Biologische afbreekbaarheid ProfiMax Eco Cleaning Capsules (ECC)

Daar ECC nieuw is voor de schoonmaakbranche en vragen of soms aannames kunnen ontstaan over waarin de capsules afbreken volgt hier een gedetailleerde uitleg over de Polyvinyl-alcohol film, (PVA) welke gebruikt wordt om de super concentraten zonder contact met gebruikers te doseren. Ten eerste dient hierbij opgemerkt te worden dat er diverse fabrikanten, soorten en kwaliteiten PVA zijn. Het zijn wetenschappelijk studies gedaan die aantonen dat de capsules helemaal afbeken en dit feit is algemeen bekend in de verpakkingsindustrie en onder wetenschappers bij Hogescholen en Univerciteiten. Zo ook in Nederland bij de TU Wagenigen en de Saxion Hogescholen (Milieubewust Verpakken) in Enschede is veel onderzoek hiernaar gedaan en is er veel kennis op dit vlak. Onderstaande informatie berust dan ook grotendeels op hun publicaties en diende als bron van onderstaande uitleg. Men verwijst hierbij ook naar het boek “Bioplastics” van Christiaan Bolck,een aanrader voor nog meer verdieping hierin.

Wat zijn capsules op basis van polyvinyl-alchohol?

PVA (of *PVOH in het Engles*) is een zogenamde Bio-kunststof gebaseerd op polyvinyl alcohol en laat geen enkele schadelijke resten na eenmaal in oplossing met water. De eigenschappen zoals de oplosbaarheid in water, biologische afbreekbaarheid, milieu verenigbaarheid, niet giftigheid, antistatisch, mechanische sterkte alsmede weerstand tegen schuring, de transpantie, helderheid en hoge dichtheid aan gas, geuren en aroma’s maken het bijzonder geschikt voor de toepassing van de specifiek hiervoor geproduceerde super geconcentreerde schoonmaak capsules zoals in gebruik bij ECC alsmede hun doel prestatie.

De verwerking vindt plaats in speciaal daarvoor samengetselde machines, die de capsules op verantwoorde wijze dichten en bijdragen aan hun uiteindelijke sterkte om een druk van van ca 15 kilo te kunnen weerstaand per capsule. De toepassing zoals geproduceerd voor ECC is niet voor vaat- of wasmachine gebruik. Er vinden dan ook geen ophopingen van biomassa of andere eventuele nadelige gevolgen plaats. De capsule valt na volledige oplossing in flacon of emmer, geheel uiteen in water en Co2, zonder ook maar enige vorm van microplastics achter te laten. Het unieke aan de ECC is dat de inhoud eveneens eenvoudig biologisch afbreekbaar is en afgestemd op het type PVA, zodat deze niet kunnen oplossen voordat ze voor hun uiteindelijke doel worden ingezet. Het is natuurlijk belangrijk de capsules met droge handen te doseren en droog te bewaren daar de PVA water aantrekt. In warm water lost de gebruikte PVA van ECC nog sneller op dan in koud water. Het heeft dus een hoge waterdoorlatendheid en vormt een uitzonderlijke barriere tegen andere dampen en gassen. De dichtheid is ca 1,25g/cm3. Door de oplosbaarheid is het natuurlijk niet recyclebaar maar oplos-afbreekbaar, het vorkomt dus inzamel en transportbewegingen alsmede reiniging, bewerking en sortering verbuikt slechts en fractie aan grondstoffen (<1 gram) per capsule. Natuurlijk blijft ECC op lange termijn zoeken naar een wateroplosbare film van herniewbare bron die helemaal geen Co2 meer achterlaat. Op dit moment is dit echter al een geweldige sprong vooruit in vergelijking met de tonnen aan onafbreekbare plastic wegwerpflessen, zakjes en containers die jaarlijks in de natuur belanden en helemaal niet afbreekbaar zijn en slechts zeer miniem gerycycled worden. Deze toepassing kan doaardoor bijdragen aan enorme vermindering van plastic zwerfafval en microplastics en voorkomt onnodig vervoer van water. De PVA kan tenslotte door zo’n 55 verschillende micro organismen worden afgebroken.

Zie ook de appendix (Bron: C.A. Finch, welke een Internationaal expert is op dit gebied.)

Microorganisms Found to Degrade PVOH

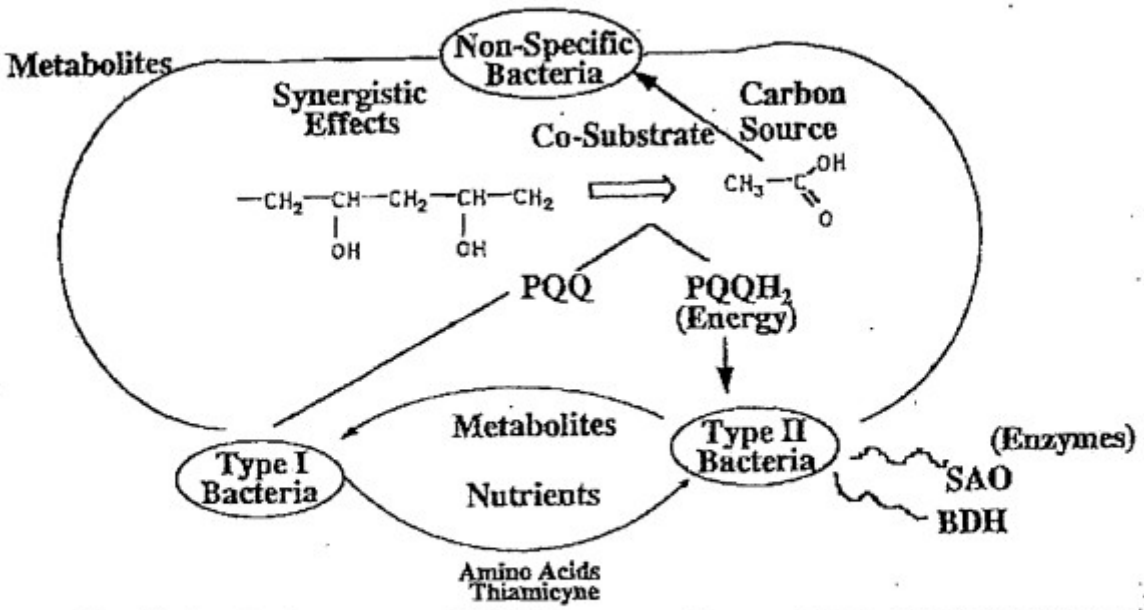
BACTERIA	
Genera	Species
Acinetobacter	2
Agrobacterium	radiobacter
Escherichia	coli
Enterobacterium	1
Proteus	mirabilis
Pseudomonas	19
Bacilius	licheniforms
Bacterium	cadaveris
Brevibacterium	2
Aerobacter	3
Alcaligenes	viscolatis
Alkalegenes	1
Arthrobacter	oxydan
Coryneform	1
Flavobacterium	1
Fusarium	lini
Micrococus	glutamicus
Neisseria	1
Sarcina	2
Xanthomonas	1

YEAST and MOLD	
Genera	Species
Aspergillus	niger
Endomyces	fibuliger
Saccharomyces	3
Nadsonia	fulvescens
Pichia	polymorphia
Rhodotorula	glutinis
Lipomyces	lipoferus
Trichosporon	cutaneum
Zygosaccharomyces	major

At Least 55 Species of Microorganisms Degrade PVOH

Bijlage 2: Uitleg microbieel metabolisme van de PVA:

Microbial Metabolism of PVOH



Non-Specific bacteria consume PVOH decomposition products or a co-substrate
Non-specific bacteria generate growth factors for PVOH degrading bacteria.
Synergistic effects are observed with non-specific bacteria.

APPENDIX 3

Biodegradability and Effluent Disposal of Polyvinyl Alcohol

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A3.1 INTRODUCTION

The biodegradability of polyvinyl alcohol has been principally studied in relation to the use of the polymer in textile manufacturing and finishing processes. The polymer has a negligible biological oxygen demand (BOD) for periods up to 30 days when exposed to non-acclimated domestic sludge microorganisms.[1] In these conditions, the polyvinyl alcohol present in an effluent does not inhibit the metabolism of existing activated sludge microorganisms. Activated sludge microorganisms can be acclimated to polyvinyl alcohol under the conditions of conventional waste water treatment processes. Studies of the long-term biodegradability of polyvinyl alcohol and other textile chemicals compared 30 day BOD results with the COD of samples, and indicated that

Polyvinyl Alcohol. Edited by C. A. Finch

activated sludge treatment removed ~94% of polyvinyl alcohol: long-term aeration is recommended for biological treatment.[2]

Biodegradation studies[3] indicate that the presence of a polyvinyl alcohol (99–99.8% hydrolysed; viscosity 25–31 cP; 'Elvanol T-25'; Du Pont) used for textile warp sizing does not inhibit the removal of other compounds during the biological disposal of textile waste, but is not consistently biodegraded unless suitable treatment conditions are employed. For consistent biodegradation performance, a food–mass ratio of ≤ 0.15 COD/MLSS (mixed liquor suspended solids) must be maintained (a ratio of ≤ 0.1 is suggested for design purposes). A saturation level (MLSS × detention time) of ≥ 8 g × days/litre should also be obtained. Under these conditions, a 75% COD and 85–97% removal of polyvinyl alcohol is obtained, partly depending on other components present. For a textile finishing plant* using polyvinyl alcohol it is estimate that:

$$\text{Solids production} = 0.3\ \text{COD removed} - 0.02\ \text{MLSS under aeration}$$

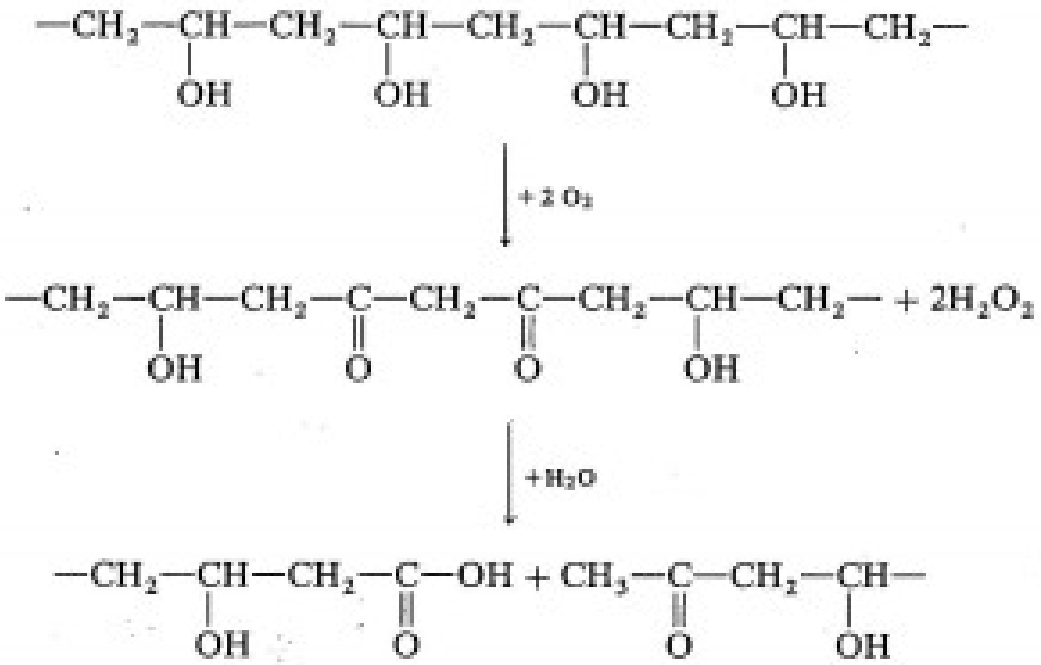
Controlled respirometric assays of polyvinyl alcohol indicate that the polymer may be completely degraded.[4] Organisms that consume polyvinyl alcohol are viable in mixed culture activated sludge. Efficiencies of mixed culture degradation of the polymer reached 13 mg h/volatile suspended solids, with 3 h influent residence time for a domestic wastewater primary clarifier effluent. Organsims that degrade polyvinyl alcohol in mixed culture remain viable under H_2O_2 treatment conditions toxic to filamentous and nitrifying organisms. Systems removing >90% of 50 mg polyvinyl alcohol/litre, >95% of 40 mg NH_3/litre, and >90% of BOD_5 operated yielding satisfactory microscopic sludge properties.

Methods for the disposal of speciality polyvinyl alcohol copolymer residues from the warp sizing of textile yarns are disucssed in Chapter 11. Other studies on degradation have been directed towards the removal of polyvinyl alcohol from sized fabrics after washing.[5] After alkaline scouring, with sodium hydroxide, the presence of residues retained on the fabric can cause difficulties with bleaching, dyeing, and printing. In addition, residual polyvinyl alcohol may be gelled and redeposited on fabric and equipment. Treatment with hydrogen peroxide indicates that the polymer undergoes oxidative degradation to yield low polymers with greater solubility. Treatment of polyvinyl alcohol mixtures with alkaline hydrogen peroxide (stabilized with a mixture of magnesium sulphate, ethylene diamine tetraacetic acid, glucoonic acid, and a non-ionic/anionic wetting agent) at 95°C for 10 min gave complete dissolution of the polymer,[6] apparently because, under these conditions, oxidative degradation prevailed over gel formation under the influence of sodium hydroxide.

* Further details on the reuse and disposal of polyvinyl alcohol mixtures used in textile warp sizing are given in Chapter 11.3.16.

A3.2 ORGANISMS AND MECHANISMS FOR BIODEGRADATION OF POLYVINL ALCOHOL

A range of organisms able to degrade and assimilate polyvinyl alcohol completely has been identified and studied in detail. The polymer is attacked by *Pseudomonas 0-3* (isolated from soil by growing cultures on nutrient agar for 12 days at 27°C) which produces and secretes a polyvinyl alcohol-degrading enzyme into the medium.[7,8] Isolation and purification of this enzyme indicated that it was an oxidase, since it degraded polyvinyl alcohol oxidatively, producing hydrogen peroxide, with degradation products including terminal carboxyl groups and methyl ketones. From these observations it was concluded that the basic degradation scheme consisted of the following stages:



The degradation of polyvinyl alcohol therefore consists of two types of reaction: oxidation of hydroxyl groups and cleavage of C—C linkages, with production of hydrogen peroxide in addition.

This mechanism has been confirmed by study of the degradation behaviour of model small molecules, such as alcohols and ketones,[6] in comparison with the degradation of polyvinyl alcohol by *Pseudomonas* sp. Some secondary alcohols were found to be oxidized but not degraded by the enzyme, whilst, amongst ketones, some 1,3-diketones such as acetylacetone and 4,6-nonanedione were degraded. A pathway for the enzymatic degradation of polyvinyl alcohol has been suggested, based on the degradation of 4,6-nonanediol by successive reactions of secondary alcohol oxidase and β-diketone hydrolase.[9] Cultures of *Pseudomonas vesicularis* PD with polyvinyl alcohol and salts at 28°C and pH 7 show gradually increased production on the degrading enzymes, notably basic

and acidic secondary alcohol oxidase (SAO), together with smaller amounts of basic and acidic β-diketone hydrolase (BDH). There are correlations between proportions of SAO and BDH.[10]

The organisms used for polyvinyl alcohol (88 % hydrolysed; d.p. = 1700) degradation have been studied.[11] The polymer is degraded by *Saccharomyces*, *Lipomyces*, or *Rhodotorula* sp. with or without addition of acetic acid, or its salts or esters. However, the polymer is only degraded by *Endomyces*, *Zygosaccharomyces*, *Pichia*, or *Nadsonia* when acetic acid or its salts or esters are added. Typically, *E. fibuliger* was cultured with shaking at 30°C for 7 days on a mixture at pH 7.0 of the above polyvinyl alcohol (0.05), sodium acetate (0.05), NH_4NO_3 (0.1), K_2HPO_4 (0.1), KH_2PO_4 (0.1), $MgSO_4$ (0.05), and yeast extract (0.01 %), to decrease the COD from 590 to 177 p.p.m., whilst COD was 540 p.p.m. without addition of sodium acetate. With *S. rouxii*, under similar conditions, the COD decreased from 590 to 70 and 95 p.p.m. with or without addition of sodium acetate, respectively. A standard method (from Hoechst) has been used to compare the biodegradability of diethylene glycol with 50 other compounds (including polyvinyl alcohol), reporting the effect of degradation time and adaptation time on the rate and degree of degradation.[12]

In more recent studies, mixed continuous cultures of polyvinyl alcohol-utilizing symbionts have been developed.[13] These are stable mixed cultures of *Pseudomonas* sp. VM15C and *Pseudomonas putida* VM15A. The former produced a polyvinyl alcohol-degrading enzyme and the latter produced an essential growth factor for polyvinyl alcohol utilization by strain VM15C. The predominant metabolzing strain was VM15C, with the growth supporter VM15A as a minor component. The growth-limiting substrate for strain VM15C in the mixed continuous culture is the growth culture produced by strain VM15A.

A microorganism for polyvinyl alcohol degradation similar to *Pseudomonas vesicularis* has been isolated, which requires thiamin as a growth factor. with glucose present, and also requires three amino acids (tyrosine or phenylalanine, isoleucine, and cystine) and has been named *P. vesicularis* var. *povalolyticus* PH.[14] Another organism believed to be a different variety of *P. vesicularis*, able to grow on polyvinyl alcohol medium without additional nutrient, has been isolated.[15]

A3.3 ANALYTICAL METHODS FOR DETERMINATION OF DEGRADATION RATES

Typical standard methods for determination of the degradation rates of polyvinyl alcohol in different effluent mixtures have been reported.

A3.3.1 ANALYTICAL PROCEDURE FOR DETERMINATION OF REPRESENTATIVE EFFLUENT MATTER BY SIMULATION, USING ACTIVATED SEWAGE SLUDGE

This method was developed for the investigation of chemical effluent from textile finishing plants:[16]

(a) Sludge is thickened by filtration through cotton cloth to 50 g of dry material/l, and stored in 10 g of aliquots in sealed bottles at $-20 \pm 2°C$.
(b) 500 g of effluent is mixed with 50 ml of 0.01 % Pluronic L-62 (surfactant) solution.
(c) Decomposition studies are carried out using 7 l of aeration cylinders with a porous bottom and an air inlet.
(d) Each cylinder is filled with sludge, 5 ml of nutrient solution ($MgSO_4.7\ H_2O$ (5); $CaCl_2.2\ H_2O$ (10); KCl (15 g/ml)), and water added to make up 5 litres.
(e) After 1 h of aeration at 1 l/min 100 g of effluent is transferred to the cylinder and the temperature adjusted to $20 \pm 2°C$. Surface tension, bacteria count, and quantiative composition were determined after 5 min, 2 and 24 h of aeration. BOD is determined on 5 min samples. Organic material is extracted with solvent (diethyl ether), dried, and analysed by chromagraphy and spectroscopy.

Under the above test conditions, polyvinyl alcohol degrades slowly, and is reported not to be toxic.

3.3.2 ANALYTICAL PROCEDURE FOR COMPARISON OF THE AEROBIC DEGRADATION RATES OF CARBOXYMETHYL CELLULOSE AND OF POLYVINYL ALCOHOL

The following method (based on the Bunch–Chambers evaluation technique) outlined is used to compare the relative degradation rates of different types of carboxymethyl cellulose (CMC), with different degrees of substitution and with polyvinyl alcohol:[17]

(a) Polymers at an initial concentration of 50 mg/l are exposed to waste water bacteria in a static, air-saturated culture medium containing yeast extract and essential inorganic salts.
(a) Adaptive transfers are then made to fresh solutions and the process repeated at weakly intervals until the rate of degradation of the samples is stabilized.
(c) After 6 weeks, the rate of degradation of carboxymethyl cellulose of degree of substitution of 0.41 stabilized at ~80 %/week, but that of CMC of degree of substitution of 0.75 only reached the same degradation rate after 16 weeks.

Parallel studies of polyvinyl alcohol under similar conditions indicated a biodegradation rate of $< 3\ \%$/week.

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