

MONOGRAPH

11th European Young Engineers Conference





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11th European Young Engineers Conference

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Introduction

Work on the 11th edition of the Conference started a short time after the end of last year's edition of EYEC. Years 2020 – 2022 was marked by the COVID-19 pandemic. For the first time in the history of the European Young Engineers Conference, we had to cancel the event and later organize it remotely on two occasions. This year, after a break of four years, we are excited to announce that we can once again gather at the Warsaw University of Technology Faculty of Chemical and Process Engineering.

The 11th edition is an incredible moment for us, the organisers of the first edition of the conference did not even dream that it would be carried for so many years. With a lot of optimism, we look forward to entering the next decade of the European Young Engineers Conference. Our team faced a major challenge as none of the members of the Scientific Club of Chemical and Process Engineering "Venturi" participated in the Conference held in a stationary form due to the pandemic. Nevertheless, we are hopeful that our efforts will enable you to have a rewarding experience, filled with engaging discussions and the exchange of ideas with your colleagues.

We would like to express our gratitude to our special guests for their captivating lectures and to the dedicated members of the Scientific Commission for their hard work during the conference. Additionally, we extend our heartfelt appreciation to all the members of the Scientific Committee who worked diligently to ensure the highest quality of submitted papers, allowing us to provide a monograph. Your invaluable assistance and guidance are greatly valued by all of us, the organizers and young scientists alike. We would like to express our heartfelt thanks to the dean and the authorities of the Faculty for their unwavering support for this initiative from the very beginning and encourage us to continue it.

> – Organising Committee Editorial Team of EYEC Monograph

1 Special guests

1.1 Prof. Sotris E. Pratsinis

Particle Technology Laboratory, Institute of Energy and Process Engineering, Department of Mechanical and Process Engineering, ETH Zürich, Zürich, Switzerland



Sotiris E. Pratsinis has a 1977 Diploma in Chemical Engineering from Aristotle Univ. of Thessaloniki, Greece and a 1985 PhD from University of California, Los Angeles. He was in the faculty of the Univ. of Cincinnati, USA from 1985 to 1998 until he was elected Professor of Process Engineering & Materials Science at ETH Zürich, Switzerland.

There he teaches Mass Transfer, Micro- & Nano-Particle Technology and Combustion Synthesis of Materials. He has graduated 46 PhDs, published 400+ articles, has filed 20+ patent families that are licensed to industry and have contributed to creation of four spinoffs. One of them (HeiQ Materials AG) was the first ever from ETH Zürich to enter the London Stock Exchange in December 2020.

He first measured the oxidation rate of TiCl₄ for synthesis of TiO₂ (a 10 billion \$ industry worldwide today) that has been recognized as "...a landmark contribution to ...(pigment) industry...". He has led the development of 2-dimensional population balances for reaction, coagulation and sintering. These models along with his proof of the rapid attainment of both self- preserving size distribution and fractal-like structure during aerosol synthesis of materials enabled creation of simple and reliable particle dynamics models that are interfaced readily with fluid mechanics greatly facilitating process design for particle manufacture and processing. For example, his model for production of optical fiber preforms was the first of its kind and still used in industry.

Motivated by this quantitative understanding, he showed experimentally, how to control flame- made particle size, crystallinity and, for the first time, morphology: from perfectly spherical particles to highly ramified agglomerates. Most notably, he developed the flame spray pyrolysis (FSP) process for synthesis of sophisticated particle compositions, up to 5 kg/h in his labs, perhaps world's largest such facility for manufacture of nanoparticles at an academic institution. With FSP he prepared novel heterogeneous catalysts (primarily for environmental remediation) and, for the first time, flame- made gas sensors and nutritional supplements as well as dental and theranostic materials. Also his FSP contributed decisively to environmental policy by identifying the origins of nanosilver toxicity and even developed processes for "curing" it.

Abstract: Aerosol processing of materials: fundamentals & applications

Aerosols are particles suspended in gases. Aerosol manufacturing offers fewer process steps than conventional wetchemistry processes, easier particle collection from gaseous than liquid streams and no liquid by-products that require costly cleaning. In addition, aerosol-made particles and films have unique morphology and high purity (e.g. optical fibers) and even metastable phases leading to materials with unique functionality resulting in novel heterogeneous catalysts, gas sensors, phosphors, battery electrodes, dental prosthetics, theranostic materials and even nutritional supplements (Kelesidis, 2021).

Then the focus of the talk will be on flame spray synthesis of materials where our laboratory has had some impact highlighting our latest breakthrough: the assembly of highlyselective gas sensing devices. This led, for example, to portable detectors of methanol in alcoholic beverages (liquor adulteration) and human breath (methanol poisoning vs. ethanol intoxication) as well to detection of exceptionally low levels of formaldehyde (few ppb) in gas mixtures (indoor air pollution) (Güntner et Pineau, 2022).

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1.2 Prof. Dr. Eng. Jörg Vienken

Technical University Mittelhessen, Giessen, Germany



Jörg Vienken graduated in Chemical Engineering at the Technical University of Darmstadt and received a Doctoral Degree in Biophysics and Bioengineering from the Technical University of Aachen, both in Germany. He was then appointed the position of an Associate Professor at the Institute for Biotechnology of the University of Würzburg, Germany.

In 1985 he switched to the medical device industry and worked for 11 years at AKZO NOBEL Membrana in Wuppertal as a Director for Clinical Research and Science Services, followed by a position as a Vice President BioSciences in Fresenius Medical Care in Bad Homburg, Germany which he held until his retirement in 2013. Then he served as one of the Nephro-Solutions AG Board Members in Hamburg. Since 2016 he works as a Freelance Advisor for the Medical Device Industry.

He has been awarded the Emil-Bücherl Award for the lifetime achievement in the realm of Artificial Organs from the European Society for Artificial Organs (ESAO) and is a distinguished fellow of ERA-EDTA, the European Dialysis and Transplantation Association.

Jörg Vienken is a Past President of the International Federation of Artificial Organs (IFAO, representing the umbrella organisation of the continental societies from Europe (ESAO), the USA (ASAIO) and Japan (JSAO)). He was a long lasting Board member of the European Society for Artificial Organs (ESAO) and served as its secretary treasurer between 1998 and 2006. He is also a Past President of the Association of German Biotech Companies (VBU-DECHEMA).

Jörg Vienken still teaches Biomaterials and Artificial Organs at several German and European Universities. He has published more than 350 scientific publications and book chapters as well as 9 own books.

Abstract: Albumin, a versatile protein acting as a molecular vacuum cleaner

Keywords: albumin, binding capacity, uremic retention solutes, pathology.

Introduction:

The protein albumin can be described as a functional molecular vacuum cleaner. Albumin efficiently binds toxins and administered pharmaceutical agents to a high degree. Recent scientific discussions circle around its deteriorated function both in kidney and liver failure.

Actual clinical observations:

The healthy kidney filters nephrotic levels of albumin as shown by the functional analysis of proximal tubular cells. Even the glomerular filtration barrier which has long been thought to be largely impermeable to albumin has now been shown to be permeable for albumin. Reasons may be referred to a charge selectivity of the glomerular membrane, a consequence of inflammatory signals or a change in molecular conformation. Complications arise when the binding capacity of albumin for toxins and pharmaceutical agents is a reduced, e.g. under pathological clinical conditions. Changes in the molecular 3D-conformation of albumin play here a role. They have been shown to be due to the presence of toxic compounds, such as indoxyl sulfate (IS). IS is considered to be one of the major uremic retention solutes. Conformational changes of albumin have also been shown to depend on both actual pH and the presence of different creatinine concentrations. This holds true for both native albumin as well as for commercially available albumin solutions to be infused.

The reality of clinical haemodialysis:

Current dialysis therapies move towards an increasing use of high flux dialysis membranes and their related treatment modalities, such as hemodiafiltration. Dialysis membranes with increased pores sizes are required for these treatment options. The current dogma, designed by nephrologists, prescribes however, that these membranes should have a cut-off below the molecular weight of albumin, i.e., below around 60.000 which reflects a membrane sieving coefficient for albumin to be far below 0.1.

New data and verifications:

A hypothesis must be advanced that a "pathological" albumin molecule with reduced binding capacities exists under pathological conditions, and thus, should be removed during hemodialysis. Consequently, the nephrologcal dogma of an albumin impermeable dialysis membranes should be questioned. Recent clinical trials with a long-term use of protein permeable membranes have shown that patient survival improves with albumin leaky membranes.

1.3 Prof. Magda H. Barecka, PhD

Department of Chemical Engineering and Chemistry and Chemical Biology, Northeastern University in Boston, Boston, MA, USA

Dr. Magda H. Barecka is an Assistant Professor at Northeastern University in Boston, Departments of Chemical Engineering and Chemistry and Chemical Biology. Her group focuses on the discovery and scale-up of electrochemical CO_2 utilization methods. Dr Barecka completed postdoctoral training at the University of Cambridge, Research Cen-



tre for Research and Education in Singapore (CARES). She developed a new approach for CO_2 utilization (Carbon Capture On-Site Recycling), as well as co-authored three patents. During her PhD studies, Dr. Barecka developed a methodology supporting implementation of intensified technologies in chemical manufacturing, which was subsequently transferred to the industry. In her free time, she enjoys hiking, snorkeling, drinking coffee and connecting to new cultures and communities.

Abstract: Accelerating the transition to carbon neutrality in Barecka Lab

In Barecka Lab, we seek to provide technically feasible and economically viable solutions to one of the biggest challenges of the 21st century: the need for transition to carbon neutrality. To achieve this goal, we need to develop capabilities of recycling carbon dioxide and using it as a sustainable feedstock for production processes. Our group explores the potential of electrochemistry and discovers new ways of turning carbon dioxide into valuable products, develops better catalysts and separation techniques, elucidates new chemical pathways and designs more efficient electrochemical reactors. We are also interested in the modeling complex electrochemical processes, evaluating their techno-economics and understanding their scalability. Our group interacts closely with the industry and renewable energy providers.

This talk will focus on how to introduce CO_2 electrolysis into established industries and allow for their full-scale decarbonization. Following a brief introduction of state-of-the-art CO_2 electrolysis, I will discuss several strategies for its stepwise deployment in chemical plants, without disrupting the existing industries and therefore not putting at risk the delivery of products that our society relies on. I will present our experimental advancements towards the development of CO_2 electrolyzers which is necessary to revolutionize the way in which manufacture diverse chemical building blocks.

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1.4 Rasa Keruckiene, PhD

Department of Polymer Chemistry and Technology, Faculty of Chemical Technology, Kaunas University of Technology, Kuanas, Lithuania



Dr. Rasa Keruckiene is a researcher at Kaunas University of Technology, Department of Polymer Chemistry and Technology. She defended her doctoral dissertation in the field of Materials Science at KTU in 2017. She has won the Best research work of Young Researcher in the field of Chemistry, Physics and Mathematics awarded by Lithuanian Academy of Sciences in 2018. Her re-

search interests and experience are in the field of the design, synthesis, characterization of organic electroactive compounds by experimental and theoretical methods as well as their thermal, electrochemical and photophysical properties investigation.

Abstract: Shaping our water technology by functional materials and electrospinning

Keywords: TADF, RTP, OLED.

Organic light-emitting diodes (OLEDs) have made great progress in display technologies due to the advantages of low weight, low power consumption, and high colour saturation (Jang et al., 2019). Organic compounds exhibiting phosphorescence and thermally activated delayed fluorescence (TADF) are versatile candidates for the improvement of device efficiency by extracting non-radiative triplet excitons, due to their ability to strong spin orbital coupling (SOC) and small singlet-triplet splitting (Δ EST) (Braveenth et al., 2021). Easily obtainable and efficient materials are preferred for the advancement of OLED technologies. Efficient luminophores with phenomena which allow to harvest triplet excitons formed under electrical excitation and convert them into light (e.g. intramolecular and intermolecular (exciplex-based) thermally activated delayed fluorescence (TADF), room temperature phosphorescence (RTP), triplet-triplet annihilation etc.) are vitally required for optoelectronic applications.

Furthermore, because of many possible benefits of organic materials including low energy processability, optical transparency, flexibility, and environmentally friendly utilization, all-organic luminophores exhibiting efficient phosphorescence at room temperature (RTP) have great potential for applications in different areas ranging from security, information encryption and optoelectronics to biological probes and optical sensing. (Xu-dong et al., 2014; Kabe et al., 2016).

Two series of naphthyridine-based TADF emitters and trifluoromethyl-based RTP oxygen sensing compounds will be presented.

Acknowledgements

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2 Scientific Commission

2.1 assoc. prof. Andrzej Krasiński

Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warsaw, Poland

Prof. Andrzej Krasiński holds PhD in chemical engineering obtained in 2005 at Faculty of Chemical and Process Engineering of Warsaw University of Technology, and in 2018 the D.Sc. (habilitation) for a comprehensive research on emulsion separation using the coalescence filtration method.



From 2019 he has been employed

as Associate Professor at afore mentioned faculty, in Chair of Integrated Processes Engineering (initially in Process Equipment Department).

Prof. Andrzej Krasiński is a co-author of more than 40 publications in peer reviewed journals, over 30 conference presentations, and 2 patents. He holds the Chartered Engineer (CEng) status obtained from IChemE. His research track is related to the separation processes, with focus on the droplets coalescence and separation of gas-liquid and liquid-liquid dispersions, pervaporation and also gas and water cleaning technologies. He has been involved in numerous industrially oriented projects, including pyrolysis of wastes, development of filtration products for the automotive industry and for the ammonia plant. Based on past experience his area of expertise covers also aggregation of particles in turbulent flows, precipitation, CFD modeling of reactive and multiphase flows, and rheology of dense suspensions.

2.2 assoc. prof. Wojciech Jerzy Nowak

Department of Materials Science, Faculty of Mechanical Engineering and Aeronautics, Rzeszow University of Technology, Rzeszow, Poland

DSc Eng. Wojciech Jerzy Nowak works as Associate Professor at Rzeszow University of Technology, Faculty of Mechanical Engineering and Aeronautics, Department of Materials Science since February 2016. He received his BSc degree in Materials Science (specialization: Organic Materials Engineering (2007)) at Rzeszow University of Technology, MSc



degree in Materials Science (specialization: Biomaterials and Composites (2010)) at AGH University of Science and Technology in Cracow and the PhD. degree in Material Science (specialization: High-Temperature Oxidation (2014)) under supervision of Prof. Lorenz Singheiser in RWTH Aachen University. During PhD. studies, he worked as a PhD. student in Forschungszentrum Juelich GmbH (2011 – 2014) in Institute of Energy and Climate Research (IEK), department: Microstructure and Properties of Materials (IEK-2) in the Group of High-Temperature Corrosion and Corrosion Protection leaded by Prof. Willem J. Quadakkers. After PhD. studies, he continued working in FZJ as a postdoctoral researcher in the Group of High-Temperature Corrosion and Corrosion Protection (2014-2016). He was additionally responsible for performing all of the analyses using glow discharge optical emission spectroscope (GD-OES). Since 2016 he has worked at Rzeszow University of Technology in the Faculty of Mechanical Engineering and Aeronautics, Department of Materials Science as an assistant professor. Between 2016 - 2020, he was responsible for the Section of Chemical Composition Analysis (P2), which is a part of the Research and Development Laboratory for Aerospace Materials at Rzeszow University of Technology; therefore, he continuously works with the GD-OES. In 2022 he received his DSc title at AGH University of Science and Technology in Cracow. His research is focused on materials dedicated for high-temperature application, especially Ni-base superalloys, protective coatings, and TBC systems, as well as high-entropy alloys, and their oxidation behavior during exposure at high temperature.

2.3 Nina Hutnik, PhD

Faculty of Chemistry, Wroclaw University of Science and Technology, Wroclaw, Poland

Since graduating in 2007, Nina Hutnik, PhD BEng, has linked her professional life with the Faculty of Chemistry at Wroclaw University of Science and Technology. She defended her doctoral dissertation at her home faculty in 2011. At present, she is employed as a teaching assistant. She specializes in chemical and process engineering as well as process design.



In particular, she focused on both - mass crystallization processes from solutions and designing crystallizers for these processes. She is a co-author of 68 articles published in foreign and domestic journals and 25 conference papers. She also participated in many foreign and domestic conferences, where she presented her research and implementation achievements. She co-authored to prepare process design for the installation which was to recover phosphates from industrial wastewater in Z.Ch. Police S.A. In the meantime, she completed postgraduate studies in Criminalistics (2012), and then Expertise of documents (2013) at the Faculty of Law, Administration and Economics at the University of Wroclaw, which enriched her research and didactic workshop. She also participated in the implementation of 6 research projects for the Ministry of Science and Higher Education (as a contractor), and in 2020 she completed the NCN SONATA11 project (as a manager). She uses her research, scientific and design experience in a creative way to teach students. She teaches chemical engineering, process engineering, technological design and design of industrial installations and industrial crystallization in all didactics forms (lectures, exercises, projects and laboratories) in the fields of Chemical and Process Engineering, Chemistry and Materials Engineering and Chemical Technology. In 2011 the International Year of Chemistry, she was awarded a medal with the image of the Nobel Prize winner Maria Skłodowska-Curie (for her work at the Faculty of Chemistry). Twice, in 2012 and 2020, she received Rector's Award. Since 2022, she has been a Leader of Accessibility at Wroclaw University of Science and Technology.

2.4 Katarzyna Jabłczyńska, PhD

Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warsaw, Poland



Dr. Katarzyna Jabłczyńska is a chemical and process engineer with a focus on micro and nanoscale functional particles. She received her PhD in Chemical and Process Engineering from Warsaw University of Technology in 2019 for her research on nanostructured systems for pulmonary drug delivery.

After completing her PhD, Dr.

Jabłczyńska worked as a postdoctoral researcher at the Particle Technology Laboratory in the Mechanical and Process Engineering Department at Swiss Federal Institute of Technology (ETH Zürich) where she researched semiconducting nanoparticles for gas sensing technology. In 2022, she returned to Warsaw as an adjunct professor.

Dr. Jabłczyńska's research centers around the synthesis and application of micro and nanoscale functional particles obtained by flame aerosol synthesis. Her particular focus is on their use in catalysis and gas sensing technology, as well as in the development of antibacterial and antivirus nanomaterials.

Dr. Jabłczyńska recently received a significant grant to establish a flame aerosol synthesis laboratory at Warsaw University of Technology, which will enable her to further advance her research in the field.

2.5 Michał Wojasiński, PhD

Head of Laboratory of Nanohydroxyapatite (LabOFn), Department of Biotechnology and Bioprocess Engineering, Faculty of Chemical and Process Engineering, Warsaw University of Technology, Warsaw, Poland



Dr. Michał Wojasiński, chemical engineer, works at the intersection of biomedical engineering, tissue engineering, and nanotechnology. He builds interdisciplinary approaches to various research and engineering problems concerning biomaterials synthesis and processing. He graduated in Chemical Engineering from the Faculty of Chemical and Process

Engineering, Warsaw University of Technology (2011). In 2019, he defended his Ph.D. thesis in chemical engineering. He took up the position of assistant professor in the same Faculty. He teaches medical nanotechnology, implantable medical devices, and bioprocess in the laboratory and introductory course into chemical engineering.

His research interest covers nanostructures formation processes – polymer nanofibers and ceramic nanoparticles – for application in tissue engineering/regenerative medicine. He works on a description of a process of air blowing of polymer fibers, called solution blow spinning, as an extension of his research project granted from the National Science Centre and his Ph.D. His recent publications deal with the chitosanbased nanofibrous materials as wound dressing, design of specific nanofibrous materials for microfluidic systems, and various methods to produce hydroxyapatite nanoparticles with controlled morphology and surface chemistry. Now, Dr. Wojasiński works on incorporating his experience in nanofibers production and synthesis of hydroxyapatite nanoparticles into 3D printing of composite materials and advanced hybrid scaffolds for tissue engineering.

3 Scientific Committee

prof. Andrzej Stankiewicz – TU Delft, Netherlands & WUT, Poland assoc. prof. Andrzej Krasiński – WUT, Poland assoc. prof. Paweł Sobieszuk – WUT, Poland Artur Małolepszy, PhD – WUT, Poland

4 Organising Committee

The eleventh edition of the European Young Engineers Conference has been organized by the following members of the Scientific Club of Chemical and Process Engineering "Venturi", students and researchers of the Faculty of Chemical and Process Engineering:

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4 Coordinators of the 11th EYEC



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Monika Klimek, BSc Coordinator of the Graphics Section Member of the Scientific Club of Chemical and Process Engineering "Venturi"

5 Monographic articles

5.1 Novel applications of zinc oxide nanoparticles as a coating agent. A short review

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KEYWORDS: coating, nanomaterials, ZnONPs, textiles, packages.

Abstract

Nanotechnology is an extensively studied field of science, where more and more results are applied in industry. One example of this phenomena is the application of metallic nanoparticles (such as zinc oxide nanoparticles - ZnONPs). Zinc Oxide nanoparticles present several interesting properties, such as UV protection, antibacterial and antifungal activity. This review concentrates on a novel application of ZnONPs-coated materials in the medicine, food and fabric industry. ZnONPs properties are maintained in a broad spectrum of coated materials, either organic (i.e. polymers) or mineral. Studies confirm that functionalisation by ZnONPs might be a promising solution for the storage of plant and meatderived food. In the medical field, ZnONPs is the perfect active coating agent for dental filling and implant surfaces. This is caused by zinc's positive effect on osteogenic processes and protection against biofilm formation. The textile industry might benefit from ZnONPs implementation because of antibacterial, UV-protection and UV-dependent self-cleaning abilities. Except many advantages, material functionalisation by ZnONPs struggles with sverals issues e.g. loss of part of material properties after modification. In future, ZnONPs coating might be a cheap and efficient way of functionalisation of everyday used materials.

Introduction

Currently, the results of nanotechnology studies are applied to a broad spectrum of everyday life products. According to press reports, the nanomaterials market has reached the size of 9.4 billion USD in 2021 and will continue to grow up to 33.6 billion in 2030. Nanomaterials are defined as regular structures, in which at least one dimension (diameter, thickness etc.) has less than 100 nm (Sun et al., 2018). Miniaturization up to the nanometre scale leads to an increase of surface to volume ratio of a specific material (compared to bulk form). Theoretically, it enlarges the catalytic potential of the material surface (Khan et al., 2019). Several studies have focused on the application potential of selected inorganic nanomaterials. One of these nanomaterials is Zinc Oxide Nanoparticles (ZnONPs), which are one of the most studied nanomaterials (Srivastav et al., 2021). ZnO itself is a very promising agent as it has been recognised as "generally safe" according to the

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Food and Drug Administration of the United States (Sun et al., 2018). This short review presents reported in the literature procedings about application of ZnONPs as a functionalysing agent for different types of materials. In this paper, we also underline current issues connected with the modification of materials using ZnONPs.



Figure 5.1.1: Zinc Oxide Nanoparticle studies – from basic research into industrial application

Properties of ZnONPss

Zinc Oxide Nanoparticles exhibit several interesting properties. The physicochemical properties of ZnONPs are similar to bulk ZnO (II) (Parihar et al., 2018). Zinc oxide itself can be described as an n-type semiconductor. Excitation of electrons from the valence band by radiation leads to its move to the conduction band. This process causes the generation of "holes" in the valence band (Verbič et al., 2019). To perform this process, radiation has to have energy at least equal to the size of the bandgap. This bandgap for bulk ZnO (II) has a value of -3.37 eV, which is equal to the energy of an electromagnetic wave of 370 nm length (Sundararaj & Chandrasekaran, 2017). Bulk ZnO (II) occur naturally in two crystallographic forms: hexagonal wurtzite (more popular) and cubic zincblende. Wurtzite-like structure develops under atmospheric pressure, hence most of described ZnONPs consists of wurtzite-like crystals. Polar symmetry between the electrostatic interaction of Zn and O atoms explains most of the physicochemical properties of ZnO (II) (Parihar et al., 2018). The crystallographic structure of ZnO (II) is then a direct cause of the bulk material properties. The literature proposes a broad variety of methods of ZnONPs synthesis. These methods can include mechanochemical, sonochemical, ultrasonic, microwave irradiation, sol-gel or precipitation techniques (Verbič et al., 2019). Nowadays, the synthesis of ZnONPs is profoundly described at the level of cost and yield efficiency. As several methods of ZnONPs synthesis require reagents, which could damage the environment severely, socalled "green ZnONPs synthesis" has been described in the literature. This approach incorporates plant extracts or whole living organisms for synthesis techniques (X. Guo et al., 2020; Kumar et al., 2020). ZnONPs described in literature represents a broad variety of shapes, which include: nanoparticle, flowerlike, nanorod, nanodiscs or spike-shaped structures (Verbič et al., 2019). Among many interesting properties of ZnONPs, antibacterial, antifungal and UV-protection abilities might be encouraging for the industry.

Antibacterial and antifungal activity

Most synthesised ZnONPs exhibit antibacterial and antifungal activity. At least three hypotheses have been proposed to explain this effect. The first hypothesis proposes Reactive Oxygen Species (ROS) dependent mechanism of toxicity. Absorption of UV light by ZnONPs lead in vitro towards a series of redox reactions on the nanomaterial surface (Sun et al., 2018). These reactions lead to the generation of ROS such as hydroxyl radical, hydrogen peroxide and superoxide. Many researchers have reported that antimicrobial activity is oxygen and illumination-dependent (Oliveira et al., 2020; Xu et al., 2013). Moreover, excessive generation of intracellular ROS has been confirmed using the Candida krusei model (Das et al., 2016). The ROS-dependent hypothesis explains that the toxicity mechanism of ZnONPs is caused by free radicals which promote the generation of DNA damages. The second hypothesis proposes free zinc ion release from ZnONPs as an explanation of cytotoxic properties. ZnO (II) itself is insoluble in an aqueous environment. However, in acidic conditions ZnO (II) can react easily to produce soluble Zn²⁺. An excessive amount of zinc ion might disrupt crucial intracellular processes, which could lead towards microorganism death. Researchers have shown, that under dark conditions, excessive zinc ion is responsible for ZnONPs toxicity in the E. coli model (Li et al., 2011). Moreover, several studies show, that ZnONPs might interact with components of bacterial cell membrane/wall. The last hypothesis suggests that this interaction leads directly towards disruption of cell membrane/wall and loss of integrity. Studies have shown, that ZnONPs causes a decrease in surface tension and structure of cell membranes (Joe et al., 2017). Additionally, the report shows that the structure of the bacterial cell wall is abnormal, which can be observed as a decrease in its thickness. Currently, there is no consensus stand about the ZnONPs mechanism of toxicity. Some studies propose that more than one mechanism of ZnONPs cytotoxicity might be required for a complete description of the process (Xu et al., 2013). ZnONPs has a toxic effect towards several groups of microorganisms (Jones et al., 2008; Moradpoor et al., 2021). The confirmed toxic effect of ZnONPs has been reported on models from genera: Aspergillus, Escherichia, Penicillium etc. A comparison of antibacterial and antifungal activity (including nanomaterial size, modification and microorganism model) has been presented in Table 5.1.1.

UV-protection properties

As described in the previous part, ZnONPs has the property of UV-light absorption. These effects are mostly caused by the semiconductor properties of bulk ZnO (II). The increase of crystallographic dimensions of ZnO crystals (e.g. diameter of the particle) leads to a decrease in the value of the bandgap between the valence and conduction band. This size-dependent effect causes a shift of absorption maximum towards higher values of wavelength and can be explained by Tauc and Davis-Mott relation. This relation connects bandgap value and light absorption properties in disordered semiconductors (Singh et al., 2011). Excellent UV-light absorption properties of ZnONPs have been currently applied in sun creams, where nanomaterial plays a role as mechanical protection (Osmond & McCall, 2010). Despite the fact of UV-protection ability, light-exposed ZnONPs might generate excessive ROS. Studies have shown that UV-light exposure to ZnONPs significantly enhances the ROS generation rate (Stankic et al., 2016). This effect is one of the major concerns in the industrial and medical applications of ZnONPs.

Synthesis of ZnONPs-functionalised materials

The current state of knowledge proposes a variety of methods for materials functionalisation using ZnONPs. However, novel methods are being still proposed. Several patents were granted, where ZnONPs coating plays the role as anti-UV (Robert Kramer et al., 2014) and antibacterial agent (Aharon Gedanken et al., 2016). Several applied works are developed using un- and modified ZnONPs (Macyk Wojciech et al., 2016). Coating methods depend on the purpose of the ZnONPs application and the properties of functionalised material. Generally, Zinc-derived nanomaterials exhibit good compatibility with a broad spectrum of organic (natural or synthetic) and mineral materials.

In the context of textile materials, several different methods of ZnONPs coating have been established, especially for: cotton, jute, polypropylene, polyamide, polyester, silk, sisal and polyurethane (including blended fabrics) (Verbič et al., 2019). One of the most popular methods for fabric functionalisation is the soaking of selected material in the suspension of the specific form of ZnONPs and drying (Mulchandani Neha & Karnad Vishaka, 2020). A more advanced modification of this method is called by the literature dip-pad-dry-cure technique (Zhu et al., 2017). Technically, the effectiveness of the dippad-dry-cure method can be modulated by the percentage of nanomaterial suspension, time and temperature of drying and curing period. Curing is crucial in soaking-based methods, as it is responsible for proper ZnONPs adhesion into functionalised material. Commonly used textiles exhibit good adhesion properties both for chemically and eco-friendly synthesised nanoparticles. Researchers bring awareness especially to ZnONPs synthesised using moulds from Fusarium and Aspergillus genera. This interests in mould-based biosynthesis include the usage o the whole organism (e.g. Aspergillus terreus) (Fouda et al., 2018) or filtrated, cell-free extract from conditioned medium (derive from Aspergillus niger or Fusarium keratoplasticum culture) (Kalpana et al., 2018; Mohamed et al., 2019). The same great interest in the functionalisation of materials is also considered by ZnONPs biosynthesised using plant extracts. Ghayempour & Montazer (2017) have soaked cotton fabrics in star-like ZnONPs. Nanomaterial itself was synthesised using Zn(NO₃)₂ and Tragacanth gum plant extract (as reaction stabilisation agent). Another novel solution for fabric coating is in situ synthesis of ZnONPs inside textiles (Belay et al., 2020). Functionalisation by in situ synthesis has shown better effectiveness of the coating. For example, El-Naggar et al. (2018) have functionalised cotton by in situ synthesised ZnONPs capped with date seed extract.

The functionalisation of materials designed for food storage includes a coating of cellulose-derived and plastic-derived materials. The literature proposes methods of functionalisation of food storage materials such as Polyethylene terephthalate (PET), Polyethylene (PE), polyvinyl alcohol (PVA), polyurethane (PU) unmodified cellulose and carboxymethylcellulose (CMC). The easiest way to functionalise paperderived materials is to soak them in ZnONPs suspension similar to textiles functionalisation. This method might be an excellent solution for coating paper pads, which are used in meat packages for the prevention of the spread of blood-borne pathogens (Hakeem et al., 2020). The most popular method for the preparation of ZnONPs-functionalised polymers is casting a mixture of nanomaterial with polymer on an inert surface (e.g. glass plates) and drying in mild conditions. The casting method is excellent for the

Species	Size (nm)	Nanomaterial modification	Results	Reference
Aspergillus	≈ 13	Flower-like	$DIZ \approx 6 \text{ mm}$	(X. Guo et al., 2020)
niger	≈ 18	Flower-like with incorporated cinnamaldehyde	$DIZ \approx 14 \text{ mm}$	(X. Guo et al., 2020)
	27.3 ± 0.5	MgZnONPs	$DIZ = 17.1 \pm 0.4 \text{ mm}$ $MIC = 1.25 \text{ mg} \cdot \text{cm}^{-3}$	(Sierra- Fernandez et al., 2017)
	76.15	-	$MIC = 16 \mu g \cdot cm^{-3}$	(Rana et al., 2018)
	20-40	Mesoporous SiO ₂ embedded ZnONPs	Growth reduction: 86%	(Mitra et al., 2015)
	30–40 Hexagonal ZnONPs		Growth reduction: 92%	(Patra et al., 2012)
Aspergillus nidulans	25	-	MIC = 3.2 mM $MFC = 18.8 mM$	(Gunalan et al., 2012)
Aspergillus flavus	25	-	MIC = 2.8 mM $MFC = 17.5 mM$	(Gunalan et al., 2012)
	60-100	Cerium doped flower-shaped ZnONPs	CFU reduction: 80%	(Hui et al., 2016)
	47.7	-	$MIC = 20 \mu g \cdot cm^{-3}$ $DIZ = 6 mm$	(Auyeung et al., 2017)
Trichoderma harzianum	25	_	$MIC = 3.8 \text{ mmol} \cdot \text{dm}^{-3}$ $MFC = 20.4 \text{ mmol} \cdot \text{dm}^{-3}$	(Gunalan et al., 2012)
Rhizopus stolonifer	25	-	$MIC = 2.4 \text{ mmol} \cdot \text{dm}^{-3}$ $MFC = 16.8 \text{ mmol} \cdot \text{dm}^{-3}$	(Gunalan et al., 2012)
Salmonella	55 ± 5	Chitosan/ZnONPs composite	CFU reduction: 100%	(Al-Naamani et al., 2016)
enterica	< 100	-	$MIC = 3.12 \mu g \cdot cm^{-3}$ $MBC = 100 \mu g \cdot cm^{-3}$	(Jayakumar et al., 2019)
Escherichia coli	55 ± 5	Chitosan/ZnONPs composite	CFU reduction: 100%	(Al-Naamani et al., 2016)
	29	latin and ZnONPs precipitated with extract of <i>Cassia fistula</i>	$DIZ \approx 10.5 \text{ mm}$	(Kumar et al., 2020)
	52.65 ± 2.58	Polyurethane functionalised with 5% MgZnONPs	CFU reduction: 93.3%	(Kasi et al., 2019)
	175.85	A. terreus synthetized ZnONPs	$MIC = 500 \mu\text{g} \cdot \text{cm}^{-3}$ $DIZ = 14.2 \pm 0.2 \text{mm}$	(Fouda et al., 2018)
	26-32	ZnONPs incorporated into cot- ton fabrics	$DIZ \approx 17.5 \text{ mm}$	(Belay et al., 2020)
	3000	Tetrapod-like ZnONPs	CFU reduction: 76% DIZ = 23.1 ± 1.3 mm	(Xu et al., 2013)
	60	Nanosized ZnONPs	CFU reduction: 65% DIZ = $19.1 + 1.5$ mm	(Xu et al., 2013)
	≈ 1000	Microsized ZnONPs	CFU reduction: 60% DIZ = 14.8 ± 1.3 mm	(Xu et al., 2013)
	163.34	Hexagonal ZnONPs	$MIC = 500 \text{ ppm}$ $DIZ = 175 \pm 0.3 \text{ mm}$	(Mohamed et al., 2019)
	135.5	Nanorod ZnONPs	MIC = 500 ppm $DIZ = 15.7 \pm 0.4 \text{ mm}$	(Mohamed et al., 2019)
	61±0.65	<i>A. niger</i> biosynthesised ZnONPs	$\mathrm{DIZ}=10\pm0.78\mathrm{mm}$	(Kalpana et al., 2018)
	212	-	CFU reduction: 85.7% DIZ = 13 mm	(El-Naggar et al., 2018)
	97	ZnONPs capped with date seed extract	CFU reduction: 99.9% DIZ = 23 mm	(El-Naggar et al., 2018)
	62	In-situ synthesised ZnONPs in	CFU reduction: 100%	(Ghayempour & Montazer,
	60	cotton tabric Polypyrrole/ZnONPs coating	DIZ = $3.3 \pm 0.1 \text{ mm}$ CFU reduction: 96%	2017) (Y. Guo et al., 2020)

(Mohammadi Arvanag et al.,

2019)

 $MIC = 400\,\mu g\cdot cm^{-3}$

 Table 5.1.1: Summary of ZnONPs antibacterial or antifungal properties of ZnONPss. Abbreviations: MIC – Minimum Inhibitory Concentration; MBC – Minimum Bactericidal Concentration; MFC – Minimum Fungicidal Concentration; CFU – Colony Forming Unit; DIZ – Diameter of Inhibition Zone.

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Species	Size (nm)	Nanomaterial modification	Results	Reference
Stapchylococcus	55 ± 5	Chitosan/ZnONPs composite	CFU reduction: 100%	(Al-Naamani et al., 2016)
aureus	175.85	A. terreus synthetized ZnONPs	$MIC = 250 \mu\text{g} \cdot \text{cm}^{-3}$ $DIZ = 19.1 \pm 0.2 \text{mm}$	(Fouda et al., 2018)
	26-32	ZnONPs incorporated into cot- ton fabrics	$DIZ \approx 22.5 \text{ mm}$	(Belay et al., 2020)
	200-500	ZnONPs incorporated into cot- ton fabrics	CFU reduction: 99.65%	(Mulchandani Neha & Kar- nad Vishaka 2020)
	300	ZnO nano-assemblies	CFU reduction: 45%	(Joe et al., 2017)
	60 30	ZnO nano-plates ZnONPs	CFU reduction: 58% CFU reduction: 72%	(Joe et al., 2017) (Joe et al., 2017)
	163.34	Hexagonal ZnONPs	MIC = 250 ppm DIZ = 18.2 + 0.7 mm	(Mohamed et al., 2019)
	135.5	Nanorod ZnONPs	MIC=250 ppm DIZ=19.5±0.2mm	(Mohamed et al., 2019)
	61 ± 0.65	<i>A. niger</i> biosynthesised ZnONPs	$DIZ = 12 \pm 0.23 \text{ mm}$	(Kalpana et al., 2018)
	212	-	CFU reduction: 83.8%	(El-Naggar et al., 2018)
	97	ZnONPs capped with date seed	CFU reduction: 99.9% DIZ = 19 mm	(El-Naggar et al., 2018)
	62	In-situ synthesised ZnONPs in cotton fabric	CFU reduction:100% DIZ = 3.1 ± 0.1 mm	(Ghayempour & Montazer, 2017)
Bacillus subtilis	175.85	A. terreus synthetized ZnONPs	$MIC = 250 \mu\text{g} \cdot \text{cm}^{-3}$ $DIZ = 20.2 \pm 0.2 \text{mm}$	(Fouda et al., 2018)
	163.34	Hexagonal ZnONP	$MIC = 250 \text{ ppm}$ $DIZ = 22.0 \pm 0.6 \text{ mm}$	(Mohamed et al., 2019)
	135.5	Nanorod ZnONPs	$MIC = 250 \text{ ppm}$ $DIZ = 23.6 \pm 0.4 \text{ mm}$	(Mohamed et al., 2019)
	212	_	DIZ = 15 mm	(El-Naggar et al., 2018)
	97	ZnONPs capped with date seed extract	DIZ = 26 mm	(El-Naggar et al., 2018)
Pseudomonas aeruginosa	175.85	A. terreus synthetized ZnONPs	$MIC = 500 \mu\text{g} \cdot \text{cm}^{-3}$ $DIZ = 14.1 \pm 0.2 \text{mm}$	(Fouda et al., 2018)
	163.34	Hexagonal ZnONPs	$MIC = 500 \text{ ppm}$ $DIZ = 16.1 \pm 0.4 \text{ mm}$	(Mohamed et al., 2019)
	135.5	Nanorod ZnONPs	$MIC = 500 \text{ ppm}$ $DIZ = 15.7 \pm 0.4 \text{ mm}$	(Mohamed et al., 2019)
	212	-	DIZ = 14 mm	(El-Naggar et al., 2018)
	97	ZnONPs capped with date seed extract	DIZ = 21 mm	(El-Naggar et al., 2018)
	65 ± 1.2	-	Biofilm inhibition: 25%	(Akhil et al., 2016)
	52 ± 2.3	PVP coated ZnONPs	Biofilm inhibition: 51%	(Akhil et al., 2016) (Akhil et al., 2016)
Kleibsiella	200-500	ZnONPs incorporated into cot-	CFU reduction: 99.55%	(Mulchandani Neha & Kar-
pneumonia	200	ton fabrics	OFIL as heating (7%	nad Vishaka, 2020)
	300 60	ZnO nano-assemblies	CFU reduction: 67%	(Joe et al., 2017)
	30	ZnONPs	CFU reduction: 100%	(Joe et al., 2017) (Joe et al., 2017)
Candida albican	62	In-situ synthesised ZnONPs in cotton fabric	CFU reduction: 100% DIZ = 3.0 ± 0.1 mm	(Ghayempour & Montazer, 2017)
	30	_	$MIC = 32 \mu g \cdot cm^{-3}$ $MFC = 64 \mu g \cdot cm^{-3}$	(Barad et al., 2017)
	60-100	cerium doped flower-shaped ZnONPs	CFU reduction: 73%	(Hui et al., 2016)
	16	Egg white coated ZnONPs	$DIZ = 25 \text{ mm}$ $MIC = 29.7 \mu\text{g} \cdot \text{cm}^{-3}$	(Shoeb et al., 2013)
Botrytis	70 ± 15	-	CFU reduction: 80%	(He et al., 2011)
cinerea	76.15	_	$\text{MIC} = 128\mu\text{g}\cdot\text{cm}^{-3}$	(Rana et al., 2018)

Species	Size (nm)	Nanomaterial modification	Results	Reference
Penicillium expansum	70 ± 15 76.15		CFU reduction: 91% MIC = $128 \mu \text{g} \cdot \text{cm}^{-3}$	(He et al., 2011) (Rana et al., 2018)
Penicillum oxaticum	27.3 ± 0.5	MgZnONPs	$DIZ = 21 \pm 0.3 \text{ mm}$ $MIC = 0.625 \text{ mg} \cdot \text{cm}^{-3}$	(Sierra-Fernandez et al., 2017)
	76.15	_	$MIC = 64 \mu g \cdot cm^{-3}$	(Rana et al., 2018)
Fusarium oxysporum	20-40	Mesoporous SiO ₂ embedded ZnONPs	Growth reduction: 90%	(Mitra et al., 2015)
21	30-40	Hexagonal ZnONPs	Growth reduction: 89%	(Patra et al., 2012)
Alternaria alternata	76.15	_	$MIC = 64\mu g \cdot cm^{-3}$	(Rana et al., 2018)

functionalisation of "classic" plastic substrates such as PU (Kasi et al., 2019) and PVA (Channa et al., 2022). Moreover, the classic casting method can be applied for the functionalisation of more eco-friendly polymers, such as CMC (X. Guo et al., 2020; Priyadarshi et al., 2021) or starch-PVA mixture (Jayakumar et al., 2019). An interesting biodegradable option has been proposed by Kumar et al. (2020). The team led by Kumar have designed a biodegradable hybrid nanocomposite of chitosan/gelatin and green synthesized zinc oxide nanoparticles. An alternative method for casting is direct spraying on polymer. Rokbani et al. (2019) have proposed the functionalisation of low-density polyethene-based films by spraying directly on polymer formed constantly by a twin screw extruder. Al-Naamani et al. (2016, 2018) have designed a method of functionalisation of PE by chitosan-ZnONPs nanocomposite. This method does not require the constant formation of the polymer but needs modification of the PE surface by plasma treatment, which enhances the adhesion of the nanocomposite. An interesting, eco-friendly and ZnONPs-functionalised alternative for traditional packages has been proposed by several researchers. In general, fruits and vegetables are dipped in a suspension of polysaccharides and ZnONPss (Anugrah et al., 2020). The proposed solution reduces the usage of plastic packages, mixes advantages of both ZnONPs and classic polysaccharide coating, and is easy to wash away.

In contrast to food storage materials and textiles, the functionalisation of materials intended for medical purposes requires higher pressure and temperature conditions. Despite harsh functionalisation conditions, ZnONPs maintains its antibacterial and antifungal properties. The most popular medical surfaces functionalised by ZnONPs are those made from Calcium hydroxyapatite (HAP) and silicate. The main reason for this is that both substances are widely used for orthopaedic and dental applications (Begam et al., 2017). Functionalised HAP coating can be applied on the titanium surface of the implants. This process can be made by deposition of ZnONPs/HAP mixture using the spin coating method (Voicu et al., 2020). After spin coating, the functionalised surface needs to be heated in aim to receive optimal crystallinity of the surface (Ohtsu et al., 2018). The used temperature extends from about 500 °C (Voicu et al., 2020) up to 650 °C (Ohtsu et al., 2018). Another method for HAP surface functionalisation requires calcination at high temperatures (circa 800 °C) and air-sintering in temperatures between 1100 and 1250 °C (Begam et al., 2017). What is interesting, parameters of sintering affect the porosity, pore size and roughness of a surface, which can modulate the effect of surface coating by ZnONPs. Another alternative for the spin coating technique might be Electro-Hydro-Dynamic Atomisation (EHDA). Memarzadeh

et al. (2015) effectively functionalise glass substrate used as dental filling using the EHDA technique. The subsequent step is heating at circa 500 °C to enhance the mechanical integrity of the coating. If the high temperature cannot be used for medical-used materials – high pressure might be an interesting alternative for functionalisation by ZnONPs. Bageshlooyafshar et al. (2019) generate scaffolds used for osteogenic differentiation by mixing ZnONPs – silicate with polyvinyl alcohol and treatment mixture with a pressure of 10 MPa until rectangular compacts generation.

In summary, functionalisation by ZnONPs can be performed using a broad spectrum of techniques and diverse materials. Although further research is needed to optimise this novel methods of the material functionalisation.

Application in the food industry

Currently, the food industry encounters with demand for better, smart and sustainable food packages. Smart food packages have to present several useful features such as protection against UV light and oxygenation, microbicidal or microbistatic effect, giving information about product condition (i.e. indicators) (Nikolic et al., 2021). Functionalisation by ZnONPs might be the answer for many of issues mentioned above.

For example, Channa et al. (2022) have designed PVA functionalised with ZnONPs to reduce photodegradation and oxidation of food. A concentration range from 0.2 to 0.8% (w/v) has been tested. What is interesting, the results show that modified PVA exhibit better thermal stability, loss of hydrophilicity and decrease in water vapour transmission rate. The effect was observed in a concentration-dependent way. Moreover, coating by ZnONPs has not changed significantly the oxygen transmission rate and bendability of PVA. Channa et al. (2022) have also shown that PVA-ZnONPs packaging is suitable for plant food storage - in comparison to uncoated PVA, the browning of apple slices has been significantly decreased. Many studies confirm the suitability of ZnONPs in packages for plant-derived food, such as okra (Abelmoschus esculentus) (Al-Naamani et al., 2018). The team led by Al-Naamani designed PE film functionalised with ZnONPs/chitosan nanocomposite. Previous paper of researchers (Al-Naamani et al., 2016) showed that designed nanocomposites have significantly decreased swelling ratio, UV-blocking properties and completely inhibit the growth of Salmonella enterica, Escherichia coli and Staphylococcus aureus. According to tested okra samples, ZnONPs functionalised LDPE packages have significantly decreased the growth of bacterial and fungal strains collected from the surface of plant samples. Functionalised LDPE film maintains in better way

moisture content, total soluble solid and pH of okra sample. Moreover, Zn²⁺ transfer from the film into the plant sample was observed but was equal to 1.8% of the total package zinc content (Al-Naamani et al., 2018). LDPE itself is a popular material for functionalisation by ZnONPs. Rokbani et al. (2019) tested ZnONPs-modified standard LDPE and anhydride-modified LDPE (AM-g-LDPE). ZnONPs-LDPE and ZnONPs-AM-g-LDPE have reduced significantly the viability of E. coli and this effect of LDPE film was maintained even after 8-month storage of material. For S.aureus only AM-g-LEDPE reduced the viability of bacteria. ZnONPs functionalisation is an ideal solution for cherry tomato packages (X. Guo et al., 2020). ZnONPs and cinnamaldehyde-modified CMC exhibit excellent mechanical properties and decrease the viability of A. niger. Modified CMC has also affected changes in weight loss, firmness and amount of soluble solids. X. Guo et al. (2020) have suggested that might be caused by the modulation of cherry tomato metabolism by active agents of the nanocomposite. Among various plastic packages, PU-based packages are also susceptible to ZnONPs functionalisation. MgZnONPsmodified PU shows perfect UV-protection properties and decreases the viability of E. coli cells (Kasi et al., 2019). Both effects were dependent on concentration manner (up to 5% w/v). ZnONPs is a useful agent for the functionalisation of a novel, biodegradable polymers. Kumar et al. (2020) create a chitosan/gelatin film functionalised with green-synthesised ZnONPs. The nano-functionalised film showed better thermal stability and antibacterial effect against E. coli and S. aureus. Jayakumar et al. (2019) have created a smart starch-PVA composite functionalised with ZnONPs and phytochemicals. The addition of ZnONPs enhances UV protection, water barrier and antibacterial (against S. typhimurium) properties. Phytochemicals derived from Syzygium cumini (Jamun) fruits were used as a colour indicator of pH.

Studies show that ZnONPs functionalised food packages are also a perfect solution for animal-derived products. CMCbased film functionalised with grape seed extract and ZnONPs effectively protects high-fat meat against the development of E. coli and L. monocytogenes (Priyadarshi et al., 2021). Moreover, ZnONPs functionalisation enhances mechanical properties of the film (e.g. UV protection and water vapour barrier) and significantly decreases lipid peroxidation which is crucial for the nutritional properties of high-fat meat. Hakeem et al. (2020) have tested the usage of ZnONPs coating in food packages for the storage of chicken meat. Researchers have immobilised ZnONPs in cellulose-absorbing pads. Functionalisation by nanomaterial has inhibited the growth of Campylobacter jejuni in raw chicken meat. What is interesting, studies have shown an increase of Zn²⁺ in chicken meat. This effect was pH-dependent and mostly caused by acidification made by naturally occurring Lactobacillus strains. Growth of Zn²⁺ concentration was reported using different bacterial models (Joe et al., 2017; Xu et al., 2013). This study (Hakeem et al., 2020) raises a significant question about the potential diffusion of nanomaterials into protected food and the safety of zinc increase for probable consumers.

ZnONPs coating in medicine

ZnONPs can play a role as a coating agent in medical textiles. This application is reviewed in the next chapter. It is reported, that ZnONPs might be applied in a broad spectrum of medical products (e.g. wound healing ointments) (Czyżowska & Barbasz, 2022). This explains, why ZnONPs coating is proposed as a promising agent in medical applications. Generally, ZnONPs has good compatibility with materials, which have any type of contact with human body surfaces (Parnia et al., 2017). This might be caused mainly by benefits taken from free zinc ions. Zinc-coated materials have excellent biocompatibility with skeleton-related tissues. It is caused by the effect of zinc on bone mineralization and protection from pathological calcification (Iqbal et al., 2014).

The main aims for the functionalisation of surface on medical products are the reduction of biofilm formation and support of regeneration of harmed organism tissues. Novel studies show that ZnONPs have huge potential as a coating agent for implant or dental filling. ZnONPs might be a promising agent in dentistry treatment. Several studies on the use of ZnONPs implantology, prosthodontics and orthodontics were performed (Moradpoor et al., 2021). ZnONPs-hydroxyapatite (HAP) nanocomposite simulating dental implants have significant antimicrobial effects (i.e. S. aureus). It has minimal toxicity towards mammalian cells, such as UMR-10 and MG-63, which are popular models in osteogenic studies. In addition, the nanoparticle-supplemented dental filling doesn't induce the release of TNF-a and IL-6 cytokines, which are crucial for the development of inflammation (Memarzadeh et al., 2015). Bageshlooyafshar et al. (2019) have created scaffolds functionalised with a zinc-silicate nanoparticle. The model of adiposederived stem cells expresses more osteogenic markers (i.e. calcium deposition, alkaline phosphatase activity, transcription of Runx2, ALP, osteonectin, and collagen I genes) compared to the unfunctionalized scaffold. An interesting conclusion about the mechanism of positive activity of ZnONPs coating for osteogenic processes can be achieved by analysing studies concentrated on characteristics of modified implant surfaces. It is reported that additional coating of stainless steel implants has excellent porous later with an enhanced attachment of osteoblasts (Ananth et al., 2018). ZnONPs-coated hydroxyapatite presents better features for osteoblast adhesion and proliferation. Moreover, the study shows that probably zinc doping, then an increase in surface roughness was responsible for ZnONPs-HAP properties (Begam et al., 2017). In another study, E. coli and S. epidermidis were effectively killed by ZnONPs/HAP composite (Ohtsu et al., 2018). An element of novelty was that the increase in the amount of ZnONPs as a doping agent did not increase bactericidal effects, which suggests, in the context of implant applications, that the ZnONPs mechanism of action is contact-related.

Antibacterial and antifungal properties of ZnONPs can be applied for protection against biofilm formation. Bacterial biofilm formation is still a crucial issue in medical treatments (Mahamuni-Badiger et al., 2020). This is especially important in case of growing microbe drug resistance. Co-doped ZnONPs films show a significant toxic effect towards S. aureus in contrast to amniotic fluid stem cells (AFSC) (Voicu et al., 2020). Polypyrrole-ZnONPs-coated Mg alloy shows better bactericidal (against E. coli) properties than an uncoated alloy (Y. Guo et al., 2020). What is interesting, Polypyrrole-ZnONPs coating generates a significant anti-corrosion effect tested using immersion assays. Moreover, MC3T3-E1 cells used as a human cell model, exhibit better viability and growth comparable to treatment using uncoated or only Polypyrrole Mg alloy. Nevertheless, several studies show apoptotic/necroticlike or genotoxic effects of ZnONPs on human-derived cells. These reports undermine the importance of the precise determination of zinc oxide nanoparticles toxicity mechanism in the specific biological model (Wang et al., 2021).

Application in the textile industry

Application studies in the modern textile industry are aiming to either design novel, interesting fabrics or modify currently used materials. Fabric modification might be recognised as useful if this modification achieved one of the several desired properties such as antimicrobial effect, UV-protection, photocatalytic self-cleaning and purification, moisture management, hydrophobicity, flame retardancy and thermal insulation (Verbič et al., 2019).

ZnONPs functionalised fabrics have perfect antibacterial, antifungal and UV-protection properties. It has been confirmed that cotton soaked with ZnONPs suspension exhibits antibacterial effects against Gram-positive and Gramnegative bacteria (Fouda et al., 2018). Literature profoundly confirms antibacterial effects of ZnONPs textiles coating, especially for E. coli and S. aureus (Kalpana et al., 2018). Moreover, antifungal effects of nanoparticle functionalisation of the fabric have been confirmed against the C. albicans model (Ghayempour & Montazer, 2017). Zhu et al. (2017) and El-Naggar et al. (2018) have confirmed independently, that functionalisation using ZnONPs enhance UPF (Ultraviolet Protection Factor) properties of the fabric. Interesting results have been presented in novel approach by Belay et al. (2020). The study compared the coating of cotton fabric by classic and in situ synthesised ZnONPs. in situ synthesis in cotton has enhanced antibacterial ability (against E. coli and S. aureus) and UV protection properties of functionalisation. This was caused by higher deposition in ZnONPs in cotton observed using Scanning Electron Microscopy. Moreover, studies show that the shape of used ZnONPs is important in the context of the effectiveness of functionalisation. Both nanorod and hexagonal ZnONPs incorporated into cotton exhibit antibacterial properties (against B. subtilis, S. aureus, P. aeruginosa and E. coli) and UV protection (Mohamed et al., 2019). But in comparison to both forms of ZnONPs, nanorods exhibit more intensified properties. Self-cleaning of the fabric is one of the most interesting, nowadays discussed properties offered by the concept of smart textiles. Studies show, that ZnONPs functionalised fabrics exhibit this ability based independently on Bismarck brown (Kalpana et al., 2018) and methylene blue (Ghayempour & Montazer, 2017; Zhu et al., 2017) decolourisation assays. The basis for this effect might be caused by the UVabsorbing properties of ZnONPs. As mentioned before, electron transfer from the valence band on the conductivity band after UV-light absorption leads toward several redox reactions, where generated ROS might be responsible for the oxidation and bleaching of stains.

For the development of smart textiles and functionalised fabric, it is important to maintain their unique abilities even after harsh exploitation. Cotton functionalised with ZnONPs exhibit significant antibacterial effects against Klebsiella Pneumoniae and S. aureus. This effect did not decrease even after 5, 10, 25 and 50 washes performed according to ISO 6330 standard (Mulchandani Neha & Karnad Vishaka, 2020). In another study (El-Naggar et al., 2018), researchers have developed cotton functionalised with uncoated or date seed extractcoated ZnONPs. Both nanomaterials show antibacterial effect against B. subtilis, S. aureus, E. coli, and P. auruginosa. Moreover, date seed extract coating reduces the toxicity of ZnONPs towards human hepatoma cells. The effect was present even after 20 washes but decreased with the number of washing. It is remarkable to report, that in contrast to the first paper, El-Naggar et al. (2018) do not confirm that have tested

fabric according to ISO 6330 standard. Despite these promising results, fabric functionalisation might affect negatively different important parameters of the material. In the case of cotton and polystyrene fabrics, functionalisation with nanomaterial leads to disruption in their structure, which decreases thermal resistance, which is directly related to thermal insulating properties (Noman et al., 2022). Overcoming this issue might be one of the crucial steps in the application of ZnONPs in the textile industry.

Conclusions

Zinc Oxide Nanoparticles evince good compatibility with a broad variety of materials commercially used in industry. Antifungal, antibacterial and UV-protection abilities are maintained even after the functionalisation of the selected material. An unspecific, multiway mechanism of ZnONPs toxicity against microbes might be an interesting option for the replacement of antibiotics. Nowadays, antibiotic-resistant microbes became an important issue in developed countries and a reduction of antibiotics usage is necessary. The durability of ZnONPs for physical conditions allows for the application of many disciplines of life such as described medicine, food industry and textile production. All presented results show that ZnONPs might be a great opportunity for the development of nanotechnology and industrial research. Future studies should be concentrated on several issues. First of all is a decrease in thermo-protective features of textiles after ZnONPs functionalisation. The second one is a reduction of ROS generation by nanomaterial surface in a situation when it is not necessary. Moreover, the lack of a complete description of the ZnONPs mechanism of action against mammal cells is the main limitation for the application of the nanomaterial in veterinary and medicine. Although several difficulties with ZnONPs application can be observed, future studies about the nanomaterial mechanism of action and application should be performed. Functionalisation of materials by ZnONPs might fill requirements for "smart" textiles, food packages and implant coatings.

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5.2 Research of solid fuel briquettes obtaining from brewer's spent grain and coffee waste

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KEYWORDS: brewer's spent grain, coffee waste, spent coffee grounds, secondary raw materials, alternate solid fuel, briquettes.

Abstract

The work describes the results of experimental studies of solid fuel production from brewer's spent grain and coffee production waste. The formation of solid fuel briquetted samples was carried out by pressing under a pressure of 9.81×106 for 60 seconds at a temperature of 150°C in the mold. The higher calorific value of the obtained solid fuel samples and dried initial material were determined for both materials. The higher calorific value of unformed brewer's spent grain is ~20 005 kJ \cdot kg⁻¹ and obtained briquettes – ~20 173 kJ \cdot kg⁻¹. In the case of coffee wastes, the higher calorific value of unformed material is ~21 583 kJ \cdot kg $^{-1}$ and ~22 147 kJ \cdot kg $^{-1}$ for obtained solid fuel sample. The obtained samples of alternative solid fuel have high calorific values, do not contain harmful impurities, do not require additional cleaning, and do not require binders. The use of brewer's spent grain and coffee production waste for the production of solid fuel will solve the problem of excessive production of industrial waste, rationalize their secondary use and avoid the negative impact of their accumulation on the environment.

Introduction

The current ecological state of the environment, the need for new energy sources, rational use of natural resources, and secondary raw materials require constant scientific research. Traditional solid fuels, such as wood and coal, need to be supplemented and replaced by alternative fuel sources, given the depletion of natural resources – forestry and mineral deposits.

As an alternative solid fuel, fast-regenerating vegetable raw materials – miscanthus and energy willow – have become widespread. However, expanding the list of energy sources and searching for raw materials with high calorific value and low cost is also necessary and important.

At the same time, there is a constant accumulation of plant waste in the food industry, which, given its characteristics, has limited secondary use. Such organic waste includes, in particular, brewer's spent grain (BSG) from breweries (Santos et al., 2003; Hassan et al., 2020) and coffee waste from coffee factories (Martinez-Saez et al., 2017; Woo et al., 2021). This raw material has a high humidity (~ $65\div75\%$) (Eliopoulos et al., 2022), as a result of which the storage and shelf life is limited (approximately 2÷3 days). Despite the possibility of secondary use as

fodder for livestock (Mussatto, 2014), fertilization of agricultural land (Aboukila et al., 2013), etc., the large volumes of generated waste make it possible to search for new ways of rational use.

A promising direction is the creation of an alternative solid fuel from these wastes of the food industry – brewer's spent grain and coffee wastes. It is known about successful studies of the creation of solid fuel samples based on dried waste from the production of food ethyl alcohol with similar parameters – alcohol distillery stillage of grain origin (Ivashchuk et al., 2022). Solid fuel briquettes from this raw material have high calorific value, combined with low ash content and residual moisture content.

The introduction of a new field of application of brewer's spent grain and coffee wastes as raw materials for alternative solid fuel can become an additional solution to the problem of significant accumulation of these industrial wastes. The low cost of raw materials will be a guarantee of the economic efficiency of the created solid fuel elements.

Experimental

The objects of the research were barley BSG obtained on the production line of Kumpel brewery (Lviv, Ukraine) and coffee wastes, which were a mixture of coffee, barley, and chicory, obtained on the production line of JV "Galca LTD" (Lviv, Ukraine). The quantitative composition of waste varies depending on the current technological processes in production.

The preparation of the initial materials consisted of drying them to the recommended values, considering the high moisture content (Chaloupkova et al., 2018; Manziy et al., 2010; Khivrych et al., 2011). Preliminary drying of raw materials was carried out on a laboratory installation for filtration drying (Ivashchuk et al., 2021), according to the advantages of using this drying method (Kobeyeva et al., 2022).

The dried test materials were subjected to hydraulic pressing on a P474A press to form samples of solid fuel briquettes. The test material was pressed under a pressure of $9.81 \cdot 10^6$. At the same time, the duration of the process was 60 s at temperatures of 20 °C and 150 °C in the mold.

To analyze the obtained samples of solid fuel, as well as the original dried raw materials, three main indicators of the experimental material were determined by calorimetric combustion: moisture content, ash content, and calorific value. All these measurements were done in accordance with the State Standards of Ukraine by the methods given in (Ivashchuk et al., 2022).

Results and discussion

The samples of researched materials were previously subjected to drying, considering the high relative moisture content, which was 77.8% wt. for brewer's spent grain and 65.24% wt. for coffee wastes. Before the production of solid fuel briquettes, the moisture content and ash content of the raw materials were determined, the results are presented in (Table 5.2.1).

Considering the heterogeneity of plant raw materials, we obtained the calorific value of the studied materials by conducting 3 parallel experiments to determine the average value. As a result, the average higher calorific value of dried brewer's spent grain was $\sim 20\,005\,kJ\cdot kg^{-1}$ or $\sim 4781\,kcal\cdot kg^{-1}$ and for spent coffee grounds was

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Table 5.2.1: The ash content and moisture content of initial dried raw materials

	Ash content, % wt.	Moisture content, % wt.
Barley brewer's spent grain	1.6÷2.3	6.5
Coffee wastes	<1	5.52

~21 583 kJ \cdot kg⁻¹ or ~5159 kcal \cdot kg⁻¹. All obtained values of calorimetric combustion, which were previously described (Ivashchuk et al., 2022), are given in (Table 5.2.2).

where m – the mass of the sample that burned during the experiment; ΔT – true temperature rises in the calorimetric experiment; q_{thread} , $q_{ampoule}$, q_{HNO_3} , q_s – the amount of energy released during the combustion of cotton thread, tery-lene ampoule, the formation of a solution of nitric acid and soot formed, respectively; Q – the higher calorific value of the dried researched materials.

The obtained experimental data of the calorific value are slightly higher than these values for alcohol distillery stillage, which was previously studied (Ivashchuk et al., 2022). In turn, this confirms the possibility and especially the effectiveness of using test materials for the production of solid fuel. Comparative values of the calorific value of the studied materials are given in (Table 5.2.3), where the calorific values of energy willow and miscanthus, as the alternative plant materials widely used in industry for the production of solid fuel briquettes, are also presented (Ivashchuk et al., 2021).

Production of solid fuel samples was carried out on a P474A hydraulic press. Pressing of the dried spent coffee grounds was carried out under a pressure of $9.81 \cdot 10^6 N \cdot m^{-2}$ for 60 seconds. The temperature in the mold was 150 °C, because of the positive results of previous studies (Ivashchuk et al., 2022).

As a result of the conducted research, experimental samples of solid fuel with strength and stable shape were obtained. The appearance of the obtained samples is shown in (Fig. 11.4.1).

Figure 5.2.1: Obtained test samples of solid fuel from: (11.4.1a) barley BSG; (11.4.1b) a mixture of CW

An important feature of the obtained prototypes was that the formation of briquettes occurred without the addition of any binders. Let us note that the work pressure was lower than the recommended values (Malovanyi et al., 2011) for the formation of fuel pellets.

The higher calorific value of obtained samples of solid fuel briquettes from dried barley BSG and coffee wastes are given in (Table 5.2.4).

The residual moisture content and ash content of obtained test samples were also determined. The obtained experimental data are given in (Table 5.2.5).

Comparing the calorific value of dried materials (Table 5.2.2) and the briquette samples (Table 5.2.5), it is noticeable that this value is slightly higher in the form of compressed solid fuel. That can be explained by the increase in the density of the material due to pressing, as well as a significant reduction in the amount of moisture in the material, which additionally evaporates during the high-temperature pressing.

The obtained solid fuel briquettes parameters almost correspond to the German standard DIN 51731: moisture content (<12%), ash content (<1.5%), calorific value (3705÷4661 kcal \cdot kg⁻¹) (García-Maraver et al., 2011). While the moisture content and ash content are within the established limits, the calorific value of solid fuel is slightly higher than the upper limit of the standard. The use of raw materials with higher humidity can slightly reduce the calorific value of the finished product, as well as reduce the cost of the drying process.

Considering the results of the conducted research, it can be argued about the advantages of using briquetted solid fuel from brewer's spent grain and coffee wastes, which include higher calorific value and suitability of the finished product for long-term storage without changing mechanical properties. In the unformed dried mixture, the moisture content will be increasing over time, which will affect the calorific value and shelf life. However, it is important to research the energy costs of the solid fuel production process and make conclusions about the feasibility of using one or another of its forms. The production of alternative solid fuel from food industry waste should in any case have an economic effect, taking into account the low cost of raw materials. Additional benefits will be in the improvement of the ecological situation due to the secondary processing of waste and the replacement of slowrenewable raw materials, primarily wood.

Conclusions

Thus, the research results showed the possibility of using brewer's spent grain and spent coffee grounds for the production of solid fuel. Due to the high moisture content, this material requires preliminary drying for long-term storage.

The results of the conducted research are samples of solid fuel made from brewer's spent grain and a mixture of coffee wastes. The higher calorific value of unformed brewer's spent grain is ~20 005 kJ \cdot kg⁻¹ and obtained briquettes – ~20 173 kJ \cdot kg⁻¹. In the case of coffee wastes, the higher calorific value of unformed material is ~21 583 kJ \cdot kg⁻¹ and ~22 147 kJ \cdot kg⁻¹ for obtained solid fuel sample.

The obtained experimental data indicate the promising and effective use of the coffee wastes for the production of solid fuel. However, it is advisable to carry out in future studies the calculation of consumption coefficients and energy calculation of the production process of solid fuel briquettes. In addition, in order to reduce energy costs, it is important to research the effect of lower temperatures on the process of forming the solid form of the briquette without negative consequences on the mechanical properties of the object.

The production of solid fuel briquettes will allow expanding the scope of brewer's spent grain and coffee production waste, and at the same time create an additional opportunity to replace traditional hard-to-renew fuel sources, such as coal and wood.

Test No ma	m g AT V		a I	<i>d</i> unio I	I a I	Q		
Test No.	m, g	$\Delta 1, v$	Yam poule, J	<i>Ythread</i> , J	$q_{\rm HNO_3}$,	$y q_s, y$	$kJ kg^{-1}$	${ m kJkg}^{-1}$
			Samp	le 1 (Brewer's	spent gra	in)		
1	0.36107	0.82688	1337.6	82.0	9.4	77.1	19953	4769
2	0.30740	0.71715	1324.2	86.9	9.1	70.5	19751	4720
3	0.36788	0.86662	1500.7	67.6	8.6	82.0	20313	4855
						The average value:	20005	4781
			Sa	mple 2 (Coffe	e wastes)			
1	0.53160	1.28797	1861.6	107.8	26.6	62.0	21433	5123
2	0.32255	0.80133	1302.1	75.2	7.7	64.0	21613	5166
3	0.37701	0.96250	1714.7	92.0	6.8	36.1	21704	5187
						The average value:	21583	5159

 Table 5.2.2: The results of experimental determination of the higher calorific value of dried researched materials according to the calorimetry of combustion

Table 5.2.3: The higher calorific value of the studied dried plant materials and their widely used analogs

	Dried spent coffee grounds	Dried barley brewer's spent grain	Dried corn distillery stillage	Energy willow	Miscanthus
Q, kJ kg ⁻¹	≈ 21583	≈ 20005	≈ 19545	≈ 17600	≈ 17500

 Table 5.2.4: The results of experimental determination of higher calorific value according to the calorimetry of combustion of solid fuel

 briquettes from barley brewer's spent grain and coffee

Test No.	<i>m</i> , g	$\Delta T, V$	gampoule, J	q _{thread} , J	$q_{\rm HNO_{\circ}}$	$J q_{s}$	_1	Q1
			Tampoure > o	nn cuu + o	111(03	13.0	kJ kg	kJ kg
	Sample 1 (150 °C, 60 s, 9.81×10^6 N m ⁻²) (Brewer's spent grain)							
1	0.50326	0.98698	-	64.2	18.6	45.8	20221	4833
2	0.36344	0.70996	-	69.8	7.7	70.5	20195	4826
3	0.46443	0.90688	-	86.1	11.2	49.2	20103	4804
						The average value:	20173	4821
		Sam	ple 2 (150 °C, 6	$50 \text{ s}, 9.81 \times 10^6$	$N m^{-2}$)	(Coffee wastes)		
1	0.53160	1.28797	-	107.8	26.6	62.0	21433	5123
2	0.32255	0.80133	-	75.2	7.7	64.0	21613	5166
3	0.37701	0.96250	-	92.0	6.8	36.1	21704	5187
						The average value:	21583	5159

Table 5.2.5: The ash content and moisture content of obtained test samples

	Ash content, % wt.	Moisture content, % wt.
Barley brewer's spent grain	1.5 ÷ 1.6	$2.5 \div 3.2$
Coffee wastes	≈ 1	≈ 1

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5.3 Microkinetic modelling of photocatalytic CO₂ conversion over MOFs

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KEYWORDS: simulation, photocatalysis, CO₂, reduction, MOFs, fuel production.

Abstract

By enabling atmospheric pressure and temperature reactions, photocatalysts promise to lower the energy required when reducing CO_2 to produce high-value fuel compounds. Yet, the progress of present techniques for discovering more effective catalysts is relatively slow.

The main goal of this study was to construct a reaction mechanism to reduce CO_2 into CO, as shown in Figure 5.3.1; however, precise kinetic data from the literature was needed to get valid results for the UiO-66 photocatalyst to achieve this, precise.

Figure 5.3.1: A Zirconium MOF, showing its components: metal nodes, in this case, Zirconium, in yellow, and linkers, in blue. On the right, the MOF reacts with sunlight to convert the CO_2 into CO. On the left, it is shown how the Zr^{4+} acts as a catalyst within the reaction as it is being regenerated

The model was created using Parest, simulating a plug flow reactor with a sacrificial agent. Next, a sensitivity analysis was designed to comprehend how the kinetic parameters impact the model. The most significant step was optimising the parameters and finding the best CO₂:S ratio.

The results show that using a sacrificial agent as a source of H^+ is quite successful, as well as the G expression for mimicking the light component. Approximating kinetic parameters show that adsorption happens, though not all products disorb. Due to the CO not disorbing, CO parameter optimisation and a sensitivity analysis were conducted to determine which kinetic parameters significantly impact the model.

To maximise the output of CO generated, it was discovered by varying the CO₂:S ratio that the amount of CO₂ at the beginning of the reaction should be higher than the amount of S. Moreover, the desorption of CO does not proceed without correctly approximating the parameters, especially the A_f .

Table 5.3.1: Nomeclature used in article

Shortening	Definition
MOF	Metal-Organic Framework
PFR	Plug Flow Reactor
TEOA	Triethanolamine

Figure 5.3.2: The routes used to produce the main byproducts of CO₂ photocatalysis (Karamian & Sharifnia, 2016)

Nomenclature

Introduction

Reducing CO₂ into usable fuels could help mitigate climate change's impacts by allowing the formation of a closed-loop carbon cycle with a net zero CO₂ increase. This process is currently being investigated through microkinetic simulation so the correct parameters, conditions and materials can be discovered before physical experiments take place to refine the experiments further, as its physical experiments are costly; to produce a commercially viable process. The microkinetic modelling will involve a rapid prototyping stage. Many iterations will be performed to determine the approximate conditions and materials that could be used before more detailed simulations occur, which will fully inform the practical experiments. This paper will focus on the chemistry of MOFs and what is required for the simulations to succeed, with plans for the future development of the simulation process and how the model will be used in future practical work already in effect.

Methods

Five phases were required to develop the micro-kinetic model; the first one investigated the source of the H^+ , a proton. The second one examines how the reaction mechanism would be generated and inputted in Parest. The third set of instructions will explain how to modify the raw data so that it may be transformed into kinetic parameters. The fourth step is the kinetic model, and the final part will describe how the kinetic parameters impact the microkinetic model.

Hydrogen ion source

The CO₂ photoreduction products with the common reductants (i.e., CO, HCOOH, HCHO, CH₃OH, CH₄, and C₂H₅OH) are often the same (Karamian & Sharifnia, 2016). The primary products may be formed using any combination of protons (H⁺), oxidising holes, and reducing electrons, as shown in Figure 5.3.2.

The reaction process for the photocatalytic synthesis of alkanes, alkenes, and syngas is explicitly described in Figure 5.3.3. According to (Takanabe, 2017), the hydrogen radical

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Figure 5.3.3: The potential reaction mechanism for the photocatalytic CO_2 generation of syngas and different hydrocarbons (Karamian & Sharifnia, 2016)

is produced when water undergoes a photocatalytic reaction, theorised to be a sustainable way to have H2 without removing methane or other natural gases from the ground. Because photocatalytic water splitting uses solar energy and matches the redox reaction type and the thermodynamics of natural photosynthesis, it is thought to be artificial photosynthesis that generates fuel (water splitting: 1.23 eV vs CO₂ reduction: 1.1 eV) (Razek et al., 2020). Most catalyst surfaces are far more strongly bound by H₂O than CO₂ (Alvarez et al., 2017). Together, these results demonstrate that although water would be a cheap and efficient reducing agent, the chemically competitive environment would produce more OH⁻ radicals to be produced and bind to the catalyst surface, which would reduce the active sites that CO_2 could attach to and thereby lower overall efficiency. Though, these OH⁻ radicals would lengthen the lifetime of the photoexcited electrons. These would also result in several more alcohol, aldehyde, and carboxylic acid groups. According to the theory in (Hart, 1961), two free hydrogen radicals may interact with CO₂ species to produce HCOOH. Subsequently, hydrogenation produces undesirable byproducts if the intended use is to produce CO. Many chemical routes have been theorised, and H₂O exhibits limited selectivity; hence, water won't be used as the feed material for this model.

Figure 5.3.3 depicts acceptable and undesirable reaction pathways. The reaction proceeds in the same manner whether H_2O or H_2 was employed as the reducing agent. According to (Narv'aez-Celada & Varela, 2022), Figure 5.3.4 is another pathway in reducing CO_2 to CO.

Viewing Figure 5.3.4 demonstrates that the route in Figure 5.3.3 needs fewer free hydrogen ions/radicals to react; given that getting H_2 gas is more costly than getting CO_2 gas, this may lower operating expenses. Also, since the H_2 gas does not produce any OH^- species when it attaches to the surface, there will be less OH^- on the catalyst to harm it. Notably, free hydrogen radicals are necessary for the reaction shown in Figure 5.3.3, while charged ions will not result in the reaction shown in Figure 5.3.3. In several photoreduction investigations, hydrogen has been used as a key reductant. However, rather than splitting water or using H_2 , a sacrificial agent, S, such as TEOA, will be used instead, producing the H^+ . On the surface of the UiO-66 linker, the absorbed hydrogen ion, according to (Subrahmanyam, 1999), would then react with photoexcited electrons from the conduction band to

Figure 5.3.4: Diagram showing the CO_2 reduction route leading to various reaction products (Narváez-Celada & Varela, 2022)

create a H \cdot , a hydrogen radical. A similar approach was shown in Figure 5.3.3. H \cdot are reactive entities that immediately interact with $CO_2^- \cdot$ to hasten its oxidation, as seen in the following section.

Equation model

The reaction mechanism for the reduction of CO2 will be similar to that described in (Kovačič, Likozar & Huš, 2020) and is described in Section 2.1 [Hydrogen ion source]. Instead of declaring $CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$, the alteration made for this microkinetic model is that each hydrogen ion reaction will be represented. The reaction process outlined in Section 2.1 [Hydrogen ion source] and discovered by (Subrahmanyam, 1999) will be followed in creating the hydrogen radical. All reactions will be taken as reversible, as both the forward and backward reactions must be examined to develop a genuine micro-kinetic model. The equations for the gaseous and aqueous species adhering to the catalyst are given in Equations 5.3.1 and 5.3.2.

$$CO_{2(g)} + \eta_{(s)} \longleftrightarrow \eta CO_{2(a)}$$
 (5.3.1)

$$S_{(aq)} + m(s) \longleftrightarrow m S_{(a)}$$
 (5.3.2)

Products are shown to have desorption from the catalyst surface in Equations 3 through 5.

$$m H_2O_{(a)}, -. m_{(s)} + H_2O_{(g)}$$
 (5.3.3)

$$\eta CO_{2(a)} \longleftrightarrow \eta_{(s)} CO_{(g)}$$
(5.3.4)

$$m S_{\text{oxi}(a)} \longleftrightarrow m(s) + S_{\text{oxi}(aq)}$$
 (5.3.5)

Compared to the activation energy computed for desorption of OH-1, which is 5.23 eV, H₂O is anticipated to desorb at a considerably greater rate (Ferro, Hodille, Denis, Piazza, & Ajmalghan, 2023). (Wang et al., 2020) discovered that the activation energy for the desorption of H2O was 1.09 eV. Hence, water has been decided to be desorbed rather than the hydroxyl ion in this reaction pathway. A transition structure between the reactants and products for an adsorption or desorption process does not exist. There would be a linear progression

Figure 5.3.5: Studying the Gibbs Free Energy graph along the reaction coordinates.

from reactants to products without the ΔG increase, as shown in Figure 5.

Listing 1 demonstrate the photon expression used to model the photocatalytic component in the model, which is incorporated in the differential equations for h^+ and e^- . When the photon hits the zirconium metal node of the MOF, it will produce h^+ and e^- , which are required in the reaction pathway.

Listing 5.1: The rate expression modelling photon interaction, as seen in the code.

$$e^{-} + \eta CO_2^{-}(a) \longleftrightarrow \eta CO_2^{\bullet-}(a)$$
 (5.3.6)

Equation 5.3.6 is obtained by cancelling out η +3CO2(a) from reactions 7 and 8, showing that the zirconium metal node in the MOF acts as a catalyst, as it regenerates.

$$\eta_4^+ \operatorname{CO}_{2(a)} + e^- \longleftrightarrow \eta_3^+ \operatorname{CO}_{2(a)}$$
(5.3.7)

$$\eta_3^+ \operatorname{CO}_{2(a)} \longleftrightarrow \eta_4^+ \operatorname{CO}_2^{\bullet^-}{}_{(a)}$$
(5.3.8)

 $CO_{2(a)}Zr$ represents the CO_2 molecule when it is attached to the catalyst surface. However, replacing this with $CO_{2(a)}$ will simplify the equations. The MOFs have two active sites, one on the Zr atom, represented as η and the linker, represented as m. Any molecule which is bonded to the surface of the MOF uses the subscript (a), meaning absorbed.

$$m S_{(a)} + h^+ + m_{(s)} \longleftrightarrow mS^{\bullet}_{(a)} + mH^+_{(a)}$$
 (5.3.9)

$$e^- + \eta CO_{2(a)} \longleftrightarrow \eta CO_2^{\bullet-}(a)$$
 (5.3.11)

$$mH_{(a)}^{+} + e^{-} \longleftrightarrow mH_{(a)}^{\bullet}$$
 (5.3.12)

$$\eta \text{CO}_2^{\bullet-}{}_{(a)} + \text{mH}_{(a)}^{\bullet} \longleftrightarrow \eta \text{CO}_{2(a)} + \text{mOH}_{(a)}^{-} \qquad (5.3.13)$$

$$mOH_{(a)}^{-} + mH_{(a)}^{+} \longleftrightarrow mH_2O_{(a)} + m_{(s)}$$
 (5.3.14)

A transition state for reactions $9 \rightarrow 14$ will exist. The forward and backward chemistry of reaction 11 is nearly identical chemically or physically, meaning it is an activated reaction. The complexes formed above are considered transition structures since they are only generated for a limited time and are quasi-stable, not genuinely stable.

Kinetic parameters

The data collected in Section "Equation model" is processed in this part to provide meaningful information that may be used to build a kinetic model.

Activated reactions

Several chemical rate equations that comprise a kinetic model all have the same basic structure as Equation 5.3.15.

$$r_{rxn} = A_f e^{\frac{E_a}{RT}} [i]^{\nu}$$
(5.3.15)

$$k = A_f e^{\frac{E_a}{RT}} \tag{5.3.16}$$

The pre-exponential factor, or the rate at which collisions happen in a reaction, is represented by the symbol A_f in the chemical rate equation. R is the ideal gas constant, T is the temperature, and $[i]^{\nu}$ is the chemical concentration raised to the power of stoichiometry. E_a stands for the activation energy or the amount of energy needed to initiate a reaction.

However, this chemical rate calculation does not consider the complexity of the molecules' structural makeup. Equation 5.3.18 illustrates how the Erying equation can be applied to the standard rate equation.

$$r_{rxn} = \frac{k_b T}{h} e^{\frac{\Delta S}{R}} e^{-\frac{\Delta H}{RT}} [i]^{\nu}$$
(5.3.17)

$$k = \frac{k_b T}{h} e^{\frac{\Delta S}{R}} e^{-\frac{\Delta H}{RT}}$$
(5.3.18)

The entropy and enthalpy must alter between the stable molecule and the quasi-stable transition structure since Equation 5.3.18 is based on the "Transition State Theory Preexponential Theory." The Boltzmann constant, k_b , Planck's constant, h temperature, T, the change in entropy between the reactant or product and the transition structure, ΔS , and the change in enthalpy between the reactant or product and the transition structure, ΔH , are all included in the equation above. The reasoning for why Equations 5.3.16 and 5.3.18 are equivalent is provided in Equations 5.3.19 \rightarrow 5.3.24 (Louie, 2013).

$$k = \nu K \tag{5.3.19}$$

$$\nu = \frac{k_b T}{h} \tag{5.3.20}$$

$$m \operatorname{S}^{\bullet}_{(a)} + \mathrm{h}^{+} + \mathrm{m}_{(s)} \longleftrightarrow \mathrm{mS}_{\operatorname{oxi}(a)} + \mathrm{mH}^{+}_{(a)}$$
 (5.3.10)

$$\Delta G = -RT \ln K \tag{5.3.21}$$

$$\Delta G = \Delta H - T \Delta S \tag{5.3.22}$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$
(5.3.23)

$$K = e^{\frac{\Delta S}{R}} - e^{\frac{\Delta H}{RT}}$$
(5.3.24)

The thermodynamic equilibrium constant K is multiplied by the frequency of vibration ν to get the rate of reaction coefficient. The vibration frequency explains the pace at which the species involved in the reaction vibrate about their equilibrium point. K specifies the chemical equilibrium point between the reactant or product and the transition structure.

Depending on whether the reaction is going forward or backwards, ΔS and ΔH , as stated, represent the change in entropy and enthalpy between the reactant or product structure and the transition structure.

Non-activated reactions

Adsorption and desorption processes, as previously mentioned, lack transition phases, necessitating a separate calculation of the rate coefficient. The activation energy for an adsorption process in this simulation is zero because the complex formed during adsorption operations always has a lower enthalpy than the sum of the individual enthalpies of the reactants, as shown in Figure 5.3.5. When looking at Equation 5.3.16, the exponential term is represented by e^0 , which equals 1, meaning that the pre-exponential component and the rate coefficient are identical. As this component can only be determined empirically, data from experiments will be used to compute it. Energy must be supplied during desorption operations because the enthalpy rises when the two molecules split, and the bonded complex becomes two independent molecules. This energy for the process, known as the activation energy, is equal to the difference in enthalpy between the complex and the total of the unbound species. The pre-exponential factor will then be determined by applying Equation 5.3.25 to the experimentally determined adsorption value and the change in entropy between the reactants and the complex.

$$\frac{A_a ds}{A_d es} = e^{\frac{\Delta S}{R}} \tag{5.3.25}$$

Kinetic model

Upon reading the desired simulated equations, the model automatically produces a series of files. This function, "testmod-2sites" is limited to two active sites and must be linked with the Parest solver library. One of the files is ddat.in which initial conditions and pressures are stated; model.c is the main file where rate equation, differential and algebraic equations can be found; param.dat is where the kinetic parameters are written. The simulated reaction takes place in a 100.000 ml plug flow reactor. It was initially thought that for the reaction to complete, the ratio of CO_2 :S should be 1:1. Despite the study's efforts to limit uncertainty.

Due to the lack of existing literature around the reaction components reaction and the uncertainty of the reaction pathways in the computational model, certain assumptions are being made in the simulation; which are listed below.

- Due to the reactor's utilisation of 1 atm of pressure and atmospheric temperature, perfect gas conditions will be assumed within the reactor.
- Octahedral nanoparticles with a size of 450 nm make up the catalysts, meaning they are all identical (Liu, Jin, & Meng, 2022).
- Since all reaction species are equal in size and occupy equivalent amounts of area on the catalyst surface, the total number of reaction sites on the UiO-66 catalyst is constant.
- Time in the simulation is measured in the reactor as the number of active sites from the start.
- The source that produces photons does so with a steady rate and wavelength. All of the energy is transmitted when the photon contacts the catalyst surface.
- Electrons that have been photoexcited always return to their ground state at the same pace.

Sensitivity analysis

The lack of kinetic parameters for this reaction pathway using UiO-66, the results with the estimated kinetic parameters have accumulated quite a lot of error. Therefore, a sensitivity analysis has been carried out to determine which kinetic parameters affect the model the most.

The sensitivity analysis works by running multiple instances of the Parest model with slightly adjusted parameters. The parameters are currently adjusted one at a time, which reduces the amount of data generated but will mean that the optimisation process, in which the best parameters for the model are discovered, needs to be done in steps.

The results of these simulations are then saved and transformed into files that list each of the kinetic parameters being changed for all the species in the simulation. To reduce the amount of data, and data processing, these results are reduced to two parameters; the standard deviation and the last partial pressure of each reactant. An adjusted parameter then groups these results to plot them by hand or script.

All of the intermediary steps performed are saved so that the results can be reproduced and to ensure that any numerical errors that are introduced can be corrected. There are many limitations when processing data, the most prominent being that the Parest model occasionally produces values smaller than the precision loss of a double, represented by – $(2^{1024}-2^{971})$, CITEME, to prevent unexpected behaviour, when reading and converting these values the analyser sets them to 0.

Results and discussion

A crucial factor in assessing if findings are meaningful is knowing how the data was obtained, its values and limits. There will be four portions to the debate. The outcomes of the reaction mechanism, first. The sensitivity analysis results follow – after the impact of the CO_2 :S ratio and parameter optimisation. Lastly, a review of the data's limitations is given, along with suggestions.

Simulation model

The rate coefficient for an adsorption reaction equals the pre-exponential component, as indicated in Section "Kinetic

Figure 5.3.6: Logarithmic production of H^+ and $H \cdot$ at 298 K and 101 325 Pa from S.

parameters". These numbers were computed using the preexponential absorption factor of 10^3 (s^{-1}) and activation energy of 0. While those values can only be determined experimentally, and no literature data was discovered for this study owing to its novelty, these values, alongside the rest, are approximates using similar studies found in the literature (Landaverde-Alvarado, Morris, & Martin, 2017).

At 298 K and 101325 Pa, the production of H^+ and H^- from using the sacrificial agent is investigated, followed by the adsorption of CO₂ and S, desorption of CO, H₂O and S_{oxi} and the production of h^+ and e^- from the photon expression.

To ensure that the sacrificial agent can be used instead of the H₂O and H₂, the production of H⁺ and H · were investigated as seen in Figure 5.3.6. It can be seen that after 100 m of length, both the H+ and H · start to form. At 10⁶ active sites, the mH⁺ starts to rise abruptly, slowing down once reaching 10^{12} sites, at which point the concentration of mH · overtakes it.

Adsorption is required for the reaction to start. Therefore, ηCO_2 and mS are particularly interesting and investigated in Figure 5.3.7. The CO₂ absorbs on the zirconium metal node quickly before flattening out, which could indicate that the active sites on the MOF are saturated. The sacrificial agent doesn't appear to be absorbing, but in reality, it does absorb on the linker, as seen in Figure 5.3.8.

The non-logarithmic graph shows that the sacrificial agent does absorb onto the MOF almost instantaneously until it levels off for most of the reaction. Then it slowly starts to decrease and then abruptly reaches zero. Comparing it with the absorbed ηCO_2 , the S absorbs simultaneously as the CO2. The last point is not reliable as it is a negative partial pressure, likely indicating that there has been a convergence error in the model due to the reaction parameters.

Desorption is needed to prevent catalyst poisoning and allow the reaction to progress. Therefore, species CO, H_2O and S_{oxi} were investigated in Figure 5.3.9; though currently, however, there is no CO being disorbed, a likely reason being the approximation of the kinetic parameters. However, some H_2O is shown to be disorbed, though two data points are missing from the graph as they were negative and could not be included on a logarithmic plot. Similarly, the sacrificial agent, which disorbs in its oxidised form, has the same issue as the H_2O , including missing data points.

Lastly, to verify that the photon expression works and the simulation considers the photocatalytic side of the model, an investigation on the production of e^- and h^+ was conducted as shown in Figure 5.3.10. This indicates that the photon expression successfully produces e^- and h^+ , which are embedded in the differential equation rather than the model equa-

Figure 5.3.7: Logarithmic absorption of and S on the MOF at 298 K and 101325 Pa.

Figure 5.3.8: Absorption of S on the MOF at 298 K and 101325 Pa.

Figure 5.3.9: Logarithmic desorption of CO, H_2O and S_{oxi} from the MOF at 298 K and 1 bar.

tions.

The total pressure times the gas's mole fraction yields the partial pressure of any given gas in a mixture. Therefore, the mole fraction of each species at any point can be calculated using Equation 5.3.26. If the mole fraction is plotted against the active sites, graphs with a similar relationship to those above would be produced.

$$x_A = \frac{p_A}{P} \tag{5.3.26}$$

Sensitivity analysis

A sensitivity analysis was carried out on each species' kinetic parameters to determine how impactful they are. There were 22 sets of kinetic parameters compromising each of A_f and E_a , and three different graphs trends have been established. Figure 5.3.11 represents the graph for the kinetic parameter A_f of equation 5.3.1 for species mH⁺.

The horizontal line means that this kinetic parameter has no impact on mH^+ since Equation 5.3.1 deals with the absorption with the CO₂, as there is no variation in standard devia-

Figure 5.3.10: Logarithmic production of e^- and h^+ due to the G expression.

Figure 5.3.11: Sensitivity analysis of parameter 0 for species 1, mH⁺; trend is not-significant.

tion. All the graphs with this trend have been categorised as non-impactful.

However, some kinetic parameters significantly impact the model, which has the trend shown in Figure 5.3.12. This specific example is for parameter 0, which is A_f of Equation 5.3.1 for species ηCO_2 . This can be seen as there is one unique value at each step; therefore, changing the parameter value will linearly change the output value too. Thus, parameter 0 has to be as accurate as possible since it will significantly affect the CO_2 absorbed.

Table 5.3.2 shows which kinetic parameters affect which species since they resulted in a trend graph similar to that in Figure 12. After the first run of the sensitivity analysis, only seven parameters have shown significant effects, meaning that those parameters must be accurate before the next run of the sensitivity analysis can be done.

There were alternative trends on the graphs produced by the sensitivity analysis, all of which were inconclusive; an example is shown in Figure 5.3.13. For these graphs, further investigation must be carried out to determine how the kinetic parameters affect the production of these species.

Figure 5.3.12: Sensitivity analysis of parameter 0 for species 13, ηCO_2 ; trend is significant.

Table 5.3.2: Table showing which parameters significantly affect what species as a result of the sensitivity analysis.

Parameter	Equation	Direction	Impacted species
A_{f}	5.3.1	Forward	ηCO ₂
E_a	5.3.1	Forward	ηCO
E_a	5.3.1	Forward	ηCO_2
E_a	5.3.2	Forward	mS _{oxi}
A_f	5.3.9	Forward	mH^+
A_{f}	5.3.9	Forward	mS
A_{f}	5.3.9	Forward	mS ·

Figure 5.3.13: Graph showing the effects of variation on parameter one on species 9, absorbed CO. The data presented in the graph is inconclusive.
Table 5.3.3: Production of CO by varying parameter 36.

	Parameter value	Unit	Unit CO production	
	17200	1/s	2,72 <i>e</i> – 31	Pa
	29500	1/s	4,72 <i>e</i> - 31	Pa
	21500	1/s	3, 73 <i>e</i> – 31	Pa
	15900	1/s	1,82e-31	Pa
	23400	1/s	6,41e-31	Pa
PARTIAL PRESSURE (PA)	1.00E-04 1.00E-10 1.00E-16 1.00E-22 1.00E-28 1.00E-34 1.00E-40 1.00E-46 1.00E-52	1,00 ^{4,00} 1,00 ^{4,00}	Laters Laters Laters Laters	LOREAN LOREAN
	Parameter 36: 172 Parameter 36: 200	PRACTIONAL	ter 36: 13400 — Parameter 36: ter 36: 12600 — Parameter 36:	20900 23400
	Parameter 36: 295	00 —— Parame	ter 36: 21500 — Parameter 36:	15900

Figure 5.3.14: Looking at CO desorption from the active sites by changing parameters 36, A_f of the forward Equation 5.3.4; parameter 37, E_a of the forward Equation 5.3.4; parameter 38, A_f of the reverse Equation 5.3.4; and parameter 39, E_a of the reverse Equation 5.3.4 with a CO₂:S ratio of 1:1 in logarithmic form.

Parameters optimisation and CO₂:S ratio

A parameter optimisation analysis has been started to determine which parameters would produce the best output. However, this is a working progress since there are 44 parameters to analyse for 19 species. However, focusing at the moment on the parameters and species in Table 5.3.2, it has found out that for parameter 1, E_a for Equation 5.3.1 in the forward direction produces no η CO₂ and no η CO with values between 100 and 1340 J mol⁻¹. Therefore, this indicates that this parameter should be left at 0 until examination of the range 0 -100 J mol⁻¹ is undertaken as it gives absorption of CO₂ and CO.

However, due to the lack of production of CO, Equation 5.3.4's kinetic parameters also impact the model. Currently, the values used are incorrect since they don't allow desorption of CO; these parameters were amongst the ones with an unusual trend in the sensitivity analysis. This may be because it depends on other parameters.

The next step was to change just parameter 36, A_f of the forward Equation 5.3.4; parameter 37, E_a of the forward Equation 5.3.4; parameter 38, A_f of the reverse Equation 5.3.4; and parameter 39, E_a of the reverse Equation 5.3.4 to notice how they impact the desorption of CO, as seen in Figure 5.3.14.

In Figure 5.3.14, nine different values for parameter 36 have been plotted to determine the best CO output. Some negative values produced cannot be plotted on a logarithmic graph, resulting in missing points. Those values are errors in the simulation, so further investigation is required to establish the actual values; this impacts the simulation as the real progression of a species is not accurate. However, in Table 5.3.3, the production of CO by varying parameter 36 can be seen. The value that produces the most at the end is 23 400 s⁻¹ with 6.41×10^{-31} Pa.

Due to the high number of files created for the simulation, the parameters shown are randomly chosen from 1054 runs for this particular scenario. This means that further analysis of all the files is required to understand a better optimisation of **Table 5.3.4:** The CO parameters changed of Equation 4, and the values in-between the randomised files were picked to analyse.

Number	Parameter	Direction	Range	Unit
36	A_f	Forward	200 - 29500	1/s
37	E_a	Forward	1370 - 1480	J/mol
38	A_{f}	Reverse	0 - 41000	1/s
39	E_a^{J}	Reverse	300 - 2840	J/mol
1.00E-03 1.00E-08 1.00E-15 1.00E-15	LOS LOELOS LOSEON LOS	100 10000 10000 10	ostal Lostal Lotting Lost	*11 1.00E*18



Figure 5.3.15: Looking at CO desorption from the active sites by changing parameters 36, A_f of the forward Equation 5.3.4; parameter 37, E_a of the forward Equation 5.3.4; parameter 38, A_f of the reverse Equation 5.3.4; and parameter 39, E_a of the reverse Equation 5.3.4 with a CO₂:S ratio of 1:2 in logarithmic form.

the parameters. In Table 5.3.4, the range of the values for the randomly chosen parameters is shown; in total, 24 arbitrary files were picked.

In Figure 5.3.14, only values for parameter 36 are plotted, and this is because, for the other parameter values, the production of CO was still zero. Since in the sensitivity analysis, only one of the four parameters was changed at a time. It could mean that parameters 37, 38 and 39 are dependent on the value of parameter 37. Another explanation is that the correct value for the other three parameters hasn't been found yet and that it might be in the middle or outside of the ranges explored.

The link between the initial CO_2 :S ratio also affects the end CO gas output. Because the kinetic parameters are independent of the initial reactant ratio, the CO parameters were investigated after the initial simulation as different ratios. The first ratio looks at a CO2:S ratio of 1:2 to show that even with more sacrificial agent, S, some CO should still be forming, even if in smaller amounts, as seen in Figure 5.3.15.

Here it can be seen that towards the end of the reactor parameter 36 with values of 1200 s^{-1} and 4900 s^{-1} producing 2.49×10^{-31} Pa, 142×10^{-31} Pa and 1.50×10^{-33} Pa of CO respectively. However, the most significant CO production was with a value of $18 400 \text{ s}^{-1}$, resulting in 2.49×10^{-32} Pa and parameter 39 having a value of $1000 \text{ J} \text{ mol}^{-1}$ producing 1.14×10^{-31} Pa of CO. But compared with the CO₂:S ratio of 1:1, there is less CO being produced because there is less CO₂ to start with. To maximise the yield of CO, there should be more CO₂ than S initially. There were some convergent errors which led to missing points in the graph. The files examined were again chosen arbitrarily, and the values of the parameters range as shown in Table 5.3.5.

The same conclusion can be made about some randomly picked values not included in the graph since they resulted in 0 production of CO. The lack of production is entirely based on the kinetic parameters, as the ratio only affects how much is produced, whereas the kinetic parameter affects whether it

Table 5.3.5: The CO parameters changed of Equation 4, and the values in-between the randomised files were picked to analyse.

Number	Parameter	Direction	Range	Unit
36	A_{f}	Forward	900 - 18400	1/s
37	E_a	Forward	130 - 860	J/mol
38	A_{f}	Reverse	2400 - 35100	1/s
39	E_a	Reverse	180 - 1990	J/mol

Table 5.3.6: The CO parameters changed of Equation 4, and the values in-between the randomised files were picked to analyse.

Number	Parameter	Direction	Range	Unit
36	A_{f}	Forward	1300 - 27200	1/s
37	E_a	Forward	380 - 750	J/mol
38	A_f	Reverse	3600 - 55200	1/s
39	E_a	Reverse	770 - 2480	J/mol

is produced.

Since more CO production would be ideal, a 2:1 ratio of CO_2 :S was investigated while still looking at changing CO parameters. The parameters in Figure 5.3.16 were randomly chosen again. The larger production can be seen that towards the end of the reactor, there is CO present when parameter 36 has a value of 1300 s^{-1} and $18\,800 \text{ s}^{-1}$ producing 5.53×10^{-32} Pa and 5.37×10^{-32} Pa respectively. However, the most CO is produced with the 7500 s^{-1} , yielding 7.98×10^{-32} Pa. Compared to the 1:1 ratio, the larger production means having a bigger amount of CO_2 favours the production of CO. For this ratio, the initial range of values for the arbitrarily chosen parameters is shown in Table 5.3.6.



Figure 5.3.16: Looking at CO desorption from the active sites by changing parameters 36, A_f of the forward Equation 5.3.4; parameter 37, E_a of the forward Equation 5.3.4; parameter 38, A_f of the reverse Equation 5.3.4; and parameter 39, E_a of the reverse Equation 5.3.4 with a CO₂:S ratio of 2:1 in logarithmic form.

Once again, the correct parameter can be in-between this range or outside of the range. So far, the parameters with a potential value leading to the production of CO are displayed in Table 5.3.7. Further investigation is needed in simulating a model that optimises parameters 36 and 39. That CO will be produced and help identify other production-limiting parameters.

Limitations

Although the output gas production figures provided by the optimised kinetic simulation for UiO-66 at a CO_2 :S ratio of 2:1 were producing CO, further research must be done before the kinetic data can be categorised to be accurate enough to start implementing this in lab or industry. This is because the

Table 5.3.7: The CO parameters of Equation 5.3.4, and the values which result in production of CO.

Number	Parameter	Direction	Value	Unit
36	A_{f}	Forward	7500	1/s
36	A_{f}	Forward	1200	1/s
36	A_{f}	Forward	1300	1/s
36	A_{f}	Forward	4900	1/s
36	A_{f}	Forward	15900	1/s
36	A_{f}	Forward	17200	1/s
36	A_{f}	Forward	18400	1/s
36	A_{f}	Forward	18800	1/s
36	A_{f}	Forward	21500	1/s
36	A_{f}	Forward	23400	1/s
36	A_{f}	Forward	29500	1/s
39	$E_a^{'}$	Reverse	1000	J/mol

theorised kinetic parameters cannot be proven until further study is done on the kinetics of the model. The findings are thus insignificant, as shown by previos Sections, and since the data obtained was insufficiently precise to provide insightful insights. This section will explore the rationale and best methods for overcoming these constraints.

In addition, the inadequate response route that was examined was another drawback. The selected reaction route was modified to reflect a better micro-kinetic model since it was the preferred reaction pathway in the gaseous state. The OH⁻ species should have been further accommodated by changing the reaction pathway as stated in Section 2.1, OH⁻ can poison the catalyst as it can't disorb due to its high activation energy. The following response should be a suggested strategy to lessen this restriction.

$$OH^- + H \cdot \longleftrightarrow H_2 O^{\bullet^-}$$
 (5.3.27)

$$H_2O^{\bullet-} \longleftrightarrow H_2O + e^-$$
 (5.3.28)

Also, by reducing the quantity of OH-1 on the catalyst, it is suggested that the conversion of the process is enhanced, as well as running parallel reactions using the different pathways of reducing the CO2 into CO, such as the one shown in Figure 5.3.4.

The results of the CO_2 :S ratio simulation, however, are no longer meaningful if more reactions are run simultaneously as additional sacrificial agent would be needed in the reactor to form the hydrogen ion and radical. However, a substantial partial pressure of CO_2 relative to S is still required for a large conversion.

The kind of kinetic model developed was the model's last significant flaw. Since this reaction is catalytic, active sites are necessary for it to proceed. Moreover, on the catalyst, the species engaged in the reaction need to be close to one another. The created kinetic model assumed that all species on the catalyst could react together, regardless of location. A Kinetic Monte Carlo (KMC) model needs to have been created to solve this issue. This kind of kinetic simulation accounts for the randomness of where a species binds to the catalyst, enabling the development of more precise kinetic models (Cheimarios, To, Kokkoris, Memos, & Boudouvis, 2021).

Conclusion

Finding kinetic rate data and designing a micro-kinetic model for the reduction of CO₂ using a sacrificial agent as the feed-

stock and Zr-UiO-66 as the catalyst was the primary goal of this study. The G expression represented the light component. However, no CO was disorbed due to the estimation of the kinetic parameters. The study's secondary objective was to determine which kinetic parameters affect the model through a sensitivity analysis. At the same time, looking at how altering the CO_2 to S ratio impacted the production of the CO gas.

Therefore, what can be concluded from this analysis is that specific parameters have a more significant impact on the model compared to others. The ones coming up in the sensitivity analysis are the kinetic parameters for the absorption of the reactants. If the E_a for the CO₂ is increased higher than 100 J mol^{-1} , then no absorption is happening. However, it has been proven to work with a value of 0 $J.mol^{-1}$. Also, it has been proven that the kinetic parameters desorbing CO are vital in getting the product. So far, 11 different values have been found for the A_f of CO and one for the reverse E_a of CO at 298.15 K and 101 325 Pa.

Unfortunately, the conclusions have limited value because of the outstanding erroneous data. Last, the reaction route must have been lengthened to enable multiple reactions with the OH^- species and more ways for the CO_2 to reduce to CO. Also, the results for the second goal showed that when CO_2 partial pressures rose, more CO was produced.

It is advised that further research is to be performed on the production of CO based on the findings of this study. The aim is to gain more precise kinetic data and better understand the chemical process. More investigation should be done on using TEOA as a sacrificial agent to reduce CO_2 , looking at various reaction paths and byproducts.

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5.4 Multiple emulsions prepared in a helicoidal flow contactor for topical drug delivery

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KEYWORDS: helical flow contactor, inflammation, multiple emulsions, pharmaceutical emulsions, release process.

Abstract

Radiotherapy is one of the main methods of cancer treatment. Irradiation with X-rays can cause a set of many disorders occurring in cells and intercellular spaces, causing symptoms such as inflammation, irritation, swelling, itching, fibrosis, or pain. This study analysed multiple emulsions as carriers of an anti-inflammatory drug for topical application, aimed at alleviating the symptoms of skin damage resulting from exposure of patients to X-ray radiation.

The aim of the study was to formulate an anti-inflammatory double emulsion containing sodium diclofenac, which could be applied to skin damaged by ionizing radiation, and to predict its effectiveness by analysing the effect on living cells. The results were compared with the classic preparation in the form of a drug solution. The emulsions were prepared by a one-step method in a helicoidal flow contactor with the inner cylinder rotating while the outer cylinder remained stationary. Waterin-oil-in-water $(W_1/O/W_2)$ emulsions have been prepared, by feeding three-phase streams to the contactor, at different flow rates and intensely mixing them. The stability of the system was assessed according to the criterion of changes in drop diameters not greater than 15% over a period of 60 days. The rheological tests of the emulsions were carried out using a rotational viscometer. In order to assess the anti-inflammatory effect of the emulsions containing sodium diclofenac, studies were carried out using irradiated suspensions of human fibroblast cells. The performance of the double emulsion was compared with the topical solution of diclofenac sodium.

All of the emulsions displayed properties of shear-thinning fluids and maintained their kinetic stability throughout the test period. It was observed that *in vitro* release of sodium diclofenac was happening gradually. The emulsions were characterised by a high drug encapsulation efficiency, above 90%. A significant increase in cell viability was observed for both – emulsions and solutions, and it was greater for the emulsions. These results proved that radiation-induced skin injury may be treated using multiple emulsions with the encapsulated anti-inflammatory drug.

Introduction

In order to alleviate the symptoms of skin damage resulting from the side effects of exposure to X-radiation and reduce the pain or discomfort of patients it is advisable to use a proper pharmaceutical preparation. This paper examines the possibility of using multiple emulsions as carriers for the topical delivery of anti-inflammatory drugs to the skin. Medicines can be encapsulated inside the internal phase of double emulsions' hierarchal structures of drops in drops. This protects them from the influence of the environment and acts as a barrier in the process of mass transfer from within. The invariability of physical, chemical, and biological properties over time is a necessary quality parameter of a pharmaceutical emulsion. In order to determine the possible shelf life of the manufactured product, it is necessary to perform stability tests of drug-containing dispersed systems. A desired feature of many pharmaceutical and cosmetic formulations is the gradual release of active substances. This enables patients to take medications less frequently, which increases comfort and ensures adherence to therapy. Moreover, using sustained- or controlled-release drug delivery systems allow the concentration of the drug to be maintained in the therapeutic range for longer periods of time. If a complete dose of medicine is instantly released, the plasma levels may exceed the therapeutic window (the dosage between the lowest therapeutic concentration and the toxic dosage), as shown in Figure 5.4.1. Diclofenac sodium salt was investigated as a



Figure 5.4.1: Time variation of drug plasma concentrations attained by using extended release product in comparison to repeated use of instant release formulation

model active pharmaceutical component in this work since it has long been a widely used nonsteroidal anti-inflammatory drug (NSAID). As with all NSAIDs, diclofenac's mechanism of action is based on the inhibition of cyclooxygenase (COX). Until 1990s both: the anti-inflammatory and gastrotoxic effects of those medicines were attributed to the suppression of a single biocatalyst. However, in 1991 Xie et al. (1991) discovered that more than one isoform of this enzyme exists. Currently, it is hypothesised that inhibition of a constitutive form - COX-1 accounts for gastric side effects, and suppression of an inducible form - COX-2 accounts for therapeutic, anti-inflammatory effects (Mitchell et al., 1991). COX enzymes catalyse the synthesis of prostaglandins - potent biological mediators involved in the expression of inflammation - from arachidonic acid. COX metabolites are abundantly released at the site of inflammation or broadly, following an infection. COX controls the characteristic signs of inflammation, especially edema and pain. NSAIDs act as competitive inhibitors of both COX forms (Yuan et al., 2009). Sodium diclofenac in topical formulations is generally considered to be safe and well-tolerated. It seems to be therapeutically effective in many inflammatory and painful diseases. Although diclofenac has some selectivity towards COX-2, it nonetheless suppresses COX-1 to a degree that may cause stomach epithelial damage if taken in high dosages for prolonged periods of time. In some cases, this could lead to gastrointestinal perforations, ulceration, bleeding, and enteropathy (Zacher et al., 2008).

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A topical formulation may reduce the risk of systemic side effects (Nokhodchi et al., 2002). This route of administration bypasses the gastrointestinal tract and delivers the drug precisely to the site of inflammation. In this work, we propose a method for preparing double water-in-oil-in-water emulsions with diclofenac sodium salt in the internal drops. Previously, diclofenac has been successfully used to reduce inflammation following exposure to radiation in animal studies (El-Ghazaly et al., 1985). This study aims to create an effective formulation, containing sodium diclofenac, to fight inflammation and prevent skin damage in cancer patients undergoing radiotherapy. We strive to create a drug delivery system with better therapeutic properties than preparations currently available on the market.

Introduction

Emulsion composition

The outer phase consisted of sodium carboxymethylcellulose (SIGMA), Pluronic P-123 (ALDRICH), Tween 80 (Fisher Bioreagents), Poloxamer 407 (SIGMA), and distilled water. The membrane phase was prepared using soybean oil (Basso) and Span 83 (Alfa Aesar) as an emulsifier. The internal phase consisted of sodium alginate (ROTH), Pluronic P-123, distilled water, methanol (Lach-Ner), and sodium diclofenac (SIGMA), as a model hydrophilic drug. A volume of 12.3 cm³ with $50 \text{ g} \cdot \text{dm}^{-3}$ solution of diclofenac sodium in methanol was added to 287.7 cm³ of the internal phase so that the concentration of the active compound in the final product was 1 mM $\cdot \text{dm}^{-3}$. Table 5.4.1 shows the weight content of individual emulsion components.

Table 5.4.1: Composition of multiple emulsion phases

Emulsion phase	Composition		
	1.91 wt.% sodium alginate, 0.24 wt. Pluronic		
Internal	P-123, 0.041 wt.% methanol, 0.0021 wt.% di-		
	clofenac sodium, distilled water		
Continuous	2 wt.% Span 83, soybean oil		
	0.25 wt.% poloxamer 407, 0.20 wt.% sodium		
Mombrono	carboxymethylcellulose (CMC), 0.25 wt.%		
Membrane	Pluronic P-123, 0.25 wt.% Tween 80, distilled		
	water		

Preparation of double emulsions in a Couette-Taylor Flow contactor

Double emulsions were prepared in a helicoidal contactor, also called a Couette-Taylor flow contactor (CTF), following a procedure proposed by Dluska et al. (2009). Liquids were pumped through the annular gap between two coaxial cylinders. The inner cylinder rotated while the outer one remained stationary. To produce $W_1/O/W_2$ type emulsions, three streams of different compositions were introduced to the contactor. The internal, membrane and external phases were fed to the annular gap of a CTF contactor as shown in Figure 5.4.2.

The inner diameter of the outer cylinder was 35 mm and the outer diameter of the inner cylinder was 25 mm. A sleeve reducing the width of the gap to 1.5 mm was put on the inner shaft (cylinder). The length of the contactor was 40 cm.



Figure 5.4.2: Scheme of the multiple emulsion's preparation by a one-step method in a helicoidal flow contactor

The incoming phase streams were: 20 cm3/min for the internal phase, 40 cm3/min for the membrane phase, and 60 cm3/min for the continuous phase. The phases were pumped to the contactor by three Masterflex L/S peristaltic pumps (Cole - Parmer Instrument Company). Emulsion samples intended for stability tests and drop size analysis were prepared using various rotational frequency settings (in the range 925-1264 rpm) to examine the impact of flow hydrodynamics on emulsion characteristics and stability. Other operating conditions such as the annular gap size, the phase volume ratios, and the phase volumetric flow rates remained constant. Analogously, a second set of fresh samples was prepared for encapsulation and drug release tests, at similar conditions.

Evaluation of emulsion stability

Except for micro-emulsions, all emulsions are inherently thermodynamically unstable. The ability of an emulsion to resist changes in its physicochemical properties over time is referred to as "kinetic stability" (McClements, 2005). The most common emulsion destabilisation mechanisms include creaming, coalescence, flocculation, Ostwald ripening, and in the extreme case phase inversion (Tadros, 2014). The term stability will be used to refer to kinetic stability throughout the rest of this paper. The emulsion stability was assessed by analysing changes in the mean droplet diameter of the internal and membrane phases. During a sixty-day study period, a series of microscopic images were taken for each sample at subsequent time points following preparation. The images were taken for each sample using an Olympus SC50 camera, an Olympus CellSens program, and an Olympus BX-60 optical microscope. The emulsions were placed on microscope slides as a thin layer and photographed in various locations of each sample.

For each image, 250 drops of the internal and membrane phases were measured at each time point using the Image-Pro Plus 2D analysis software (Media Cybernetics, Inc.). The arithmetic (Eq. 15.4.1), Sauter (Eq. 5.4.2) and de Brouckere (Eq. 5.4.3) mean diameters, as well as polydispersity indexes (Eq. 5.4.4), were calculated.

$$d_{10} = \frac{\sum_i N_i d_i}{\sum_i N_i} \tag{5.4.1}$$

$$d_{32} = \frac{\sum_{i} N_{i} d_{i}^{3}}{\sum_{i} N_{i} d_{i}^{2}}$$
(5.4.2)

$$d_{43} = \frac{\sum_{i} N_{i} d_{i}^{4}}{\sum_{i} N_{i} d_{i}^{3}}$$
(5.4.3)

$$PDI = \frac{d_{43}}{d_{32}} \tag{5.4.4}$$

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Where; d_i – drop diameter; N_i – number of drops of d_i size in population.

Emulsions were considered stable if the Sauter diameters of both phases did not change by more than 15% over a period of 60 days, relative to the measurement taken immediately after emulsion formation.

Rheological measurements

Rheological properties were tested using a RheolabQC C-LTD80/QC rotational viscometer (Anton Paar). The emulsion samples were thermostated during the measurements. The tests were carried out at temperatures of 24 °C and 37 °C. Measurements were carried out at a lower temperature to determine the properties of the emulsion immediately after preparation and at 37 °C, corresponding to the conditions of application to the skin.

In-vitro drug release and encapsulation efficiency study

The *in vitro* drug release study was performed using the dialysis membrane. Dialysis membranes with an appropriate molecular weight cut-off (MWCO) of 14 kDa were used in this procedure. A suitable high MCWO value allows the drug to diffuse from the internal to the external medium through the semi-permeable dialysis membrane (Kim et al., 2021). 2.5 cm³ of the tested emulsion and 2.5 cm³ of phosphate buffer (PBS) were added to the dialysis bags. The samples were diluted to avoid plugging the membrane pores. Sealed bags were immersed inside tubes filled with PBS to a volume of 50 cm³. The samples were thermostated at 37 °C with a buffer pH of seven to simulate the surface conditions of skin inflamed following irradiation (Auerswald et al., 2019). Maintaining a constant pH level is important because CMC is a pH-sensitive polymer and changes in acidity affect the diffusion rates of the encapsulated drugs (Rowe et al., 2009). In order to determine diclofenac concentration changes in the external medium, samples of the liquid in which the membranes were immersed were taken at fixed time intervals. After collecting 2 cm³ of the sample from each tube, the external medium was replenished with buffer - to a volume of 50 cm³. To assess the amount of medicine released from the internal droplets and encapsulation efficiency, samples of the external phase were diluted, filtered through syringe filters (nylon, 0.45 µm, Bionovo), and analysed by a spectrofluorimeter (Jasco, Model FP-6500).

In-vitro therapeutic effect study

The K21 fibroblast line was chosen to study the effect of emulsion-encased diclofenac on irradiated human cells. Cells were cultured in 10 cm diameter dishes in F10 Hams' (F-10 Nutrient Medium) supplemented with 10% fetal bovine serum (FBS) and 1% penicillin-streptomycin (Pen/Strep) solution to protect against infections. Cells were grown to 80-90% confluence and passaged with trypsin. K21 fibroblasts were cultured in an incubator at 37 °C and 5% CO2. The medium was withdrawn from the cell culture and 5 cm3 of PBS was added to each dish. The cells in PBS were then irradiated (Crosslinker CL-1000) with UV doses of $15 \text{ J} \cdot \text{m}^{-2}$. UV radiation at approximately $15 \text{ J} \cdot \text{m}^{-2}$ has a similar biological impact on a monolayer of cells on a plate as a dose of ionizing radiation of 2 Gy (Pan et al., 2013; Han et al., 2014), which is a fraction dose commonly used in radiotherapy (Kirkpatrick et al., 2010; Ling et al., 2010; Castle & Kirsch, 2019). One of the dishes where the cells were growing was not irradiated as an experimental control. After irradiation of the cells, PBS was drawn from the dishes, and 10 ml of complete medium (F-10 + 10% FBS + 1% Pen/Strep) was added to each dish. The fibroblasts were then further cultured in an incubator (37 °C, 5% CO₂). After 24 h, pictures were taken under a microscope (NIKON). PBS was extracted from the cells before treating them with a diclofenac solution or the emulsion. A volume of $10^{-4}dm^3$ of the prepared media was added to them and incubated for72 h. Cell viability was measured after 24, 48, and 72 h of incubation. $10^{-5}dm^3$ of Presto Blue reagent were added to the wells of a multi-well plate containing cells, and after 4 h, relative fluorescence was measured (at the wavelength of 535/590 nm) using the DTX880 Multimode Detector (Beckman Coulter).

Results and discussion

Characteristics of sodium diclofenac-loaded emulsions

All obtained emulsion samples were milky white, opaque, and optically homogenous liquids.

Creaming was visible in samples that had been left unstirred for more than a day. This effect was easily reversible by shaking. Using different contactor cylinder frequency settings, water-in-oil-in-water multiple emulsions (D1 \rightarrow 925 rpm; D2 \rightarrow 976 rpm, D3 \rightarrow 1155rpm, and D4 \rightarrow 1254 rpm) with varying average droplet sizes were obtained. Drop sizes for the membrane phase ranged from 18.59 µm for D3 to 25.15 µm for D1, while those for the internal phase - from 7.62 µm for D3 to 9.89 µm for D1, as shown in Figure 5.4.3.



Figure 5.4.3: Sauter mean diameters of multiple emulsion drops as a function of the rotational frequency in the CTF contactor

All of the produced systems remained kinetically stable during the 60 days. The emulsions were characterised by a relatively low polydispersity index, ranging from 1.20 to 1.39 for the membrane phase and from 1.44 to 2.06 for the internal phase.

A high degree of sodium diclofenac encapsulation was observed for all samples tested, ranging from 91.7% to 95.8%. Within 141 hours, most of the drug contained within the internal phase of the emulsion was gradually released (Figure 5.4.8). During this time, the medicine was released in mass fractions from 0.84 to 0.89 of the initially encapsulated amount. Figures 5.4.4 and 5.4.5 depict examples of a diameter size distribution and a microscopic photograph of an emulsion. The samples were generally characterised by a monomodal distribution of drop diameters.

All emulsions created in this study all exhibited a shearthinning rheology fluid properties. As seen in Figures 5.4.6 and 5.4.7 apparent viscosity decreases with increasing shear stress. This is a desirable feature for pharmaceutical and cosmetic preparations administered topically to the skin. This allows the quick spread of the product layer across the skin, fol-



Figure 5.4.4: Drop size distribution for the multiple emulsion sample (D3)



Figure 5.4.5: Microscopic image of multiple emulsion (D3)



Figure 5.4.6: The rheological curve of emulsion D4 at 37 °C

lowed by the deposition of a thin layer of the product on its surface (Suñer-Carbó et al., 2019).

The active ingredient is diffused through all emulsion phases as part of a multi-stage release process. The mathematical description of this mechanism is complex and should include the structure of the emulsion (drop size and volume packing fraction), drug transport parameters in the form of effective diffusion coefficients and drug consumption (Dluska et al., 2017, 2022).

Parameters such as drop size, composition, and rheological properties of the emulsion may be altered to control the drug release rates (Dluska et al., 2020). Table 5.4.2 illustrates the results of the viability of K21 cells following UV irradiation without (control) and with the addition of solutions or emulsions (D1) containing diclofenac.

The viability of cells in the control sample significantly de-



Figure 5.4.7: The emulsion rheological curve of emulsion D3 at 24 °C



Figure 5.4.8: The emulsion rheological curve of emulsion D3 at 24 °C

Table 5.4.2: The results of cell line K21 viability for diclofenac solutions, emulsions, and control

time [h]	24	cell viability [%] 4 diclofenac solution diclofenac emulsion		
24	43	56	76	
48	24	58	88	
72	7	81	95	

creased after the irradiation. In samples containing diclofenac solutions and emulsions, a gradual rise in viability can be observed with incubation. The increase in cell viability visible in diclofenac-treated samples was greater when drug-loaded emulsions were applied. The effect was also dose-dependent in the considered drug concentration range. All of the excipients used for the formulation are generally regarded as nontoxic and non-irritant at utilized concentrations and are commonly included in topical emulsions (Rowe et al., 2009).

Conclusions

In this study double water-in-oil-in-water emulsions were proposed as carriers for the topical delivery of NSAID drugs. The multiple emulsions were prepared by a one-step process using a CTF contactor. Samples were characterised by a relatively low polydispersity index, which demonstrates the homogeneity of the drops and allows for dose measurement reproducibility. The release of the active substance occurred in a gradual manner, which suggested that presented emulsions could be used as extended release formulations. Drug-carrying multiple emulsions are a promising alternative to instant release products currently widely available on the market. The rate of drug release decreased over time, which is beneficial because it enables the patient to receive an initial active dose of the medication fast, and maintain its concentration for a longer period of time. An in-vitro study on irradiated skin cells suggested that the proposed emulsion-based formulation was more effective in promoting cell viability than instant release products (represented by a solution of diclofenac). The observed stability of the emulsions at room temperature makes them more convenient to store. However, their long-term shelf-life is yet to be examined. These findings indicate that the tested double emulsions could be used to treat skin inflammations caused by radiotherapy in the treatment of cancer. To adjust the drug release rates, emulsion preparation conditions in the CTF contactor may be changed, such as the inner cylinder rotational frequency (to change the structure and drop diameters), apparatus dimensions (contactor gap width), and emulsion composition (to adjust viscosity and drug transport rate). All these factors above alter encapsulation efficiency and drug release rates (Dluska et al., 2020, 2022). Different doses of the drug may be encapsulated if needed. The above mentioned properties of the created multiple emulsions make them promising carriers of anti-inflammatory drugs and other active substances, especially if an extended release is desired.

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6 Abstracts: Analytical chemistry & nanotechnology

6.1 A modulation of response in a lymphoblastic leukaemia on zinc oxide nanoparticles through a polyethylene glycol coating

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KEYWORDS: ZnONPs, leukaemia, PEG, cytotoxicity.

One of a parameter, which defines nanomaterials, is the high surface-to-material volume ratio. The nanomaterial surface characterises its properties (for example an ability to catalyse reactive oxygen species-related reactions) and potential application. Understanding the mechanism of cytotoxicity of the one, selected nanomaterial is crucial for its practical application, where zinc oxide nanoparticles (ZnONPs) are a good example of it. Surface modification of the zinc oxide nanoparticle would allow for assessment of the nanomaterial surface in disruption of homeostasis of the selected cellular model.

For the assessment of the role of nanomaterial surface in ZnONP cytotoxicity, the CCRF-CEM cell line was incubated with bare or polyethylene glycol-coated zinc oxide nanoparticles. Low molecular weight markers of redox homeostasis, such as reduced glutathione or NADPH, were measured as same as the main enzymes of antioxidative defence (CAT, SOD, GPx). Experiments also include quantitation of reactive oxygen species generation, membrane fluidity and expression of genes response for zinc homeostasis maintenance in human cells.

Results of experiments indicate moderation of the effect of a decrease in the amount of reduced glutathione and increased reactive oxygen species generation when the uncoated and modified nanomaterial is compared. Nanoparticle coating leads towards an upturn of membrane fluidity and inhibition of increased catalase activity. It has been shown an increase in mRNA level for metallothionein 2A and a decrease in the expression of zinc plasma membrane transporters independently for the nanomaterial surface coating.

An explanation for received results is reduction of access to nanomaterial functional surface by the nanoparticle coating. This process generates a spatial impediment and leads to decrease contact between nanomaterial and the acidic environment of autophagosomes, which are generated during ZnONP endocytosis. In acidic conditions, ZnONPs effectively release free zinc ions. Received results correlate with the current state of knowledge connected with the ZnONP surface modification and support the hypothesis considering free zinc ion release as the main factor of the toxicity of zinc oxide nanoparticles.

6.2 Bio-based polysaccharide nanoparticles as a promising carriers for hydrophobic drugs delivery

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Keywords: dextran, surfactants, nanomicelles, self-assemblydrug delivery.

Although cancer diseases has been explored for decades, they still exist as one of the leading causes of death worldwide. Nowadays, the knowledge that the use of nanocarriers may support conventional chemotherapy strongly expands cancer research. Among many types of nanoparticles, polymeric micelles got extraordinary attention, primarily due to their small size, high biocompatibility, and the possibility of additional functionalization (eg. towards selective targeting or environmentally-triggered drug release). These physicochemical properties translate directly into their advantages in the context of anti-cancer drug delivery systems. Another key advantage is the relatively easy methods (nanoprecipitation and solvent evaporation) of self-assembling micelles synthesis and the possibility of process upscaling. Nevertheless, the difficulties associated with their characterization may occur.

In the presented work, dextran – a natural polymer produced by Leuconostoc mesenteroides, was modified. The novel macromolecular surfactants were obtained by the permanent bonding of long hydrophobic hydrocarbons (lauric acid and 11-aminoundecanoic acid), as well as by attaching cancer-targeting molecule (folic acid) to the dextran chains. Different degrees of substitution to dextran chains allowed us to screen the synthesized structures toward the best characteristics.

The obtained nanoparticles size ranges were between 50-200 nm (DLS), which partially confirmed the micellar character of obtained nanovesicles. Measured negative surface charge allows for assumptions that produced nanoparticles would not rapidly aggregate and have a great potential to be applied in human serum. Obtained new materials were confirmed by Fourier Transform Infrared Spectroscopy and Nuclear Magnetic Resonance Spectroscopy. Nanoparticles formation was studied by Dynamic Light Scattering to evaluate size distribution. Attempts to determine critical micelle concentration by utilizing pyrene as a fluorescent probe and surface tension measurements were made. The following studies will be carried out on the cytotoxicity and selectivity of obtained nanomaterials.

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7 Abstracts: Bioengineering, biotechnology, biomedical engineering

7.1 Particle Image Velocimetry of 3D-printed blood vessels

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KEYWORDS: Particle Image Velocimetry, micro-PIV, 3D printing, anatomical vascular models.

The study of biomedical fluid dynamics using non-intrusive visualizing methods on a micro-scale has become possible using a proper 3D inkjet printing process. This printout is fully transparent and allows fluid dynamics measurements to be carried out inside the printout using measurement techniques such as PIV.

The Computed Tomography of the patient with atherosclerosis was 3D printed with inlet diameter around 4 mm and measured with different constant flow rates. The procedure to obtain a proper 3D printed model with high-quality optical access usable for Particle Image Velocimetry has been discussed. Extremely important is fluid with a corresponding refractive index. The results of the PIV shows a multi-stitched color-code vector map from the axis cross-section along the whole 3D printed model.

Figure 7.1.1 shows one example of the obtained PIV results. The results of this work show that 3D prints allow for the creation of desired geometry and can be used to investigate severe pathologies of the human circulatory system.



Figure 7.1.1: Vector statistic and velocity magnitude $(m \cdot s^{-1})$ along whole blood vessel for Re = 432.

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7.2 Poly(1,3-propanediol citrate)-based nonwovens for ex-vivo cell culturing

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KEYWORDS: citric acid, citrate-based polyesters, nonwovens, electrospinning.

At present, there are several types of biodegradable polyesters on the market. One of their applications is the fabrication of artificial extracellular scaffolds. They can be used as matrices for ex-vivo cell culturing and offer new possibilities for reconstructing damaged tissues. The premise of tissue engineering is to combine autologous cells and synthetic scaffolds, creating temporary support for the growing tissue and the formation of a three-dimensional structure. Poly(1,3-propanediol citrate) is considered interesting for tissue engineering applications. It is a polyester based on citric acid, a substance taking part in natural human metabolic pathways.

This work reports the synthesis and study of poly(1,3-propanediol citrate). The polyester structure was characterised by FTIR, NMR and the end-group titration methods. Polymer films were obtained and characterised. In several mass content ratios, nonwovens of poly-L-lactide and various poly(1,3propanediol citrates) were made via electrospinning. Swelling properties were characterised, and gel content was calculated. The degradation time of the polymer films was studied. Two liquids (water and diiodomethane) were used for calculating total surface energy by measuring liquid contact angle values. Based on that, the effect of the poly(1,3-propanediol citrate) addition on the surface hydrophilicity was examined. Cytotoxicity tests were performed to assess the suitability of nonwovens for eventual longer culturing. The studied nonwovens appear to be noncytotoxic.

Performed studies allow for considering possible applications in the field of biomaterials and tissue engineering.

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7.3 Chitosan-based modifications of porous polylactide bone substitutes

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Keywords: polylactide, chitosan, surface modifications, spongy bone substitutes.

Bones are prone to mechanical damage, e.g. fractures and contusions. Bone tissue is capable of regeneration, but only to a limited extent. If the damage is too vast, it requires special treatment. In that case, porous biomaterial substitutes are of use, providing an attachment site in the form of an artificial scaffolding for the reconstruction process. Polylactide (PLA) may be used for preparing such substitutes as it is non-toxic and bioresorbable. To reduce the hydrophobicity of polylactide scaffolds, surface modification can be conducted, e.g. by applying hydrophilic chitosan layers, improving cell adhesion and proliferation.

Porous polylactide substitutes have been obtained via the freeze extraction variant of the phase inversion method. The substitutes were modified by coating them with a bioactive layer of chitosan. Different types of chitosan have been used. Chosen properties of the substitutes have been studied. The presence of chitosan on the scaffolds was confirmed by infrared spectroscopy, elemental analysis and scanning electron microscopy. Both the external and internal surfaces were examined. The effect of chitosan addition was examined by analysing bulk absorbability, open porosity (hydrostatical weighing) and elasticity (static compression). The application of chitosan decreases open porosity and bulk absorbability. After modification, the elasticity of the substitute decreases due to the high rigidity of chitosan. Cytotoxicity tests were performed to assess the suitability of substitutes for eventual in vivo studies.

Chitosan-based surface modifications of PLA substitutes for bone regeneration affect their structure and properties. Chitosan can be found mainly on the lateral surface of the substitutes, whereas the interior of the substitutes is poorer in the polymer. Prepared substitutes can be pre-qualified as suitable for spongy bone reconstruction.

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7.4 Stability of nanobubbles in water solutions of chosen surfactants

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Keywords: nanobubbles, nanodispersion, stability, pluronic, carbon dioxide.

Nanobubbles, due to their unique properties, have become the subject of research by scientists around the world. New methods of generating bubble nanodispersions are still being sought and developed. The research, that allows us to understand their nature and find innovative applications in chemical engineering is still being carried out.

A long time of interfacial contact and increased specific surface area are one of the few properties that allow not only for the intensification of processes, but also the use of nanobubbles in the fields of biology and medicine. One of the applications constituting the basis for the following work is the generation of a time-stable carbon dioxide nanodispersion for use in carboxytherapy, leading to the reduction of foot ulcers for diabetic patients.

A set of experiments were carried out with the aim of examination of the influence of changes in hydrodynamic conditions, physicochemical parameters, and generation time as independent variables on the stability of the produced carbon dioxide nanodispersion in aqueous solutions of selected biocompatible surfactants.

A prototype system consisting of a porous membrane and a disc stirrer was used to generate dispersions of nanobubbles. The densities of the nanobubble diameter distributions were measured, and the Sauter diameter was calculated on their basis.

We found out that the Sauter diameter of nanobubbles is affected by the change of rotation rate of the stirrer (shear stress), the critical micellar concentration of surfactant and the time of generation. These three parameters should be considered when designing the process of nanobubble generation with surfactant.

The results obtained in this work allowed us to extend the knowledge on the methods of generation of a stable nanodispersion of the tested gas in aqueous solutions of selected surfactants.

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7.5 Pseudo-gel ternary systems of xanthan gum in water-ethanol solutions for industrial applications

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Keywords: xanthan gum, ethanol, pseudo-gels.

Thickening agents are widely used in many industries. The choice of the thickening agent is very important, as it determines both the properties of the final product, and the technological production process.

Xanthan gum is an anionic polysaccharide built from repetitive units of β -D-glucose connected in C₃ position with trisaccharide chain made up of two D-mannose molecules linked by D-glucuronic acid. The water solution of xanthan gum demonstrates characteristics of pseudo-gel, with the relaxation time increasing exponentially as a function of time. The increase in viscosity of the aqueous xanthan solution is due to the entanglement of polysaccharide chains and intermolecular interactions. The solubility and intermolecular association capacity of aqueous xanthan gum solutions can be influenced by various factors, especially alcohols, which promote conformational changes in the structure and leads to a gelation process.

The study investigated the effect of pseudo-gel ternary systems as thickening agents for industrial applications. Formulations differing in the mass proportion of xanthan gum and the solvent ratio were used to get model mouldings. Additionally, the rheological properties of selected suspension powder masses were investigated. The loss of mass during drying under different conditions was evaluated (50 °C/72 h; 115 °C/45 min). Thermal stability of mouldings and pseudo-gel systems was examined with DSC-TG. The internal structure of the samples was assessed based on the absorption, porosity and lipophilicity tests. SEM imaging was used to visualize the internal structure. A hardness test with surface analysis using a profilometer was carried out.



Figure 7.5.1: Graphical abstract presenting research results on pseudo-gel ternary systems of xanthan gum

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7.6 Synthesis and performance properties study of poly(1,2-ethanediol citrate) for bioengineering

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Keywords: citric acid, ethylene glycol, polycondensation, optimization.

The prevalent challenge facing tissue engineering is the lack of adequate vascularization to support the growth, functionality and viability of tissue substitutes that require blood vessel supply. Hence, new biomaterials among aliphatic polyesters are still in demand for the production of cellular scaffolds. In response to today's challenges in regenerative medicine, a new class of biomaterials based on citric acid and diols has been reported.

There is currently no literature focusing on poly(1,2-ethanediol citrate). Both citric acid and 1,2-ethanediol have medical applications and are fully resorbable by cells. Citric acid is the key metabolite in the Krebs cycle. Ethylene glycol is used in cosmetics as a moisturizing agent. The multifunctionality of both citric acid and 1,2-ethanediol is favorable for postprocessing. Polymer chain cross-linking via thermal polycondensation sacrifices valuable pendant carboxyl and hydroxyl chemical groups.

The synthesis of poly(1,2-ethanediol citrate) has been developed in catalyzed reaction with water removal by Dean-Stark apparatus. A wide range of products, differing in form and molecular weight, were obtained depending on synthesis conditions. The polyester structure was characterized by FTIR and NMR spectroscopy. The influence of temperature and catalyst content on the degree of esterification and conversion of acid groups in citric acid is described. The optimization was performed with the criterion of maximizing the degree of esterification. A preliminary assessment of cytotoxicity was carried out as part of the study. Preliminary studies show the potential of poly(1,2-ethanediol citrate) for further research towards tissue engineering applications.



Figure 7.6.1: The concept of synthesis and performance properties study of poly(1,2-ethanediol citrate) as a new material in bioengineering

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7.7 Application of computational fluid dynamics to assess the risk of hemolysis in patients with atherosclerosis.

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KEYWORDS: hemolysis, atherosclerosis, CFD.

Computational fluid dynamics is a frequently used tool in biomedical engineering. As part of this research, several blood flow simulations were performed for different shapes of cholesterol constrictions. The presence of contractions in blood vessels causes a local increase in linear velocity and an increase in shear stresses. If the stresses are high enough, the continuity of the surface of the erythrocyte may be interrupted, and consequently the hemolysis may occur.

A series of modified geometries of blood vessels differing in narrowing parameters such as cross-sectional area or degree of eccentricity were used. The geometries were developed based on the real geometry of the blood vessel obtained based on computed tomography. The simulation was performed using the ANSYS Fluent software with the new model of blood rheology model – Population Balance based Rheology implemented.

Based on the analysis of a number of different shapes of the narrowing and flow values, a correlation was obtained connecting the shape of the narrowing hydrodynamic parameters with the value of maximum stresses in the area of the narrowing. These dependencies may, in the future, help to quickly pre-analyze the risk of hemolysis without the need for timeconsuming calculations using advanced software and may become part of routine diagnostics.



Figure 7.7.1: Contour plot of shear stresses [Pa] on the blood vessel wall for a constriction with an area of 9% of the area before the constriction for a flow of 3.12 mL s^{-1} .

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7.8 Lab scale *in vitro* urolithiasis model for rapid screening of substances of various origins

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KEYWORDS: urolithiasis, in vitro model, dynamic flow model, kidney stones, disease modelling.

About 32-40% of patients in Ukraine turn to urologists every year precisely because of urolithiasis. Drug treatment of this disease is not so common, although it is the third optimal way of treating this disease. Therefore, for preclinical research, the creation of a model that will be as similar as possible to the human body is a significant improvement.

The purpose of work: creating a lab scale model for studying the influence of substances of various origins on the process of urolithiasis for future usage in research and clinical trials. We analyzed existing studies, related to our topic that included laboratory models, discovered their imperfections in comparison with the human excretory system and created a new model, taking into account all these points: the control of the speed of urine movement in the system, the temperature regime, the presence of cycles of urine accumulation in the bladder, the length of these cycles and the dimensions all components of the installation. We are using artificial synthetic urine, 2 flasks, silicone tubes, peristaltic pump, 3 filters and a urine bag.



Figure 7.8.1: Lab scale in vitro urolithiasis model

The result of our work was the creation of our model simulating the conditions of the human excretory system:

- the structure;
- the temperature regime (37±0.5 °C);
- the speed of movement of liquid through the system is 0.4- $0.5 \text{ ml} \cdot \text{min}^{-1}$.

Also we determined the types of analysis for monitoring the operation:

- titration of calcium;
- microscopy of the general sample;
- weighing of deposits;
- measurement of the size of stones.

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7.9 Application of mathematical modeling technology in upper limb prosthetics

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KEYWORDS: prosthetics, upper limb prosthesis, mathematical modeling, static mathematical modeling, dynamic mathematical modeling, pediatric prosthetics.

Nowadays, the development of prosthetics is becoming an increasingly important issue, especially in Ukraine number of patients with traumatic amputations continuing to grow. Since prostheses are devices that a person use for a long time, these devices must meet ergonomic, functional and aesthetic requirements. These requirements should include ease of use, lightness, durability and attractiveness. To achieve the best results, the engineers need to create a good mechanical design, internal mechanism and choose the best materials. So, it will be useful to find a method which can help to find best engineering solutions.

The purpose of work: analise an application of mathematical modeling in designing upper limb prosthetics. Mathematical modeling is the derivation of a certain mathematical function that provides a qualitative and quantitative understanding of observations, which is useful for responding to them. Mathematical modeling is often seen as a preliminary phase of prosthesis development, in example before the creation of a controlled physical object. Using articles from different internet scientific editions was found main problems in prosthetics that can be solved by mathematical modeling, namely:

- determination of the design, which takes into account the parameters of the patient's body parts;
- evaluation and parametrization of parts movements;
- creating of wear resistance of control devices;
- calculation of wear resistance and critical loads of the material.

Since the human body has a complex structure and shape, creating a model of a body part is quite a challenge but using static mathematical modeling can help make it easier. Another important aspect of modeling is body movements. Dynamic mathematical modeling is used for this purpose. This method allows you to evaluate how to describe the bending motion of a particular part. CAD systems make it possible to parameterize the geometry and perform other engineering tasks to ensure aesthetics and functionality. Having such a model of the prosthesis, it is then possible to study loads, deformations and displacements, to estimate the weight of the future product. This approach can also significantly improve pediatric prosthetics, where the most difficult aspect is the correct selection of the right size of the prosthesis and manufacture of a large number of prostheses for the patient during his or her growth.

In a result, mathematical modeling can speed up the time of modeling prototypes and products, calculate the cost of materials, and predict the behaviour of circuit elements and the model as a whole.

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7.10 Controlled formation of highly porous polymer-calcium phosphate granules with defined structure

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Keywords: tissue engineering, biomimetic scaffolds, biomaterials.

Autologous iliac crest bone transplants are dangerous, yet still considered the gold standard in patients afflicted by bone resection. Living human cells can reconstruct tissue when they can proliferate in an environment enabling 3D growth. Ideal scaffolds should provide good transport of oxygen and nutrients, a large surface-to-volume ratio, conditions for cell adhesion, and mechanical integrity of the original tissue. The granulated form is appreciated in dentistry, where removed tooth cavities can be conveniently filled with granulated biomaterial. Pore size in the scaffold can be controlled by manipulating the particle size, which is essential for the early stages of regeneration.

This work presents the manufacturing of porous, polylactic acid (PLA)- β -tricalcium phosphate (β -TCP) granulates. Our goal was to prepare a synthetic biomaterial suitable for cell attachment and proliferation in bone defects or resections. The solvent-induced phase separation (SIPS) process has been successfully adapted for obtaining composite PLA/β-TCP porous particles in the 0.8 -1.2 mm diameter range, with 69 - 89% porosity. Two types of biomedical PLA were used - Biomer L9000 and Resomer LR706S. DoE approach was used to determine standardised effects of process parameters - PLA, β-TCP and emulsifier concentrations, temperature, and mixing speed. Granulates were thermally fused into 12 mm diameter porous discs. The scaffolds have been proven non-cytotoxic to L929 cells in vitro. The osteogenic potential of prepared scaffolds has been measured in vitro with alkaline phosphatase activity in human mesenchymal stem cells culture for 3 weeks. Cells were visualised with confocal microscopy and alizarin red staining to show calcium deposits produced by cells. Those studies revealed that Resomer granulates had been overgrown with elastin fibres, and calcium staining can be visible after 3 weeks.

Prepared granulates could potentially build the synthetic bone regeneration scaffold upon thermal assembly. They can be fused into shapes with desired porosity, mimicking the structure of natural bone tissue. Further in vivo tests are the next step in testing the usefulness of our developed alternative to auto-, allo- or xenografts as applied to regenerate damaged bone tissue.

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7.11 Color calibration in the study of the vitamin C oxidation process using deep neural networks

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Keywords: color calibration, deep neural networks, vitamin C, oxidation.

The purpose of this work is to recognize the state of oxidation of vitamin C based on the color of its solution in distilled water. Vitamin C is a vital ingredient in many food sources. Establishing the state of oxidation of vitamin C could be used as one of the ways to assess the freshness of food.

Several steps were taken in order to prepare the dataset. First, the template of shades of yellow was created derived from colors of oxidized vitamin C in a solution of a fixed concentration in different stages. The second step was the main data collection, which included preparation of vitamin C solution in distilled water and recording the oxidation state during time intervals by taking photos of the solution with the previously mentioned template within the frame of the picture. Differently concentrated solutions were tested to find the one with optimal oxidation rate. The third step included the calibration of images based on the template included in the pictures. The RGB values of the images were recalculated in a way that caused the template values in the images to match their real values. After calibration images of the solution were divided into smaller parts to enlarge the dataset. The last step consisted of the design and improvements of a deep neural network that would allow to establish the oxidation state of vitamin C. Various models were tested. Different network architectures were considered and various optimization techniques were investigated. In addition, several activation functions were incorporated into the implementation process.

The optimal model which could be used to recognize the oxidation state of vitamin C could be an indicator that it could be possible to establish the freshness of food based on its color. Of course there is a need to take into consideration different dyes used in the food industry, however, it would be a step which would be considered in the future experiments.

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7.12 Influence of colour space model of an image in melanoma detection.

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Keywords: colour space models, deep neural networks, melanoma.

The aim of this work is to compare various algorithms designed for automated diagnosis of melanoma which is the most lethal skin cancer. Especially, the influence of colour space model of an image in melanoma detection is analysed.

As for now, a painless technique used for an early detection of melanoma is dermoscopy, or epiluminescence microscopy (ELM). Thanks to that, it is possible for the doctor to evaluate the patterns of shape, pigmentation and size of skin lesions. Nevertheless, it can be time consuming and the automated method which would allow to detect the melanoma by analysing picture of the lesions, would highly improve the early detection process.

Various studies show, that different colour space models, can influence the results of neural network classification with the use of images. Presented study tries to establish whether this aspect can be used in the medical field, in particular, in previously mentioned melanoma detection. The dataset, obtained from Kaggle Melanoma Detection Dataset, is divided into three sets: training dataset (2000 images), validation dataset (150 images) and test dataset (600 images). Each dataset contains images of melanoma, nevus and seborrheic keratosis. Results of detection for various colour space models, such as, RGB, HSV, YUV and CIELab with the usage of several neural networks are compared. The exemplary neural networks used are, among others, ResNet and DenseNet. Moreover, different number of network architectures and various optimalization techniques are used. The possible application are discussed and further development is debated.

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7.13 Application of rocking-motion disposable bioreactor for proliferation of Nicotiana tabacum BY-2 cells expressing recombinant proteins

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Keywords: recombinant proteins, plant expression systems, BY-2, agroinfection.

Among leading products of the biopharmaceutical industry, recombinant proteins occupy an unwavering position among newly developed pharmaceutical products. Considering the high costs and limitations of conventional expression systems plant-based approach becomes competitive solution for recombinant protein manufacturing due to costeffectivity, lack of animal components and adaptability to scale-up procedures in various bioreactor systems. In the presented study we aimed to investigate optimal culture conditions in rocking-motion bioreactor for efficient proliferation of *Nicotiana tabacum* BY-2 cell suspension expressing selected recombinant proteins.

An originally designed plasmid carrying expression cassette for the gene of interest under the control of CaMV 35S constitutive promoter was synthesized based on the pCAM-BIA1305.1 vector and isolated. For the purpose of thesstudy a gene for the receptor-binding domain of Sars-CoV-2 glycoprotein was used as a potential vaccine antigen. The obtained plasmids were introduced via electroporation to Agrobacterium tumefaciens. Transformed bacteria were used for further agroinfection procedure of *N. tabacum* BY-2 cells and resulting transformants were transferred for 7 days to a selective LS medium containing hygromycin B and cefotaxime. Transformed BY-2 cell suspensions were cultured for ten days in ReadyToProcess WAVE 25 system equipped with a 2-litre Cellbag disposable container. Various mixing parameters and relative growth kinetics were investigated.

Application of rocking-motion disposable bioreactor demonstrated 1,47-fold higher proliferation of BY-2 cells compared to conventioanal cultures maintained in the flasks. Analysis of culture parameters shows dissolved oxygen concetration as the main growth limiting factor requiring intensification of mixing parameters along with culture duration. Moreover, proteomic analysis proved significant product expression.

The presented study demonstrated an efficient method of BY-2 cells proliferation in rocking-motion disposable bioreactor allowing for efficient recombinant protein manufacturing via a plant expression system.

7.14 Remodeling of calcium phosphate to hydroxyapatite in a batch reactor

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Keywords: 3D printing, bone scaffolds, polycaprolactone, polylactide, tricalcium phosphate.

3D printing is a promising technique for obtaining bone implants. However, 3D printed bone implants, especially those printed using fused deposition modelling, are still in the experimental phase despite decades of work. Research on new materials faces numerous limitations, such as reagents' cost and machines' high prices to produce filaments for 3D printing polymer-ceramic composites for fused deposition modelling. We propose another way – a simple, low-cost, and fast method of obtaining polymer-ceramic filaments using apparatus consisting of parts available in a hardware store. Obtained polymer and polymer-ceramic filaments can be used in almost every popular and commercially available 3D printer. We hope that it could lower the price of tailored biomedical implants and accelerate using 3D printed implants in therapy.

The method's versatility for producing the filaments was demonstrated on two different biodegradable polymers – poly(L-lactic acid) and polycaprolactone – and different concentrations of calcium phosphate – β -tricalcium phosphate – in the composite, up to 50% by weight. Polymers were dissolved in dichloromethane and mixed with ceramic. Obtained solutions were poured on a glass bed and dried at 50 °C. The obtained polymer and polymer-ceramic foils were melted in a stainless-steel container of the pressure filament extruder. The melted polymers were extruded through a 2.85 mm nozzle using 4 bar air pressure and collected as 1 m long filament segments. For screening purposes, numerous scaffolds were 3D printed from the obtained filaments on a ZMorph VX commercial 3D printer.

Structural, mechanical, and biological tests show that the scaffolds 3D printed with composite filaments extruded in the proposed device are suitable for bone implants, as their structure, mechanical, and non-cytotoxic properties are evident. Moreover, the proposed method of composite forming is a simplification of the processes of screening materials for manufacturing and researching 3D printed materials with potential applications in the regeneration of bone tissue.

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7.15 Multiple emulsions prepared in a helicoidal flow contactor for topical drug delivery

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Keywords: helical flow contactor, inflammation, multiple emulsions, pharmaceutical emulsions, release process.

Radiotherapy is one of the main methods of cancer treatment. Irradiation with X-rays can cause a set of many disorders occurring in cells and intercellular spaces, causing symptoms such as inflammation, irritation, swelling, itching, fibrosis, or pain. This study analysed multiple emulsions as carriers of an anti-inflammatory drug for topical application, aimed at alleviating the symptoms of skin damage resulting from exposure of patients to X-ray radiation.

The aim of the study was to formulate an anti-inflammatory double emulsion containing diclofenac, which could be applied to skin damaged by ionizing radiation, and to predict its effectiveness by analysing the effect on living cells. The results were compared with the classic preparation, in form of a solution. The emulsions were produced by one-step method in a helicoidal flow contactor with the inner cylinder rotating while the outer cylinder remained stationary. Water-in-oil-inwater $(W_1/O/W_2)$ emulsions have been prepared, by feeding three phase streams to the contactor, at different flow rates and intensely mixing them. The stability of the systems was assessed - its criterion was the lack of changes in Sauter diameters (acceptable error margin ±15%). The rheological properties tests of the emulsions were carried out using a rotational viscometer. In order to assess the anti-inflammatory effect of the emulsions containing diclofenac, studies were carried out using irradiated suspensions of human fibroblast cells. The performance of the double emulsion was compared with diclofenac sodium topical solution.

All of the emulsions displayed properties of shear thinning fluids and maintained their kinetic stability throughout the test period. It was observed that diclofenac release in vitro was happening gradually. The emulsions were characterised by a high drug encapsulation efficiency, above 90 %. Significant increase in cell viability was observed for both – emulsions and solutions, it was greater with the emulsions, and dose-dependent. These results proved that radiation-induced skin injury may be treated using multiple emulsions with the encapsulated anti-inflammatory drug.

7.16 Novel chemical modification in bio-based polymer materials

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Keywords: biomaterials, composites, wood filler, chemical modification.

Depleting deposits of non-renewable raw materials are forcing scientists to develop new alternatives with the use of renewable materials, so a lot of research work has been done in the field of using wood to produce wood-polymer composites (WPCs), which combines the advantages of the constituent materials while reducing the polymer content. In order to increase the application potential of WPCs, attention should be directed to solving existing problems during the manufacture, use and recycling of these composites, which are induced by WPCs insufficient thermal stability, low resistance to microorganisms or insufficient interfacial stability. To this end, an innovative modifying method of wood with a modifier of natural origin has been developed.

As part of the work, studies of physicochemical and structural properties were carried out, evaluating the material's ability to potentially be used in industry and everyday life. Values of the parameters such as tensile strength and elongation of the studied composites, which are directly related to interfacial compatibility of the constituent materials, were obtained thanks to performed mechanical testing. Thermal properties expressed through the relationship of weight loss under increasing temperature were determined using thermogravimetric analysis. Moreover, phase transitions were analysed by differential scanning calorimetry, and the following parameters were determined: melting and crystallization temperatures, degree of crystallinity and half-time of crystallization. The effect of the presence of wood and wood modification on the crystalline structure of WPC composites was investigated by X-ray diffraction. The study was conducted for composite samples made by injection molding, with increasing content of non-modified and modified wood filler from 0 to 30%.

Simultaneous analysis of the results of structural and thermo-mechanical properties of the material made it possible to comprehensively evaluate the influence of the carried out processes on the behavior of obtained WPC composites with wood modified using a modifier of natural origin. The data resulting from the studies provide an introduction to the subject of biomaterials based on synthetic polymers with the concurrent use of plant-based chemical modified fillers.

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7.17 Innovate photocurable resin-based composites for biomedical applications

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Keywords: additive manufacturing, DLP 3D, composites, biomaterials.

Transdermal drug delivery is a medical innovative solution which, compared to conventional methods, can reduce pain, make it easier to personalize drug delivery and reduce gastrointestinal side effects. One of the ways to deliver drugs through the skin is usage of microneedle systems. There are 4 basic types of microneedles: solid, coated, dissolving and hydrogel, which all of them are mainly made of polymers. Due to the huge variety of drugs, there is a need of research to find a suitable material that is compatible with the drug, what means chemical inertness and allowing the drug to be released into the human body through the stratum corneum. Because of that, there was a research undertaken on composite samples made of photocurable resin and hydrophilic drug.

The conducted studies were chosen with a view to the possibility of future application of the resin-drug composite for microneedle systems. For this purpose, an FTIR-ATR study was performed, through which the dependence of the crosslinking degree of the resin on the drug content was obtained. Crosslinking has a significant influence on performance properties of the photocurable resin and its ability to the water absorption. Tensile and flexural strength tests were performed, particularly relevant in the context of removing needles from the skin after the drug delivery process. Evaluation of the resin-drug systems in terms of changes in hydrophilicity was examined using the contact angle measurement method. The specimens with 3 differ drug concentration were manufactured by using of the digital light processing method, which makes it possible to produce very small parts with complex designs, such as microneedles. Printing parameters were constant to facilitate evaluation of the drug presence effect on the properties of the composites.

Due to the performed tests, the suitability of the used resin as a matrix for transdermal microneedle systems was determined, primarily in terms of strength properties and its compatibility with the selected polar drug. The obtained results confirm the validity of further research aimed at obtaining new biocompatible polymer-drug composites with the possibility of their processing by 3D printing methods.

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8 Abstracts: Kinetics & thermodynamics

8.1 Stability of the liquid crystalline nematic ferroelectric phase in binary mixtures

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KEYWORDS: nematic liquid crystals, ferroelectric, phase diagrams.

In 2017, there was information about a new liquid crystal phase (nematic ferroelectric phase). The compound in which it was discovered was RM734¹. Mandle and Kikuchi provided information on new liquid crystal compounds exhibiting a nematic-nematic phase transition. Two distinct nematic phases separated by a first-order phase transition have been discovered².

The aim of the work was to investigate the nematic stability of the ferroelectric phase in binary mixtures. Nine nitro and cyano compounds resembling rods with scarred structures were selected for the study (Fig. 8.1.1).

The results of the research allowed to determine the influence of the structure of compounds on the behavior of the N_f phase.

The main conclusion regarding the occurrence of the N_f phase is the presence of a terminal nitro, methoxy or ethoxy group and a pendant methoxy group in the structure. Probably the wedge shape of the molecule imparted by the polar nitro group is favored by the N_f phase.



Figure 8.1.1: General formula of the compounds: $R=CH_3O$, C_2H_5O , C_5H_{11} , C_3H_7 ; z=1 or 0; $X_1=H$, F; $X_2=CH_3O$, H, F; $X_3=H$, F; $X_4=H$, F; $X_5=H$, F

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8.2 Fuel cells running on recirculated formic acid

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Keywords: DFAFC, recirculation, fuel utilization.

Today we are moving towards living in a zero-waste society that aims to make the most efficient use of our food, materials, and energy. In the case of a Direct Formic Acid Fuel Cell (DFAFC) we can try to extract the energy from the fuel cell as long as there are formic acid (FA) molecules in the tank. This is because the electrical energy is derived from electrochemical reaction: FA oxidation and oxygen reduction. The idea behind the research was to find the best model of delivering fuel to the DFAFC with an eye to getting reasonable efficiency and maximising fuel utilization.

Three systems were tested during laboratory experiments in order to get to know the possibilities and limitations of each way of fuel delivery to the DFAFC:

- 1. DFAFC with no recirculation of the fuel
- 2. DFAFC with step-by-step recirculation of fuel
- 3. DFAFC with continuous recirculation of fuel

Both experiments with fuel recirculation are conducted in the closed system. Step-by-step recirculation means that the fuel at the outlet is returned to the inlet when the inlet tank has run out of the fuel. Continuous recirculation means that the inlet and outlet tank is the same fuel vessel.

Every experiment was initially run on the same FA concentration and the same fuel stream during the whole experiment. While conducting the experiment, voltage and current values were recorded, fuel samples at the DFAFC outlet were taken, and their concentrations were measured in high pressure liquid chromatography analyser at the end of experiment. Due to the voltage-time characteristics with a fixed value of current, systems could be compared regarding the efficiency of DFAFC in the function of time as well as FA concentration.

In the present study, the best results were obtained for the step-by-step model of recirculation. Compared to the DFAFC with continuous recirculation, the step-by-step recirculation model worked much longer for the demanded current. Moreover, the DFAFC performed with a greater power density. Additionally, more energy was extracted from one tank of fuel. These performance advantages are due to the short intervals needed to prepare the fuel cell for another cycle of work, which allowed removing products from the reaction area, and catalyst regeneration. Taking it into consideration, this research can be a start of developing the system of periodically working DFAFCs.

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¹ Mandle R. J., Cowling S. J., Goodby J. W Chemistry European Journal, 23 (58), 14554–14562, 2017

² X. Chen, E. Korblova, D. Dong, X. Wei, R. Shao, L. Radzihovskyb, M.A. Glaser, J.E. Maclennan, D. Bedrov, D.M. Walba, and N.A. Clark, Physical Sciences, Volume 117, Pages 14021–14031, 2020

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9 Abstracts: Material engineering

9.1 Synthesis and research of micro-nitrocellulose as an additive for non-ideal high-energy materials

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KEYWORDS: nitrocellulose, non-ideal, energetic materials.

Cellulose nitrate (V) also known as nitrocellulose (NC) is a polymer of cellulose nitrate esters with β -1,4 bonds between monomers. It is obtained by nitration of cellulose. This macro-molecule has different applications depending on the degree of nitration.

Nitrocellulose with a low degree of nitration is used in paints, varnishes, inks, etc., while nitrocellulose with a high degree of nitration (>12.5 wt.%) is used in high-energy materials. High-energy materials containing nitrocellulose include dynamites and broadly defined propellants. Propellants containing nitrocellulose include smokeless gunpowder.

Due to its high-energy properties, NC has been used as an additive to non-ideal high-energy materials to improve their performance. The subject of this work is to investigate microstructured nitrocellulose as a new additive for non-ideal low-density high-energy materials to improve their performance, with a special focus on ANFO.

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9.2 Composite alginate membranes with dispersed MQFP hard magnet network as a new concept for highly efficient pervaporative dehydration of ethanol/ water mixture

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KEYWORDS: pervaporation, alginate, ethanol dehydration, composite membrane.

Pervaporation is a technique enabling liquid homogenous mixtures to separate. Biopolymer composites membranes are more and more common in pervaporation. Therefore in our research we proposed to add MQFP powder into sodium alginate (SA) membrane in order to improve separation efficiency of ethanol/water mixture in the pervaporation process. Hard magnetic nature and high degree of dispersibility in SA solution are great features of filler, which may improve removal of water from ethanol solution.

Magnetic particles have been recently considered as appealing functional fillers in composite membranes used for versatile purposes. SA/MQFP membrane was prepared using solvent evaporation method. To begin with, SA was dissolved in water and then MQFP powder with different grain size was added. After evaporation of water membranes were crosslinked with calcium chloride to preserve from material dissolution. Prepared membranes were studied in pervaporation cell due to the separation properties of ethanol/water system. The extensive physicochemical characterization of SA/MOFP was performed by means of scanning electron microscopy (morphology), and magnetometry (magnetic properties), and theoretical modelling. In addition, positron annihilation lifetime spectroscopy (PALS) was used to analyse voids sizes between polymer chains in membranes. We showed that SA/MQFP membrane had better hard magnetic properties than magnetic powder separately. Best separation results were obtained for membranes with lower amount of MQFP powder, which were also characterized with the best hard magnetic properties.

The obtained results showed that addition of such filler impacted on the excellent water/ethanol separation, especially for membrane filled with 1 wt% of magnetic powder with grain of 5 microns. In this case separation factor reached 12 271 and flux 2.48 kg m⁻² h⁻¹, respectively. These results indicate that the pervaporation process with membranes filled with hard-magnet are a viable approach for the complete dehydration of ethanol, which could find the application for production of bioethanol in an industry.

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9.3 Synergistic effect of tetranuclear iron (III) molecular magnet and magnetite for high-performance ethanol dehydration through alginate membrane

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KEYWORDS: synergistic effect, single-molecule magnet, magnetite, sodium alginate, hybrid membrane, pervaporation, ethanol dehydration.

The alginate membranes filled with various proportions of mixed magnetite and molecular magnet were investigated in the process of ethanol dehydration via pervaporation. The results show that the synergistic effect of combining these powders significantly improves the efficiency of the process.



Figure 9.3.1: Comparison of results obtained for membranes containing 2 wt% magnetite and 8 wt% molecular magnet with those with magnetite and molecular magnet separately.

The concept of synergy is one of the major topics studied in many areas and is responsible for producing materials with advantages of mixed components. In this paper, we used the combination of molecular magnet and magnetite in different proportions as a filler for alginate matrix applied in the process of ethanol dehydration. We expected that the combination of powders positively influences the pervaporation efficiency due to the good magnetic properties of magnetite and excellent dispersion of molecular magnet.

The results showed that the membranes with mixed filler showed much better separation abilities compared to the membranes filled with magnetite or molecular magnet separately. Moreover, better results were achieved for membranes containing significantly more molecular magnet than magnetite. Consequently, the best results were obtained for a membrane containing 8 wt% of molecular magnet and 2 wt% of magnetite, for which PSI and separation factor were equalled to 8439 kg m⁻² h⁻¹ and 3426, respectively.

9.4 Dopamine electropolymerization reaction in the presence of transition metal ions on the surface of titanium nanotubes

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Keywords: nanotubes, polydopamine, electropolymerization, photocatalysis.

Nowadays, we often face the problem of constantly growing environmental pollution. Photocatalytic degradation of organic pollutants may be one of the ways of the environment cleaning. The material that can be used in this process are TiO_2 nanotubes, which are gaining interest due to their chemical stability and photocorrosion resistance. Unfortunately, the wide band gap, makes that the light absorption of TiO_2NTs is limited only to UV light radiation. Fortunately, thanks to the modifications of TiO_2NTs , it is possible to increase the photosentivity of the material. Thanks to its high conductivity, polydopamine is a polymer that is an interesting material for photocatalytic research. In addition, thanks to the electropolymerization reaction, it is possible to quickly obtain a homogeneous layer.

The aim of the research was to check how dopamine electropolymerization reactions and the properties of the obtained material are influenced by the addition of transition metal ions. The first step was to obtain matrices for electropolymerization reactions. For this purpose, I made anodizations in order to obtain a layer aligned nanotubes. Dopamine electropolymerization reactions in the presence of transition metal salts were performed using the cyclic voltammetry technique. During the reaction, I used salts of various metals, i.e. copper and nickel. In the case of a given metal, I also checked the effect of the counterion, salt concentration and pH of the solution used for electropolymerization. Then, Iexamined the photochemical properties of the obtained samples using linear voltammetry in the presence of visible and ultraviolet light, as well as electrochemical properties by examining the conductivity. The above studies made it possible to determine the optimal synthesis conditions in relation to potential photocatalytic properties. For samples showing interesting properties, I also performed material stability test.

The research allowed me to determine not only the impact of the presence of transition metals, but also specific parameters. The obtained results show that the metal addition increases the photoactivity not only in relation to pure TiO_2 nanotubes, but also to nanotubes coated with polydopamine obtained in the reaction without metal addition.

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9.5 Remodeling of calcium phosphate to hydroxyapatite in a batch reactor

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Keywords: hydroxyapatite, precipitation, calcium phosphates.

Hydroxyapatite (HAp) is the most desirable and one of the most studied forms of calcium phosphate. It is found, among others, in human bones and teeth. HAp has the lowest solubility of all forms of calcium phosphate. Moreover, it has many properties of a promising biomaterial. There are many methods of HAp synthesis, but one of the most popular and straightforward methods is precipitation. In precipitation, calcium precursors and phosphate precursors are mixed in a solution. Then transition forms of various calcium phosphates are formed, and finally, HAp is obtained.

In this work, we present the analysis of which forms of calcium phosphate occur after a specific synthesis time at 40 $^{\circ}$ C in a batch reactor and which morphology they have when, instantaneously after initial precipitation, a constant dosage of aqueous ammonia solution raised the pH of the mixture.

In the experimental part of this work, we carried out 12 hydroxyapatite syntheses at 40 °C in a batch reactor using the precipitation method with the continuous addition of ammonia solution for increasing the pH over time up to about 10. The syntheses were performed for 0, 1, 2, 3, 4, 5, 6, 7, 8, 16, 20, and 24 h. The obtained samples were centrifuged, cleaned, dried, and ground before the comprehensive analysis. Moreover, we collected samples of the water phase from the reactor for analysis.

Fourier transform infrared spectroscopy spectra indicate that the samples obtained by synthesis for 3 h had water, hydrophosphate- and hydroxyapatite-specific bonds in their structures. X-ray fluorescence spectrometry shows that the molar ratio of calcium to phosphorus increased from a level of 1.00 to about 1.67 over the reaction time, indicating that the final product was HAp remodeled from previously occurring other forms of calcium phosphate. The zeta potential of all investigated samples ranged from -30 mV to 30 mV, meaning that particles are unstable and could agglomerate. Scanning electron microscopy images show that for the first 3 h, the particles have an irregular structure (dominated by agglomerates made up of spherical particles). After 4 h, remodeled calcium phosphates start taking the form of plates. However, as time pass, the particles take on an increasingly irregular structure - inclusions in the form of spheres appear on the plates. Only after 16 hours does the visible form of the plates reappear, and after 24 h, particles become fully developed and free of inclusions.

Knowing the occurrence of a given morphology depending on specific synthesis conditions makes it possible to design the precise production of HAp as needed, for example, as an admixture in 3D printing or as molecules used in diagnostics.

9.6 Injectable hydrogel materials based on chitosan enriched with retinol and resveratrol

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Keywords: hydrogel, chitosan, retinol, resveratrol.

Injectable hydrogel materials are an extremely attractive group of biomaterials. They are known for a many beneficial properties such as high swelling, controlled degradation, appropriate rheological parameters, surgical handiness, biocompatibility and the ability to mimic the native extracellular matrix. Hydrogels are often used as carriers of biologically active substances (e.g. retinol or resveratrol), which can be released from their structure during the degradation of the material. Retinol is known for its anti-inflammatory and antibacterial properties, stimulation of the production of collagen and elastin, and formation of blood vessels. On the other hand resveratrol, in addition to antimicrobial properties, has great antioxidant properties.

The subject of this study are injectable hydrogel materials based on chitosan cross-linked with dextran dialdehyde. Materials were enriched with retinol or resveratrol in the amount from 1 to 10%.

The aim of this study was to evaluate the effect of presence of two biologically active substances on the cross-linking process and physicochemical, biological and rheological properties of hydrogels. The materials were incubated in PBS solution in order to assess their degradation and the release rate of retinol and resveratrol. The antioxidant test was performed using ABTS method. After the materials were freeze-dried their microstructure and morphology were evaluated by SEM microscopy and ATR-FTIR spectroscopy. Additionally, a rheological properties were investigated, while the preliminary *invitro* studies were carried out on Hs680 fibroblasts.

The conducted study showed that the presence of retinol and resveratrol influenced the structural, physicochemical, rheological and biological properties of hydrogel materials. Moreover resveratrol showed a greater tendency to be released from the materials into the PBS during incubation and increased the antioxidant properties compared to materials with retinol. The obtained hydrogel materials have promising multifunctional properties and great potential for use as injectable materials for tissue engineering.

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9.7 Development of MoS₂/ZnO/CNMs photocatalysts for hydrogen evolution reaction

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KEYWORDS: HER photocatalysts, zinc oxide, molybdenum disulfide, carbon nanotubes.

One of the materials showing photocatalytic activity is zinc oxide (ZnO), which may be combined with hydrogen evolution reaction (HER) catalysts, such as molybdenum dislufide/carbon nanotubes ($MoS_2/CNTs$) heterostructures, in order to obtain efficient HER photocatalysts. The aim of the research was to develop new method of obtaining $MoS_2/ZnO/CNTs$ structures and investigate their application as HER photocatalysts.

In experiments ZnO was obtained both by sol-gel and microwave-assisted solvothermal method. Subsequently, it was deposited on MoS₂/CNTs catalysts with the use of the following mixing devices: ultrasonic homogenizer and high pressure homogenizer. ZnO and MoS₂/CNTs structures were mixed in different weight ratios. Photocatalysts obtained by those methods showed varying physical, structural and catalytic properties.

In order to investigate photocatalysts' composition, physical and structural properties, thermogravimetric analysis, Fourier transform infared spectroscopy, and scanning electron microscope analysis were conducted. Research allowed determining catalysts' composition, size as well as their particles' surface properties. Furthermore, ZnO photocatalytic activity was examined by its capability to decomposite methylene blue solution while being exposed to the light of an appropriate wavelength. MoS₂/ZnO/CNMs electrochemical and photocatalytic properties were examined by linear sweep voltammetry (LSV) and photochronoamperometry measurements. LSV analysis allowed investigating HER activity by determining catalysts' overpotential and Tafel slope, while the photochronoamperometry measurements allowed determining their degree of excitation while being exposed to the light of appropriate wavelength.

The results of the research indicate that above-mentioned methods allow obtaining photocatalitically active ZnO particles as well as $MoS_2/ZnO/CNTs$ heterostructures showing HER photocatalytic activity. Research enabled the selection of potentially best method of obtaining ZnO and $MoS_2/ZnO/CNTs$ structures from the photocatalytic point of view. It also allowed determining the best weight ratio of the materials used among the ones examined.

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9.8 Gemini ionic liquids as new modifiers for renewable fillers

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Keywords: gemini, imidazolium ionic liquids, nanocellulose, functionalization.

Polymer composites with lignocellulosic fillers in the form of wood, cellulose or nanocellulose are gaining interest from research centers. One of the limitations of using this type of polymer filler is the problem of appropriate dispersion and the formation of filler agglomerates in the matrix, which has a direct impact on the final strength parameters. In addition, these materials may be characterized by increased water adsorption. In order to improve adhesion between filler and polymer, various techniques are used to modify renewable fillers, including acetylation or esterification. Unfortunately, these methods are characterized by a number of drawbacks - for example the high toxicity of the organic solvents used. Therefore, it is reasonable to look for new, more ecological, as well as more efficient methods of modifying lignocellulosic materials.

In the present work, an attempt was made to functionalize a nanocellulose filler, previously obtained by enzymatic hydrolysis reaction with cellulase from a microorganism of the genus Trichoderma, using dimeric imidazolium gemini-type ionic liquids. The efficiency of the polysaccharide modification reaction was determined, as well as the supermolecular structure of potential plastic fillers was defined. An integral research stream was the characterization of the obtained cellulose nanofiller by defining its morphological and dispersion parameters.

The carried out functionalization of the cellulose filler with innovative modifiers proved to be an effective method of polysaccharide modification and ensured the formation of a stable spatial structure between renewable nanoparticles limiting the formation of aggregates and did not cause structural changes in the studied materials.

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9.9 Polymer nanocomposites based in polysaccharide/inorganic systems

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Keywords: nanocellulose, inorganic oxide, hybrid fillers, nanocomposites.

Increasing emphasis is being placed on production of functional polymer composites combining excellent mechanical properties, high UV and gas barrier properties, antibacterial characteristics and biodegradability. As a result, there is growing interest in using renewable fillers as novel fillers for polymer plastics through the use of cellulose or its nanometric alternative – nanocellulose. It is worth noting that in order for this material to exhibit high application potential, it should be properly modified – for example by combining inorganic metal oxides in correlation with polysaccharide material.

The presented problems were the motivation to try to synthesize hybrid nanofillers based on nanocellulose obtained by cellulases from the microscopic fungus Trichoderma reesei and selected inorganic metal oxides. The morphological parameters and the thermal stability of the modified hybrid systems were determined. The next step was to obtain nanocomposite films and define their supermolecular structure, as well as barrier and nucleation properties.

It was found, the high potential of the applied modification technique towards obtaining novel hybrid nanofillers and additionally proved that the barrier, nucleation and structural properties of the nanocomposite systems depend on the type of used filler.

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10 Abstracts: Mathematical modeling, simulations & optimization

10.1 Computational Fluid Dynamics of Hollow Fiber Membrane Contactor for CO₂ Absorption

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Keywords: CO_2 capture, hollow fiber membrane contactor, mathematical modelling, CFD.

 $\rm CO_2$ emissions represent 65% of the total greenhouse gases. There are different solutions to reduce the $\rm CO_2$ emissions, the post-combustion gas-liquid absorption process using amines can be considered one of the most attractive technologies, due to the maturity, ability to handle large flue gases volumes, and cost-effectiveness. In order to intensify the $\rm CO_2$ absorption process, the use of Hollow Fiber Membrane Contactor (HFMC) brings many advantages, the most significant being a much larger mass transfer area compared with packed bed columns.

In this work, a comprehensive three-dimensional (3D) Computational Fluid Dynamic (CFD) model for CO_2 absorption using HFMC in MEA solution is developed, using Comsol Multiphysics. The model considers the mass transfer of CO_2 from the gas phase, through membrane pores, in the liquid phase, followed by the chemical reaction with MEA. The developed CFD model was validated based on experimental data published in the literature. The simulation results of CFD model are used to determine the HFMC CO_2 capture capacity, and also the concentration profiles of CO_2 (Figure 10.1.1) and MEA in gas, membrane compartment, and liquid phase, in different operating conditions, for steady state and dynamic configuration, in the 3D space. The influence of the number, length, porosity and tortuosity of the membranes, flow path of the two phases, etc., on the absorption efficiency is also determined.



Figure 10.1.1: Surface CO_2 concentration profile in the tube (gas phase) and membrane.

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10.2 Experimental study and CFD modeling of fragmentation of titanium dioxide water suspension in a stirred ball mill

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KEYWORDS: stirred ball milling, deagglomeration, CFD.

The need for ultrafine powders arises from the development of such industrial branches as: cosmetic, pharmaceutical, ceramic, paint. The degree of fragmentation, the morphology and the size distribution of the received particles are all factors which determine the properties of the engineered product: its rheology, its homogeneity (due to variating solubility), the rate of active ingredient release, the kinetics of reactions, in which the product is being used and their influence on the efficiency of catalysts. Notably there is a growing application of nanoparticles because of their exceptional physicochemical properties: large specific surface area and high chemical reactivity.

A confirmed way of obtaining submicron- and nanoparticles is stirred ball milling due to the power efficiency of the process, the devices' simple construction, high size-reduction rates and low wear contamination. The fragmentation occurs from suspension attrition resulting from balls' complex motion and from their impacts with solid particles. The amount of generated stress energy determines different breakage mechanisms of particles and as a result a certain size distribution and a quality of the powder. The learning of the process course and of the variables affecting it is relevant for the optimization of the working conditions required for a specific outcome.

The aims of the study were to qualitatively characterise mechanisms of deagglomeration in a water suspension of titanium dioxide and employ the CFD to model an influence of rotational speed of a mill stirrer on the velocity field of the solid-liquid mixture consisting of the suspension and the balls, the kinetic energy of the milling medium and the energy dissipation rate in particular zones in the grinding chamber, as well as on the power consumption of the mill. Moreover, a deployment of 3D-printed working parts of the mill shaft was investigated.

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10.3 New flow field design enhancing the reagent distribution uniformity in direct formic acid fuel cell

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KEYWORDS: fuel cell, interconnectors, flow field, mass transport.

The ongoing climate change and depleting fossil fuel resources force the energy sector to transition towards more sustainable and efficient technologies such as fuel cells which convert fuel chemical energy into electricity and heat via electrochemical reactions. Most popular fuel cells operate on hydrogen, but the promising alternative is to utilize liquid fuel such as formic acid, which is easier to store and transport, and has higher volume energy density than hydrogen. Hence, the our study focused on a Direct Formic Acid Fuel Cell (DFAFC).

All reactants are distributed in the system by flow channels milled in interconnectors. Fuel starvation zones, which can occur due to insufficient diffusive transport in laminar flow, especially in porous electrodes, result in a sharp voltage drop. Fuel cell voltage influences a system efficiency and depends on the reactant concentration at the reaction surface. Therefore, uniform reagent distribution is crucial for stable and efficient fuel cell performance.

This study aimed to develop a new flow field design enhancing reagent distribution uniformity in a DFAFC. The proposed flow pattern can be divided into three sections: a distributor zone – dividing the inflowing stream between the row of channels; a mesh zone – the area of intersecting channels; and a collector zone – collecting all the fluid to the one outlet, assuring the uniform outflow from the channels.

The proposed flow field design was investigated numerically using ANSYS Fluent software and experimentally using the DFAFC, with the interconnectors being representations of the system designed virtually. All CFD simulations and experiments were performed for the range of inlet flow rates and current densities to determine current-voltage characteristics.

The current study allowed a comparison between the standard serpentine flow pattern and the proposed mesh-type flow field design on two levels: inspecting the hydrodynamic conditions, reagent concentration and residence time distribution using numerical modeling in the design phase, and examining the prototyped system experimentally. The research underlined the CFD simulations' advantage in the development of fuel cell reagent distribution system, minimizing the cost of prototyping, and maximizing the benefits from the new flow field design.

10.4 Optimization of the synthesis of cross-linkable poly(glycerol itaconate) for tissue engineering purposes

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Keywords: poly(glycerol itaconate), tissue engineering, optimization, biomaterials, bone scaffolds.

Tissue engineering is an intensively developing field of science. Poly(glycerol itaconate) (PGItc) is a synthetic polymer that can be modified due to a double bond in the side chain. It is formed from substrates that are non-toxic and used as components in the pharmaceutical and medical industries. Hence, it is conceivable that PGItc in the future may find application, for example, as a cellular scaffold for filling bone defects.

This study aimed to obtain and optimize the synthesis of PGItc in such a way as to obtain the highest possible degree of conversion. Preliminary experiments were conducted to select the reactants and determine the optimization conditions for the synthesis of the polyester. According to the Box-Behnken model, optimization experiments were performed with itaconic anhydride and glycerol using mathematical planning of experiments. The experiments were conducted without solvent and catalyst. FTIR, ¹H NMR, and ¹³C NMR analyses of the obtained products were performed. The degree of esterification was determined by titration methods. The input variables of the process were the ratio of substrate functional groups, temperature, and reaction time. The optimized output variables were: the degree of esterification (SE_{tit}), the degree of esterification calculated from the analysis of ¹H NMR spectra (SENMR), and the degree of itaconic anhydride conversion, which was calculated from the analysis of $^{13}\mathrm{C}$ NMR spectra ($\% X_{13C}^{NMR}$). Statistical models were created. The significance of the changed synthesis parameters was checked in each case. Optimal conditions for conducting the process were determined. The product with esterification degree equal to 62.3% (SE_{tit}) and 70.4% (SE_{NMR}) was obtained. The degree of anhydride conversion was 62.8%.

Performing the experiment under optimal conditions confirmed that running the reaction at a ratio of OH/COOH of 1.5, at 140 °C, for five hours makes it possible to obtain PGItc oligomers with a high degree of conversion.

Acknowledgements

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10.5 Titanium dioxide particles breaking in an industrial ball mill – experimental and CFD modelling

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KEYWORDS: eulerian granular, granular temperature, stresses, breaking-up.

To obtain a satisfactory quality of a suspension, solid particles must have a certain size. In the production process, particles tend to aggregate and agglomerate, which leads to large clusters. The process of breaking those clusters is commonly used in industrial applications. Food, cosmetics and drug industries use it to obtain small enough particle size distribution. This process also requires a large amount of energy. Therefore, a study of a particle-breaking mechanism and device efficiency could improve the process and lower the cost of production and lower energy consumption.

Breaking up the process requires using specific devices. In industry, many crushing devices are used. Ball mills are one of the most common constructions, due to their simplicity and high capacity. In those devices, the milling chamber is filled with beads. The high-speed rotations of the shaft cause movement of the filling bead. As a result of collisions between beads and between beads and chamber wall thigh values o stresses are generated. Those stresses cause the breakage of grinding particles on smaller parts.

In this work, computational fluid dynamics simulations were applied to predict the efficiency of ball mills in breaking suspension particles. The eulerian model was applied to find the interactions between solid mill beads and the liquid phase. The kinetic theory of collisions was applied to find the collision frequency of beads and collision frequency. The usage of CFD methods allows for comparing different types of mill geometry and process parameters on a particle breaking efficiency.

Acknowledgements

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10.6 Coupling the Worlds of Theory and Experiment in Materials Science – several case studies from the perspective of computational chemistry

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KEYWORDS: density functional theory, electrochemistry, sensing, multiscale modeling.

Progress in electrochemistry over several decades paved the way to a huge range of applications. In particular, electrochemical sensors represent a solid resolve for detection of various biologically relevant markers. Their importance for realization of a personalized medicine paradigm cannot be omitted.

However, electrochemical fields are rich in many cases, where results of applied science greatly advance the theoretical understanding. The question of how the material really works on the profound level of quantum mechanics typically remains unanswered. Therefore, there is a strong need to employ methods of computational physics and chemistry to fill the discrepancy between theory and experiment. In this presentation I would like to show examples of cases where this philosophy can be applied, in particular for studies of the interactions between gold nanocubes (AuNC) with different surfaces. Through the density functional theory (DFT) calculations it was possible to link experimentally observable macroscopic properties of electrodes - such as the rate constants and morphologies - with the molecular properties of their constituents. Those results were then used to select the most optimal parameters for further experiments and guide the electrodes modifications towards the biosensing of nucleic acids.

The aim of this presentation is to show the possibilities of DFT to close the gap between the experiment and theory in electrochemical sensing on the AuNC assemblies example.



Figure 10.6.1: Intermolecular interactions between AuNC and different surfaces in presence of ferrocyanide redox marker

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10.7 Microkinetic modelling of photocatalytic CO₂ conversion over MOFs

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KEYWORDS: simulation, photocatalysis, CO₂ reduction, MOFs, fuel production.

Carbon dioxide contributes to the greenhouse effect and global warming. Figure 10.7.1 shows a sunlight-assisted photocatalytic process that transforms CO_2 into hydrocarbon fuel utilising Metal Oxide Frameworks (MOFs). Over 10,000 MOF structures were discovered in the Cambridge Structural Database in 2021¹.

This project aims to reduce solid-state rocket engines' climatic effects. Falcon 9's rockets create 337 tonnes of CO_2 every launch but may be used to manufacture sustainable hydrocarbons².

MOFs feature a highly modular structure with long-range crystallinity, allowing various active sites and strong adsorption characteristics. Some metal nodes and organic ligands enable photocatalytic alteration, making MOFs catalytic under visible light. This highly catalytic condition might enable artificial photosynthesis on earth or space, potentially creating a new frontier³. A microkinetic model might replace years of effort to find viable MOF catalysts and optimise operating conditions. The microkinetic model presented in this research employs kinetic parameters to simulate conversions and selectivity in an idealised Plug Flow Reactor (PFR)⁴.

The reaction network shows how CO_2 may be transformed into hydrocarbon fuels. Refined kerosene may be used as a rocket, jet fuel, or automotive octane.



Figure 10.7.1: A Zirconium MOF, showing its components: metal nodes, in this case, zirconium, in yellow, and linkers, in blue. On the right, it is shown that the MOF is reacting with sunlight to convert the CO_2 into CO. On the left, it is shown how the Zr^{4+} acts as a catalyst as it is being regenerated.

10.8 Simplified approach for CFD simulation of hemodynamics inside mitral paravalvular leak

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KEYWORDS: paravalvular leak, hemolysis, hemodynamics, CFD, dynamic mesh.

To study the hemodynamics inside the left heart affected by a mitral paravalvular leak (PVL), simulations were performed using computational fluid dynamics (CFD) software. They were focused on parameters characterizing the risk of hemolysis, that is, the destruction of erythrocytes due to shear stress. It was assumed that hemolysis occurs in areas with stresses above 300 Pa.

In this work, validity of the simplified approach to left heart (disease affected) modelling was tested. In this test a left heart, affected by mitral paravalvular leak, derived from computed tomography (CT) was investigated. First, we compared two approaches to left ventricle contraction: using left ventricular motion, that is dynamic mesh, and static mesh, where the mesh motion was ignored. Next, whether it is necessary to include real shape of the left heart in the simulation of hemodynamics inside mitral paravalvular leaks. Simulations were performed for the unsteady phase of cardiac contraction using a non-Newtonian viscosity model (Carreau-Yasuda).

The study showed that the differences between "static" and "dynamic" approach are rather insignificant, and the use of static mesh can be considered justified in the PVL analysis. Moreover, analysis of the parameters describing blood flow through the PVL channel provides comparable results between the simplified and real LV model. This means that simplification of LV geometry can be used in further research and medical diagnosis. Regarding the PVL, area of shear stress above 300 Pa occurs only near the walls of the PVL-LV junction. The shape of this connection (channel entry) is considered to have a significant effect on the risk of hemolysis.

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10.9 Computational fluid dynamics of influence on process parameters and geometry of catalyst wire on the ammonia oxidation process

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KEYWORDS: ammonia oxidation, platinum-rhodium catalyst, catalyst degradation, CFD.

The world's food demand increases rapidly, making pressure to increase fertiliser production where ammonia oxidation on the platinum-rhodium catalyst mesh is a critical stage. The most significant drawback is catalyst degradation caused by harsh operating conditions. This work concerns the effect of process parameters on efficiency.

Computational fluid dynamics allows examining the relationship between wire geometry and momentum, heat and mass transfer by analysis of flow fields. This work aims to maximise the efficiency of nitrogen oxide conversion and minimise the degradation of the catalyst. The diameters of wires forming a woven gauze ranged between 0,06-0.09 mm are expected to give the highest conversion rate of nitrogen oxide. The concentration meshes in catalyst woven gauze are 1024 cm^{-2} .

The velocity, pressure and concentration fields for different contact times were obtained. It can be observed that there are stagnation areas behind the wires, which is the essential region of the considered process. The temperature difference ranges between several degrees in the front and back of the single wire, which expresses the problem of platinumrhodium wire degradation associated with the presence of "cold spots" on the catalyst's surface.



Figure 10.9.1: Contours of mass fraction of nitrogen oxide, contact time: 0.0002 s, wire diameter: 0.09 mm.

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11 Abstracts: Process equipment & environmental protection

11.1 Filtration drying of secondary raw materials of organic origin

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Keywords: brewer's spent grain, spent coffee grounds, production wastes, filtration drying, secondary raw materials.

In the food industry, there is a constant accumulation of plant waste, which, given its characteristics, has limited secondary use. The examples of such organic waste are, in particular, brewer's spent grain from breweries and spent coffee grounds from coffee factories. These raw materials have a high humidity (\sim 70÷75%), as a result the storage and shelf life is limited and is approximately up to 3 days. That is why it is important to research the kinetics regularities of the test materials drying – from the point of view of its economic and promising for practical use.

Brewer's spent grain and spent coffee grounds were dried using a highly efficient method of the filtration drying in order to remove excess moisture. The research of the kinetics of filtration drying of brewer's spent grain and spent coffee grounds were carried out with variable height of the layer of dispersed materials (40, 80, 120 and 160 mm), temperature of the drying agent (50, 70, 80 and 90 °C) and its speed. The kinetic dependencies were obtained, an example is shown in Figure 11.1.1.



Figure 11.1.1: Kinetics of filtration drying of brewer's spent grain at different layer heights (t=70 °C).

It was established that the drying time of the researched materials increases with an increase in the height of the layer of the test materials, with a decrease in the temperature and speed of the drying agent.

The obtained experimental data will be used for the mathematical analysis of the drying of these raw materials.

11.2 Scale-up of PET glycolysis process applying recyclable catalysts

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Keywords: *depolymerisation of PET*, glycolisys, optimization, scale-up, catalyst, recycling.

With the chemical recycling of plastic waste, the monomers of the polymer can be purely recovered and used to resynthesise the plastic material with high purity and quality. In our previous research, we optimised the glycolysis of poly(ethylene terephthalate) (PET) applying organocatalysts supported on silica gel with experimental design, achieving full conversion and 89% bis(2-hydroxyethyl) terephthalate (BHET) yield. To continue the research, we aimed to optimise the scale-up reaction conditions.

First, we examined more thoroughly the catalytic effect of the unmodified silica gel. We applied 50 wt% silica gel in a 6-fold scale-up reaction, which was carried out under the previously optimised conditions (190 °C and 12.6 eq. ethylene glycol (EG)) with a longer reaction time (10 h). Under these conditions, complete conversion and 72% BHET yield were obtained. We also investigated the effect of the particle size with ANOVA; however, it was not proved to be significant. We also carried out a 23 two-level factorial design, examining the temperature, the catalyst amount, and the EG/PET molar ratio as factors. We also conducted an 18-fold preliminary scale-up reaction, applying trialkyl amine-functionalized silica gel. With 15.5 mol% catalyst, 12.6 eq. ethylene glycol, 5 h reaction time and 190 °C, full conversion, and 72% BHET yield were achieved.

To summarise, we successfully used unmodified silica gel as a catalyst in the glycolysis of PET and built up an experimental design for the process. We also carried out a preliminary scaleup reaction applying trialkyl amine-functionalized silica gel, based on which we plan to create a two-level experimental design. Our further goal is to set up linear models for the use of both the unmodified and modified silica gels and optimise the reaction parameters.

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11.3 Design and prototype of an automatic reagent dosing device for use in a wave-mixed single-use bioreactor system

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Keywords: wave-mixed bioreactor, microcontroller programming, 3D modelling, 3D printing.

Wave-mixed single-use bioreactors are modern devices widely used in bioengineering. Advantages of single-use systems over conventional stirred bioreactors made from glass or stainless steel include bigger application flexibility and easier preservation of sterility inside the culture vessel. Liquid mixing in wave-mixed bioreactors occurs due to wave-induced agitation caused by the oscillations of the rocking platform. This mixing mechanism achieves lower shear stress values than stirred tank bioreactors, which can prevent damage to the cultured cells or tissues. A drawback noticed in the bioreactor system used for the research was that liquid dosing through the syringe port could only be done manually. This could pose a problem, especially when precise and repeatable liquid dosing to the reactor is necessary.

The goal of this work was to create an automatic reagent dosing device compatible with syringes with a standardised Luer Lock connection for use in a *ReadyToProcess* WAVE 25 system. The first step of the design involved creating 3D models of a syringe and stepper motor holder and a clamp for mounting on the rocking platform. The parts were designed using AutoCAD and Fusion 360 software and later printed with a Prusa i3 MK3S+ 3D printer. The second design step was to create an electronic circuit and a microcontroller program to operate the stepper motor driving the dosing mechanism.

The syringe plunger and the stepper motor are connected with a rack-and-pinion mechanism. The circuit is controlled by an Arduino Uno R3 board. The device is operated with an interface consisting of an LCD screen, indicator diodes and a set of switches. The user can enable and disable the device, pull the syringe plunger in and out, and set a system into configuration mode, which in the current prototype allows for adjusting the volume of the substance dose.

The device enables the user to inject a precise amount of a substance into the bioreactor container. The operation of the dosing system is repeatable and reliable. This development will allow for easier precise liquid dosing via the syringe port on the single-use culture container.

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11.4 Research of solid fuel briquettes obtaining from brewer's spent grain and coffee waste

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KEYWORDS: brewer's spent grain, coffee waste, spent coffee grounds, secondary raw materials, alternate solid fuel, briquettes.

One of the challenges nowadays is reuse of secondary raw materials, which very often cannot be stored for a long time and, when spoiled, become a factor of environmental pollution. About 15–20 kg of brewer's spent grain (BSG) are formed for every 100 L of beer, which is almost 31% of the initial mass of malt. On average, 1 ton of coffee product accounts for about 2 tons of coffee waste (CW).

Considering the high content of lignin in BSG and a mixture of CW, it is possible to assert the possibility and perspective of using these waste for the alternate solid fuel production.

The objects of the research were barley BSG obtained on the production line of brewery "Kumpel" (Ukraine) and CW – a mixture of coffee, barley, and chicory waste from JV "Galca LTD" (Ukraine). Examples of the solid briquettes are shown in Fig. 11.4.1.



Figure 11.4.1: Obtained test samples of solid fuel from: (11.4.1a) barley BSG; (11.4.1b) a mixture of CW.

The raw materials after the filtration drying process and formed solid briquettes were analyzed with calorimetric combustion. On the average, the higher calorific value of unformed BSG is ~20 005 kJ kg⁻¹ and for the obtained briquettes – in range from ~20 173–20 298 kJ kg⁻¹; for the dried unformed CW mixture it is ~21 583 kJ kg⁻¹ and for the CW briquettes ~22 147–23 095 kJ kg⁻¹.

The obtained experimental data indicate the promising and effective use of BSG and the CW mixture for the alternate solid fuel production. This solution should also be cost-efficient – the low price of raw materials, absence of need for additional binders and specials technological cleaning procedures.

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11.5 Calorimetric method for determining the microwave heating efficiency of materials

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Keywords: microwave heating, heating efficiency, calorimetric method, methane pyrolysis.

Electrification of chemical processes can help to reduce the carbon footprint of various industries worldwide. Therefore, several unconventional heating methods that proved their potential at the laboratory and pilot scales have been investigated to be widely introduced in the industry. Among different unconventional heating methods, microwave heating is especially attractive due to several unique properties, including volumetric, uniform, and selective heating.

This work aims to provide a simple calorimetric method for determining the microwave heating efficiency of materials. Although this work seeks to investigate possible catalysts for microwave-assisted decomposition (or pyrolysis) of methane, the proposed calorimetric method is more general and can be used for various materials.

In this work, silicon carbide (four fractions), nickel catalyst on Al_2O_3 carrier and commercial activated carbon were tested. The catalysts were heated in a small quartz vessel. The local temperatures of the catalyst bed were measured by three fibre optic sensors at different heights. An additional sensor was placed outside the quartz vessel in a multimode microwave cavity. The tests were conducted at a microwave frequency of 2.45 GHz with microwave powers of 16–24 W.

In general, silicon carbide and activated carbon showed similar microwave heating efficiencies, while a much worse result was obtained for the nickel catalyst.



Figure 11.5.1: Temperature profiles during microwave heating and cooling of different materials

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12 Abstracts: Other

12.1 Investigation of application and recycling of lipophilic organocatalyst in asymmetric synthesis

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Keywords: silica aerogels, condensation kinetics, reaction-limited aggregation, nucleation and growth, cellular automata.

Nowadays, chiral, bifunctional organocatalysts, which can be used to catalyse asymmetric syntheses in an enantioselective way, are getting more popular than ever. Enantioselective catalysis is fundamental in the pharmaceutical industry because the two enantiomers of the product can have different biological effects.

Recycling and reusing catalysts are essential to improve the environmental and economic footprint. During my work, I modified a cinchona squaramide-based organocatalyst with octadecyl side-chains. Furthermore, the catalyst was applied in asymmetric Michael additions, for instance, in the production of the chiral intermediate of baclofen. The recycling was based on the lipophilic character of the catalyst. After the reaction, the non-polar solvent was changed to a polar one. As a result, the catalyst precipitated and was separated by centrifugation.

The catalyst was reused in four more catalytic cycles without a significant decrease in the catalytic activity, achieving excellent yield (82–96%) and enantiomeric excess values (90–92%).



Figure 12.1.1: Recycling of the lipophilic catalyst

Acknowledgements

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12.2 Development and application of a new, bio-based solvent

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Keywords: alternative solvent, green chemistry, carbon-carbon coupling, methylation, bio-based solvent.

With the tightening of the environmental regulations, alternative solvents are getting greater attention, which may be capable of replacing the traditional, environmentally harmful solvents. They have a lower tension, and they are not toxic nor flammable. In many cases, they can also be manufactured from bio-based materials.

In my research work, I aimed to synthesise an alternative solvent with the advantageous properties mentioned above. I have successfully determined the most important physical properties of the solvent and investigated its stability. Furthermore, it was successfully applied in carbon–carbon coupling reactions like Suzuki and asymmetric Michael reactions. Finally, it was applied as a cosolvent to hydrolyze PET and PC polymers.

The newly synthesised solvent has shown many of the common beneficial properties of the alternative solvents. It has also performed well in coupling reactions. Furthermore, it turned out to be an excellent cosolvent in the hydrolysis of polymers with a full conversion and yields (>80%).



Figure 12.2.1: Properties of the new, bio-based solvent

Acknowledgements

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12.3 Statistical analysis of the obtaining of alginate microparticles

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KEYWORDS: fuel cell, interconnectors, flow field, mass transport.

The aim of the work was to optimize the process of obtaining alginate microcapsules based on mathematical methods of experiment planning. Two fractional plans were prepared (using an ultrasonic homogenization process and a rotor-stator mechanical homogenizer) with one point in the center of the plan. It was checked whether the input parameters significantly affect the output parameters. In both cases, the group of input parameters includes the concentration and the rate of instillation of the cross-linking agent, as well as the amplitude (in the case of the ultrasonication method) or the rotor rotation speed.





Statistical analysis was performed based on one-way analysis of variance (ANOVA). The significance of differences was assessed using the F test. In all cases, the p value <0.05 was considered statistically significant. Utility function profiles have been developed taking into account independent parameters. As a result of the analysis, approximation profiles were obtained, which allowed to optimize the composition of the reaction composition and process parameters.

12.4 Optimisation for polycarbonate methanolysis applying a recyclable heterogeneous organocatalyst

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KEYWORDS: polycarbonate, depolymerysation, methanolysis organocatalysis.

Poly(bisphenol A carbonate) (BPA-PC) is considered one of the most popular thermoplastics thanks to its good mechanical properties and versatility. Methanolysis, a method of chemical recycling, is a simple and economical way to degrade BPA-PC.

We investigated the methanolysis of BPA-PC to bisphenol A (BPA) monomer and dimethyl carbonate (DMC). The degradation process was performed by studying the activity of three commercially available organocatalysts (Si-TEA, Si-GUA, Si-THU) and one organocatalyst grafted onto silica gel (Si-TBD) prepared by us (Figure 12.4.1). Of these, the one modified with 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) showed the best results: conversion above 98% and 65% yield in 4 hours. Therefore, the Si-TBD catalyst was used to explore the main reaction parameters: temperature, catalyst:BPA-PC ratio, and methanol:BPA-PC ratio. According to the preliminary experiments, an experimental design was set up for optimizing the methanolysis of BPA-PC.

In conclusion, the methanolysis of BPA-PC was optimised, achieving 94% BPA yield. The applied Si-TBD catalyst can be recycled in several cycles without significant loss in its catalytic activity.



Figure 12.4.1: Methanolysis of BPA-PC applying a heterogeneous catalyst

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