XVII IMEKO World Congress
Metrology in the 3rd Millennium
June 22–27, 2003, Dubrovnik, Croatia

COMPLEX ANALYTICAL PROCEDURE FOR THE CHARACTERIZATON OF MODIFIED ZEOLIZE AND FOR THE ASSESSMENT ITS EFFECTS ON BIOLOGICAL WASTEWATER TREATMENT

Peter Princz[1], *József Oláh*[1], *Scot Smith*[2], *Kirk Hatfield*[2]

[1]Living Planet Environmental Research, Ltd. Budaörs, Hungary; [2]University of Florida, Gainesville, USA

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 [1].

In order to determine the chemical composition and the stability of the CAP modified zeolite (SMZ), as well as predict its effects on the biological treatment of wastewater, total organic carbon (TOC), Fourier transform infrared (IR) spectroscopic measurements, as well as laboratory and pilot scale biological degradability tests were carried out.

The data of TOC and IR measurements showed that using the patented zeolite modification method 1-3 mg CAP could be chemically attached to the surface of 1 g natural zeolite of 100 µm grain size. The stability test of SMZ showed that 93 % of the CAP-zeolites bonds remained stable at even pH 9 after 3 days.

The pilot scale experiments in harmony with the laboratory ones applying SMZ resulted in significantly better effluent water quality and verified that SMZ additive was capable to increase the capacity of WTPs expressed in chemical oxygen demand (5-40%), biochemical oxygen demand (50-40%), organic nitrogen removal (40-70%), ammonical-nitrogen removal (50-80%), phosphorous removal (15-20%) and suspended solids removal (30-40%).

Keywords

***Z**eolite, wastewater, analysis*

1 INTRODUCTION

The most often used wastewater treatment method is the aerobic biological one in which the organic pollutants are decomposed by bacteria in the presence of oxygen. The culture of bacteria forms a living, activated sludge. The capacity and the loadability of WTPs 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.

The traditional Zeoflocc® method based on the application of natural zeolite [2, 3], however had a significant drawback. Development of the biomass on the zeolite surface was a slow process, consequently the additive became effective only after 5 - 7 days.

One of the most promising approaches to accelerate the immobilization of bacteria on the surface of zeolite particles was the pre-treatment of zeolite with CAPs. The patented additives used for wastewater treatment are the physical mixture of zeolite, CAPs and other materials [4, 5, 6]. Our earlier experiments showed however, that the zeolite-CAP mixture was not stable enough in aqueous media. As a consequence of the week physical absorption, CAP molecules were easily remobilised 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 media. Consequently there is no joint zeolite-CAP effect.

Taking into consideration that the efficiency of zeolite-CAP additive considerably depends on the CAP content of SMZ, (1) bond-strength examination, (2) CAP content determination, (3) stability tests, as well as (4) laboratory and (5) pilot scale biological degradability tests were performed in order to predict the effects of SMZ on wastewater treatment.

2 EXPERIMENTAL

2.1 Bond strength examination

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

10 g of SMZ (particle size < 100 µm) 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.

2.2 Determination of the chemically bound CAP content of SMZs

Quantity of the chemically bound CAP content of different SMZ products was determined in the form of organic carbon by total organic carbon (TOC) measurements. SMZs were washed through with TOC-free water to remove the mechanically adhered CAP molecules. Thereafter the TOC of the "unwashable" CAP content of SMZs was determined.

1g of SMZ was suspended in 1 litre of TOC-free water. The suspension was settled and decanted. The above treatment of washing was repeated 5 times.

2. 3 Stability test of the zeolite-CAP bond

Examination of the stability of zeolite-CAP bond was as follows: 130g of SMZ containing 3 $mg_{\text{"unwashable"TOC}}/g_{zeolite}$ was suspended in 1 litre of TOC-free water. The suspension was intensively stirred and the TOC concentration in the aqueous phase was measured as a function of pH (pH: 4.5, pH: 7.1, pH: 9.1) and time (0.5 - 72 hour)

2.4 Laboratory scale biological degradability tests

In order to quantify the effects of SMZ on the effluent water quality and sludge settling properties, laboratory experiment were carried out using different zeolite-CAP products.

An innovative respirometer was developed for modelling the operation of the biological WTPs 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 schematic diagram of the equipment is shown in Fig. 1. The parameters of experiments (flow rate, hydraulic detention time, biological loading, sludge concentration, sludge age, recirculation ratio, excess sludge removal) set on the respirometer were calculated on the basis of the operational data of the WTP of Szob.

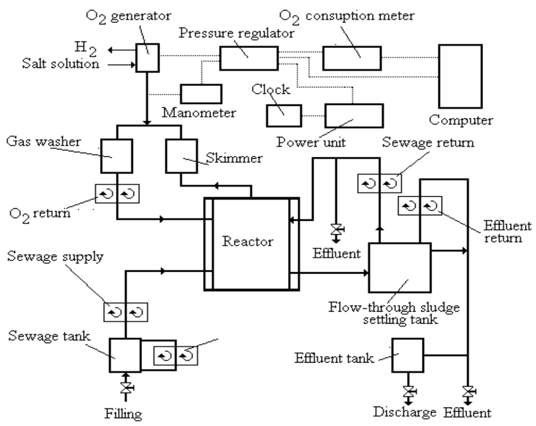

Fig. 1 Continuous Respirometer Schematic Diagram

Description of respirometric experiments is as follows:

2,000 ml wastewater containing 6 g activated sludge and 600 mg SMZ (10% SMZ related to the sludge content) was poured into the biological reactor of respirometer. The reactor was continuously aerated and fed with row wastewater containing SMZ in 30 mg/l. The feeding rate of the raw wastewater and the rate of recirculation was set to 4,000 ml/day (twelve-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 and the sludge sedimentation was examined. The experiments were carried out without SMZ additive and different SMZs.

2.5 Pilot scale experiments

The wastewater treatment technology using SMZ was installed and set to work at the WTP of Szob in Hungary. The operators to ensure the reliable examination of the effects of SMZ divided the WTP into two identical cleaning lines. One of the lines, the so-called SMZ one, was fed with SMZ. The other line, the reference one, served as a control.

The main technical data of the WTP of Szob are summarized in Table 1.

Table 1 Technical Data for the WTP of Szob

Character of influent wastewater:	Domestic and industrial
Total hydraulic capacity of WTP:	1,000 m^3/day
Volumetric capacity of zeolite line:	500 m^3/day
Volumetric capacity of reference line:	500 m^3/day
Technical specifications of both 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:	2,021 kg
• Volume of secondary settling tank:	235 m^3
• Dry sludge concentration in the secondary settling tank:	10,6 kg/m^3
• Dry-sludge quantity in the secondary settling tank:	2,491 kg

The experiments started on March 2001 and were completed on January 2002. The daily quantity of the applied SMZ ranged between 7 and 14 kg.

Wastewater and sludge samples were taken twice a week. Daily average water samples were collected from the influent wastewater and from the effluent water of SMZ and Reference lines. Sludge samples were taken from both aeration tanks and recirculation systems.

Water samples were analysed for pH, COD, filtered COD (COD_f), BOD_5, TOC, NH_4-N, Kjeldahl-N, NO_3–N, total-P and suspended solids. The quality parameters of sludge analyses 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.

3 RESULTS AND DISCUSSION

3.1 Bond strength examination

The IR spectrums of different SMZs, 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 SMZs are shown in Table 2 and Fig. 2. The data show that CAP molecules change 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 is stronger than a physical adsorption.

Table 2 Absorption bands of natural zeolite and the mixture of H-form zeolite and CAP

Sample type	Adsorption bands
	3700-3200 cm^{-1}
Natural zeolite	3740, 3637, 3555, 3406,3220
0.1 $g_{CAP}/10g_{zeolite}$*	3740, 3637, 3555, 3400, 3196
0.2 $g_{CAP}/10g_{zeolite}$*	3636, 3555, 3400, 3200
0.4 g $g_{CAP}/10g_{zeolite}$*	3638, 3554, 3400, 3200
	1st group
Natural zeolite	1210, 1155, 1137 (doublet)
0.1 $g_{CAP}/10g_{zeolite}$*	1212, 1155, 792, 725, 600
0.2 $g_{CAP}/10g_{zeolite}$*	1210, 1153, 789, 720,598
0.4 g $g_{CAP}/10g_{zeolite}$*	1212, 1157, 789, 723, 598
	2nd group
Natural zeolite	1075, 1026, 1008 (doublet)
0.1 $g_{CAP}/10g_{zeolite}$*	1073, 1054, 1034 (triplet)
0.2 $g_{CAP}/10g_{zeolite}$*	1076, 1032 (doublet)
0.4 g $g_{CAP}/10g_{zeolite}$*	1086,1069, 1031, 969

Legend: *: AP/zeolite ratio during zeolite modification

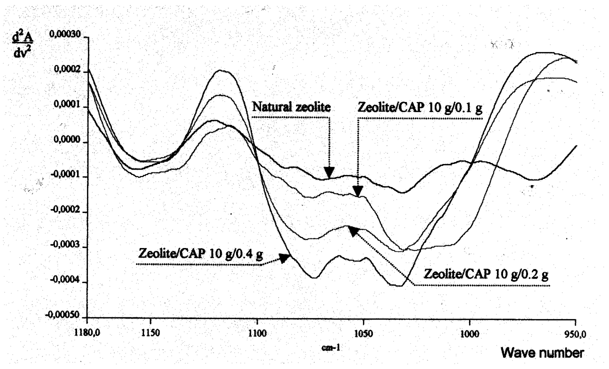

Fig. 2 Second derivatives of the absorbency of natural and modified zeolites as a function of wave number

3. 2 Determination of the chemically bound CAP of SMZ

The TOC data of a Hungarian natural zeolite treated with Polyacrylamine (molecule weight: 50.000) are summarized in Table 3. The data show that

- CAP molecules can not be attached chemically to the natural zeolite (there is no the ″unwashable” TOC-increase on the zeolite),
- If the zeolite is in H- or NH_4 form or natural zeolite are treated with the acidic solution of CAP the ″unwashable” TOC-increase ranges between 1 and 3 $mg_{TOC}/g_{zeolite}$, i.e. max. 3 mg CAP can be chemically attached to the surface of 1 g natural zeolite of 100 µm grain size.

3. 3 Stability test of the zeolite-CAP bond

The TOC data of stability tests are summarized in Table 4 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 390 mg/L, it can be stated that more than 93 % of the CAP-zeolite bonds remained stable at even pH 9 after 3 days.

Since the pH of communal wastes is always below 9, the zeolite-CAP connection can be considered stable in the process of wastewater treatment.

Table 3 Relationship between the quantity of CAP used for modification and the TOC content of zeolite-CAP product

Type of zeolite and treatment with CAP	TOC content ($mg_{TOC}/g_{zeolite}$)				
Natural zeolite	2.18	2.40	2.34	2.30	2.20
Zeolite – CAP mixture	1.85	2.11	2.19	2.10	2.17
H- zeolite + CAP	1.85	4.68	4.34	3.92	3.04
NH_4- zeolite + CAP	1.67	4.56	4.31	3.75	3.16
Zeolite + acidic CAP	1.57	4.56	4.31	3.75	3.16
Quantity of CAP (g) used for 10 g of zeolite	0.0 g	4.0 g	0.4 g	0.2 g	0.10 g

Table 4 Examination of CAP-zeolite bond strength as a function of pH and time

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	15.3	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: H-form of zeolite was used for producing SMZ examined

3.4 Laboratory scale biological degradability tests

Some typical data of the laboratory scale measurements are summarized in Table 5 and 6. The data show that

- the application of SMZ, regardless of its kind, resulted in better effluent quality in the case of all water parameters and sludge settling properties expressed in Sludge Volume Index (SVI),
- application of SMZs having chemical zeolite-CAP bonds (H-form zeolite + CAP, NH_4-form zeolite + CAP, Zeolite + acidic CAP) yielded the most significant water and sludge quality improvement
- the water and sludge quality improvement increased with the SMZ concentration,

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Table 5 Water quality data of the laboratory-scale biological degradability experiment using different SMZ products

Waste-water	Type of SMZ	COD (mg/L)	BOD_5 (mg/L)	NH_4-N (mg/L)	SVI (ml/g)
Influent		975	313	8.63	
	No SMZ addition	101	39	3.63	128
	Natural zeolite + CAP	75	29	1.20	68
	H-form zeolite + CAP	61	24	1.13	50
	NH_4-form zeolite + CAP	65	22	1,13	52
	Zeolite + acidic CAP	60	24	1,13	53

Note: Influent wastewater originated from the WTP of Szob
Applied SMZ concentration is 10 % in $g_{SMZ}100/g_{sludge}$ unit

Legend: COD: Chemical oxygen demand
BOI_5: Biochemical oxygen demand,
NH_4-N: Ammonical nitrogen, Org.-N: Organic nitrogen

Table 6 Water and sludge quality data of the laboratory-scale biological degradability experiment carried out with the effluent water of the WTP of Szob

Waste-water	SMZ addition	COD (mg/l)	BOD_5 (mg/l)	TOC (mg/l)	NH_4-N (mg/l)	Kjeldahl-N (mg/l)
Influent		975	313	395	8,63	75,1
Effluent	0 % SMZ	101	39	10	3,63	69,2
	5 % SMZ	87	29	8,6	2,05	59,2
	8 % SMZ	70	26	7,5	1,85	57,0
	10 % SMZ	61	24	7,1	1,13	56,5
Waste-water	SMZ addition	NO_3-N (mg/L)	Total-P (mg/L)	SS (mg/L)	OUR (mg/gh)	SVI (ml/g)
Influent		0,1	17,9	260	-	
Effluent	0 % SMZ	0,1	12,8	82	15.2	128
	5 % SMZ	0,2	10,4	65	16.5	83
	8 % SMZ	0,3	10,0	57	17.8	56
	10 % SMZ	0,4	9,8	53	19.0	50

Note: H-form of zeolite was used for producing SMZ applied

Legend: COD: Chemical oxygen demand
BOI_5: Biochemical oxygen demand
TOC: Total organic carbon
NH_4-N: Ammonical nitrogen
NO_3-N: Nitrate nitrogen
Total-P: Total phosphorous
SS: Suspended solids
OUR: Oxygen uptake rate (mg_{02}/g_{sludge}hour)
SVI: Sludge volume index
%:: SMZ content of the activated sludge ($g_{SMZ}100/g_{sludge}$)

3.5 Pilot scale experiments

Results of the pilot scale experiment are introduced on the example of BOD_5.

The BOD_5 values measured in the effluent water of SMZ and Reference lines are shown in Fig. 3. It can be seen that usually both cleaning lines operated satisfactorily between March and September. In October and November however, the water quality frequently exceeded the related standard value (25 mg BOD_5/l) and the effluent water quality in the Reference line became extremely poor in many cases. Differences between the water qualities of the two cleaning lines were the most significant in the season of high load.

The correlation between the BOD_5 values measured in the two cleaning lines at the same time is shown in Fig. 4. This figure shows that at smaller concentrations the relationship is a linear one that changes to logarithmic one at higher concentrations.

Fig. 5 shows the improvement of effluent water quality as a function of the quantity of SMZ used. It can be seen that the percentile values of BOD_5 decrease directly proportionate with the SMZ concentration.

The pilot scale experiments verified the results of the previous laboratory scale ones, namely, the application of SMZ having chemically bound CAP increased

- the decomposition rate of organic compounds expressed in COD by about 5 - 40%,
- the biodegradation of organic nitrogen compounds by 40 - 70%,
- the nitrification rate by 50 -80%,
- the rate of phosphorous removal by 15 – 20%,
- the rate of suspended solids removal by 30 - 40%,
- the sludge settling rate expressed in SVI by 30 - 60%.

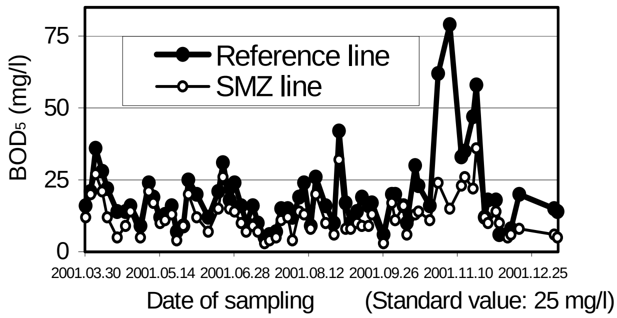

Fig. 3 BOD_5 values measured in the effluents of the Reference and SMZ lines of the WTP of Szob

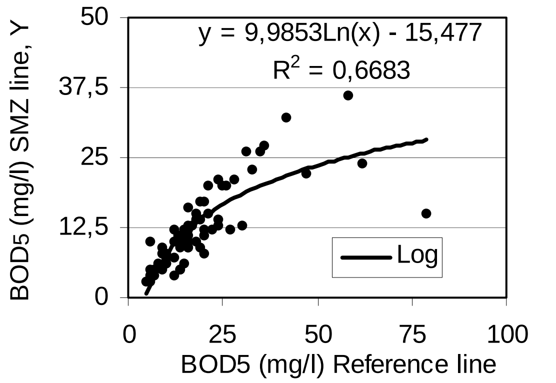

Fig. 4 Relationship between the BOD_5 values measured in the effluents of the Reference and SMZ lines at the WTP of Szob

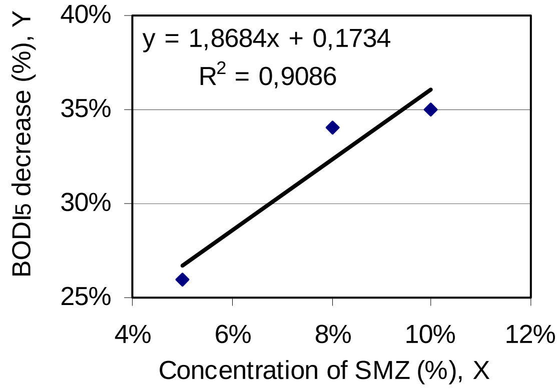

Fig. 5 Differences between BOD_5 values measured in the Reference and SMZ lines of the WTP of Szob WTP vs. SMZ concentration

4 CONCLUSION

Based on the analytical examinations, the laboratory and pilot scale tests it can be stated that the

- creation of chemical connection between zeolite particles and CAP molecules makes necessary the pre-treatment of natural zeolite or CAP,
- chemically bound CAP content of SMZ has an important role in the development of the positive

effects of SMZ 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 water treatment.
- laboratory scale (respirometric) experiments are eminently suites to predict the expected effects of SMZ on effluent water and sludge quality,
- application of SMZ in biological wastewater treatment considerably enhances the operation of WTPs.

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Authors

Dr. Peter Princz, Living Planet Ltd., H-2040Szivárvány u. 10 Budaörs. Hungary Phone/fax: +36 1 334-0047, e-mail: lplanet@hungary.net

Dr. József Oláh, Living Planet Ltd., H-2040Szivárvány u. 10 Budaörs. Hungary Phone/fax: +36 1 334-0047, e-mail: lplanet@hungary.net

Prof. Dr. Scot Smith, University of Florida Gainesville, Florida 32611-2083 USA, Phone: +352 392 4990, Fax: +352 392 4957, e-mail: ses@ce.ufl.edu

Prof. Dr. Kirk Hatfield, University of Florida Gainesville, Florida 32611-2083 USA, Phone: +352 392 4975, Fax: +352 392 4957, e-mail: khatf@ce.ufl.edu