Summary of the final report
for Willy Hager Foundation
on the project

Investigation on system conditions for the biodegradation of polyvinyl alcohol

Duration: January 2020 – May 2023

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2023

1 Introduction

1.1 Motivation

Based on United Nations Sustainable Development Goals 2015 (SDGs), as stated in goal 14, is to reduce the environmental impacts from plastics and existing polymers (Walker, 2021). There are continuous and increasing efforts from all over the world to develop new synthetic sustainable material which is harmless to the environment based on different end-of-life scenarios. This includes the EU initiative (Directive 2019/904) for the disposal of single-use plastics. Biodegradable options are considered as alternatives to conventional polymers.

Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer which is applied in huge scale in industry with utilization that exceeds one megaton due to its specific properties. The increasing application of PVA in multiple areas such as textiles, foods, medicine, industry, construction, and chemicals has led to high level of emissions to the environment. The existence of PVA in the environment at high concentrations have different consequences starting from its ability of plastic particles to adsorb dangerous contaminants, to altering gas exchange and oxygen transfer in affecting the aqua life and ecosystem, to causing pollution when it leaks to groundwater, aside with long existence without biodegradation in marine environments.

Therefore, it is significant to investigate and develop degradation methods, including physical-chemical methods such as chemical oxidation (for instance Fenton process or photocatalytic degradation processes) which still requires more investigations to reduce the application costs and increase their efficiency to ensure complete degradation and avoid producing toxic or intermediate compounds. Biodegradation of PVA is considered a very promising field with respect to classify PVA as fully sustainable material, since it proves that is completely biodegradable with considering the presence of certain conditions and procedures. Related organisms with their enzymatic activities are proven to be able to degrade PVA as mentioned in previous studies.

To ensure practical application of PVA biodegradation, certain system conditions in wastewater treatment plant under aerobic/anaerobic conditions must be met to ensure the occurrence of biodegradation. These conditions including temperature (18 -33 °C), adaptation of organisms which has certain limitations considering the conditions in muncipal WWTP, low F/M ratio (0.15 kg BOD/ kg SS.d) pH, solubility of PVA, dissolved oxygen and others.

In textile industries, which are responsible of high wastewater volumes due to its necessity in the production process, these conditions are not met, where high COD loads including high PVA concentrations (500 mg/L) which is responsible for 30 to 70% of COD loads, temperatures above 33°C and non or partial adaptation of organisms occur, with availability of other easy biodegradable compounds as carbon source. Which all led to discharging wastewater without meeting the requirements of water quality parameters. Also, temperature range which is considered a crucial factor in biodegradation process, is either difficult to be met since these industries apply high temperatures in the manufacturing process, or due to high climate temperature in manufacturing countries, such as Bangladesh and China.

The aim of this project is to investigate the system conditions which is necessary to achieve high PVA biodegradation, considering low – high temperature ranges, pH, adaptation to high temperatures, type and specification of PVA and its effects in biodegradation process, and specify the related strains which are able to degrade PVA, and their effects in increasing the kinetic rates of biodegradation.

1.2 Objective

1.2.1 General aspects

The majority of the available specialist literature related to PVA biodegradation under aerobic conditions lacks on investigation of biodegradation aspects at high temperatures, adaptation aspects and combination between biodegradation capacity of the sludge represented in kinetic rates, related strains and enzymatic activities and applicability aspects. Previous investigations (Sträßner,1995; Schönberger, 1997; Rolsky & Kelkar, 2021) showed that there is no degradation possible at 40°C and initial investigations confirm these aspects. There are also missing details about the specifications of system conditions necessary for biodegradation using different microbiocoenosis. There is also a lack of information regarding to the main strains that could degrade PVA under high temperatures, with technical applicability of the cultures containing these strains. For all of these mentioned aspects, there are a considerable need for research here to help in the implementation of the application of process development.

1.2.2 PVA spectrometric measurement method

To ensure high accuracy of the planned experiments, PVA method were investigated by testing different factors; including specifications of PVA, absorbance wavelengths, types of water, reaction time, age of applied solutions, and types of filtration.

1.2.3 Optimum system conditions for PVA biodegradation

Without meeting certain system conditions, PVA is not biodegradable under aerobic conditions. Therefore, specific parameters were tested depending mainly in F/M ratio and temperature and applying municipal microbiocoenosis using batch tests to specify the optimum system conditions based on kinetics.

1.2.4 Adaptation effect in biodegradability of PVA

In the batch test, the effect of adaptation of municipal sludge is tested to be applied for different aspects. Firstly, after adaptation phase at optimum temperature, the potential of microbiocoenosis is tested to degrade PVA at higher temperature range where it was not possible to degrade before (36-42°C). secondly, investigation whether the adaptation of degrading organisms is a concentration dependant phase or there are other factors have an essential role in adaptation. Low concentrations of PVA should specify the minimum concentration which is necessary for full adaptation of PVA.

1.2.5 Industrial sludge potential in PVA biodegradation at high temperature

Adapted sludge to PVA biodegradation is investigated. This includes a series of biodegradation experiments to specify the temperature, concentration, and pH ranges, with testing the degradation as a proof of biological effect. Also, parametric and process comparisons between the different sludge types were included with microscopic analysis to provide more details and specifications.

2 Summary

Step 1: Literature research/procurement of materials

The specialist articles published to date lack investigations on the biodegradation of PVA of under high temperatures; considering ranges (31-49°C). Initial investigations at ISWA showed that it is possible to achieve biodegradation at high temperatures if the process is opitimised. Also, it is very essential from practical prospects (especially in textile industry) to identify in depth the optimum system conditions to biodegrade PVA in activated sludge systems. It is also worth mentioning that many of previous studies related to strains and enzymatic activities but did not investigate applicable aspects and results with respect to real treatment plants with biodegradation aspects.

Therefore, investigating different microbiocoenosis will bring detailed information about optimisation options for the design and operation of wastewater treatment plants, which all were investigated in detail in this project.

The lab was mobilized with all necessary equipment, materials, and chemicals necessary for experimental sets and analytics, including water baths to control specific temperatures and reduce temperature fluctuation, a thermal sensor to measure temperature for each vessel through time of the experiment, pH and oxygen meters.

Step 2: Design of Zahn-Wellens method

D-optimal design guarantee the minimization of the forecast or confidence interval of the calculated estimation parameters (regression coefficients, standard errors, etc.). D-optimal advantage compared to the other methods is the free choice of the test levels and the independence of the number of tests from the number of levels of the factors. This also reduces the test efforts and increases the extraction of various information from the tests.
D-optimal design of experiment diagnostic show very good planning quality based on statistical indicators. The number of experiments were reduced from 20 to 12 sets, with high D-efficiency of 97.8% and G-efficiency of 56.1% as shown in figure 2.1.

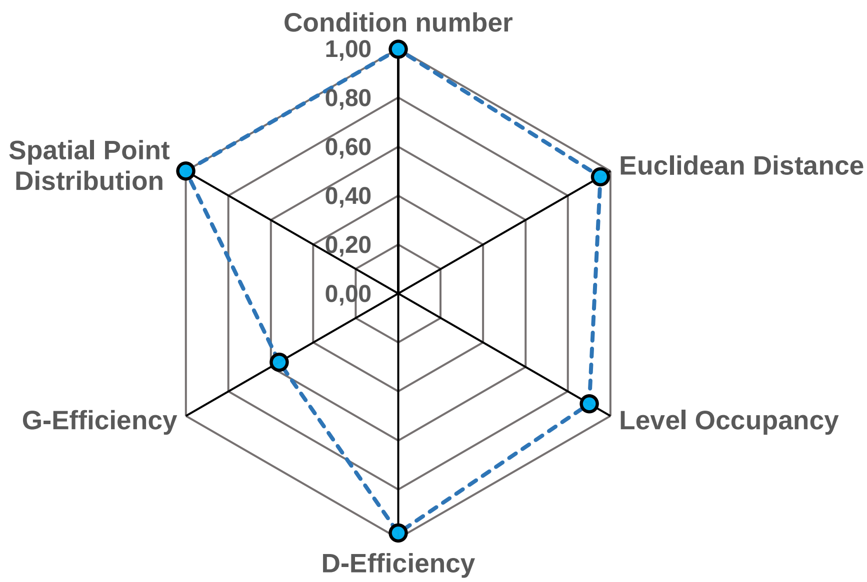

Figure 2.1: Diagnostic parameters for assessment of design of experiment

Also, DOC sampling plan were made to minimize DOC samples with conservation of tracking the values through the experiments and have comparable results with PVA measurements.

Step 3: Laboratory tests for PVA biodegradability

PVA spectrometric method

- It was found that molecular weight of PVA has high effect on absorbance values with variations up to 60-70%, with higher absorbance values for lower PVA MWs.
- Different optimum wavelengths found between 630 and 680 nm according to the MWs of PVA, and 680 nm was applied for all types to generate comparable results.
- For reaction times, peak value was found after 20 min.
- The minimum effect of filtration was found using membrane and paper filter for fully solubilised PVA with differences between 2-4.5%. Also, no significant differences were observed between old and new PVA solutions, which confirms that PVA is stable over time.

Optimum system conditions

- Abiotic elimination checks by applying abiotic vessel containing test medium and PVA (at two concentrations 10 mg/L and 100 mg/L) without inoculum. It was found that there is no drop in PVA concentration at these concentrations due to adsorption or air stripping.

- 200 and 500 mg/L had high concentration losses due to foaming varied between 10 and 30%. 18°C showed lower degradation kinetics. The adaptation phase was highest; it took 9-11 days depending on concentration. The degradation lasted till day 11-19 depending on concentration with highest degradation rate of 31 mgPVA/ gSS.day.
- 23 °C showed less adaptation (7 days) with better degradation kinetics (7 days for 10 and 30 mg/L, 12 days for 500 mg/L), the highest degradation rate was around 60 mgPVA/ gSS.day.
- 28 °C and 33°C showed the least adaptation days (5-6 days) with minimum degradation phase at 28 °C (2 days at 30 and 100 mg/L). The highest degradation rate was 70 mgPVA/ gSS.day.
- Determination of kinetics showed that Kbio at 28 °C had values based (0.3 -0.33 L/(gSS d)), with highest k(d^{-1}) at 28 °C of 100 mg/L. Optimised regression analysis showed high representation of the values to the investigated range of parameters with a significance of 90% and optimum variance inflation factor of 1.089. The results of regression 3-D graphs shown in figure 2.2 and detailed values with standard deviations in figure 2.3.

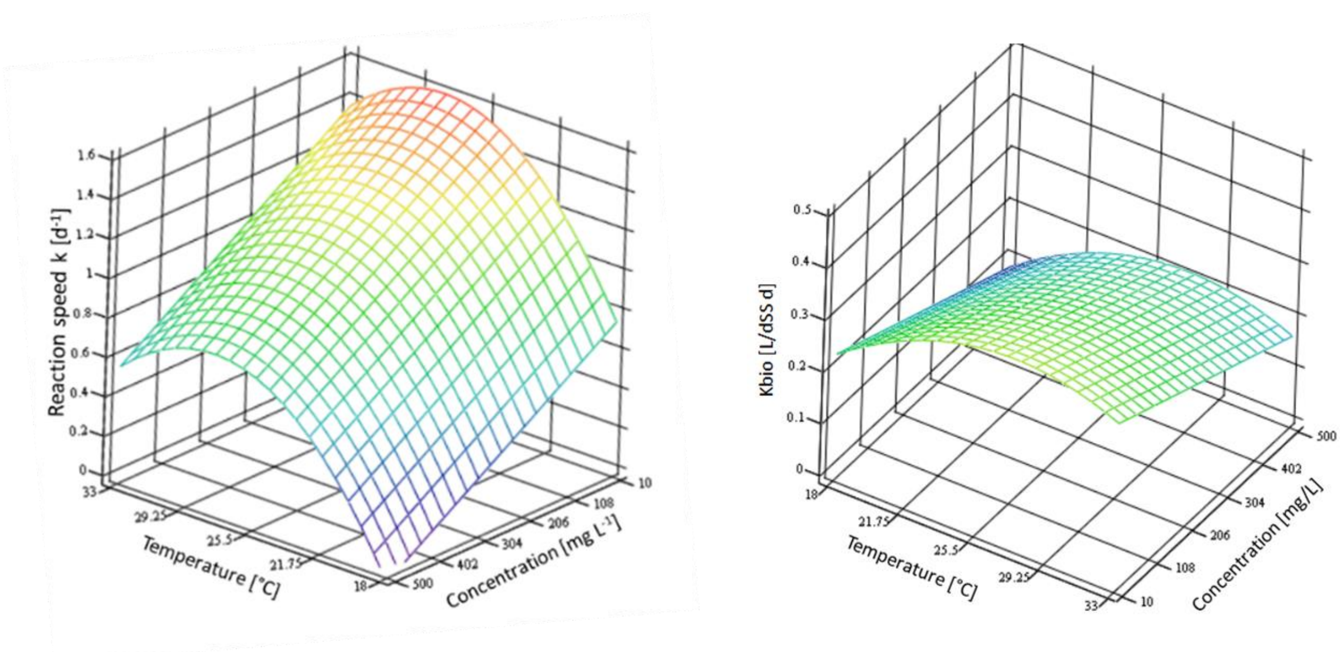

Figure 2.2: Regression 3-D model (temperature, concentration) with Kbio (right) and k(left)

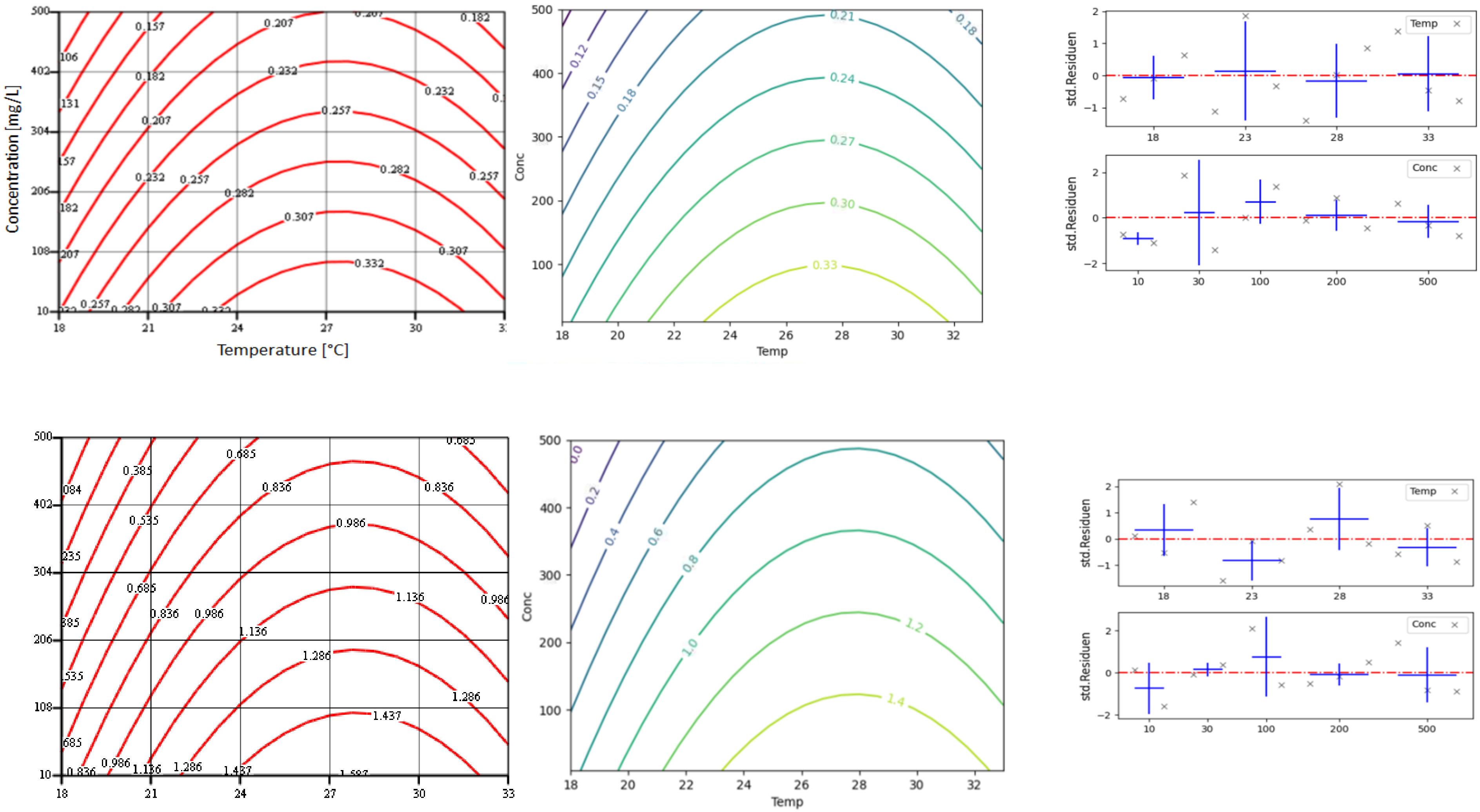

Figure 2.3: k values before and after optimisation with standard deviations using the model for .(k 1st graphs) and (Kbio 2nd graphs).

Two phases experiments

- Optimum conditions of 100 mg/L at 28°C were applied in this experiment. The adaptation phase showed matching degradation rates for all test vessels. After test reset at 9th day, the sludge was adapted to achieve full degradation at 28 and 36 °C. The degradation stopped at 38-42°C, and DOC showed higher values than in the test reset, which indicates cell lysis or rupture of microbial cells.

Different types of PVA and threshold concentration experiments

- No significant difference in biodegradation of different molecular weights of PVA was determined and same kinetics were found.
- It is found that adaptation happens even at a minimum tested concentration of 1 mg/L, which proves that adaptation is not only a concentration dependent, but also temperature has its effect. Full adaptation was found at 5 mg/L and 10 mg/L since full degradation witnessed after test reset.

Adapted Sludge investigations

- Parameters measurements showed high COD, sulphate, PVA and temperature values with the existence of starch; also pH values proved that the sludge is functioning under alkaline conditions.

- No adaptation phase. The degradation started immediately from the first hours of experiments. High kinetics witnessed since more 90% degradation of substrate 100 mg/L PVA achieved in the first day at all high temperatures (36-42 °C). DOC values showed same kinetics as PVA with lower DOC eliminations with more than 90% for 36, 38 and 80% for 40 and 42°C.

- Proof of biological activity showed that less than 10% of PVA elimination was due to adsorption to the dead sludge or a chemical reaction using autoclaved sludge and autoclaved supernatant, where 95% degradation happened using normal active sludge in the first day at same test conditions (40°C, 100 mg/L PVA, 1 g/L SS).

- pH testing range showed highest degradation of 55% which happened after 3 hrs at pH of 7.5, which represent the optimum value for this microbiocoenosis.

- The degradation reached 70% and 30% for 45 and 49°C and stopped at the first day of experiment which confirms the limits of temperature for this type of sludge. It is also noted that DOC values were increasing through the days of experiment with ratios 30% to 100% at 45 and 49 °C.

- PVA Concentration range (60 -2000 mg/L) at 40 °C were tested and kinetics shows high degradation rates varied between 450 and 650 mg PVA/gSS.day, which is 7-9 times higher than municipal sludge (70 mg PVA/gSS.day at optimum conditions) , and high k(d-1) of 3.5 which is twice higher compared to municipal sludge with 1.95 at optimum conditions.

- Comparison of yearly variations of parameters showed high variations in COD, Ntot, temperature in Cilander treatment plant, with low ammonium concentrations and high SVI. Oxygen consumption rates comparison showed less values at cilander compared to LFKW (initial value 6 and 5 mg/L at cilander compared to 10 mg/L at LFKW). This proves high mortality of the organisms due to many factors, the major one is long sludge age.

- Comparison of calculated kinetics based on the performed experiments are summerised in Table 2.1. It can be concluded sludge not only started the biodegradation immediately, but also showed around double values in modelled k and Kbio. The degradation rates are higher up to 7-8 times than municipal sludge even after adaptation, which demonstrates the potential of adapted sludge in PVA biodegradation even at high temperatures (as shown in figure 2.4) which was never proved before in specialised articles and previous PVA biodegradation studies.

Table 2.1: Kinetics comparison for the different types of sludges.

Parameter	Adapted sludge (40°C)	Municipal sludge (opt.C.) (28°C)
kbio (L/(gSS d))	0.7	0.32
k (d^{-1})	3.52	1.9
dc/dt (mg/(l·d. gSS))	500- 600	60- 70
Maximum tested PVA concentration (mg/L) without toxic effect	2000	1000
Foaming effect	Very low	high
Adaptation (days)	0	5-11

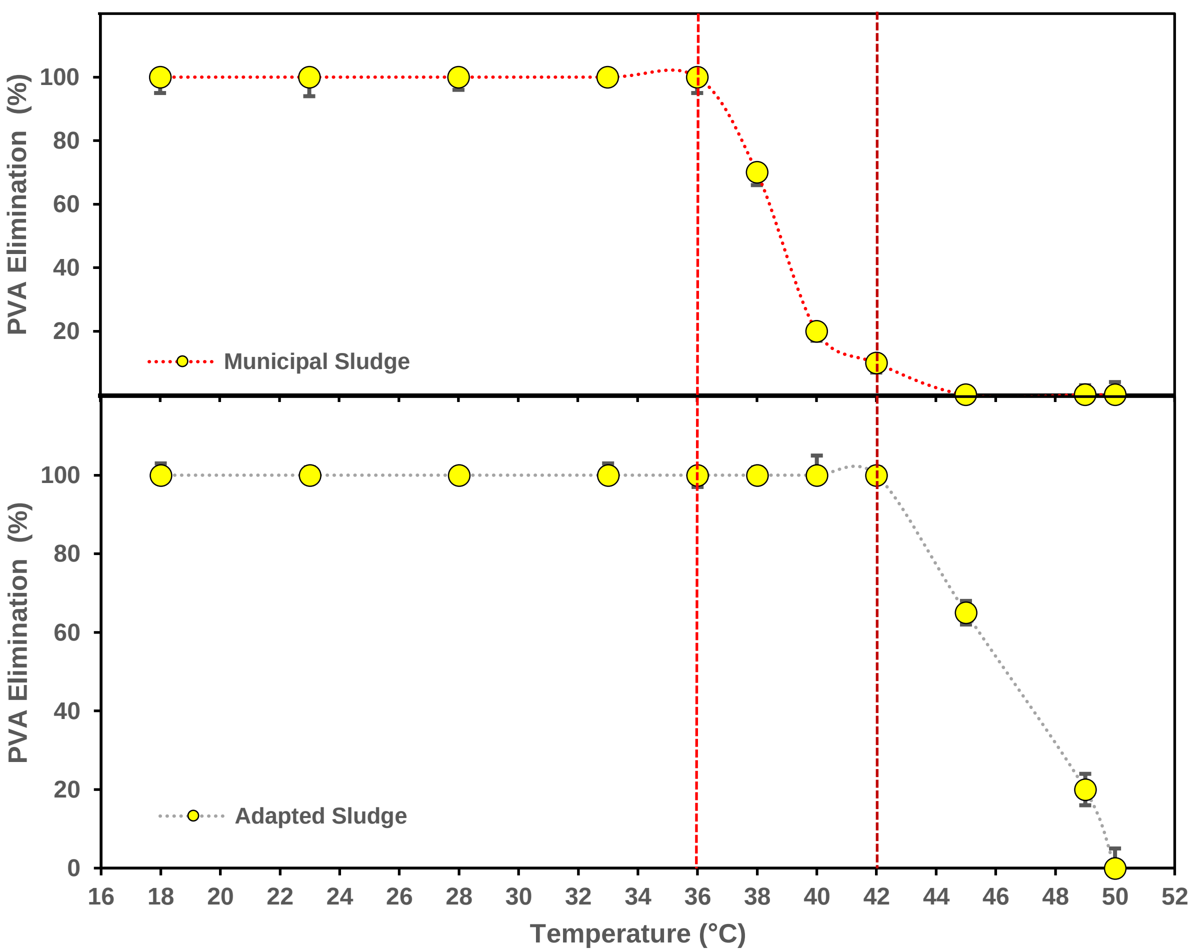

Figure 2.4: Comparison of two sludges on temperature range and PVA elimination

Exploitation activities

A patent related to this research project is submitted for registration at The Technologie License Büro (TLB).

Also, publications are going to be submitted soon in international, peer-reviewed journals, conferences and the use of the results in a dissertation are planned.

- Polyvinyl Alcohol: Overview in production, properties, applications and impacts on environment, with current and future degradation potential to achieve sustainability.
  (This publication as demonstrated in the report includes **all** references related to PVA which is published till 2022).
- improved spectrometric method for high-accuracy measurement of different types of Polyvinyl alcohol
- Identifying the optimum system conditions for biodegradation of Polyvinyl alcohol under aerobic conditions using batch reactors.
- Kinetic study and statistical analysis of system conditions for biodegradation of polyvinyl alcohol.
- Effect of Polyvinyl alcohol properties and threshold concentration on biodegradation of polyvinyl alcohol using batch reactors.
- A detailed comparison of Municipal and adapted sludge for degradation potential of PVA under high temperatures.

In addition, several student theses were awarded as part of this project:

- Sachit Dhakal (2021): Study of biodegradation of polyvinyl alcohol (PVA) as a function of Food-To-Mass ratio. Master thesis.
- Md Shahriar Kabir (2022): Investigation on system conditions for the biodegradation of polyvinyl alcohol. Master thesis.
- Jian Zhang (2022): Korrelation des biologischen Abbaus von PVA in verschiedenen Testsystemen. Master thesis.

References

Abegglen, C., & Siegrist H. (2012). *Mikroverunreinigungen aus kommunalem Abwasser*. Bern: Bundesamt für Umwelt.

Aguiar, P. F. de, Bourguignon, B., Khots, M., Massart, D., & Phan-Than-Luu, R. (1995). D-optimal designs. *Chemometrics and Intelligent Laboratory Systems*, *30*, 199–210.

Ajmi, K., Vismara, E., Manai, I., Haddad, M., Hamdi, M., & Bouallagui, H. (2018). Polyvinyl acetate processing wastewater treatment using combined Fenton's reagent and fungal consortium: Application of central composite design for conditions optimization. *Journal of hazardous materials*, *358*, 243–255.

Alonso-López, O., López-Ibáñez, S., & Beiras, R. (2021). Assessment of Toxicity and Biodegradability of Poly(vinyl alcohol)-Based Materials in Marine Water. *Polymers*, *13*(21).

Battersby, N. (1990). A review of biodegradation kinetics in the aquatic environment. *Chemosphere,*, *21*, 1243-1284.

Anonymous (2003), Reference Document on Best Available Techniques for the Textile industry. https://eippcb.jrc.ec.europa.eu/reference/Bref/txt_bref_0703.pdf

Behera, S. K., Kim, J.-H., Guo, X., & Park, H.-S. (2008). Adsorption equilibrium and kinetics of polyvinyl alcohol from aqueous solution on powdered activated carbon. *Journal of hazardous materials*, *153*(3), 1207–1214.

Ben Halima, N. (2016). Poly(vinyl alcohol): review of its promising applications and insights into biodegradation. *RSC Advances*, *6*(46), 39823–39832.

Bisschops, I., & Spanjers, H. (2003). Literature review on textile wastewater characterisation. *Environmental technology*, *24*(11), 1399–1411.

Boyer, R. F. (2012). *Biochemistry laboratory: Modern theory and techniques.* (2nd ed.). Boston: Prentice Hall.

Chakravorty, S., Helb, D., Burday, M., Connell, N., & Alland, D. (2007). A detailed analysis of 16S ribosomal RNA gene segments for the diagnosis of pathogenic bacteria. *Journal of microbiological methods*, *69*(2), 330–339.

Chen, J., Zhang, Y., Du, G.-C., Hua, Z.-Z., & Zhu, Y. (2007). Biodegradation of polyvinyl alcohol by a mixed microbial culture. *Enzyme and Microbial Technology*, *40*(7), 1686–1691.

Chiellini, E., Corti, A., D'Antone, S., & Solaro, R. (2003). Biodegradation of poly (vinyl alcohol) based materials. *Progress in Polymer Science*, *28*(6), 963–1014.

Chiellini, E., Corti, A., Del Sarto, G., & D'Antone, S. (2006). Oxo-biodegradable polymers – Effect of hydrolysis degree on biodegradation behaviour of poly(vinyl alcohol). *Polymer Degradation and Stability*, *91*(12), 3397–3406.
Chiellini, E., Corti, A., Del Sarto, G., & D'Antone, S. (2006). Oxo-biodegradable polymers – Effect of hydrolysis degree on biodegradation behaviour of poly(vinyl alcohol). *Polymer Degradation and Stability*, *91*(12), 3397–3406.
Chou, W.-L. (2010). Removal and adsorption characteristics of polyvinyl alcohol from aqueous solutions using electrocoagulation. *Journal of hazardous materials*, *177*(1-3), 842–850.

Chowdhury, M. N. K., Ismail, A. F., Beg, M. D. H., Hegde, G., & Gohari, R. J. (2015). Polyvinyl alcohol/polysaccharide hydrogel graft materials for arsenic and heavy metal removal. *New Journal of Chemistry*, *39*(7), 5823–5832.

Chung, J., Kim, S., Choi, K., & Kim, J.-O. (2016). Degradation of polyvinyl alcohol in textile waste water by Microbacterium barkeri KCCM 10507 and Paenibacillus amylolyticus KCCM 10508. *Environmental technology*, *37*(4), 452–458.

Corti, A., Solaro, R., & Chiellini, E. (2002). Biodegradation of poly(vinyl alcohol) in selected mixed microbial culture and relevant culture filtrate. *Polymer Degradation and Stability*, *75*(3), 447–458.

Cox, D., & Reid, N. (2000). *The Theory of the Design of Experiments*: Chapman & Hall/CRC.

DeMerlis, C. C., & Schoneker, D. R. (2003). Review of the oral toxicity of polyvinyl alcohol (PVA). *Food and chemical toxicology an international journal published for the British Industrial Biological Research Association*, *41*(3), 319–326.

Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung (2017). Allgemeine Angaben (Gruppe A) – Teil 51: *Kalibrierung von Analysenverfahren – Lineare Kalibrierfunktion (A 51).* (DIN 38402-51).

Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung (2013). Allgemeine Angaben (Gruppe A) – Teil 60: *Analytische Qualitätssicherung für die chemische und physikalisch-chemische Wasseruntersuchung (A 60)* (DIN 38402-60).

Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung (1999) *Quantitative Bestimmung der kultivierbaren Mikroorganismen*. (DIN 38402-60).

Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung (1997). Water analysis - Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC). (DIN EN 1484 – 1997-08).

Dong, Y., Bian, L., & Wang, P. (2019). Accelerated degradation of polyvinyl alcohol via a novel and cost effective heterogeneous system based on Na2S2O8 activated by Fe complex functionalized waste PAN fiber and visible LED irradiation. *Chemical Engineering Journal*, *358*, 1489–1498.

European Commission (2003): Best Available Techniques Reference Document for the Textiles Industry, https://eippcb.jrc.ec.europa.eu/sites/default/files/2019-11/txt_bref_0703.pdf

Finley, J. H. (1961). Spectrophotometric determination of polyvinyl alcohol in paper coatings. Journal of Analytical Chemistry, 33, 1925–1927.

Gallo, F., Fossi, C., Weber, R., Santillo, D., Sousa, J., Ingram, I., Nadal, A., & Romano, D. (2018). Marine litter plastics and microplastics and their toxic chemicals components: the need for urgent preventive measures. *Environmental sciences Europe*, *30*(1), 13.

Gooch, J. W. (Ed.) (2007). *Encyclopedic Dictionary of Polymers*. New York, NY: Springer New York.

Hamad, D., Mehrvar, M., & Dhib, R. (2014). Experimental study of polyvinyl alcohol degradation in aqueous solution by UV/H2O2 process. *Polymer Degradation and Stability*, *103*, 75–82.

Hashimato, S., & Fujita, M. (1985). Isolation of a bacterium requiring three amino acids for polyvinyl alcohol degradation. *Fermentation technology*, *63*, 471–474.

He, Y., Wang, X., Xu, J., Yan, J., Ge, Q., Gu, X., & Jian, L. (2013). Application of integrated ozone biological aerated filters and membrane filtration in water reuse of textile effluents. *Bioresource technology*, *133*, 150–157.

Henze, M., van Loosdrecht, M., & Ekama G. (2008). *Biological wastewater treatment: Principles, modelling and design*. London: IWA Pub.

Hoffmann, J., Řezníčková, I., Kozáková, J., Růžička, J., Alexy, P., Bakoš, D., & Precnerová, L. (2003). Assessing biodegradability of plastics based on poly(vinyl alcohol) and protein wastes. *Polymer Degradation and Stability*, *79*(3), 511–519.

Holkar, C. R., Jadhav, A. J., Pinjari, D. V., Mahamuni, N. M., & Pandit, A. B. (2016). A critical review on textile wastewater treatments: Possible approaches. *Journal of environmental management*, *182*, 351–366.

Hou, Q., & Wang, X. (2017). The effect of PVA foaming characteristics on foam forming. *Cellulose*, *24*(11), 4939–4948.

Hsu, L.-J., Lee, L.-T., & Lin, C.-C. (2011). Adsorption and photocatalytic degradation of polyvinyl alcohol in aqueous solutions using P-25 TiO2. *Chemical Engineering Journal*, *173*(3), 698–705.

ISO (1999). International Organization for Standardization. (1999). Water quality – Evaluation of ultimate aerobic biodegradability of organic compounds in aqueous medium – Static test (Zahn-Wellens method). (ISO Standard No. 9888).(9888:1999).

Jia, Y., Bai, S., Park, C. B., & Wang, Q. (2017). Effect of Boric Acid on the Foaming Properties and Cell Structure of Poly(vinyl alcohol) Foam Prepared by Supercritical-CO 2 Thermoplastic Extrusion Foaming. *Industrial & Engineering Chemistry Research*, *56*(23), 6655–6663.

Joshi, D., Chun-Fung, Y., & Pritchard, J. (1979). Determination of Polyvinyl alcohol via it complex with boric acid and iodine. *Analytica Chimica Acta*, *104*, 153–160.

Julinová (2018). Water-soluble polymeric xenobiotics – Polyvinyl alcohol and polyvinylpyrrolidon – And potential solutions to environmental issues: A brief review. https://www.sciencedirect.com/science/article/pii/S0301479718310016.Accessed 25.03.2023.

Kang, S.-F., Liao, C.-H., & Chen, M.-C. (2002). Pre-oxidation and coagulation of textile wastewater by the Fenton process. *Chemosphere*, *46*(6), 923–928.

Katsoyiannis, A., Zouboulis, A., & Samara, C. (2006). Persistent organic pollutants (POPs) in the conventional activated sludge treatment process: model predictions against experimental values. *Chemosphere*, *65*(9), 1634–1641.

Kawai, F., & Hu, X. (2009). Biochemistry of microbial polyvinyl alcohol degradation. *Applied microbiology and biotechnology*, *84*(2), 227–237.

Kim, B. C., Sohn, C. K., Lim, S. K., Lee, J. W., & Park, W. (2003). Degradation of polyvinyl alcohol by Sphingomonas sp. SA3 and its symbiote. *Journal of industrial microbiology & biotechnology*, *30*(1), 70–74.

Kim, S., Kim, T.-H., Park, C., & Bai Shin, E. (2003). Electrochemical oxidation of polyvinyl alcohol using a RuO_2/Ti anode, *155*(S0011-9164(03)00238-8), 49–57.

Klomklang, W., Tani, A., Kimbara, K., Mamoto, R., Ueda, T., Shimao, M., & Kawai, F. (2005). Biochemical and molecular characterization of a periplasmic hydrolase for oxidized polyvinyl alcohol from Sphingomonas sp. strain 113P3. *Microbiology (Reading, England)*, *151*(Pt 4), 1255–1262.

Kromidas, S. (2011). *Validierung in der Analytik.* (2. überarbeitere Auflage). Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA.

Kumar, K., Singh, G. K., Dastidar, M. G., & Sreekrishnan, T. R. (2014). Effect of mixed liquor volatile suspended solids (MLVSS) and hydraulic retention time (HRT) on the performance of activated sludge process during the biotreatment of real textile wastewater. *Water Resources and Industry*, *5*, 1–8.

Kwang Keun Choi, Chul Hwan Park, Sang Yong Kim, Won Seok Lyoo, Sang Hun Lee, & Jin Won Lee (2004). Polyvinyl Alcohol Degradation by Microbacterium barkeri KCCM 10507 and Paenibacillus amylolyticus KCCM 10508 in Dyeing Wastewater, *14*(5), 1009–1013.

Lacasse, K., & Baumann, W. (2004). *Textile Chemicals, Environmental Data and Facts.* (1 st edition). Berlin, Heidelberg: Springer-Verlag Berlin Heidelberg.

Lei, L., Hu, X., Yue, P. L., Bossmann, S., Göb, S., & Braun, A. (1998). Oxidative degradation of polyvinyl alcohol by the photochemically enhanced Fenton reaction. *Journal of Photochemistry and Photobiology* (116), 159–166.

Lin, C.-C., Lee, L.-T., & Hsu, L.-J. (2013). Performance of UV/$S_2O_8^{2-}$ process in degrading polyvinyl alcohol in aqueous solutions. *Journal of Photochemistry and Photobiology A: Chemistry*, *252*, 1–7.

Lin, C.-C., Lee, L.-T., & Hsu, L.-J. (2014). Degradation of polyvinyl alcohol in aqueous solutions using UV-365 nm/$S_2O_8^{2-}$ process. *International Journal of Environmental Science and Technology*, *11*(3), 831–838.

Lipsa, R., Tudorachi, N., Grigoras, A., Vasile, C., & Gradinariu, P. (2015). Study on Poly(vinyl alcohol) Copolymers Biodegradation. *Memoirs of the Scientific Sections of the Romanian Academy*.

Lucas, N., Bienaime, C., Belloy, C., Queneudec, M., Silvestre, F., & Nava-Saucedo, J.-E. (2008). Polymer biodegradation: mechanisms and estimation techniques. *Chemosphere*, *73*(4), 429–442.

Magwene, P. M. (2020). Biology 723: Statistical Computing for Biologists. https://bio723-class.github.io/Bio723-book/multiple-regression.html. Accessed 26.04.2023.

Marušincová, H., Husárová, L., Růžička, J., Ingr, M., Navrátil, V., Buňková, L., & Koutny, M. (2013). Polyvinyl alcohol biodegradation under denitrifying conditions. *International Biodeterioration & Biodegradation*, *84*, 21–28.

Matsumura, S., Kurita, H., & Shimokobe, H. (1993). Anaerobic biodegradability of polyvinyl alcohol. *Biotechnology Letters*, *15*(7), 749–754.

Matsumura, S., & Tanaka, T. (1994). Novel malonate-type copolymers containing vinyl alcohol blocks as biodegradable segments and their builder performance in detergent formulations. *Journal of Environmental Polymer Degradation*, *2*(2), 89–97.

Mejía, G. A. I., López, O. B. L., & Mulet, P. A. (1999). Biodegradation of poly (vinylalcohol) with enzymatic extracts of phanerochaete chrysosporium. *Macromolecular Symposia*, *148*(1), 131–147.

Metcalf, & Eddy (2003). *Wastewater Engineering.* (4th ed.): McGraw Hill.

Mohod, A. V., & Gogate, P. R. (2011). Ultrasonic degradation of polymers: effect of operating parameters and intensification using additives for carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA). *Ultrasonics sonochemistry*, *18*(3), 727–734.

Montgomery, D. (1997). *design and analysis of experiments.* (5th edition). United states: John Wiley & sons.

Mori, T., Sakimoto, M., Kagi, T., & Sakai, T. (1996). Isolation and Characterization of a Strain of Bacillus megaterium That Degrades Poly(vinyl alcohol). *Bioscience, biotechnology, and biochemistry*, *60*(2), 330–332.

Mritunjay Chaubey (2021). *Wastewater Treatment Technologies.* (1st ed.): Wiley-Blackwell.

Nogi, Y., Yoshizumi, M., Hamana, K., Miyazaki, M., & Horikoshi, K. (2014). Povalibacter uvarum gen. nov., sp. nov., a polyvinyl-alcohol-degrading bacterium isolated from grapes. *International journal of systematic and evolutionary microbiology*, *64*(Pt 8), 2712–2717.

Nogi, Y., Yoshizumi, M., & Miyazaki, M. (2014). Thalassospira povalilytica sp. nov., a polyvinyl-alcohol-degrading marine bacterium. *International journal of systematic and evolutionary microbiology*, *64*(Pt 4), 1149–1153.

OECD (2008). Test No. 314: Simulation Tests to Assess the Biodegradability of Chemicals Discharged in Wastewater. OECD Guidelines for the Testing of Chemicals, Section 3. Paris: OECD Publishing.

Opwis, K., Knittel, D., Kele, A., & Schollmeyer, E. (1999). Enzymatic Recycling of Starch-Containing Desizing Liquors. *Starch - Stärke*, *51*(10), 348–353.

Pandey, S., & Sarkar, S. (2017). Anaerobic treatment of wastewater using a two-stage packed-bed reactor containing polyvinyl alcohol gel beads as biofilm carrier. *Journal of Environmental Chemical Engineering*, *5*(2), 1575–1585.

Polaris (2023). Global Polyvinyl Alcohol Market Size Report, 2022 - 2030. https://www.polarismarketresearch.com/industry-analysis/polyvinyl-alcohol-market. Accessed 28.03.2023.

Pritchard, J., & Akintola, D. (1972). Complexation of Polyvinyl alcohol with Iodine, *19*, 877–888.

Procházková, L., Rodríguez-Muñoz, Y., Procházka, J., & Wanner, J. (2014). Simple spectrophotometric method for determination of polyvinylalcohol in different types of wastewater. *International Journal of Environmental Analytical Chemistry*, *94*(4), 399–410.

Pšeja, J., Charvátová, H., Hruzík, P., Hrnčiřík, J., & Kupec, J. (2006). Anaerobic Biodegradation of Blends Based on Polyvinyl Alcohol. *Journal of Polymers and the Environment*, *14*(2), 185–190.

Qian, D., Du, G., & Chen, J. (2004). Isolation and Culture Characterization of a New Polyvinyl Alcohol-Degrading Strain: Penicillium sp. WSH02-21. *World Journal of Microbiology and Biotechnology*, *20*(6), 587–591.

Ghaly, A., Ananthashankar, R., Al hattab (2014). Production, Characterization and Treatment of Textile Effluents: A Critical Review. *Journal of Chemical Engineering & Process Technology*, *05*(01).

Rieger, B., Künkel, A., Coates, G. W., Reichardt, R., Dinjus, E., & Zevaco, T. A. (2012). *Synthetic Biodegradable Polymers*, 245. Berlin, Heidelberg: Springer Berlin Heidelberg.

Rolsky, C., & Kelkar, V. (2021). Degradation of Polyvinyl Alcohol in US Wastewater Treatment Plants and Subsequent Nationwide Emission Estimate. *International journal of environmental research and public health*, *18*(11).

Rongrong, L., Xujie, L., Qing, T., Bo, Y., & Jihua, C. (2011). The performance evaluation of hybrid anaerobic baffled reactor for treatment of PVA-containing desizing wastewater. *Desalination*, *271*(1-3), 287–294.

Rosen, M. J., & Song, L. D. (1996). Dynamic Surface Tension of Aqueous Surfactant Solutions 8. Effect of Spacer on Dynamic Properties of Gemini Surfactant Solutions. *Journal of Colloid and Interface Science*, *179*(1), 261–268.

Rowe, R., Sheskey P., & Quinn, M. (Eds.) (2009). *Handbook of pharmaceutical excipients.* (6. ed.). London: APhA (PhP) Pharmaceutical Press.

Russo, M. A. L., O'Sullivan, C., Rounsefell, B., Halley, P. J., Truss, R., & Clarke, W. P. (2009). The anaerobic degradability of thermoplastic starch: polyvinyl alcohol blends: potential biodegradable food packaging materials. *Bioresource technology*, *100*(5), 1705–1710.

Sakai, K., Hamada, N., & Watanabe, Y. (1986). Degradation Mechanism of Poly(vinyl alcohol) by Successive Reactions of Secondary Alcohol Oxidase and β -Diketone Hydrolase from Pseudomonas sp. *Agricultural and Biological Chemistry*, *50*(4), 989–996.

Saxena S. K (2007). Polyvinyl alcohol (PVA)- Chemical and Technical Assessment (CTA). In J. W. Gooch (Ed.), *Encyclopedic Dictionary of Polymers* (p. 772). New York, NY: Springer New York.

Schonberger, H., Baumann, A., & Keller, W. (1997). Study of Microbial Degradation of Polyvinyl Alcohol (PVA) in Wastewater Treatment Plants. *No. 8*, *86*, 9–17.

Schweikl, H., Schmalz, G., & Gijttke, C. (1996). Mutagenic activity of various dentine bonding agents. *Biomoteriols*, *17*, 1451–1456.

Shan, J., Guan, Y., Zheng, Q., Han, J., Liu, Q., & Pu, Z. (2009). Application of urea/H 2 O 2 activation-oxidation system in degradation of PVA and desizing of polyester/cotton fabric. *Journal of Applied Polymer Science*, *113*(2), 860–867.

Shimao, M., Taniguchi, Y., Shikata, S., Kato, N., & Sakazawa, C. (1982). Production of polyvinyl alcohol oxidase by a symbiotic mixed culture. *Applied and Environmental Microbiology*, *44*(1), 28–32.

Shimao, M., Yamamoto, H., Ninomiya, K., Kato, N., Adachi, O., Ameyama, M., & Sakazawa, C. (1984). Pyrroloquinoline Quinone as an Essential Growth Factor for a Polyvinyl alcohol)-degrading Symbiont, Pseudomonas sp. VM15C. *Agricultural and Biological Chemistry*, *48*(11), 2873–2876.

Shokri, A. (2021). Using NiFe2O4 as a nano photocatalyst for degradation of polyvinyl alcohol in synthetic wastewater. *Environmental Challenges*, *5*, 100332.

Song, Q., Chen, X., Tang, L., & Zhou, W. (2021). Treatment of polyvinyl alcohol containing wastewater in two stage spiral symmetrical stream anaerobic bioreactors coupled a sequencing batch reactor. *Bioresource technology*, *340*, 125702.

Spahr, S., Teixidó, M., Sedlak, D. L., & Luthy, R. G. (2020). Hydrophilic trace organic contaminants in urban stormwater: occurrence, toxicological relevance, and the need to enhance green stormwater infrastructure. *Environmental Science: Water Research & Technology*, *6*(1), 15–44.

Sun, W., Chen, L., Zhang, Y., & Wang, J. (2015). Synergistic effect of ozonation and ionizing radiation for PVA decomposition. *Journal of environmental sciences (China)*, *34*, 63–67.

Suzuki, T. (1976). Purification and Some Properties of Polyvinyl Alcohol-degrading Enzyme Produced by Pseudomonas O-3. *Agricultural and Biological Chemistry*, *40*(3), 497–504.

Tang, B., Liao, X., Zhang, D., Li, M., Li, R., Yan, K., Du, G., & Chen, J. (2010). Enhanced production of poly(vinyl alcohol)-degrading enzymes by mixed microbial culture using 1,4-butanediol and designed fermentation strategies. *Polymer Degradation and Stability*, *95*(4), 557–563.

Tchobanoglous, G., Stensel, H., Tsuchihashi, R., & Burton, R. (2014). *Metcalf & Eddy. Wastewater Engineering: Treatment and Reuse, 5th Edition.*: McGraw Hill.

Thomsen, V., Schatzlein, D., & Mercuro, D. (2003). Limits of Detection in Spectroscopy. *Spectroscopy*, 18, 112–114.

Tsujiyama, S., & Okada, A. (2013). Biodegradation of polyvinyl alcohol by a brown-rot fungus, Fomitopsis pinicola. *Biotechnology letters*, *35*(11), 1907–1911.

Tsujiyama, S., Nitta, T., & Maoka, T. (2011). Biodegradation of polyvinyl alcohol by Flammulina velutipes in an unsubmerged culture. *Journal of bioscience and bioengineering*, *112*(1), 58–62.

Vaclavkova, T., Ruzicka, J., Julinova, M., Vicha, R., & Koutny, M. (2007). Novel aspects of symbiotic (polyvinyl alcohol) biodegradation. *Applied microbiology and biotechnology*, *76*(4), 911–917.

Venkatesan, A. K., & Halden, R. U. (2014). Brominated flame retardants in U.S. biosolids from the EPA national sewage sludge survey and chemical persistence in outdoor soil mesocosms. *Water research*, *55*, 133–142.

Walker, T. R. (2021). (Micro)plastics and the UN Sustainable Development Goals. *Current Opinion in Green and Sustainable Chemistry*, *30*, 100497.

Wei, Y., Fu, J., Wu, J., Jia, X., Zhou, Y., Li, C., Dong, M., Wang, S., Zhang, J., & Chen, F. (2018). Bioinformatics Analysis and Characterization of Highly Efficient Polyvinyl Alcohol (PVA)-Degrading Enzymes from the Novel PVA Degrader Stenotrophomonas rhizophila QL-P4. *Applied and Environmental Microbiology*, *84*(1).

W.E. Boyce, R.C. DiPrima(1995). Gewöhnliche Differenzialgleichungen, Spektrum Akademischer Verlag

Weiner, R. (1997). Boyce, W. E; DiPrima, R. C.: Gewöhnliche Differentialgleichungen. Einführung — Aufgaben — Lösungen. Heidelberg etc., Spektrum, Akademischer Verlag 1995. XV, 699 S., 150 Abb., DM 78.–. ISBN 3-86025-151-1 (Spektrum Lehrbuch). *ZAMM - Journal of Applied Mathematics and Mechanics / Zeitschrift für Angewandte Mathematik und Mechanik*, *77*(4), 294.

Woo, P. C. Y., Teng, J. L. L., Wu, J. K. L., Leung, F. P. S., Tse, H., Fung, A. M. Y., Lau, S. K. P., & Yuen, K.-Y. (2009). Guidelines for interpretation of 16S rRNA gene sequence-based results for identification of medically important aerobic Gram-positive bacteria. *Journal of medical microbiology*, *58*(Pt 8), 1030–1036.

Yamatsu, A., Matsumi, R., Atomi, H., & Imanaka, T. (2006). Isolation and characterization of a novel poly(vinyl alcohol)-degrading bacterium, Sphingopyxis sp. PVA3. *Applied microbiology and biotechnology*, *72*(4), 804–811.

Ye, B., Li, Y., Chen, Z., Wu, Q.-Y., Wang, W.-L., Wang, T., & Hu, H.-Y. (2017). Degradation of polyvinyl alcohol (PVA) by UV/chlorine oxidation: Radical roles, influencing factors, and degradation pathway. *Water research*, *124*, 381–387.

Yu, H., Gu, G., & Song, L. (1996). Degradation of Polyvinyl Alcohol in Sequencing Batch Reactors. *Environmental technology*, *17*(11), 1261–1267.

Zahn, R., & Wellens, H. (1974). Ein einfaches Verfahren Zur Prüfung der biologischen Abbaubarkeit von Produkten und Abwasserinhaltsstoffen. Chemiker Zeitung, 98, 228–232.

ZDHC, 2. Wastewater Treatment Technologies- The roadmap to zero programme. In *Chaubey (Edition) 2021 – Wastewater Treatment Technologies* (pp. 67–102).

Zhang, S.-J., & Yu, H.-Q. (2004). Radiation-induced degradation of polyvinyl alcohol in aqueous solutions. *Water research*, *38*(2), 309–316.

Zhu, G., & Ge, M. (2021). Study on efficient degradation of polyvinyl alcohol in aqueous solution. *Environmental Challenges*, *4*, 100176.