0.7	5.6	0.1	6.7	974
		Efl. Z	7.1	68	29	4	6	0.01	0.2	0.1	2.4	34
		Efl. C.	7.2	78	35	6	9	0.01	0.5	0.1	3.0	52
2001. 07. 23.	310	Efl.	6.6	1274	874	225	249	43.1	8.3	0.1	9.8	464
		Efl. Z	7.6	38	29	5	7	0.03	0.2	0.1	3.5	72
		Efl. C.	7.7	67	57	7	10	0.08	0.9	0.1	4.2	102

Sam- pling date	Wastewater (m ³ /d)		pH	COD	COD _f	BOD ₅	TOC	NH ₄ -N	Org-N	NO ₃ -N	Total-P	Susp. solids
	Quantity*	Type										
2001. 07. 26.	390	Infl.	7.5	824	243	247	257	23.7	10.8	0.2	10.6	912
		Efl. Z	7.5	25	20	11	9	0.03	0.4	0.1	4.1	20
		Efl. C.	7.5	37	28	15	10	0.03	0.5	0.1	5.0	52
2001. 07. 30.	365	Infl.	6.6	558	423	110	148	18.0	6.7	0.1	7.8	220
		Efl. Z	7.3	38	29	12	12	0.2	0.3	23.1	0.1	102
		Efl. C.	7.4	58	48	15	17	0.7	0.3	0.1	0.1	132
2001. 08. 02.	360	Efl.	5.7	1279	798	176	224	9.7	12.8	0.1	8.9	384
		Efl. Z	7.4	52	33	4	5	0.04	0.6	0.1	2.6	42
		Efl. C.	7.4	82	44	12	14	0.04	0.6	0.1	3.2	54
2001. 08. 06.	310	Infl.	7.3	634	242	178	198	26.0	5.8	0.1	11.2	120
		Efl. Z	7.5	19	9	14	13	0.3	0.1	16.1	2.8	38
		Efl. C.	7.3	28	19	19	22	0.4	0.1	18.4	3.6	42
2001. 08. 09.	390	Infl.	6.7	811	699	206	215	9.7	7.5	0.1	9.7	349
		Efl. Z	7.4	19	14	13	10	0.07	0.6	6.1	2.6	38
		Efl. C.	7.4	33	23	24	17	0.1	0.9	1.5	3.5	88
2001. 08. 13.	360	Efl.	6.0	848	705	239	252	11.9	9.2	<0.1	9.0	434
		Efl. Z	7.1	23	19	8	10	0.2	0.5	23.7	8.0	124
		Efl. C.	7.3	242	56	9	12	0.6	0.6	20.0	11.2	326
2001. 08. 16.	425	Infl.	7.1	668	464	116	139	18.5	6.6	0.1	6.7	200
		Efl. Z	7.4	37	25	20	16	0.1	0.3	0.1	2.8	80
		Efl. C.	7.6	37	28	26	21	0.1	0.3	0.1	3.5	86
2001. 08. 22.	350	Infl.	6.4	1156	361	316	340	25.1	8.8	0.1	6.8	507
		Efl. Z	7.3	42	30	10	13	0.1	0.1	0.1	2.1	93
		Efl. C.	7.3	63	36	16	20	0.1	0.1	0.1	3.0	115
2001. 08. 27.	410	Infl.	7.0	454	288	198	220	16.3	7.9	0.1	8.1	104
		Efl. Z	7.4	26	9	6	9	0.3	0.1	8.5	3.6	20
		Efl. C.	7.4	49	17	10	14	0.3	0.2	9.3	4.1	41
2001. 08. 30.	350	Infl.	6.8	1730	399	865	805	57.6	45.2	0.1	8.6	179
		Efl. Z	7.4	150	38	32	37	0.02	0.6	0.1	3.0	50
		Efl. C.	7.6	228	48	42	50	0.02	0.9	0.1	3.5	92
2001. 09. 03.	390	Efl.	6.7	1261	452	370	398	51.5	16.0	0.1	11.5	670
		Efl. Z	7.3	75	65	8	10	0.02	2.7	0.1	3.5	22
		Efl. C.	7.4	113	75	17	20	0.03	2.8	0.1	4.0	180
2001. 09. 06.	420	Infl.	6.3	800	630	237	257	6.20	10.2	0.1	10.6	544
		Efl. Z	7.5	56	52	8	12	0.05	1.0	0.1	3.7	16
		Efl. C.	7.6	94	80	10	15	0.05	1.0	0.1	4.3	48
2001. 09. 10.	395	Infl.	5.9	1018	672	319	338	19.4	11.0	0.1	4.9	124
		Efl. Z	7.3	38	19	10	13	0.6	0.1	8.4	1.0	52
		Efl. C.	7.3	48	22	14	19	1.4	0.2	8.8	1.8	96
2001. 09. 13.	415	Efl.	5.8	960	540	246	261	11.0	9.9	0.1	8.3	266
		Efl. Z	7.2	29	17	9	10	0.02	0.4	0.1	3.0	26
		Efl. C.	7.3	67	26	19	23	0.02	0.9	0.1	3.8	98
2001. 09. 17.	400	Infl.	6.2	1829	1774	914	890	3.1	15.4	0.1	6.9	138
		Efl. Z	7.3	27	18	9	8	0.01	0.5	12.1	3.9	26
		Efl. C.	7.3	46	27	16	16	0.01	0.8	10.8	4.3	49
2001. 09. 19.	390	Infl.	6.6	431	319	214	186	4.4	4.9	0.1	10.7	206
		Efl. Z	7.4	66	56	13	15	0.01	0.1	10.8	3.0	37
		Efl. C.	7.4	75	66	17	23	0.01	0.1	10.0	3.6	59

Sam- pling date	Wastewater (m ³ /d)		pH	COD	COD _f	BOD ₅	TOC	NH ₄ -N	Org-N	NO ₃ -N	Total-P	Susp. solids
	Quantity*	Type										
2001. 09. 26.	410	Efl.	6.3	1038	463	234	265	3.5	11.3	0.1	8.9	428
		Efl. Z	7.5	37	28	3	6	0.01	0.4	0.1	2.8	24
		Efl. C.	7.5	46	32	6	11	0.01	0.4	0.1	3.6	88
2001. 10. 01.	470	Infl.	6.1	1494	832	344	362	3.0	13.3	0.1	9.2	596
		Efl. Z	7.3	66	47	17	21	0.7	0.4	0.8	0.7	56
		Efl. C.	7.5	76	57	20	28	1.5	0.7	1.5	1.1	136
2001. 10. 03.	410	Infl.	4.8	3898	3804	2171	2350	10.3	10.0	0.1	7.7	401
		Efl. Z	7.7	47	37	11	15	0.03	0.2	0.1	2.9	50
		Efl. C.	7.6	75	56	20	27	0.04	0.5	0.1	3.8	108
2001. 10. 08.	450	Efl.	7.1	609	290	174	210	10.6	8.9	0.1	16.1	548
		Efl. Z	7.7	66	38	16	13	0.04	0.2	5.4	5.1	144
		Efl. C.	7.7	94	51	16	15	0.04	0.4	2.3	7.0	152
2001. 10. 10.	390	Infl.	5.7	1209	778	290	319	12.3	9.3	0.1	11.3	476
		Efl. Z	7.4	66	42	6	11	0.04	0.1	3.8	4.1	72
		Efl. C.	7.4	95	61	10	19	0.05	0.4	3.1	5.1	89
2001. 10. 15.	450	Infl.	6.9	592	449	124	149	31.	9.6	<0.1	4.8	330
		Efl. Z	7.3	36	18	13	10	0.3	0.4	46	1.8	120
		Efl. C.	7.6	126	36	30	25	0.8	0.6	46.8	2.3	200
2001. 10. 17.	485	Efl.	5.4	1820	780	268	300	26.4	5.4	0.1	10.4	572
		Efl. Z	7.4	67	49	14	18	0.3	0.1	0.1	3.2	68
		Efl. C.	7.6	103	58	23	29	0.6	0.1	0.1	4.1	144
2001. 10. 24.	470	Infl.	6.1	1041	431	297	325	24.6	9.3	0.1	9	592
		Efl. Z	7.4	63	45	11	14	0.1	0.8	7.7	0.3	16
		Efl. C.	7.4	260	36	16	19	0.2	0.4	3.1	2.5	118
2001. 10. 29.	445	Infl.	6.3	1475	1078	265	310	24.6	11.1	0.1	11.8	596
		Efl. Z	7.6	104	38	24	30	0.1	3.1	0.1	1.7	104
		Efl. C.	7.6	274	85	62	59	0.2	0.2	0.1	1.8	230
2001. 11. 05.	460	Efl.	7.4	983	390	209	234	49.3	10.5	0.1	18.5	770
		Efl. Z	7.5	102	74	15	19	17.4	11.2	17.0	3.6	80
		Efl. C.	7.5	519	130	79	69	22.9	13.7	17.0	9.5	572
2001. 11. 12.	450	Infl.	6.5	987	804	299	331	14.5	7.2	0.1	9.2	480
		Efl. Z	7.4	96	46	23	26	1.7	0.1	9.2	5.9	101
		Efl. C.	7.5	142	55	33	38	7.2	3.0	8.5	4.6	128
2001. 11. 14.	465	Infl.	6.6	804	676	232	265	18.9	12.6	0.1	12.3	360
		Efl. Z	7.4	174	27	26	32	0.1	0.4	0.1	4.0	230
		Efl. C.	7.4	256	50	35	55	0.1	0.8	0.1	4.8	350
2001. 11. 19.	490	Efl.	6.8	870	320	278	356	20.7	12.2	0.1	10.2	450
		Efl. Z	7.3	82	36	22	25	0.3	0.8	10.8	2.0	100
		Efl. C.	7.3	159	62	47	56	4.3	1.2	7.3	2.5	190
2001. 11. 21.	430	Infl.	6.6	1085	498	314	345	42.	18.1	0.1	14.3	386
		Efl. Z	7.3	98	76	36	31	0.3	0.3	5.3	0.1	44
		Efl. C.	7.2	169	67	58	59	0.5	0.7	7.1	5.3	24
2001. 11. 26.	425	Infl.	6.7	917	709	285	308	26.4	8.3	0.1	3.9	160
		Efl. Z	7.2	52	35	12	18	0.6	0.5	11.5	1.4	58
		Efl. C.	7.1	61	35	12	20	0.7	0.3	9.2	1.1	58
2001. 11. 28.	425	Efl.	6.4	917	700	264	298	23.5	4.6	0.1	9.8	350
		Efl. Z	7.3	76	47	10	16	0.2	0.2	6.1	1.5	70
		Efl. C.	7.2	95	61	18	31	0.1	0.2	17.6	2.0	202

Sam- pling date	Wastewater (m ³ /d)		pH	COD	COD _f	BOD ₅	TOC	NH ₄ -N	Org-N	NO ₃ -N	Total-P	Susp. solids
	Quantity*	Type										
2001. 12. 03.	450	Infl.	6.6	3058	1872	1136	1324	330	0.1	0.1	16.8	888
		Efl. Z	7.2	47	47	14	15	0.1	0.2	0.1	1.8	20
		Efl. C.	7.2	94	66	18	29	0.1	0.1	15.4	2.1	78
2001. 12. 05.	390	Infl.	7.0	1218	560	245	276	37.8	2.4	0.1	11.6	308
		Efl. Z	7.2	47	28	10	15	0.1	0.1	0.1	3.8	116
		Efl. C.	7.4	66	37	6	20	0.1	0.2	0.1	4.3	82
2001. 12. 10.	465	Efl.	6.6	487	112	122	146	29.9	10.1	0.1	20.7	236
		Efl. Z	7.3	37	23	5	9	0.5	0.3	12.3	5.2	142
		Efl. C.	7.3	84	37	6	18	0.5	0.1	16.5	6.2	54
2001. 12.12	470	Infl.	6.5	1441	628	319	342	57.2	39.1	0.1	5.9	419
		Efl. Z	7.4	55	37	6	12	0.05	0.2	10.4	1.9	62
		Efl. C.	7.4	55	46	8	12	0.09	0.2	8.5	2.4	58
2001. 12.17.	350	Infl.	6.5	969	625	245	265	42.2	6.8	0.1	23.2	188
		Efl. Z	7.4	77	45	8	11	0.06	0.9	8.4	5.3	92
		Efl. C.	7.4	195	136	20	21	0.08	2.1	6.9	6.7	72
2002. 01. 07.	210	Efl.	7.1	99	60	31	35	24.2	12.8	0.1	13.4	250
		Efl. Z	7.2	60	29	6	12	0.2	0.3	3.2	3.2	25
		Efl. C.	7.2	86	37	15	25	1.9	0.5	4.0	3.7	40
2002. 01. 09.	250	Infl.	7.1	101	75	35	31	8.5	25.4	1.0	18.7	198
		Efl. Z	7.2	58	32	5	10	0.1	0.4	2.0	4.5	16
		Efl. C.	7.2	125	45	14	26	0.6	0.9	2.5	5.6	31
2002. 01. 14.	310	Efl.	7.1	106	73	38	34	2.10	12.0	1.0	13.4	328
		Efl. Z	7.2	66	30	12	17	0.10	0.2	0.1	3.9	62
		Efl. C.	7.2	122	52	27	35	0.3	0.4	0.1	4.6	85

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Legend: *: hydraulic load of one cleaning line (half of plant load)
 Inf.: Influent
 Efl.: effluent of cleaning line employing CAPMZ
 Efl. C.: effluent of control cleaning line
 COD_f: COD of filtered sample

Table B: Sludge Quantity and Quality Data of Experiments Accomplished at the WWTP of Szob

Sampling date	Cleaning line	Sludge concentration (g/L)		30-minute sludge sedi- mentation		Excess sludge	
		Aeration basin	Recirculation system	(ml/L)	SVI (ml/g)	Concentration (g/L)	Quantity (m ³ /day)
30 March 2001	CAPMZ	6.5	8.5	880	135	8.5	170
	Control	6.0	7.6	990	165	7.6	152
02 April 2001	CAPMZ	6.9	7.2	910	132	7.2	144
	Control	5.2	6.8	840	162	6.8	136
05 April 2001	CAPMZ	7.5	9.5	900	120	9.5	190
	Control	6.2	7.0	780	126	7.0	140
09 April 2001	CAPMZ	6.7	7.6	410	61	7.6	152
	Control	6.9	8.9	590	86	8.9	178
12 April 2001	CAPMZ	5.9	8.0	340	58	8.0	160
	Control	7.4	8.4	760	102	8.4	168
18 April 2001	CAPMZ	6.9	8.0	750	109	8.0	200
	Control	7.0	8.0	860	123	8.0	200

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1 Sampling date	Cleaning line	Sludge concentration (g/L)		30-minute sludge sedimentation		Excess sludge	
		Aeration basin	Recirculation system	(ml/L)	SVI (ml/g)	Concentration (g/L)	Quantity (m ³ /day)
23 April 2001	CAPMZ	4.9	6.4	590	120	6.4	128
	Control	5.8	7.1	840	145	7.1	142
26 April 2001	CAPMZ	4.4	6.6	410	93	6.6	132
	Control	5.0	8.4	610	122	8.4	168
02 May 2001	CAPMZ	4.3	8.1	340	79	8.1	162
	Control	5.8	7.5	550	95	7.5	150
07 May 2001	CAPMZ	4.8	7.3	380	80	7.3	146
	Control	6.1	6.9	580	96	6.9	138
10 May 2001	CAPMZ	7.3	9.5	850	116	9.5	190
	Control	7.3	9.2	870	119	9.2	184
14 May 2001.	CAPMZ	6.4	8.7	720	112	8.7	174
	Control	7.2	11.7	890	123	11.7	234
17 May 2001.	CAPMZ	7.2	11.6	620	86	11.6	232
	Control	6.6	8.3	640	96	8.3	166
21 May 2001.	CAPMZ	8	11.0	450	68	11	220
	Control	7.1	8.3	630	88	8.3	166
24 May 2001.	CAPMZ	9.3	11.3	780	84	11.3	226
	Control	7.3	8.4	590	81	8.4	168
28 May 2001.	CAPMZ	8.4	9.2	770	92	9.2	184
	Control	7.5	8.8	760	101	8.8	176
31 May 2001.	CAPMZ	7.6	8.5	710	93	8.5	170
	Control	7.5	10.1	710	95	10.1	204
5 June 2001.	CAPMZ	12.8	14.8	900	70	14.8	296
	Control	5.7	11.4	760	133	11.4	228
12 June 2001.	CAPMZ	10.1	13.9	670	66	13.9	278
	Control	8.5	14.6	750	88	14.6	292
18 June 2001	CAPMZ	8.9	14.8	890	100	14.8	296
	Control	8.8	13.1	930	106	13.1	262
21 June 2001	CAPMZ	8.0	9.3	850	106	9.3	186
	Control	7.5	9.7	870	116	9.7	194
25 June 2001	CAPMZ	7.3	13.3	400	55	13.3	266
	Control	7.6	13.7	580	76	13.7	274
28 June 2001	CAPMZ	7.9	9.5	820	104	9.5	190
	Control	8.3	9.9	950	114	9.9	198
02 July 2001	CAPMZ	10.1	8.7	900	89	8.7	174
	Control	7.2	9.8	1000	138	9.8	196
05 July 2001	CAPMZ	7.1	12.8	740	104	12.8	256
	Control	7.0	10.4	850	122	10.4	208
09 July 2001	CAPMZ	8.6	11.2	880	102	11.2	224
	Control	7.6	10.9	960	127	10.9	218
12 July 2001	CAPMZ	8.3	10.1	880	106	10.1	202
	Control	8.4	11.4	920	108	11.4	228
16 July 2001	CAPMZ	8.2	9.3	860	105	9.3	186
	Control	8.6	11.5	950	110	11.5	230
19 July 2001	CAPMZ	9.3	11.4	500	53	11.4	228
	Control	8.5	13.0	850	99	13	230

Sampling date	Cleaning line	Sludge concentration (g/L)		30-minute sludge sedimentation		Excess sludge	
		Aeration basin	Recirculation system	(ml/L)	SVI (ml/g)	Concentration (g/L)	Quantity (m ³ /day)
23 July 2001	CAPMZ	12.7	14.5	950	75	14.5	290
	Control	8	8.9	900	113	8.9	178
26 July 2001	CAPMZ	11.1	12.7	940	85	12.7	254
	Control	7.9	9.7	900	114	9.7	194
30 July 2001	CAPMZ	9.4	13.8	570	61	13.8	276
	Control	7.4	9.9	510	69	9.9	198
02 Aug. 2001	CAPMZ	9.2	15.9	750	82	15.9	318
	Control	7	11.2	770	110	11.2	224
06 Aug. 2001	CAPMZ	7.6	11.5	380	50	11.5	230
	Control	7	8.1	560	79	8.1	162
09 Aug. 2001	CAPMZ	6.9	10.8	500	72	10.8	216
	Control	7.2	10.6	730	101	10.6	212
13 Aug. 2001	CAPMZ	7.9	10.6	700	89	10.6	212
	Control	6.7	8.9	770	114	8.9	178
16 Aug. 2001	CAPMZ	7.9	9.1	560	71	9.1	182
	Control	7.2	8.9	800	110	8.9	178
22 Aug. 2001	CAPMZ	9.9	23.9	710	72	23.9	478
	Control	8.1	15.7	720	89	15.7	314
27 Aug. 2001	CAPMZ	10.2	10.7	910	89	10.7	214
	Control	8.5	21.4	850	100	21.4	428
30 Aug. 2001	CAPMZ	21.1	13.3	780	37	13.3	266
	Control	7.7	12.3	700	91	12.3	246
03 Sept. 2001	CAPMZ	9.1	15.1	680	75	15.1	302
	Control	8.4	13.0	840	100	13	260
06 Sept. 2001	CAPMZ	7.9	10.2	840	106	10.2	204
	Control	6.4	7.6.0	750	117	7.6	152
10 Sept. 2001	CAPMZ	7.6	9.0	910	119	9.0	180
	Control	6.7	6.2	850	127	6.2	124
13 Sept. 2001	CAPMZ	16	16.1	720	45	16.1	322
	Control	13.1	13.1	820	62	13.1	262
17 Sept. 2001	CAPMZ	7.3	9.3	900	123	9.3	186
	Control	5.6	6.5	890	159	6.5	130
19 Sept. 2001	CAPMZ	5.8	8.8	640	110	8.8	176
	Control	6.5	8.7	780	120	8.7	174
26 Sept. 2001	CAPMZ	10.7	12.2	500	46	12.2	244
	Control	9.5	8.8	820	86	8.8	176
01 Oct. 2001	CAPMZ	8.9	10.2	920	103	10.2	204
	Control	6.9	8.4	900	130	8.4	168
03 Oct. 2001	CAPMZ	10.3	9.1	900	87	9.1	182
	Control	8	7.8	930	116	7.8	156
08 Oct. 2001	CAPMZ	9.2	12.2	850	92	12.2	244
	Control	7.1	8.8	750	106	8.8	176
10 Oct. 2001	CAPMZ	8.6	21.6	760	88	21.6	432
	Control	7.2	23.2	780	108	23.2	464
15 Oct. 2001	CAPMZ	10.6	11	850	80	11.0.0	220
	Control	8.0	9.2	800	100	9.2	184

Sampling date	Cleaning line	Sludge concentration (g/L)		30-minute sludge sedimentation		Excess sludge	
		Aeration basin	Recirculation system	(ml/L)	SVI (ml/g)	Concentration (g/L)	Quantity (m ³ /day)
17 Oct. 2001	CAPMZ	9.9	11.4	750	75	11.4	228
	Control	7.5	10.0	780	104	10	200
24 Oct. 2001	CAPMZ	10.8	13.7	800	74	13.7	274
	Control	12	20.6	650	54	20.6	412
29 Oct. 2001	CAPMZ	19.1	20.1	700	37	20.1	402
	Control	4.3	10.6	710	165	10.6	212
05 Nov. 2001	CAPMZ	15.2	14.2	820	54	14.2	284
	Control	6.0	7.9	910	152	7.9	158
12 Nov. 2001	CAPMZ	7.1	9.3	750	106	9.3	186
	Control	3.6	5.1	480	133	5.1	102
14 Nov. 2001	CAPMZ	5.8	6.2	900	155	6.2	124
	Control	4.3	5.6	820	190	5.6	112
19 Nov. 2001	CAPMZ	5.0	5.6	840	168	5.6	112
	Control	3.1	5.8	800	258	5.8	116
21 Nov. 2001	CAPMZ	4.5	5.2	700	155	5.2	104
	Control	4.0	4.2	770	192	4.2	84
26 Nov. 2001	CAPMZ	5.0	4.7	940	188	4.7	94
	Control	4.4	4.1	950	216	4.1	82
28 Nov. 2001	CAPMZ	8.0	6.0	950	118	6	120
	Control	4.4	5.4	970	220	5.4	108
03 Dec. 2001	CAPMZ	4.1	5.5	950	231	5.5	110
	Control	4.7	5.2	980	208	5.2	104
05 Dec. 2001	CAPMZ	9.4	5.5	980	104	5.5	110
	Control	7.0	5.2	980	140	5.2	104
10 Dec. 2001	CAPMZ	5.8	6.8	930	160	6.8	136
	Control	5.4	6.3	920	170	6.3	126
12 Dec. 2001	CAPMZ	7.0	12.7	920	131	12.7	254
	Control	4.6	12.1	470	102	12.1	242
17 Dec. 2001	CAPMZ	7.7	12.2	940	122	12.2	244
	Control	5.2	13.1	840	161	13.1	262
7 January 2002	CAPMZ	8.2	13.0	800	98	13	260
	Control	5.6	14.2	710	128	14.2	284
9 January 2002	CAPMZ	5.2	7.1	510	98	7.1	142
	Control	5.2	9.2	650	125	9.2	184
14 January 2002	CAPMZ	5.9	9.2	480	81	9.2	184
	Control	6.4	7.9	650	101	7.9	158

Technical Annex 2: Description and Users Guide of ZeoRapMod Model, 1 piece CD

Model for Assessing the Improvement of the Biological Degradability of Wastewaters and that for the Changes in Treatment Cost, upon the Application of Modified Zeolites (ZeoRap[®])

DESCRIPTION AND USERS GUIDE

The model called ZeoRapMod was made on the basis of the experimental data of a joint NATO (Science for Peace 972494) and Ministry for Education (OMFB-02467/2000) Project. A short project introduction can be found in English and Hungarian languages under the menu item “**Guide/About Project**”. A more detailed description of the Project is found on the following homepage: www.living-planet.hu. Both the experiments and the model concern biological wastewater treatment plants (WTP) consisting of an aeration basin and a secondary settling tank. The schematic diagram of these WTPs is shown on the software main page).

The model-software was developed in order to enable the WTPs’ technical managers and operators to (1) predict the water and sludge quality improvements upon the application of ZeoRap[®] technology, (2) determine the optimal ZeoRap[®] dosage rate and (3) assess the cost-benefit affects of the ZeoRap[®] technology on wastewater treatment.

About the model-software

The model-software was developed on the basis of the data of the industrial-scale experiments carried out during the above named NATO-OMFB Project. The data analysis was focussed on the determination of the improvement of the pollutant removal efficiency of the treatment system upon the dosage of ZeoRap[®]. This was done by writing mass balances of the form of differential equations for either on the entire system or its partial units (depending on the data on a given experiment). In doing so the removal rate of the system or part of it was represented by a single lumped reaction rate coefficient K_{rem} . (This parameter is called “the model coefficient” on the screens of the software). Therefore, the model developed is not a process model or design tool for treatment systems, but it is a mass balance model, which defines the relation between the pollutant concentrations of the influent and the effluent of the system. (If you wish to see the model equations click on the tab “**Model Equations**”). Next we tried to identify the relationship between the rate coefficient K_{rem} and the ZeoRap[®] dosage rate. Further on, this relationship was transformed into one, which specifies the relation between the improvement of the pollutant removal efficiency (that of the model coefficient) [%] and the ZeoRap[®] dosage rate [%, $kg_{ZeoRap}/100*kg_{dry\ sludge}$]. On the screen the user sees these functions only, when he/she decides so by clicking on the respective menu item “**Model/Select model**” (see below in paragraph 6 of the chapter “Instruction for users” for more details). The model selection step can also be skipped and then the model uses a default model function. This model function, selected in one of the above mentioned two ways, is used in the programme for calculating the improvement of the efficiency of the wastewater treatment system upon ZeoRap[®] dosage.

A similar relationship was identified between the Sludge Volume Index (SVI) and the ZeoRap[®] dosage rate, as well as the SVI improvement as a function of ZeoRap[®] dosage was also determined.

The software also offers a cost-benefit analysis for the selection of the appropriate (optimum) ZeoRap[®] concentration. The data needed for this are to be entered by the user, using the respective menu item and include (1) the environmental penalty values of the relevant (effluent) standard, (2) the respective limit values of the standard for the location of the given plant, (3) the costs of the ZeoRap[®] technology (investment cost and the unit price of ZeoRap[®]). If the user does not specify the penalty rates and standard limit values, then the programme uses the respective Hungarian standard [Joint decree of KöM-KöViM No. 9/2002. (III.22)].

For the model calculations the user can select from among the models of the different experiments.

This was necessitated by the fact that the results obtained for the various pilot experiments were not comparable with each other. If the user does not select a model version then the programme uses a default model function.

Instructions to users

The language of the programme can be selected from the main menu (“**Language-Nyelv**”) from among English and Hungarian. Each of the steps can be reached also from the main menu. The use of the programme is facilitated by the “**Next**” and “**Back**” keys, shown on the bottom of the screen, following a pattern of work steps.

The main menu items are as follows (*tab captions are in italic letters*):

Data	
	New model data
	Open model file...
	Save model file ...
	Technical data
	Water Quality data
	Cost – Efficiency parameters
	<i>Penalty</i>
	<i>Cost</i>
Model	
	Select model
	Run model
	<i>Results tabulated</i>
	<i>Results graph</i>
	<i>Cost-benefit tabulated</i>
	<i>Cost-benefit graph</i>
	<i>SVI</i>
Language - Nyelv	
	Magyar – Hungarian
	Angol – English
Guide	
	<i>Main page</i>
	<i>Project introduction</i>
	<i>Users guide</i>
	<i>Model equations</i>
About...	

Below we give a typical sequence of work-steps for the user:

1. Enter first the main menu item “**Data**” and start “**New model data**” entering the main technical and flow data of your WTP. If you continue a work, which was started earlier, saving the results into a file, you may read in these data by clicking on “**Open model file**”. Next the data can be edited using the menu item “**Technical data**”.

After having selected an item by clicking on one of the rows of the table, you may enter your data for that item by a “slider” which can be found on the bottom of the screen. The using of arrows of the keyboard can make fine-tuning of the slider, else you are to use the mouse. (The keyboard cannot be used for entering data.) The error (if any) made in entering data (from the point of view of correct mass and water balances) is also presented if you click on the button “**status of calculated data**”, specifying also the type of error.

2. Clicking on the “**Next**” key you move to the screen for entering water quality data. Do enter the concentration data of the influent and effluent of your plant for each of the parameters you want to consider. Here you enter the data also by the slider and the “move arrows”.
3. Clicking on the “**Next**” key you move to the screen for showing the model results. The means of visualising the results can be selected from among the “tabs” on the top of the screen. These are:

alising the results can be selected from among the “tabs” on the top of the screen. These are:

- “**Results tabulated**”, which show for each of the parameters you have selected (rows) and for various ZeoRap[®] dosage rates (columns) the expectable pollutant concentration and annual load of the effluent. Where the model yields negative data a zero (0) appears in the cell;
 - “**Results graph**”, which show the graphical form of the table. You see the result of a single parameter at a time, and then you may select other one by clicking on the parameter list on the left side of the screen;
 - “**Cost-benefit tabulated**”, which shows as a function of ZeoRap[®] dosage (columns) the variation of expectable costs and savings by calculating the following components:
 - “Concentration over limit (mg/l)”, that is the difference between the predicted effluent concentration and the effluent standard value relevant to the site (standard value should be by the user)
 - “Predicted penalty (1000 currency unit/year)”, which is calculated on the basis of the total excess load (corresponding to the excess concentration) and the environmental penalty rate. The penalty value is calculated for each water quality parameter considered by the user and then summed up to yield the total predicted penalty (The environmental penalty rate for each component should be entered in cost/kg_{pollutant} unit.);
 - “Cost of ZeoRap[®] treatment (1000 currency unit/year)”, which is calculated as the sum of the annual amortization of the investment (of ZeoRap[®] feeder) and the operation costs (of ZeoRap[®] technology);
 - “Cost - benefit [1000 currency unit/year]”, which is calculated by comparing the environmental penalty cost belonging to the traditional wastewater treatment technology to the sum of the “extra-costs” and “penalty remained” belonging to the ZeoRap[®] technology. The ZeoRap[®] technology results in cost-saving in cases where penalty saving (penalty decrease) exceeds the total cost of ZeoRap[®] treatment. The cost to benefit analysis in this case will result in a positive figure.
 - “**Cost-benefit graph**”, which shows the variation of the “Predicted penalty”, “Costs of ZeoRap[®] treatment” and “Benefit” as a function of the applied ZeoRap[®] concentration. The “Benefit” curve may have (in certain cases) a maximum value, which points out the optimum dosage rate of ZeoRap[®]. In this case the programme marks this optimum point;
 - “**SVI**”, which shows, both in graph and table, the variation of SVI values as a function of ZeoRap[®] concentration. (SVI is a good indicator of sludge settling properties. (The lower the SVI the better the sludge quality.)
4. Clicking on the “**Next**” key, on the screen which visualizes the results, you move to the screen for saving your model results obtained so far; You also can do so by entering the main menu item “**Data/Save model file**”. The saved file will contain all technical, water quality and model data and the user may continue the work later by reading the data when entering the main menu item “**Data/Open model file**”.
 5. The data needed for the calculation of costs and savings (for that of the predicted penalty and the cost of ZeoRap[®] application) can be entered from the menu item “**Data/Costs-Efficiency parameters**”. Here the user may enter the standard limit values of the effluent concentrations, the relevant penalty rates, as well as the investment and operation costs of the ZeoRap[®] technology. If the user does not specifies penalty rates and standard limit values, the programme uses the respective Hungarian standard [Joint decree of KöM-KöViM No. 9/2002. (III.22)].
 6. From the main menu item “**Model/Select model**” the user may view all the models available in the programme. First you select a parameter using the “tabs” on the top of the screen, then you can select the experiment the model of whose you wish to use (selecting also from regression functions of the first or second order type). In the upper part of the screen there is a table for model selection. At this point the graphical form of the model function appears in the lower left corner of the screen. On the right side window, next to the graph, you find basic information and data on the experiment, the model of which you have selected. These data and information may help you in selecting the WTP (and its model), which is closest to your own WTP. If you do not select a model the software uses a default model function.