Study Of Microbial Degradation Of Polyvinyl Alcohol (PVA) In Wastewater Treatment Plants

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Introduction

For environmental and other reasons, it's important to overview the manufacture and chemical characterization of PVA as well as the PVA load of textile effluents discharged and the current level of knowledge on the microbial degradation of PVA. The evaluation conducted in Germany is based on experimental data collected between 1990 and 1992 which indicates that PVA is microbially degradable in conventional mechanical-biological wastewater treatment plants if fixed system requirements such as adaptation, constant influx, food to microorganisms ratios (F/M) under 0.15 kg BOD s/kg MLSS x d, and temperatures above 15°C are present.

The temperature dependence of the microbial degradation of PVA, up to now inadequately investigated, is presented in detail on the basis of experimental data and the results of laboratory investigations. Results show there is a drastic fall in the efficiency of PVA degradation through activated sludge in existing wastewater treatment plants at temperatures below 10-12°C. This may be attributed to the fact that at this temperature level, the wash-out rate of the PVA-degrading microorganisms is higher than the growth rate and their concentration is no longer sufficient for a quantitative degradation of the incoming PVA loads.

An important area of application of polyvinyl alcohol (PVA) is its use as sizing agent in the textile industry, for which it is the oldest fully synthetic polymer. Sizing agents are placed on the fibers before the weaving process to protect them. After the weaving process, the sizing agent has fulfilled its role. In subsequent finishing processes it is a disturbance and must therefore be completely washed out by more than 90%. This textile pretreatment process results in a high wastewater load, which amounts to a COD of 40-80% of the entire load from a textile finishing industry[3,4,5,6,7].

Table I: Specific COD- and BODs-values of the important sizing agents.

Kind of sizing agent	spec. COD-value [mg O2/g]	spec. BODs-value [mg O2/g]
Starch	900 -1000	500-600
Carboxymethylcellulose (CMC)	800 - 1000	50 - 90
Polyvinyl alcohol (PVA)	ca. 1700	30 - 80
Polyacrylates	1350 - 1650	< 50
Galaktomannanes	1000-1 150	400
PES-dispersions	1600 - 1700	< 50
Protein sizes	1 200	700 - 800

1) in consideration of the moisture percentage of commercial products
2) with non-adapted inocculum

Many investigations have been published about the microbial degradation of PVA. According to these sources, PVA is biologically degradable under certain conditions. These conditions are not always present in wastewater treatment plants and may lead to the exceeding of prescribed standards, especially of the sum parameter COD. This study investigates the requisite conditions for the microbial degradation of PVA. The chemical basis of PVA and an evaluation of its extent of use as a sizing agent. Although the data were gained from only one plant in Germany, the results relate directly to plants of a similar nature in other countries.

Technically, PVA (Figure 1) is manufactured overall through radical chain polymerization (in an organic solvent-usually methanol) of vinyl acetate with ensuing hydrolysis (saponification). The different PVA types result from variation of the reactions and procedure conditions (e.g. different methanol percentages for the control of the degree of polymerization or different catalyst concentrations to influence the residual acetyl group content etc). In the practical technical sense the molecular weight (degree of polymerization) and the residual acetyl group content (degree of hydrolysis or saponification) are the proper first line terms. Figure 2 shows a fully hydrolyzed (saponified) and a partially hydrolyzed PVA in idealized form, that is without reference to the steric configuration and without acetyl chain and main chain branchings.

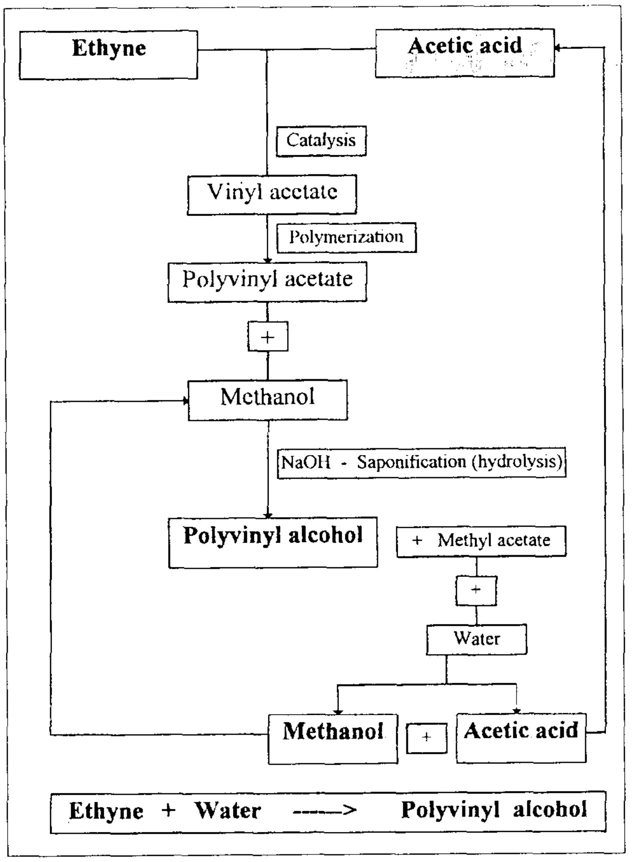
The molecular weight of technical

PVA is Gaussian shape distributed. The interpretation of considering the biological oxygen-demand (BOD) and the degradation curves, one should note, is that technical PVA could include lower molecular weight parts as well as chemicals remaining from the polymerization (especially methanol and acetic acid), which are more quickly and easily biodegraded than PVA polymers.

PVA quantities

According to an elaborately detailed estimate, about 15,000 tonnes of sizing agents are emitted yearly in the united Germany. The semi and fully synthetic sizing polymers (PVA, polyacrylates, CMC, polyesters) cover a share of about 45%. The imported textiles are predominantly produced with native sizing agents. Considering the import/export relationship, the amount of sizing agents that reaches the wastewater system from German textile finishing industries runs between 12,000 and 14,000 tons per year, respectively, about 14,000 t COD per year. The absolute share of PVA lies in a magnitude of 1,000 tons per year. The mass specific COD and BODs values for the most important sizing agents which are

Figure 1: Flow sheet of the industrial manufacture of PVA.



included in the previous estimate are shown in Table I.

The BOD5 value for PVA should be compared to the displayed values of methanol and acetic acid content as well as in given cases to the lower molecular weight PVA content which are, or can be present in technical PVA.

Microbial degradation

Biological degradability is not only a characteristic or a property of organic compounds, but also a system condition. In many cases the system with its requirements determines whether an organic chemical inside degrades or not and at what kinetic. The saying compound x is biologically degradable..." is often worthless without the specification of the system conditions. PVA is an outstanding example of this. As shown in the following, this polymer is quantitatively degraded in the system "biological wastewater treatment plant/activated sludge system" under the system conditions

- adapted microbial population,
- low food to microorganisms ratios (F/M) in [kg BOD5 or kg COD or kg PVA/kg MLSS x d] - (MLSS = Mixed Liquor Suspended Solids)
- constant influx and
- temperatures over 18°C.

In contrast, PVA passes through the same system largely unchanged under the conditions

- temporary influx and low input concentration so that no adaptation is possible,
- high F/M,
- temperatures under 10°C

This means that for the microbial PVA degradation the system conditions are crucial.

In the early 70's, on the basis of envisaged COD limits for the effluents of biological wastewater treatment plants in the US and in Japan, extensive and detailed investigations were conducted about the microbial degradation of PVA. These investigations have been somewhat forgotten in the German speaking regions. There it is clearly stated that PVA is degraded in mechanical- biological wastewater treatment plants, but specific conditions must be maintained.

These conditions are essentially:

- steady PVA influx
- sufficiently low F/M and sufficiently high sludge age and
- adaptation of the microorganisms, which as a rule demands several weeks.

Solely, the influence of temperature was not taken into account. These results are summarized in Table II. Table II also contains results of investigations which were obtained in the 80's and 90's. These relate to results of biological degradation tests which were conducted in the laboratory. They restate the knowledge which was determined between the beginning and middle of the 70's.

The investigations shown in Table II were performed exclusively with undefined mixed cultures of microorganisms, particularly with activated sludges from

Table II: Compilation of data for the biodegradation of polyvinyl alcohol (PVA) in different tests.

Year	Characterization of the test	PVA-degrad.rate [%]	Adaptation necessary for degrad.	F/MPVA [g PVA/ g MLSSxd]	Explanations/remarks	Lit.
1973	contin. laborat.-ETP	60	yes	0.46	adaptation time: 35-40 d	[10]
1973	contin. pilot-ETP	75	yes	0.32	PVA-percent. of COD-influent conc.: 60%; F/M_{COD}=0,9	[10]
1973	contin. pilot-ETP	>90	yes	0.02	F/M_{COD}=0,11; F/M_{BOD5}=0,06; infl. conc.: COD=700-1100 mg O_2/l, BOD_5=400-600; PVA=160 mg/l (30% of COD); no adsorption to the sludge; no loss of adaptat. after 7d (this time also depends on F/M); PVA-degrad. do not correlate with C-degrad,; spec. PVA-analysis	[10]
1974	Zahn-Wellens-test	>90	yes	-	adaptation as a prerequisite for PVA=degrad. is explained in detail	[11]
1975	contin. laborat.-ETP	>80	yes	<0.1	F/M_{COD}<0,1; in praxis, F/M is the key parameter for predicting the extend of microbial PVA-degradation	[12]
1975	contin. pilot-ETP	93	yes	0.05-0.25	1 m^3-plant; 200d-test; T: 20-27 °C; PVA-infl.: 100-1300 mg/l	[13]
1976	contin. laborat.-ETP	>80 -95	yes	<0.1-0.3	F/M_{COD}<0,1-0,3; use of fully adapted activated sludge; T: 20-23 °C; PVA-infl.=200 mg/l resp. 60-70% of COD-infl; no PVA-degrad. at F/M_{PVA}>1; spec. PVA-analysis	[14]
1978	Zahn-Wellens-test	>80	yes	-	no elimination through adsorption, no remarkable difference of the biodegradation between fully and partially saponified PVA	[15]
1980	Zahn-Wellens-test	>90	yes	-		[16]
1984	Zahn-Wellens-test	>80	yes	-	adaptation time at pH 8-9 is shorter than at pH 7 and tendentiously shorter in case of low-Viscosity PVA	[17]
1988	Zahn-Wellens-test	80	yes	-	adaptation time: 20d	[18]
1990	Zahn-Wellens-test	98-100	yes	-		[19]
1990	coupled-units-test	29	yes		no explanation for the low biodegradation rate	[19]
1992	Zahn-Wellens-test	80	yes	-	adapted activated sludges: 80 % degradation after 7d; non-adapted activated sludges" 0-18% degradation after 7d	[20]
1992	semibatch-test	90	yes	-	90% PVA-degrad. after 5d with 1 g/l PVA and fully adapted activ. sludge, adaptation is faster in case of partially saponified PVA, spec. PVA-analysis	[21]

legend: ETP = Effluent Treatment Plant; F/MCOD = Food/Microorgan. ratio related to COD in [g COD/g MLSS x d]; spec. PVA-analysis = PVA-degradation was controlled by PVA-specific analysis; MLSS=Mixed Liquor Suspended Solids; infl.=influent; COD=Chemical Oxygen Demand; BOD=Biological Oxygen Demand.

Figure 2: Simplified structural formula for polyvinyl alcohol (without acetyl chain and primary chain branching as well as without the three-dimensional structure) with the main distinction << fully and partially hydrolyzed >> resp. << fully and partially saponified >>

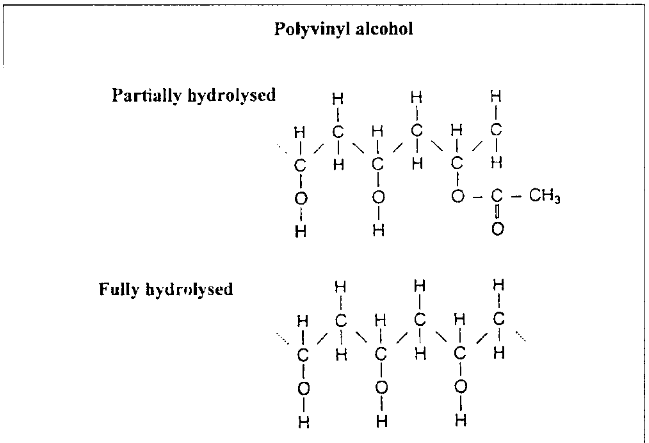
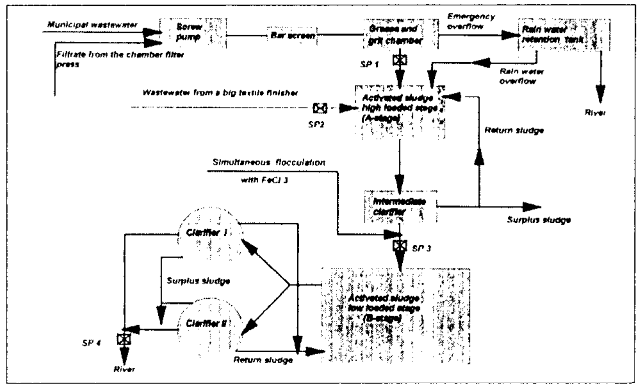


Figure 3: Flow Sheet of a Municipal Wastewater Treatment Plant in Münsterland, Germany with a percentage of textile Wastewater - in Case of Dry Weather - of 40-50 % (Status l992 before the extension of the plant with an ozonation, an activated carbon adsorption and a sand filtration stage) The wastewater of a big textile finishing industry plant was discharged to this plant by a separate pipe; SP1 - SP4 = Sampling points 1-4.



wastewater treatment plants. The degradation was followed with sum parameters such as COD or TOC/DOC. here are also numerous investigations about PVA degradation which were performed with defined strains of bacteria. An attempt was made to identify the microbial degradation path(s). According to a literature research by StraBner there are 29 publications from the period 1969-1991-with one exception all were from Japan-which show that *psuedomonas* are able to degrade or assimilate PVA.

We investigated the functions of a two-stage wastewater treatment plant located in Munsterland, in the North of Germany. The two biological stages are conceived according to the so called AB-process[2]*. Thereby, in the first A-stage, high F/M (F/M,BoD~ = 3-4 kg BOD5/kg MLSS x d) is applied, so that quickly growing microorganisms dominate which only metabolize carbon hydrogen bonds. In the B-stage, on the other hand, the growth of microorganisms with longer generation times (nitrificants and "degradation specialists") is possible, whereby nitrogen oxidation (nitrification) occurs and more difficultly degradable bonds can be replaced microbially[z3]. The flow diagram of this slant is shown in Figure 3.

Since 1992 an ozonation plant, an activated carbon adsorption stage as Nell as a sand filtration have been added. However, for the microbial PVA degradation considered here, that is not relevant. Of special significance is that the wastewater of a large full scale textile finishing industry is discharged to he wastewater treatment plant via a separate pipe. Moreover, a smaller textile finishing industry discharges its wastewater into the public sewer sysem.

Self-monitoring

The operator of the wastewater treatment plant takes flow proportional 24-hour composite samples at four different sampling points (SP) daily. As shown in Figure 3, the procedure concerns both influxes (municipal wastewater and from the textile finisher) as Nell as the sampling of the intermediate clarifier and the final clarifiers. At SP 1, SP 2 and SP 4 there are flow meters for he continuous measurement of the wastewater flow. COD is determined daily in all samples, PVA once weekly, at times every two weeks at the outlet of the intermediate (SP 3) and of the final clarifiers (SP 4). During a half year measurement plan in 1992 both influxes (SP 1 and SP 2) were also thoroughly analyzed for PVA. The original values of this measurement plan are summarized in Table III. Table IV contains the subsequent evaluations. According to the above, the textile wastewater discharged to the plant by a separate pipe amounts to approx. 40-50% of the total flow of wastewater. The percentage of COD load of the textile finisher runs between 55 and 75%.

From the desizing process an average of 200-300 kg of PVA flows daily into the wastewater treatment plant. About l0-40 kg PVA per day enter the plant with the municipal wastewater, originating mostly from the second textile finisher discharging to the public sewer system.

The inflowing PVA load represents about 10% of the COD influx load. This relatively high percentage and the observation that the COD effluent concentration of the wastewater treatment plant clearly increases in winter, allowed the assumption that PVA is no longer quantitively degraded at low temperatures, and this could be the cause of the COD increase during winter months. Therefore, the wastewater treatment plant operator began to follow the PVA degradation. For this a PVA specific investigation method was needed which is described as follows.

Table III: *COD- and PVA-Concentrations resp. Loads in the Influents, in the outlet of the A-stage and in the Effluent of a Municipal Wastewater Treatment Plant in Munsterland, Germany (See Figure 3) with a high Percentage of Textile Wastewater.*

Date	Wastewater flow in [cbm/d]			COD-Concentration in [mg O_2/l]				COD-Load in [kg O_2/d]				PVA-Concentration in [mg /l]				PVA - Load in [kg /d]			
1992	Mun. SP 1	TFI SP 2	Total	Mun. SP 1	TFI SP 2	IC SP 3	Effl. SP 4	Mun. SP 1	TFI SP 2	IC SP 3	Effl. SP 4	Mun. SP 1	TFI SP 2	IC SP 3	Effl. SP 4	Mun. SP 1	TFI SP 2	IC SP 3	Effl. SP 4
15.01.	6059	1885	7944	218	930	333	151	1321	1753	2645	1200	5.9	114	39	21	36	215	310	167
20.01.	5996	2686	8682	192	834	304	151	1151	2240	2639	1311	2.7	99	32	25	16	266	278	217
28.01	4158	2472	6630	412	812	425	171	1713	2007	2818	1134	6.8	61	35	27	28	151	232	179
04.02.	4570	2693	7263	323	890	414	180	1476	2397	3007	1307	3.9	86	34	24	18	232	247	174
27.02.	4629	2520	7149	204	992	331	185	944	2500	2366	1323	7.0	119	36	-	32	300	257	-
03.03.	4095	2008	6103	186	918	310	133	762	1843	1892	812	4.7	92	31	16	19	185	189	98
09.03.	3704	2832	6536	294	1054	327	183	1089	2985	2137	1196	3.4	94	43	18	13	266	281	118
17.03.	8555	3835	12390	174	874	272	143	1489	3352	3370	1772	4.1	78	25	18	35	299	310	223
25.03.	7887	3984	11871	192	1070	331	161	1514	4263	3929	1911	4.3	94	39	22	34	374	463	261
02.04	5135	3367	8502	235	1034	359	158	1207	3481	3052	1343	2.4	102	43	13	12	343	366	111
14.04.	5413	2871	8284	296	1082	359	139	1602	3106	2974	1151	5.2	76	31	7	28	218	257	58
21.04.	3667	2403	6070	243	890	247	127	891	2139	1499	771	3.1	62	30	10	11	149	182	61
08.05.	4053	3144	7197	380	1095	360	149	1540	3443	2591	1072	5.2	57	37	2	21	179	266	14
12.05.	4728	2802	7530	280	936	351	107	1324	2623	2643	806	4.9	70	36	2	23	196	271	15
20.05.	4087	3325	7412	347	976	482	117	1418	3245	3573	867	4.1	71	35	0.6	17	236	259	4
27.05.	3426	3308	6734	265	902	484	86	908	2984	3259	579	10.4	73	44	<0.1	36	241	296	<1
17.06.	3126	2951	6077	353	980	392	95	1103	2892	2382	577	15.0	117	57	2	47	345	346	12
22.06.	2446	1746	4192	374	972	321	72	915	1697	1346	302	7.0	117	47	1	17	204	197	4
02.07.	2901	2946	5847	519	902	502	80	1506	2657	2935	468	8.7	71	47	0.3	25	209	275	2
07.07.	3969	2831	6800	480	1047	519	86	1905	2964	3529	585	9 2	95	45	0.6	37	269	306	4
20.07.	2463	2341	4804	412	764	259	45	1015	1788	1244	216	4.6	58	27	0.6	11	136	130	3

Legend:
SP 1-4 = Sampling Points 1-4 as illustrated in Figure 3; SP 1 = Influent municipal wastewater; SP 2 = Influent TFI; SP 3 = IC outlet; SP 4 = Effluent - discharging point; Mun. = Municipal wastewater; TFI = Textile finishing industry, which discharges its wastewater to the treatment plant via a separate pipe according to Figure 3; IC = Intermediate Clarifier; Effl. = Effluent
For the analysis 24-h composite samples were taken during half a year in 1992.

Specific PVA analysis

The blue color reaction of PVA with iodine was already reported in 1927 later, it was determined that this greenish-blue color reaction is considerably more sensitive in the presence of boric acid. From this the test methods for PVA were developed. The photometric method for the determination of PVA in coated papers, published by Finley in 1961 was later modified by Hoechst AG for wastewater analysis". Thereby, the interfering influence of starch is taken into account. This disturbing influence is often present in conjunction with desizing and must be considered. The Hoechst method does not mention the time dependence of the formation of the greenish to blue PVA-boric acid-iodine complex which was already shown in 1964. A new work recognizes that and has recommended the application of extinction measurement according to a set time interval (e.g. 15 minutes)".

This work contains the following important conclusions for the analysis of PVA in wastewater:

- the individual PVA types (various degrees of polymerization and hydrolysis) differentiate themselves only slightly according to color intensity of the PVA-boric acid-iodine complex.

Figure 4: Corresponding PVA/COD elimination rates and waste water temperature of the low loaded stage of the effluent treatment plant, which can be seen from Figure 3; data from 1990-1992.

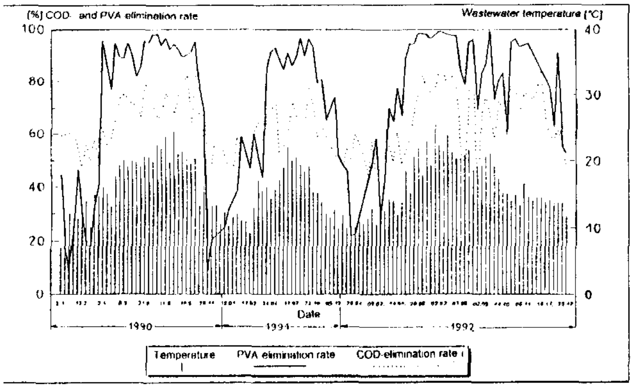
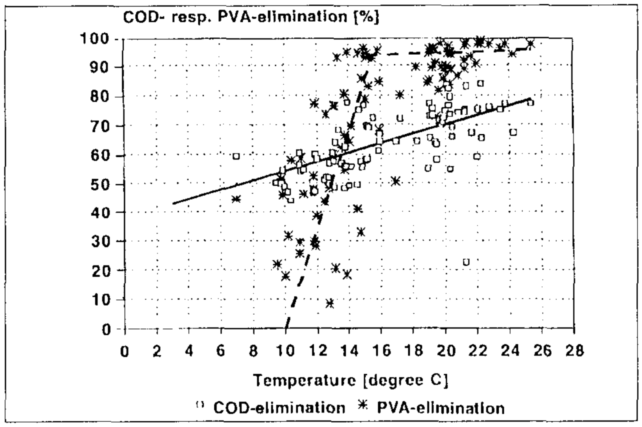


Figure 5: Correlation of PVA and COD elimination rates from Figure 4 with the wastewater temperature; data from 1990-1992.



- a correlation for the extinction of the PVA-boric acid-iodine complex exists neither with the degree of hydrolysis nor with the degree of polymerization (viscosity)
- the COD correlates well with the previously mentioned Hoechst method following the microbial degradation of PVA
- the method according to Finley and, therewith, also the Hoechst method are applicable to the analysis of wastewater.

For the determination of PVA degradation in the previously mentioned wastewater treatment plant, the Hoechst method was applied. In this manner, the samples were not filtered but only sedimented. The photometric determination proceeded 15-30 minutes after the addition of the reagents (boric acid and iodine-calcium-iodide solution). Present starch was enzymatically depolymerized before.

Evaluation and interpretation

The results of the half year measurement plan conducted in 1992 show that in the high loaded activated sludge stage (A-stage), the COD elimination rates strongly vary by 2050%. This can be attributed firstly to the equally strongly varying COD influx loads and to the various retention times (shortened particularly by occurrences of rain). In the A-stage with F/M of more than 34 kg BODs/kg MLSS x d with the predominant, fast-growing microorganisms there, which at first attack carbon bonds, PVA is not degraded (see PVA elimination rates in Table IV). The variations in the PVA elimination rates in the A-stage range from zero to values in the positive and negative range. This can be explained by the fact, that the sampling did not take into account the delayed retention time.

In every case it becomes significant that no stable, noteworthy PVA degradation takes place. On the contrary, in the low loaded activated sludge stage (B-stage) PVA elimination rates reach up to 99% at F/M under 0.1 kg BODs/kg MLSS x d. Thereby the values in the literature (see Table II) are confirmed. However, the elimination rates can also be under 20%. Because this appeared to be related to the low wastewater temperatures, the effect was pursued in detail to the correlation between PVA degradation in the low loaded stage and wastewater temperature therein.

To this end, not only the values of the measurement program in 1992 (see Tables III and IV) but also all the determined PVA and COD concentrations and loads in the years 1990 to 1992 were evaluated; from the input and output of the low loaded stage as well as the corresponding wastewater temperatures. Within this time frame, corresponding data for 108 days were available. In Figure 4 the determined PVA and COD elimination rates together with the associated temperature in the time period (1990-l 992) are recorded.

This graph shows directly how PVA degradation efficiency breaks down at wastewater temperatures under 12°C and only recovers again at temperaures above 15°C. At temperatures above 18°C - 20°C elimination rates of more than 90% are reached. The COD elimination decreases proportionally to he decreasing PVA degradation through which the observed COD increase in the cold seasons is essentially explained. The degradation of other organic compounds is, however, not as temperature dependent as the PVA degradation. Otherwise, the COD elimination would have to decrease even further.

The observable breakdown of the elimination rates in 1992 can be attributed to the expansion program on the wastewater treatment plant, which began at that time. For this, individual tanks were taken out of operation and the retention times in the activated sludge stage sank sharply.

Table IV: Proportional Percentages of Municipal Wastewater resp. Textile Wastewater with respect to the Flow, COD- and PVA-Load and COD- and PVA-Elimination Rates of a Municipal Wastewater Treatment Plant in Munsterland, Germany (See Figure 3) with a high Percentage of Textile Wastewater.

							Elimination rate				
Date	Wastewater flow Percentages of the total flow in [%]		COD-load Percentages of the total influent load in [%]		PVA-load Percentages of the total influent load in [%]		High loaded stage in [%]		Low loaded stage in [%]		Temperature of the efflue. in [°C]
1992	Mun.	TFI	Mun.	TFI	Mun.	TFI	COD	PVA	COD	PVA	
15.01.	76.3	23.7	43.0	57.0	14.3	87.7	14.0	- 23.5	54.7	46.2	9.9
20.01.	69.1	30.9	33.9	66.1	5.7	94.3	22.2	+ 1.5	53.3	21.9	9.5
28.01.	62.7	37.3	46.0	54.0	15.6	84.4	24.2	- 29.6	59.8	22.9	10.0
04.02.	62.9	37.1	38.1	61.9	7.2	92.8	22.3	+ 1.2	56.5	29.4	10.9
27.02.	64.8	35.2	27.4	72.6	9.6	90.4	31.3	+ 22.6	44.1	-	11.2
03.03.	67.1	32.9	29.3	70.7	9.3	90.7	27.4	+ 7.4	57.1	48.4	12.8
09.03.	56.7	43.3	26.7	73.3	4.6	95.4	46.8	- 0.7	44.0	58.1	10.4
17.03.	69.0	31.0	30.8	69.2	10.5	89.5	30.4	+ 7.2	47.4	28.0	11.9
25.03.	66.4	33.6	26.4	73.6	8.3	91.7	32.0	- 13.5	51.4	43.6	12.5
02.04.	60.4	39.6	25.7	74.3	3.4	96.6	34.9	- 3.1	56.0	69.8	14.2
14.04.	65.3	34.7	34.0	66.0	11.4	88.6	37.9	- 4.5	60.6	77.4	11.9
21.04.	60.4	39.6	29.4	70.6	6.9	93.1	50.5	- 13.8	48.6	66.7	13.8
08.05.	56.3	43.7	30.9	69.1	10.5	89.5	48.0	- 33.0	58.6	94.6	15.2
12.05.	62.8	37.2	33.5	66.5	10.5	89.5	33.0	- 23.8	69.5	94.4	20.5
20.05.	55.1	44.9	30.4	69.6	6.7	93.3	23.4	- 2.4	75.7	98.3	22.1
27.05.	50.9	49.1	23.3	76.7	13.0	87.0	16.3	- 6.9	82.2	-	17.8
17.06.	51.4	48.6	27.6	72.4	12.0	88.0	40.4	+ 11.7	75.8	96.5	19.3
22.06.	58.3	41.7	35.0	65.0	7.7	92.3	48.5	+ 10.9	77.6	97.9	25.4
02.07.	49.6	50.4	36.2	63.8	10.7	89.3	29.5	- 17.5	84.1	99.4	22.3
07.07.	58.4	41.6	39.1	60.9	12.1	87.9	27.3	+ 3.2	83.4	96.7	21.4
20.07	51.3	48.7	36.2	63.8	7.5	92.5	55.6	+11.6	82.6	97.8	21.3

Legend:
Mun. = Municipal wastewater; TFI = Textile finishing industry,
The calculations were done by hand of the values given in Table III.

In Figure 5 the correlation of the PVA and COD elimination rates is depicted With respect to the temperature. Accordingly, temperatures above 18°C are effective for PVA elimination rates of more than 80% in biological wastewater treatment plants. Naturally the system conditions of "adapted microbial populations" and F/M,PvA < 0.1 kg PVA/kg MLSS x d with F/M,BoD~ < 0.15 kg B0Ds/kg MLSS x d (see Table II) must 3150 be present. Temperatures above 20°C are optional while at temperatures under 10°C the degradation at the given retention times is greatly hindered. This indicates exactly the temperature level at which the metabolism of the nitrifying bacteria also decreases significantly.

The nitrifying bacteria can also be attributed to the psuedomonas. As mentioned, numerous psuedomonas have been isolated which can attack/degrade PVA microbially. The growth rate of the PVA degrading microorganisms is less at temperatures under IO*C-12°C than the wash-out rate, which leads to elimination rates at this temperature level gradually retreat to under 20%.

These results could be interpreted even more clearly with a mathematical model of the PVA degradation. But the available data presented are not sufficient for its application. The "Activated Sludge Model No. 1" of the IAWPRC work group[31,32] is recommended as a model.

At first glance it does not seem plausible that the mixed water temperature in a wastewater treatment plant with 40-50% textile wastewater can actually fall under 15*C, because textile wastewater comes in at 30-35°C. In the present

Figure 6: Elimination and mineralization of PVA in the Zahn-Wellens-Test with non-PVA-adapted activated sludge from a municipal wastewater treatment plant (WTP Teufen - see Figure 8).

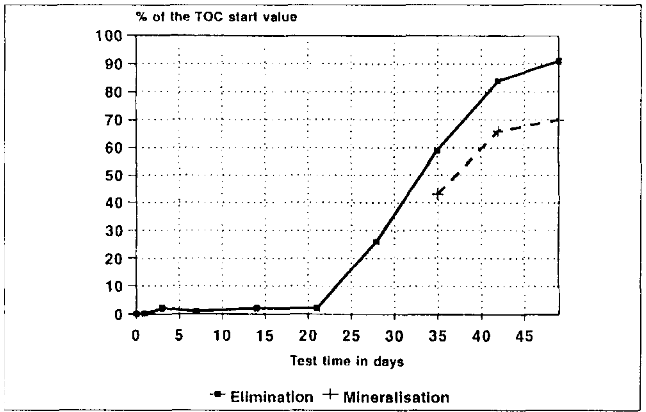
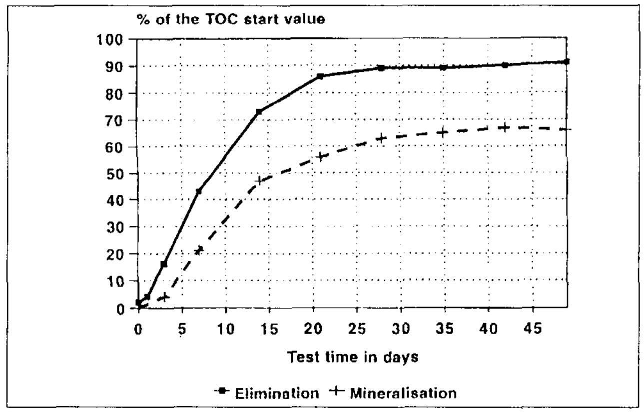


Figure 7: Elimination and mineralization of PVA in the Zahn-Wellens-Test with PVA-adapted activated sludge from a municipal wastewater treatment plant with a high percentage of textile wastewater (WTP Dornbirn - see Figure 8).



case, it not only cools greatly at the ambient external temperatures in a large mixing and equalization tank of the textile finishing industry (not contained in Figure 3) with a retention time of several days, but also in the high loaded stage and in the intermediate clarifier, so that the reported temperatures can be explained. Within this background it should be tested whether the temperature level could be elevated ı the low loaded stage even at very cold temperatures through insulation and/or covering procedures as well as through direct discharge of hot rinsing waters from the textile finishing industry to the low loaded stage.

The strong temperature dependence of microbial PVA degradation determined at the wastewater treatment plant in Munsterland was to be conditionally investigated and these observations to be reproduced or fully carried out in the laboratory of the EMPA in CH-St. gallen. A modified Zahn-Wellens test was used as a test method, which was cconducted according to the 1981 OECD standard and meanwhile evaluated[a] and conducted also as a Euronorm. ‘hereby, the recommendations of the EMPA St. Gallen (lower test substrate concentration and lower biomass concentration) were considered. Additionally, mineralization of organic compounds was determined by measuring carbon dioxide.

The investigations of the temperatture dependence of various PVA degrading microbial populations was combined with the determination of the PVA degradation potential of those activated sludges. The municipal effluent treatment plant Teufen does not receive wastewater from a textile finisher. Meanwhile, in the Habis plant only textile wastewater is treated. The other wastewater treatment plants lie between these extremes. The influence of the textile wastewater can at first be compared to the degree of adaptation and respectively the PVA degradation capability of the present activated sludges of the concerned plants, with the assumption that the textile finishing industries connected to them also finish weaved textiles.

Laboratory investigations

The PVA elimination curves contained herein corroborate completely the previous publications (see Table II), particularly those from Zahn and Wellens from the years 1974 and 1980. The elimination curve for a municipal activated sludge is shown in Figure 6.

It must be recognized that after a lag phase, which includes the adaptation time, the degradation takes place with the typical exponential profile and PVA is degraded up to 90% after a total of 50 days. The PVA removal was followed using DOC. To be certain that a microbial degradation of PVA really takes place, the carbon dioxide development was detected as mentioned above as a direct measure of mineralization.

Figure 7 shows the result for an activated sludge that is well adapted on PVA. The PVA elimination and mineralization occurs directly. In Figure 8 further elimination curves for activated sludges of various origins are shown. This figure does not contain the mineralization curves, because in every case the PVA elimination occurs due to microbial degradation. Other elimination mechanism could not observed.

The elimination time shown previously in Figure 6 with the activated sludge from the wastewater treatment plant Teufen is significantly longer compared to the other wastewater treatment plants. This is understandable, since it involves a wastewater treatment plant to which household wastewater flows exclusively. A “PVA contact” is, accordingly, not made to this activated sludge in a small area, while it is the case in the others where textile wastewater comes in.

The curve shape in Figure 8 further indexes that many adaptation levels are possible and finally PVA can be removed by all activated sludges up to about 90%.

The temperature dependence of chemical and microbiological reactions and the microbial growth has been a part of our basic knowledge for a long time. As reinforcement, we initiated laboratory investigations for the observable temperature influence in the present wastewater treatment plant which could be reproduced in the Zahn-Wellens tests. A complementary factor is whether the degradation by more easily degradable organic bonds can be significantly less influenced by temperature. Additionally PVA degradation with adapted activated sludge was followed in one case at room temperature, at 15°C and 10°C while at the same time the degradation curves of an easily degradable sizing agent (a mixture of galactomannan and starch) was taken. The results exhibit the same response as from industrial practice. Figure 9 shows the PVA elimination curves at the three temperature levels mentioned heretofore.

From this the strong temperature dependence of microbial PVA degradation becomes meaningful. In the wastewater treatment plants at the given retention times and at low F/I\A of under 0.15 BOD_5/kg MLSS x d, temperatures under 10°C-12°C lead to growth rates which are smaller than the wash-out rates. With this, the concentration of the PVA degrading microorganisms, and therefore the PVA elimination, strongly decreases.

The 10°C curve in Figure 9 demonstrates that in the Zahn-Wellens test, which is static and contrary to the dynamic systems of existing mechanical biological wastewater treatment plants, no biomass are released which require microorganisms around 35 days to increase to such a mass that the PVA degradation occurs noticeably. Extremely revealing by comparison is the degradation of an easily degradable sizing agent based on galactomannan/-starch (Figure 10).

As expected, a definite temperature dependence shows here, but which is in large measure not as marked as with PVA. This corresponds with the observations in practice (Figure 4) in which COD degradation does not retreat to the same extent with temperature as PVA degradation. This leads to the hypothesis that the easily degradable sizing agent is more degraded by other microorganisms than PVA, for whose degradation more temperature sensitive species are necessary. □ □ □

Figure 8: Elimination of PVA in the Zahn-Wellens-Test with activated sludges of different PVA-adaptation degree from various municipal wastewater treatment plants (WTP).

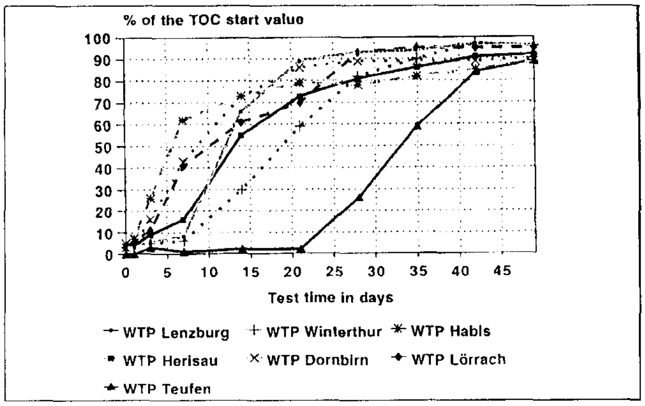


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Figure 9: PVA-elimination curves in the Zahn-Wellens-Test at three different temperatures with PVA-adapted activated sludge from a municipal wastewater treatment plant (WTP).

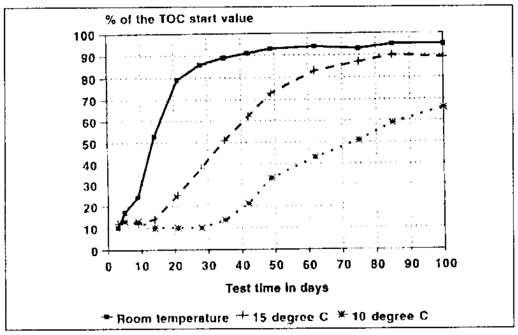
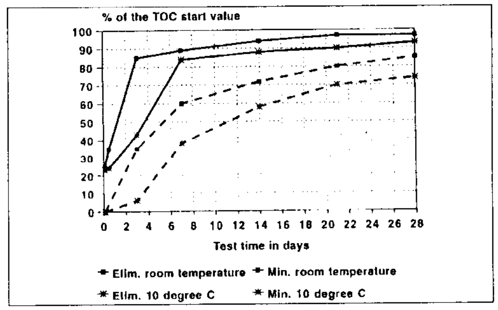


Figure 10: Elimination curves in the Zahn-Wellens-Test of an easily biodegradable natural sizing agent at two different temperatures with activated sludge from a municipal wastewater treatment plant (WTP).



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