Ninth National Conference on Chemistry

Science and Technology for Better Life

18th National Symposium on Polymers

Book of Abstracts

29 September – 1 October 2016, Sofia, Bulgaria

Union of Chemists in Bulgaria

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Faculty of Chemistry and Pharmacy
St. Kliment Ohridski University of Sofia
Sofia, Bulgaria

Union of Chemists in Bulgaria

The Organising Committee appreciates financial support by ACM2 Ltd., AQUACHIM Ltd., Biotechlab Ltd., and Branch chamber of pulp and paper industry

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Ninth National Conference on Chemistry
Science and Technology for Better Life
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Sofia 2016

Compiled by V. Beschkov, Ch. Bonev, I. Havezov
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ORGANISATION

Institutions

Union of Chemists in Bulgaria
Federation of Scientific Technical Unions in Bulgaria
Union of Scientists in Bulgaria
Bulgarian Academy of Sciences
University of Chemical Technology and Metallurgy, Sofia
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Conference Organiser

Company for International Meetings Ltd.

Schedule

Thursday, 29th September 2016

Hall 130 foyer

08:30–18:00	**Registration and information:** Company for International Meetings

Hall 130

09:15–09:30	**Opening session:** Organising Committee (V. Beschkov)
09:30–10:15	PL1. Plenary lecture: V. Bankova
10:15–11.00	PL2. Plenary lecture: Y. Osada
11.00–11.30	**Coffee break**

Session 1 Symposium 7: 18th National symposium on polymers

11:30–12:00	7-K1. Keynote lecture: P. Petrov
12:00–12:30	7-K2. Keynote lecture: M. J. Carrero, A. M. Borreguero, M. J. Ramos, M. Jimenez, J. F. Rodríguez
12:30–13:00	7-K3. Keynote lecture: B. Trzebicka
13:00–14:00	**Lunch break**
14:00–14:30	7-K4. Keynote lecture: P. Shestakova, H. Gruncharova, E. Vassileva
14:30–15:00	7-K5. Keynote lecture: R. Bryaskova, D. Pencheva, St. Dimov, M. Iliev, T. Kantardjiev
15:00–15:30	Oral presentations (7-O1-O2)
15:30–16:00	**Coffee break**
16:00–17:00	Oral presentations (7-O3-O6)
17:00–18:00	Poster flash presentations (7-P1-P23)

Hall 445

Session 2 Symposium 9: Pulp, paper and packaging: paper for pure nature

11:30–12:00	9-K1. Keynote lecture: P. Chingov, P. Fisera
12:00–13:00	Oral presentations (9-O1-O4)
13:00–14:00	**Lunch break**
14:00–14:45	Oral presentations (9-O5-O7)
14:45–15:30	Poster presentations (9-P1-P25)
15:30–16:00	**Coffee break**
16:00–17:30	Poster presentations (9-P1-P25, continued)

Hall 507

Session 3 Symposium 4: Analytical chemistry

11:30–12:00	4-K1. Keynote lecture: Y. Zhang, M. Miró, S. D. Kolev
12:00–13:00	Oral presentations (4-O1-O4)
13:00–14:00	**Lunch break**
14:00–15:30	Poster presentations (4-P1-P7)
15:30–16:00	**Coffee break**

Hall 547

Session 4 Symposia 2 and 8: Organic chemistry and technology. Pharmaceutical chemistry and technology

11:30–12:45	Oral presentations (2-O1-O5)
13:00–14:00	**Lunch break**
14:00–14:45	Oral presentations (8-O1-O3)
14:45–15:30	Poster presentations (2-P1-P13, 8-P1-P4)
15:30–16:00	**Coffee break**
16:00–17:30	Poster presentations (2-P1-P13, 8-P1-P4, continued)

Hall 210 foyer

18:30–21:00	**Welcome reception at Faculty of Chemistry and Pharmacy**

Friday, 30th September 2016

Hall 130 foyer

08:30–18:00	**Registration and information:** Company for International Meetings

Hall 130

09:30–10:15	PL3. Plenary lecture: B. Galabov
10:15–11.00	PL4. Plenary lecture: S. Pispas

11.00–11.30	**Coffee break**

Session 5 Symposium 7: 18th National symposium on polymers

11:30–12:00	7-K6. Keynote lecture: S. K. Smoukov
12:00–12:45	Oral presentations (7-O7-O9)
13:00–14:00	**Lunch break**

Session 6 Symposium 7: 18th National symposium on polymers, Session dedicated to the 80th anniversary of Professor Stoyko Fakirov

14:00–14:15	Introduction: I. Shopov
14:15–15:00	7-K7. Keynote lecture: K. Friedrich: A tribute to Professor Stoyko Fakirov (invited)
15:00–15:30	7-K8. Keynote lecture: A. Lederer
15:30–16:00	**Coffee break**
16:00–16:45	Oral presentations (7-O10-O12)
16:45–17:30	Greetings
17:30–19:00	Poster presentations (7-P1-P23)

Hall 445

Session 7 Symposium 6: Chemical engineering and environmental protection

11:30–12:00	6-K1. Keynote lecture: Ch. Boyadjiev
12:00–12:30	6-K2. Keynote lecture: S. Pişkin
12:30–13:00	Oral presentations (6-O1-O2)
13:00–14:00	**Lunch break**
14:00–14:15	Oral presentation (6-O3)
14:15–15:30	Poster presentations (6-P1-P12)
15:30–16:00	**Coffee break**
16:00–17:30	**Discussion: Novel materials for clean environment** (Chair: V. Beschkov)

Hall 507

Session 8 Symposium 1: Physical chemistry and electrochemistry

11:30–13:00	Oral presentations (1-O1-O6)
13:00–14:00	**Lunch break**
14:00–14:30	Oral presentations (1-O7-O8)
14:30–15:30	Poster presentations (1-P1-P2)
15:30–16:00	**Coffee break**

Hall 547

Session 9 Symposia 3 and 5: Inorganic chemistry and technology. Catalysis

11:30–12:00	5-K1. Keynote lecture: T. Tabakova, E. Kolentsova, D. Dimitrov, K. Ivanov, P. Petrova, G. Avdeev, D. Nihtianova, M. Manzoli
12:00–12:30	5-K2. Keynote lecture: M. Gabrovska
12:30–13:00	5-K3. Keynote lecture: K. Chakarova, K. Hadjiivanov, M. Mihaylov, S. Andonova, N. Drenchev, E. Ivanova
13:00–14:00	**Lunch break**
14:00–15:30	Poster presentations (3-P1-P11, 5-P1-P9)
15:30–16:00	**Coffee break**

Hall 704

Session 10 Symposium 10: Education in chemistry

11:30–12:45	Oral presentations (10-O1-O5)
13:00–14:00	**Lunch break**

Saturday, 1st October 2016

Hall 130 foyer

08:30–14:00	**Registration and information:** Company for International Meetings

Hall 130

09:30–10:15	PL5-Plenary lecture: I. Panaiotov
10:15–11.00	PL6-Plenary lecture: M. Stamm
11.00–11.30	**Coffee break**
11:30–12:15	PL7-Plenary lecture: V. I. Slaveykova
12:15–13:00	PL8-Plenary lecture: T. Spassov
13:00–13:15	**Closing session:** Organising Committee (V. Beschkov)

Programme

(as of 1st September 2016)

Thursday, 29th September 2016

Hall 130 foyer

8:30	18:00	**Registration and information**	Company for International Meetings

Hall 130

9:15	9:30	**Opening session**	V. Beschkov Organising Committee
9:30	10:15	PL1. Plenary lecture: Propolis chemistry: a look inside the beehive and beyond	V. Bankova
10:15	11.00	PL2. Plenary lecture: Intelligent gels: approaches to artificial soft tissue	Y. Osada
11.00	11.30	**Coffee break**	
Session 1	**Symposium 7: 18th National symposium on polymers**		
11:30	12:00	7-K1. Keynote lecture: Co-assembly of block copolymers: a strategy toward multifunctional nanocarriers	P. Petrov
12:00	12:30	7-K2. Keynote lecture: Functionalisation of propylene and ethylene oxide copolymers for the synthesis of polymer-drug conjugates	M. J. Carrero, A. M. Borreguero, M. J. Ramos, M. Jimenez, J. F. Rodríguez
12:30	13:00	7-K3. Keynote lecture: Thermoresponsive nanocarriers of active species	B. Trzebicka
13:00	14:00	**Lunch break**	
14:00	14:30	7-K4. Keynote lecture: Novel NMR methods in polymer science in Bulgaria: diffusion NMR and magic angle spinning (MAS) NMR for investigation of structure, dynamics and interactions in polymer hydrogels	P. Shestakova, H. Gruncharova, E. Vassileva
14:30	15:00	7-K5. Keynote lecture: Synthesis, characterisation, and behaviour of polymer-stabilised silver nanoparticles for biomedical applications	R. Bryaskova, D. Pencheva, St. Dimov, M. Iliev, T. Kantardjiev
15:00	17:00	**Oral presentations**	
15:00	15:15	7-O1. Functionalised hydrophilic polymers for modification of biomacromolecules or nanocarriers	N. Koseva, V. Mitova, I. Tsacheva, P. Shestakova, A. Kowalczuk, M. Karayianni, S. Pispas
15:15	15:30	7-O2. Star nanocarriers of nucleic acids	B. Mendrek, Ł. Sieroń, I. Żymełka-Miara, B. Trzebicka, A. L. Sieroń, A. Dworak, A. Kowalczuk

15:30	16:00	**Coffee break**	
16:00	16:15	7-O3. Polymer-based gene-delivery vector systems with entrapped gold nanoparticles	E. Haladjova, G. Mountrichas, S. Pispas, S. Rangelov
16:15	16:30	7-O4. Numerical analysis of controlled/living radical polymerisation	K. V. Grigorova, V. T. Toncheva, G. Georgiev
16.30	16:45	7-O5. Hybrid polymer/silica materials based on poly(N,N-dimethylacrylamide) copolymers: synthesis, properties and potential application	L. Todorova, C. Novakov, D. Christova
16:45	17:00	7-O6. Polymer surfaces for biomedical application	A. Utrata-Wesołek, W. Wałach, N. Oleszko, D. Szweda, J. Anioł, A. L. Sieroń, A. Klama-Baryła, G. Kitala, M. Kawecki, A. Dworak
17:15	18:00	**Poster flash presentations (7-P1-P23)**	

Hall 445

Session 2 Symposium 9: Pulp, paper and packaging: paper for pure nature

11:30	12:00	9-K1. Keynote lecture: Industry 4.0 for batch cooking process at Mondi Stambolijski	P. Chingov, P. Fisera
12:00	13:00	**Oral presentations**	
12:00	12:15	9-O1. Modern approach applied in the process of structural and graphic design of consumer packaging for cosmetics	A. Radoslavov, M. Koleva
12:15	12:30	9-O2. New deinking technology for digital printed paper	A. Bozhikov, P. Transka, K. Savov
12:30	12:45	9-O3. Lignosulphonate and waste technical hydrolysis lignin as adhesives for eco-friendly fibreboard	N. Yotov, V. Savov, S. Petrin, I. Valchev
12:45	13:00	9-O4. Comparative analysis of topochemical kinetic equations applied to cellulase hydrolysis of lignocellulosic biomass	N. Yavorov, I. Valchev, G. Radeva
13:00	14:00	**Lunch break**	
14:00	14:45	**Oral presentations**	
14:00	14:15	9-O5. Dyeing of offset printing paper with new reactive dyes: influence on paper properties and ageing	D. A. Todorova, P. M. Miladinova, V. N. Blyahovski
14:15	14:30	9-O6. Reuse of sludge from wastewater treatment in production of recycled paper for corrugated packaging solutions	D. Elenkova, S. Ladzhov, V. Yavorova, I. Valchev
14:30	14:45	9-O7. Bentonite as a cleaning agent for pitch deposition on paper machine	R. Zahariev
14:45	15:30	**Poster presentations (9-P1-P25)**	
15:30	16:00	**Coffee break**	
16:00	17:30	**Poster presentations (9-P1-P25, continued)**	

Hall 507

Session 3 Symposium 4: Analytical chemistry

11:30	12:00	4-K1. Keynote lecture: A novel hybrid flow system for the online fractionation and speciation of bioaccessible inorganic and organic mercury in environmental solid samples	Y. Zhang, M. Miró, S. D. Kolev
12:00	13:00	**Oral presentations**	
12:00	12:15	4-O1. Spectral interferences in the determination of rhenium in molybdenum and copper concentrates by inductively coupled plasma optical emission spectrometry	M. Karadjov, N. Velitchkova, O. Veleva, S. Velichkov, N. Daskalova
12:15	12:30	4-O2. Supramolecular bioinorganic chemistry: an interdisciplinary challenge for the Faculty of Chemistry and Pharmacy at Sofia University	A. Ahmedova, N. Burdzhiev, D. Momekova, R. Mihaylova, S. Stoykova, J. Zaharieva, G. Momekov, P. Shestakova
12:30	12:45	4-O3. A comparative study of the effects of salinomycin, monensin, and DMSA on the biodistribution of cadmium, calcium, copper, iron, and zinc in Cd-intoxicated mice	K. Kamenova, Y. Gluhcheva, S. Arpadjan, Ju. Ivanova
12:45	13:00	4-O4. Chromate-imprinted sorbent supported on silica spheres for preconcentration and determination of Cr(VI) in textiles	T. Yordanova, M. Mitreva, I. Dakova, I. Karadjova, P. Vasileva
13:00	14:00	**Lunch break**	
14:00	15:30	**Poster presentations (4-P1-P7)**	
15:30	16:00	**Coffee break**	
16:00	17:30	**Poster presentations (4-P1-P7, continued)**	

Hall 547

Session 4 Symposia 2 and 8: Organic chemistry and technology. Pharmaceutical chemistry and technology

11:30	13:00	**Oral presentations**	
11:30	11:45	2-O1. Synthesis of substituted proline derivatives as potential Seprase inhibitors	V. Mihaylova, N. Mateeva, Ts. Iliev, I. P. Ivanov, D. Tasheva
11:45	12:00	2-O2. Diastereoselective aza-Michael addition catalysed by chiral ketopinic acid derived complex	Y. Hassan, R. Klein, P. T. Kaye
12:00	12:15	2-O3. Effective removal of heavy metal ions using glycerol and starch xanthate	A. D. Mohammed, D. A. Young, J. Hendriks, H. C. M. Vosloo
12:15	12:30	2-O4. Kinetics and mechanism of inhibited lipid autoxidation in presence of 4-substituted coumarins	V. D. Kancheva, S. Angelova, A. Slavova-Kazakova
12:30	12:45	2-O5. Biscoumarins: a challenge to synthesis	A. I. Koleva, N. I. Petkova, R. D. Nikolova
13:00	14:00	**Lunch break**	
14:00	14:45	**Oral presentations**	
14:00	14:15	8-O1. Efficient drug delivery: characterisation of peptide-based complex of doxorubicin	G. Gocheva, N. Ilieva, K. Peneva, A. Ivanova

14:15	14:30	8-O2. Transfer of a drug-peptide complex through model cell membranes	N. Ivanova, A. Ivanova
14:30	14:45	8-O3. Micellar solubilisation of hydrophobic drugs	Z. Vinarov, D. Radeva, S. Tcholakova, N. Denkov
14:45	15:30	**Poster presentations (2-P1-P13, 8-P1-P4)**	
15:30	16:00	**Coffee break**	
16:00	17:30	**Poster presentations (2-P1-P13, 8-P1-P4, continued)**	

Hall 210 foyer

18:30	21:00	**Welcome reception at Faculty of Chemistry and Pharmacy**

Friday, 30th September 2016

Hall 130 foyer

8:30	18:00	**Registration and information**	Company for International Meetings

Hall 130

9:30	10:15	PL3. Plenary lecture: Application of spectroscopic and theoretical methods in elucidating reaction mechanisms	B. Galabov
10:15	11:00	PL4. Plenary lecture: Functional nanostructures from amphiphilic block copolymers and other building blocks	S. Pispas
11:00	11.30	**Coffee break**	
Session 5	**Symposium 7: 18th National symposium on polymers**		
11:30	12:00	7-K6. Keynote lecture: Bottom-up methods for nanostructured functional polymers and composites	S. K. Smoukov
12:30	12:45	**Oral presentations**	
12:00	12:15	7-O7. Polybenzimidazole-based anion conductive polymer electrolyte membranes for AEM fuel cells and electrolysers	H. Penchev, P. Ublekov, G. Borisov, V. Sinigersky
12:15	12.30	7-O8. Mechanical and tribological behaviour and biomineralisation ability of hydroxyapatite-modified hydrogels	L. Sorochynska, S. Grishchuk, B. Wetzel
12.30	12:45	7-O9. Polymer-containing photovoltaics: current state and new perspectives	G. Grancharov, V. Gancheva, P. Mokreva, R. Kalinova, P. Petrov, E. Lazarova, C. Dikov, G. Popkirov, P. Vitanov, M. Sendova-Vassileva
13:00	14:00	**Lunch break**	

Session 6 Symposium 7: 18th National symposium on polymers, Session dedicated to the 80th anniversary of Professor Stoyko Fakirov

14:00	14:15	Introduction: I. Shopov	
14:15	15:00	7-K7. Keynote lecture: From solid-state postcondensation of neat polymers to mutifunctional nanofibrillar polymer composites: a tribute to Professor Stoyko Fakirov on the occasion of his 80th birthday (invited)	K. Friedrich
15:00	15:30	7-K8. Keynote lecture: Advanced separation and characterisation of multifunctional polymer systems	A. Lederer
15:30	16:00	**Coffee break**	
16:00	16:45	**Oral presentations**	
16:00	16:15	7-O10. Functionalisation of self-assembling copolymers for nanoencapsulation of phase changing materials	S. Grishchuk, G. M. Florescu, B. Wetzel
16:15	16:30	7-O11. Polymer nanocrystals in aqueous dispersions	M. Krumova, S. Mecking
16:30	16:45	7-O12. Polyacrylate and polymethacrylate based interpenetrating polymer networks as drug delivery systems	M. Simeonov, A. Lederer, S. Boye, B. Kostova, E. Vassileva
16:45	17:30	Greetings	
17:30	19:00	**Poster presentations (7-P1-P23)**	

Hall 445

Session 7 Symposium 6: Chemical engineering and environmental protection

11.30	12:00	6-K1. Keynote lecture: A new approach to modelling the mass transfer processes in industrial column apparatuses	Ch. Boyadjiev
12:00	12:30	6-K2. Keynote lecture: Sol-gel hydrothermal synthesis of titanium dioxide nanoparticles	S. Kasap, M. S. Yilmaz, S. Pişkin
12:30	13:00	**Oral presentations**	
12:30	12:45	6-O1. Ultrasound-assisted extraction and nanofiltration of bioactive compounds from *Sideritis*	B. Tylkowski, A. Trojanowska, C. Quintas, I. Tsibranska
12:45	13.00	6-O2. Study of the energy potential of vinasse	P. G. Velichkova, T. V. Ivanov, I. G. Lalov
13:00	14:00	**Lunch break**	
14:00	14:15	**Oral presentation**	
14:00	14:15	6-O3. Magnetically assisted fluidised bed bioreactor for bioethanol production	P. G. Velichkova, T. V. Ivanov, I. G. Lalov
14:15	15:30	**Poster presentations (6-P1-P12)**	
15:30	16:00	**Coffee break**	
16:00	17:30	**Discussion: Novel materials for clean environment**	V. Beschkov (chair)

Hall 507

Session 8 Symposium 1: Physical chemistry and electrochemistry

11:30	13:00	**Oral presentations**	
11.30	11:45	1-O1. Electrostatic equations in quadrupolar media	R. Slavchov, I. Dimitrova, Tz. Ivanov
11:45	12:00	1-O2. A theoretical identification of the [10]annulene configurations isolated by Masamune's group	R. Palmeiro, F. J. Nañez, D. Rivero, O. Castaño
12:00	12:15	1-O3. Self-shaping droplets: from formation mechanisms to potential applications	N. Denkov, S. Tcholakova, I. Lesov, D. Cholakova, S. K. Smoukov
12:15	12.30	1-O4. Role of surfactant adsorption layers for dynamic foam properties	S. Tcholakova, N. Denkov
12.30	12:45	1-O5. Adsorption of ions at a non-ionic surfactant spread monolayer interface	T. Peshkova, I. Minkov, R. Slavchov
12:45	13:00	1-O6. Phase formation and structure of glass-ceramics by Fe-Ni waste vitrification	A. Kamusheva, S. Vladimirova-Atanasova, B. Ranguelov, G. Avdeev, D. Karashanova, A. Karamanov
13:00	14:00	**Lunch break**	
14:00	14:30	**Oral presentations**	
14.00	14:15	1-O7. Kinetic parameters of anodic oxidation of titanium alloys in a fluoride-containing electrolyte	M. Stancheva, M. Bojinov
14:15	14:30	1-O8 Effects of cold plastic deformation on the mechanical characteristics and corrosion behaviour of low-alloyed (2%Cr) steel	D. Ivanova, G. Ilieva, L. Fachikov
14:30	15:30	**Poster presentations (1-P1-P2)**	
15:30	16:00	**Coffee break**	

Hall 547

Session 9 Symposia 3 and 5: Inorganic chemistry and technology. Catalysis

11:30	12:00	7-K1. Keynote lecture: Design of novel catalysts for CO and VOCs abatement	T. Tabakova, E. Kolentsova, D. Dimitrov, K. Ivanov, M. Manzoli, P. Petrova, G. Avdeev, D. Nihtianova
12:00	12:30	7-K2. Keynote lecture: Impact of magnesium dopant on the properties and performance of nickel-based catalysts	M. Gabrovska
12:30	13:00	7-K3. Keynote lecture: Guest molecules in metal-organic frameworks: FTIR spectroscopic studies	K. Chakarova, K. Hadjiivanov, M. Mihaylov, S. Andonova, N. Drenchev, E. Ivanova
13:00	14:00	**Lunch**	
14:00	15:30	**Poster presentations (3-P1-P11, 5-P1-P9)**	
15:30	16:00	**Coffee break**	

Hall 704

Session 10 Symposium 10: Education in chemistry

11:30	12:45	**Oral presentations**	
11.30	11:45	10-O1. Student's attitudes related to science and scientists: stereotypes, peculiarities, implications	A. Gendjova
11:45	12:00	10-O2. Bulgarian university ranking system: indicators for student motivation to choose university education in the chemical sciences professional field	A. Tafrova-Grigorova, M. Kirova
12:00	12:15	10-O3. Key set of skills of the successful science teacher in constructivist learning environment	V. Tzvetkov, E. Boiadjieva
12:15	12.30	10-O4. Results of an international study on constructivist practices in chemistry education	I. Emilov, A. Tafrova-Grigorova
12.30	12:45	10-O5. A study of the floral migration and floral specialisation of worker bees	Z. H. Garova
13:00	14:00	**Lunch break**	

Saturday, 1st October 2016

Hall 130 foyer

8:30	14:00	**Registration and information**	Company for International Meetings

Hall 130

9:30	10:15	PL5. Plenary lecture: Behaviour of nanosized drug carriers at model interfaces	I. Panaiotov
10:15	11.00	PL6. Plenary lecture: Polymers for high energy-density batteries	M. Stamm
11.00	11.30	**Coffee break**	
11:30	12:15	PL7. Plenary lecture: Small particles - large implications? What aquatic microorganisms tell us about environmental impact of engineered nanomaterials	V. I. Slaveykova
12:15	13.00	PL8. Plenary lecture: Micro- and nanoporous metals by dealloying of glasses	T. Spassov, L. Mihaylov
13.00	13.15	**Closing session:** Organising Committee (V. Beschkov)	

PL1. Propolis chemistry: a look inside the beehive and beyond

V. Bankova

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Propolis is a plant-derived resinous bee product, which serves dual purposes in the beehive: it is a building material and protective substance against infectious microorganisms. Propolis has a long history of application in the traditional medicine of numerous nations as a remedy for treating wounds, burns, sore throat, stomach disorders, etc. Propolis solutions are still among the most popular homemade remedies in South-Eastern Europe, including Bulgaria. Propolis has attracted the attention of modern scientists since about 50 years with its diverse pharmacological activities: antibacterial, antiviral, antioxidant, anticancer, immunomodulating, and many others accompanied by low toxicity. These pharmacological properties of propolis inspired the study of propolis chemistry. Chemical studies revealed that bee glue is characterised by a remarkable chemical variability: because in different phytogeographic zones bees collect the resinous material from different plants, the chemical composition of propolis varies significantly.

This variability is a serious obstacle to propolis standardisation and accordingly, to its official acceptance into the main stream of the healthcare system. On the other hand, the chemical diversity of propolis in different ecosystems has made it a source of new biologically active molecules, mainly antioxidative, antibacterial, and anticancer agents. Our chemical studies of propolis samples from all over the world have revealed numerous new propolis constituents including new chemical entities, natural products of different chemical types as flavonoids, phenolic acids and their esters, di- and triterpenes, and stilbenes. Many of these compounds showed significant antimicrobial and antioxidant activities. Using the knowledge of chemical composition, we were able to identify many propolis plant sources, thus shedding new light on the bee-plant relationships. The importance of propolis for honeybees themselves was also a subject of our research interests: we have demonstrated the importance of propolis and some of its individual constituents for the health of the bee colony and especially in resistance of bees to two of the most dangerous pests: American foulbrood and varroa mites.

The chemical knowledge about propolis allowed us to develop a new approach to propolis standardisation, based on the distinct chemical profiles of propolis of specific plant origin. This approach makes possible the wide application of propolis in standardised and controlled products: food additives, cosmetics, over-the counter preparations, medical devices, etc.

PL2. Intelligent gels: approaches to artificial soft tissue

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Materials, which consist of cross-linked polymer network with water filling the interstitial spaces of the network, are called polymer hydrogel. The polymer network sustains the water and prevents it from flowing out through the strong interaction between the network and water.

Human body largely consists of the soft tissue, which is made of hydrogels of filamentous proteins and/or polysaccharides networks. Soft tissue can further be divided into connective tissue (ligaments, tendons, cartilage) and organs such as vein, nerve, and muscle. One can notice that the network of these biological tissues exists in highly hierarchical and charged states and enables to generate mechanical power (muscle), sustain mechanical stress (ligaments, tendons), and lubricate effectively under stress (cartilage) as highly swollen tissue while keeping its solidity as gel state. It would be one of the ultimate goals for gel science to design hydrogels with 'emergent functions' which biological soft tissues possess and eventually to replace them. In this lecture, attempts and future prospects to obtain artificial soft tissue: artificial muscle and artificial connective tissue using synthetic polymer gels will be discussed.

PL3. Application of spectroscopic and theoretical methods in elucidating reaction mechanisms

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Application of theoretical quantum chemistry methods have become an invaluable approach to evaluating fine details of chemical reaction pathways. Nevertheless, the outcomes of computational modelling may depend on the level of theory applied, how the reaction medium is simulated, and other factors. Additionally, multiple pathways are possible for many processes and theory cannot always resolve satisfactorily which mechanism dominates. On the experimental side, spectroscopy has proved the method of choice in kinetic studies. In favourable cases, spectroscopic methods may also provide information on key reaction intermediates. In this talk, the combined application of quantum chemical modelling and spectroscopic (IR, UV, NMR) methods in evaluating the mechanisms and quantifying reactivity for several organic reactions will be discussed. The following organic reactions are considered: electrophilic aromatic substitution (halogenation, nitration, sulphonation), aminolysis of carbamates, and S_N2 reactions.

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PL4. Functional nanostructures from amphiphilic block copolymers and other building blocks

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Amphiphilic block copolymers have the ability to self-organise in a variety of nanometre scale structures usually as a response to external physicochemical stimuli changes, as well as to interact with a variety of other building blocks, toward the formation of hybrid and functional nanostructures. These distinctive abilities allow the utilisation of amphiphilic block polyelectrolytes, in particular, in a number of practical applications.

In this presentation, we will discuss our resent results on the design and synthesis of new amphiphilic block copolymers and block polyelectrolytes, their self-assembly in aqueous solutions and surfaces, and their interaction with proteins, nucleic acids, low molecular weight surfactants, and inorganic nanoparticles, producing colloidal and surface nanostructures of different morphologies and functionalities [1–4]. The ultimate goal is to understand and master ways for controlling self-assembly of macromolecular materials and the creation of functional nanostructures able to find use in applications related to drug and gene delivery, enzymatic catalysis, biomimetics and biotechnology, and thin film designs.

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PL5. Behaviour of nanosized drug carriers at model interfaces

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Nowadays a real revolution in galenics occurs. The traditional forms of drug administration give up one's place to the new drug delivery systems. During the last decades, an important progress has been made by tailoring various kinds of micro- and nanosized molecular assemblies used as drug carriers. These include small unilamellar vesicles (SUV); lipid nanocapsules (LNC) with a core of triglycerides (TG) covered by a soft layer of polyethylene glycol (PEG) and stabilised by phospholipids (PL); biodegradable polyester matrix of poly-α-hydroxy acids (PLAGA); more complex structures of commercially available lung surfactant (LS), containing phospholipids (PL) and proteins (P); coacervates containing plant proteins like alpha-gliadin and cage molecules like beta-cyclodextrin.

From the physicochemical point of view, a better understanding of their behaviour in living environment seems indispensable. Despite the complexity of the living systems, it is possible to produce generic models of the reorganisation at membrane interfaces of molecular assemblies by considering simple model systems.

Some experimental results and theoretical description of complex phenomena occurring during the reorganisation of SUV, LNC, PLAGA matrix, LS, and alpha-gliadin coacervates at model membrane interfaces will be briefly reported. Further attention will be paid to recently studied cases of interaction between Paclitaxel (Ptx)-loaded LNC and 2D and 3D mucous membrane models and formation of beta-cyclodextrin-beta-carotene inclusion complex.

PL6. Polymers for high-energy-density batteries

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This talk is dedicated to the 80th birthday of my longstanding collaborator and friend Professor S. Fakirov

The storage of energy is a challenge for the effective use of regenerative energy sources like wind and solar energy. Efficient and high energy-density batteries could help in this respect and at the same time make e-mobility more acceptable due to more affordable batteries with higher range. Besides other concepts, lithium-sulphur batteries would provide a solution since they promise a much higher energy density and capacity compared to conventional Li-ion batteries. There are, however, still many problems to be solved. Polymers can be used for the design of cathodes, which contain sulphur in a porous conductive structure [1]. Nanoporous carbon cathodes for lithium-sulphur batteries can be produced by pyrolysis of gyroid replicas based on polystyrene-poly-4-vinyl pyridine (PS-P4VP) block copolymer sacrificial templates. A freestanding gyroid carbon network of highly ordered and interconnected porous structure is fabricated by impregnating the carbon precursor solution into the gyroid block copolymer nanotemplates and subsequently carbonising them at elevated temperature in an inert medium. A wide range of analytical tools is employed to characterise fabricated porous carbon materials [2]. Prepared nanostructures exhibit a fascinating morphology of high surface area and uniform porosity with interconnected three-dimensional networks. These nanoporous templates with gyroid structure provide high cycling stability of lithium-sulphur batteries over more than 100 cycles [3]. They can affect the so-called polysulphone shuttle and dendride formation, which limit battery lifetime. Polymers are also used for separator, solid electrolytes, and binders for Li-anode, and last but not least, as casing and packaging materials for batteries.

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PL7. Small particles - large implications? What aquatic microorganisms tell us about environmental impact of engineered nanomaterials

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Engineered nanomaterials (ENMs) are promising materials finding wide use in a broad range of new commercial and industrial applications that are expected to contribute to significant improvement of the life. However, the newly engineered material properties also bear the potential for unintended and yet not completely elucidated hazards for environmental and human health. ENMs are considered a new class of emerging contaminants with a potential to harm the organisms in the environment. According to currently accepted paradigms, to produce biological effect, contaminants (e.g. ENMs) should first interact with organisms through adsorption and crossing the biological barriers. However, developed for other conventional contaminants (e.g. toxic trace metals), the validity of such paradigms for ENMs as well as the establishment of 'dose-response' relationship is still to be proved. In this presentation, we explore the frontiers of our knowledge of this tiny world to understand how the metal containing ENMs could affect aquatic microorganisms and how in turn microorganisms affect ENMs properties and behaviour. More specifically, the interactions of inorganic nanomaterials with two environmentally relevant unicellular eukaryotic organisms: green alga and protozoa with inorganic nanoparticles will be addressed. The complexity of the behaviour of ENPs in the environment will be highlighted and the importance of environmental transformations and trophic linkages for a proper environmental impact and risk assessment of ENMs and for a weighing the 'benefits versus risks' of nanotechnologies will be discussed.

PL8. Micro- and nanoporous metals by dealloying of glasses

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Micro- and nanoporous metals received an increasing research interest in the last years due to their high surface area, good electrical and thermal conductivity, and outstanding mechanical stability [1–3]. These structures are considered for a wide range of applications in catalysis, sensing devices, filtering, biotechnology, etc. Dealloying, realised by selective electrochemical/chemical dissolution of less noble components of an alloy, is one of the routes to produce porous materials. The remaining more noble elements diffuse along the solid-electrolyte interface and reorganise into a nanoporous structure with bicontinuous ligaments. The pore size in the dealloyed structure is dependent on alloy composition. Sun et al. [4] have shown for the first time the formation of a nanoporous structure by dealloying the more-noble component. They demonstrate that a process involving electrodeposition of a homogeneous single-phase Ni_xCu_{1-x} binary alloy followed by electrochemical etching of Cu from the alloy can form nanoporous Ni films. The formation of a passive oxide film on nickel in sulphamate solutions allows the selective electrochemical etching of copper. These results show a general strategy for fabrication of nanoporous structures by electrochemical dealloying where the more active component is passivated and hence is kinetically rather than thermodynamically stable. This strategy is important, for example, in the fabrication of nanoporous structures from transition metal elements.

In the present study, rapidly quenched multicomponent Zr-Ni-based bulk glass-forming alloys were exposed to chemical and electrochemical selective dissolution. Various types and concentrations of the electrolyte were applied in respect to selective dissolution of Zr. For the electrochemical dealloying 1-M saturated water solution of NaF was found to produce most efficient result. The effect of the electrode potential on the dissolution process was also found to be essential. In most cases, the etching takes place at a constant rate in three dimensions indicating a surface controlled dissolution process. The etching rate was found to be very high, as the entire dealloying process takes place in several minutes. As a result three-dimensional homogeneous microporous structures were obtained under different conditions (electrochemical potential, temperature, dissolution time). Moreover, the evolution of the morphology and microstructure of the nanoporous material at different stages of dealloying was investigated by electron microscopy (SEM and HR TEM) and EDS microanalysis. The resulting ligaments microstructure ranges from tens to hundred nanometres. The changes in the ligament composition and microstructure at different dealloying times are correlated to the mechanism of dealloying. Additionally, the microstructure evolution is related to the electrocatalytic activity of nanoporous alloy. The electrocatalytic activity for hydrogen evolution reaction of the dealloyed ribbons was found to be improved compared to the as-cast alloys.

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1-Physical chemistry and electrochemistry

1-O1. Electrostatic equations in quadrupolar media

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The classical Poisson's equation ($\nabla^2\phi = -\rho/\varepsilon$; ϕ – electrostatic potential, ρ – free charge density) underlies the Debye-Hückel theory for activity coefficients, the DLVO theory for disjoining pressure, etc. In this equation, the continuous medium is represented by the dielectric permittivity, ε, which says that the medium is built up of polarisable dipoles. When the continuous medium is slightly polar or non-polar (for example liquid CO_2, C_6H_6) i.e. the molecules have small dipole moment or do not possess any and only their polarizability is left, then we may take into account quadrupole moment and quadrupolarisability of the molecules. The quadrupolar analogue of Poisson's equation is: $\nabla^2\phi - L_Q^2\nabla^4\phi = -\rho/\varepsilon$, where the presence of quadrupoles in the medium is hidden in the so called quadrupolar length, L_Q. The derived quadrupolar equation was applied to some electrostatic problems and the main corollaries are summarised:

(i) The quadrupolar terms in the electrostatic equations lead to regularisation of the electrostatic potential.

(ii) All surfaces between dielectrics possess normal surface dipole moment.

(iii) Onsager model for dielectric fluid is generalised for quadrupolar medium: dielectric permittivity and the quadrupolar length of the medium are related to the basic molecular characteristics (dipole and quadrupole moment, polarisability, and quadrupolarisability).

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1-O2. A theoretical identification of the [10]annulene configurations isolated by Masamune's group

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Masamune and coworkers isolated two crystalline [10]-annulenes (A and B) and proposed that A and B consisted of mono-trans and all-cis configurations of 9,10-dihydronaphthalene. Other authors have proposed a double-trans configuration for B instead of the all-cis one. Theoretical works released so far have studied the conformational exchange of mono-trans conformers and the mechanism obtained at correlated levels matches the one proposed by Masamune, although MP2 and DFT fail in order to calculate the relative energy between C_2 and C_s conformations. On the contrary, MP4 and CCSD render C_2 conformation as the more stable one, consistent with the five peaks showed by the C^{13}-NMR spectrum below −100°C. However, it remains to be elucidated all-cis and double-trans conformational exchange mechanism, which is the aim of our work. On the other hand, we have calculated the energy barriers of the cyclisation to 9,10-dihydronaphthalene of the three configurations, in order to compare them to the Masamune's experimental results.

We have found out the pathways of those mechanisms at CASSCF level using 10 electrons in an active space constituted by 10 π orbitals. Subsequently, dynamic electronic correlation has been taken into account by CCSD in order to refine the energy barriers between the conformers, and by CASSCF MP2 to correct the energy barriers of the cyclisation to 9,10-dihydronaphthalene. The NMR spectra in function of temperature have been simulated and compared with the Masamune's dynamical NMR studies on A and B.

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1-O3. Self-shaping droplets: from formation mechanisms to potential applications

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Recently we reported a conceptually new bottom-up approach where internal phase transitions in oil droplets transform them into micrometer-sized, fluid objects with complex shapes, such as regular polyhedra, platelets shaped as hexagons, triangles, squares, and toroids. Furthermore, many of these shapes spontaneously form micrometer and sub-micrometer in diameter fibres, which resemble in shape the flagella of the living cells. Experimentally, the system is realised as the oily drops are dispersed in appropriate long-chain surfactant solutions and are slowly cooled down in a temperature range around the freezing point of the oil. Under these conditions, molecular multilayers of intermediate plastic phases are formed at the oil-water interface, which are able to deform the drop surface and to self-assemble into long fibres. These systems appear as a convenient toolbox for studying the mechanisms of morphogenesis (structure and shape genesis) in nature from minimal in composition and structure molecular components. Furthermore, under appropriate conditions, we observed a spontaneous process of drop bursting and fragmentation into numerous much smaller emulsion drops. This novel process of self-emulsification incorporates three new highly efficient drop breakup mechanisms, which encompass several branches of science: elasto-capillarity, hydrodynamic jet stability, and surface wetting. We show that the studied methods are applicable to various oil-surfactant combinations and are scalable to technological applications.

1-O4. Role of surfactant adsorption layers for dynamic foam properties

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Recently our group has performed several related studies on the factors controlling foamability, bubble size after foam shearing, foam rheology, and rate of bubble Ostwald ripening in aging foams. Five different types of foam stabilisers were studied: (i) low-molecular mass surfactants which form adsorption layers with low shear and dilatational elasticities and viscosities; (ii) low-molecular mass surfactants which were specifically chosen to provide high dilatational elasticity of the surfactant adsorption layers, at negligible shear elasticity; (iii) natural surfactants from plant extracts, called saponins, which form adsorption layers with high dilatational and shear elasticities; (iv) solid particles which form a network (weak gel) in the continuous phase of the foam, without adsorbing on the bubble surface, and (v) solid particles adsorbing on the surface of the bubbles and stabilising the foam films.

The performed analysis showed that the foamability is controlled by the Gibbs elasticity of the dynamic adsorption layers, which depends primarily on the kinetics of surfactant adsorption. Two master curves for nonionic and ionic surfactants were found to describe the foam volume, as a function of Gibbs elasticity, which demonstrates an additional important contribution of the electrostatic repulsions for ionic surfactants (beside the steric repulsion operative for nonionic surfactants). The bubble size in sheared foams and foam rheological properties are controlled by the surface dilatational modulus as determined at low surface deformation. Depending on a specific foam stabiliser, the rate of bubble Ostwald ripening in aging foams could be controlled by the resistance to the gas transfer of the aqueous core of the foam films, the resistance of the surfactant adsorption layers, the surface elasticity of the adsorption layer at large deformations, the characteristic desorption time of the stabilising species, or the yield stress of the continuous phase for gelled systems. Bubble Ostwald ripening was completely arrested only when the solid particles were adsorbed on the air-water interface. The mechanistic explanations of all these trends have been described and verified with model experiments.

1-O5. Adsorption of ions at a non-ionic surfactant spread monolayer interface

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The motivation for this study is the Hofmeister series of activity of ions. The adsorption of ions at a water-air and water-oil interface shows special properties. Small ions (Cl^-) desorb equally from water-air and water-nonpolar oil. For larger ions, this is not the case: Br^- ions desorb less from water-oil than from water-air, and I^- ions adsorb on water-oil. This brings us to the conclusion that when the hydrophobic phase is changed from air to oil an attraction potential appears. We lean towards the idea that the force is a combined hydrophobic attraction that is not affected by the type of hydrophobic phase and van der Waals repulsion that exists only at a water-air interface. To examine this hypothesis, we developed an experimental procedure to 'add gradually' the oil phase to the surface by using surfactants that form an oil-like liquid-expanded (LE) phase. A change in the area of the monolayer of a non-soluble surfactant allows for the thickness and density of the LE film to be varied. Obviously, while the LE film is thinner, ions shall interact with the interface as with water-air. An interface with a dense monolayer will have the properties of water-oil. This way, the variance of the area allows varying the ion-interface interaction by a gradual 'switch off' of the van der Waals force without changing the hydrophobic. Our main experimental goal was to determine the adsorption of electrolyte. The Gibbs isotherm contains a $\Gamma d\mu$ term for the adsorbed surfactant, which makes it difficult to determine the adsorption of the electrolyte. The solution for the problem is to determine the equilibrium spreading pressure of a surfactant crystal at the surface of electrolyte solutions with varying concentrations.

1-O6. Phase formation and structure of glass-ceramics by Fe-Ni waste vitrification

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Hazardous residues from ferronickel smelting plant were mixed with glass cullet and vitrified for 2 h at 1400°C. After a short and low-cost thermal cycle (45–60 min nucleation at 650°C and 30–60 min crystallisation at 730–750°C), a fine crystalline bulk glass-ceramic was obtained.

Due to increased amounts of chromium, iron, and magnesium oxides in residue composition, the parent glass was characterised by a very high crystallisation trend. In addition, the phase formation was particular, which led to a complex structure of the final material.

The crystallisation process and the development of the glass-ceramic structure were studied by SEM-EDS, TEM, and XRD analytical techniques.

Our results elucidate that the phase formation starts during the melt cooling with the precipitation of preliminary Fe-Mg-Cr spinel crystals. Consequently, these crystals act as centres for further epitaxial growth of a pyroxene phase. Thus, a part of the complex glass-ceramic arrangement is formed. However, the main structure is a result of the tendency for liquid-liquid immiscibility of the parent glass. After the nucleation treatment, this immiscibility leads to the formation of 0.5–1.0 µm pyroxenes as the main crystal phase, while without nucleation treatment the pyroxene phase consists of 3.0–5.0 µm spherulites. In addition, we observed some tiny olivine crystals that also act as nuclei for pyroxene growth.

1-O7. Kinetic parameters of anodic oxidation of titanium alloys in a fluoride-containing electrolyte

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Anodic film growth on different Ti alloys (Ti-6Al-4V, Ti-15Mo-3Nb-3Al, and Ti-12%Mo-6%Zr-4.5%Sn), typically used in technological and medical applications, was investigated using electrochemical and surface analytical techniques. Electrochemical measurements were carried out using a three-electrode configuration featuring the titanium alloy with an exposed area of 4 cm^2 as working electrode, a Pt mesh as a counter electrode, and an Ag/AgCl/3 M KCl electrode (E = 0.200 V vs. SHE) as a reference. Ethylene glycol (EG, 99.9%), containing 0.6 M H_2O and 0.11 M NH_4F was used as electrolyte. Prior to anodic oxidation, the samples were chemically polished in a 1:3 mixture of HF (40 wt.%) and HNO_3 (65 wt.%) until a mirror finish was obtained. First, the steady-state current-potential curves, and electrochemical impedance spectra in a wide potential range (0.1–5 V vs AgCl/Ag) were registered, which pointed to two parallel reaction pathways: film growth/dissolution and titanium dissolution through the film. The steady-state thickness of the barrier layer was found to be a linear function of the applied potential, indicating a constant field growth of the oxide. Second, film composition, as depending on alloy type and applied potential, was assessed using X-ray photoelectron spectroscopy. XPS analysis revealed the presence of a non-stoichiometric oxide containing mainly Ti^{4+} and a certain amount of Ti^{3+}, with a certain degree of hydroxylation. Mo and Al were found to be enriched in the oxides, and evidence of transpassive oxidation/dissolution of Mo was found. Third, a kinetic model of the process is proposed and its parameters are estimated by quantitative comparison with the current-potential curves, EIS, and XPS data.

1-O8. Effects of cold plastic deformation on the mechanical characteristics and corrosion behaviour of low-alloyed (2%Cr) steel

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Steels with increased content of chromium (1÷3%) are widely used in practice for manufacturing of welded steel constructions working under corrosion attacks of sea water and atmosphere, underground and waste waters, aggressive technological media, etc.

Chromium does not change considerably the mechanical and functional characteristics of the alloys but significantly increases the corrosion resistance: about 2–3 times with respect to the non-alloyed mild steels.

This work reports results on a study addressing the effects of cold plastic deformations (up to 80%) on the mechanical characteristics, microstructures as well as the corrosion behaviour (in model solutions) of low-alloyed (Cr) carbon steel. The study was carried out with various physical and electrochemical methods.

The results obtained reveal that the increase in the degree of plastic deformation raised the tensile strength, the yield strength, and the hardness of the steel samples (about 2 times), while the relative elongation reduces by about one order of magnitude. Moreover, grain sizes increase about 3 times, but the residual stresses increase the degree of deformation up to about 50% and decrease when the deformation exceeded these value. It was established that during the deformation process the preferable grain orientation is {100}.

The model aqueous solutions of sulphuric acid allow observing the effect of the plastic deformation on the corrosion rate: the highest corrosion rate was observed when the deformation degree attained a range of 40–50%. The general corrosion behaviour of the untreated steel altered in a localised attack in the deformed samples along the elongated grains.

1-P1. Electrochemical preparation of NiCoCu and NiMoCu alloys as catalysts for hydrogen generation: a preliminary study

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NiCoCu and NiMoCu alloys of different elemental composition were obtained. The influence of deposition procedure on the electrochemical behaviour and physical properties of the deposits was established. The effect of coating morphology, composition, and structure on the catalytic activity for hydrogen evolution reaction in 6M KOH was determined.

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1-P2. Characterisation by atomic force microscopy of gold nanoparticles functionalised with azocasein for protease colorimetric enzyme assay

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In the last decades, gold nanoparticles (GNPs) have found various applications in the fields of medicine, biology, pharmacology, and chemistry. Their ubiquitous physical and chemical properties have promoted them as excellent drug delivery and diagnostic systems. A colorimetric assay based on surface plasmon resonance of metal nanoparticles have proved to be applicable for sensor systems in the enzyme catalysis because of its simplicity, sensitivity, and low cost [1,2].

The preparation of stable suspensions of gold nanoparticles (GNPs) modified with proteins is a prerequisite for their use as an analytical tool for colorimetric analysis. We propose a convenient experimental procedure for reproducible production of azocasein-functionalised GNPs. Azocasein is a red-coloured protein, which is a nonspecific protease substrate with wide application in biochemistry practice for enzyme activity determination. Hydrolysis of the casein releases the azo dye into the media where it is detected by absorbance at 440 nm.

The GNPs were functionalised with azocasein in a stable suspension with an optimised concentration of the azocazein. We also proposed a test for protease activity using azocasein-modified GNP. We applied UV-Vis spectroscopy for following the enzyme reaction on the surface of gold nanoparticles and the shift of surface plasmon resonance maxima. We studied the possibility of using azocasein-functionalized GNPs for enzyme sensor.

For characterisation of azocasein-functionalised GNPs we performed a systematic imaging by means of atomic force microscopy (AFM). A series of sample AFM images were taken in the course of the proteolytic enzyme reaction that characterised the morphology changes and GNPs size.

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2-O1. Synthesis of substituted proline derivatives as potential Seprase inhibitors

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Seprase (fibroblast activation protein, FAP) is a type II transmembrane serine protease, belonging to the prolyl oligopeptidase family. This family comprises serine proteases that cleave peptides preferentially after proline residues. The unique expression profile of FAP, coupled with studies indicating its important role in supporting tumour growth and metastasis, has generated interest as a therapeutic target. FAP inhibitors possess potential antitumor activity and some of them have been used as drugs. The most effective FAB inhibitors contain 2-cyanopyrrolidine scaffold or are pyrrolidine-2-carbaldehydes.

In this study we present the synthesis of new 3,5-diarylsubstituted proline derivatives (nitriles and esters) as potential Seprase inhibitors. Substituted proline derivatives are synthesized by the reaction path: Michael addition of [(diphenylmethylene)amino]acetonitrile to different chalkones, containing fluorine, methyl, methoxy groups in one of the aromatic rings, is performed using LiOH as a base and ultrasound irradiation in EtOH or under phase-transfer catalyst conditions. Substituted 2-amino-5-oxonitriles with protected amino group are converted to Δ^1-pyrroline-5-carbonitriles by hydrolytic cyclization under acidic conditions. Reduction of some Δ^1-pyrrolinecarbonitriles by $NaCNBH_3$ gives substituted pyrrolidine-2-carbonitriles. Methanolysis under anhydrous conditions and the following reduction of the azomethine bond give rise to substituted pyrrolidine esters. Saponification of the ester group of methyl-3,5-diphenylpyrrolidine carboxylate produces matching 3,5-disubstituted proline.

2-O2. Diastereoselective aza-Michael addition catalysed by chiral ketopinic acid derived complex

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New (+)-ketopinic acid derived Mn(III) complex, which possesses pseudo C_2-symmetry, was synthesised as chiral catalyst candidate. The ligand was prepared by refluxing (+)-ketopinic acid with ethylene diamine in chloroform. Treatment of the ligand with manganese(II) acetate tetrahydrate in refluxing ethanol gave rise to the as a brown amorphous powder complex. Characterisation of the ligand and the corresponding complex was achieved using NMR, IR spectroscopy, and elemental analysis. Aza-Michael addition of piperidine to the racemic Baylis-Hillman adducts in the presence of the chiral catalyst (10 mol.%) was found to yield anti adducts exclusively (with up to 91% yield).

2-O3. Effective removal of heavy metal ions using glycerol and starch xanthate

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Glycerol and insoluble starch xanthates (ISX) were synthesised and effectively used in the removal of Pb, Cd, and Cu from aqueous solutions. The insoluble metal complex formed between the sulphur atoms in the xanthates and the heavy metals were easily separated. Lower dosage of glycerol xanthate (GX) was required in each case, with an optimum molar ratio (M^{2+}/GX) of two. Moreover, the use of glycerol xanthate required no pH adjustments to give a 100% heavy metal removal within the range of the detection limit. As for the ISX, there was a remarkable metal scavenging activity when the ISX contained high amount of sulphur per molecule (~10%) and when the pH was adjusted to six. Butyl xanthate was also synthesised to make a reasonable comparison with the glycerol and insoluble starch xanthate. The xanthates from these two sustainable materials (starch and glycerol) proved to be more effective in metal scavenging activity. FTIR and CHNS elemental analyses were used to prove the evidence of xanthation and, in addition, ^{13}C NMR was used to characterise the glycerol xanthate.

2-O4. Kinetics and mechanism of inhibited lipid autoxidation in presence of 4-substituted coumarins

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Coumarins are a large group of 1,2-benzopyrones derivatives widely distributed in natural plant sources. They have been studied *in vivo* and *in vitro* for their biological activities: anti-inflammatory, anti-carcinogenic, anti-viral, anti-thrombotic, anti-allergic, hypo-lipidemic, and antioxidant activity. The antioxidant activity as well as biological activity of these compounds is strongly influenced by their chemical structure. The tendency to form mutagenic and toxic 3,4-coumarin epoxide intermediates during metabolic degradation of 3,4-unsubstituted coumarins has limited their pharmaceutical application. Design of novel derivatives of coumarins (as drugs) may be a good strategy to overcome this problem. In contrast, 4-substituted coumarins do not induce the formation of the epoxide. For this reason, they could be better candidates for pharmaceutical use.

The study of the antioxidant inhibiting activity is an exciting challenge from both experimental and theoretical viewpoints. A comprehensive knowledge of the chemical and functional properties and antioxidant activities of 4-methyl-, and 4-hydroxy-coumarin derivatives could help to develop design strategies of non-toxic coumarins with antioxidant activity. Here, we present the structure-antioxidant activity relationships of over 40 4-substituted coumarin derivatives (mainly 4-methyl-, and 4-hydroxy-coumarins) using combined experimental and theoretical approaches: radical scavenging activity, chain-breaking antioxidant activity during inhibited lipid autoxidation, and density functional theory to calculate quantum chemical features. The fundamental role of catecholic moiety in the inhibiting activity and the importance of the third and fourth substituents for the molecular structure are discussed.

2-O5. Biscoumarins: a challenge to synthesis

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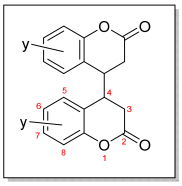

Coumarins and their analogues have shown to be useful as antitumoural and anti-HIV agents and as CNS-active compounds. Furthermore, they have been reported to have multiple biological activities: anti-coagulant, anti-inflammatory, anti-microbial, antioxidant as well as good enzyme inhibition properties [1].

During the research of the properties of coumarin compounds and their derivatives, several biscoumarins were isolated from plants and later been synthesized [2]. There are different types of dimerised coumarin systems from which 3,3'-, 4,4'-, 3,8'-, 3,6'-, 8,8'-, and 8,6'-biscoumarins are known. Few synthetic procedures for such compounds were reported in the literature based on the total synthesis of 4,4'-biisofraxidin, electroreductive hydrocoupling or electrochemical reduction [3]. All of these methods have some disadvantages: long reaction time, unsatisfactory yields, or requirement of complex equipment. Herein, we present a new simple experimental procedure for biscoumarin synthesis based on radical generation during organometallic reagents formation.

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2-P1. Theoretical study of the tautomeric preference and self-association processes of maleic and phthalic hydrazide

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Maleic hydrazide, 1,2-dihydropyridazine-3,6-dione, is a synthetic compound which has a plant growth regulating action, and claimed to be selectively toxic to plants but not to bacteria, fungi, etc. It is supposed to be a mutagen and a carcinogen in cell cultures and animals, but no evidence is available on human carcinogenicity. Maleic hydrazide acts either as a purine analogue (can form base pairs with uracil and thymine), or as a pyrimidine analogue (forming base pairs with adenine). The tautomerism of maleic hydrazide has been the subject of many experimental and computational studies. For the monomeric compound, all the theoretical assessments of relative energies of tautomers agree with the experiment and favour the oxo-hydroxy form. Phthalic hydrazide, 2,3-dihydro-1,4-phthalazinedione, in the solid state also exists in oxo-hydroxy form, while in solution the dioxo form is favoured.

The relative stabilities of maleic hydrazide and phthalic hydrazide tautomers and dimers have been studied computationally with the HF, DFT (B3LYP and M06) and MP2 methods with 6-31+G(d,p) basis set.

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2-P2. Synthesis and transformation of substituted 2-phenylimidazoles with application in supramolecular bioinorganic chemistry

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The development of suitable carriers of anticancer agents has emerged as one of the most promising approaches to overcome the adverse biochemical interactions that limit their effectiveness. The inclusion of the active substance in nanosized molecular assemblies generally leads to an increase of the selectivity based on enhanced permeability and retention effect. Suitable compounds for these purposes appear to be 2-substituted-1*H*-imidazol-4(5)-carbaldehydes which readily form imines with 2-(pyridin-2-yl)ethan-1-amine. In the presence of Cu(II) and Pd(II) such imines turn into ligands that form pH dependent, self-assembled complexes capable of decomposing at right pH value. This provoked our interest in the synthesis of modified imidazole-4(5)-carbaldehyde. The fragment that we expect to provide the desired antitumour activity is pyrene, which is incorporated in the structure of the ligand in positions that do not alter the coordination properties of the ligand and do not sterically interfere the process of self-association.

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2-P3. Molecular design of specific substrates for Seprase

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Fibroblast activation protein alpha (FAP, Seprase) is proline-specific enzyme, which belongs to the small family of serine integral membrane peptidases. The enzymes of this class have an important role in cancer disease and in particular, the FAB expression correlates with the invasiveness of human melanoma and carcinoma cells.

The widely used substrate of FAP Z-Gly-Pro-AMC is not specific. Recently, new highly specific fluorogenic substrate N-(quinoline-4-carbonyl)-D-Ala-Pro-AMC was proposed, but its disadvantage is the high concentration needed for the enzyme quantification in biological samples.

Based on own results and modelling of enzyme-substrate complexes by molecular mechanics a molecular design of chromogenic substrates for FAP was made. Two peptide series of *p*-nitroanilides were synthesised, with the following general formulas: Xaa-Gly-Pro-pNA and Xaa-D-Ala-Pro-pNA (Xaa = amino acid, In = isonicotinic acid, pNA = 4-nitroaniline).

The initial rates of FAB-catalysed substrate hydrolysis were determined. The decreasing order of the initial rates is βAla-D-Ala-Pro-pNA > βAla-Gly-Pro-pNA > In-Gly-Pro-pNA > In-D-Ala-Pro-pNA > D-Asp(Gly-Pro-pNA). These results show that β-Ala at P3 position is preferred to D-Asp and isonicotinic acid. These substrates are not hydrolysed by dipseptidyl peptidase IV. In contrast to other substrates, we have found that the In-D-Ala-Pro-pNA peptide is not hydrolysed by prolyl endopeptidase. In-D-Ala-Pro-pNA is a highly specific chromogenic substrate for FAP, which could have practical application.

2-P4. New approach to the benzo[a]quinolizidine ring system

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Recently the benzo[a]quinolizidine ring system became of a great significance since it was found to be a key subunit in the alkaloids of the *Schulzeines* and *Ipecac* species, which possess diverse physiological activities. Many methods for the construction of synthetic molecules that incorporate such a tricyclic ring system are known hitherto. Most of them include the closure of ring B or C or both.

We investigated the reaction of dihydroisoquinolines with cyclic anhydrides as a one-step approach to the benzo[a]quinolizidine system. In this manner, heterocyclic analogues of the desired system were also made. The structure and relative configuration was established by means of 1D and 2D NMR techniques. In the case of 1-methyldihydroisoquinoline the formation of a new unexpected product was observed. The compounds prepared bare the potential to become building blocks for future synthetic bioactive molecules.

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2-P5. Methoxy-substituted aroylhydrazones: synthesis, characterisation, and DFT calculations

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Aroylhydrazones have been intensively investigated in the recent years due to their coordination properties and diverse biological applications. Hydrazones derived by condensation of salicylaldehyde and different acid hydrazides possess especially high antiproliferative activities.

A series of methoxy-substituted salicylaldehyde-based aroylhydrazones have been designed by varying the position of the methoxy group in salicylaldehyde moiety. The compounds have been synthesised by Schiff-base condensation method in ethanol. The molecular structure of the hydrazones has been characterised by elemental and thermogravimetric analyses, IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. The effect of the position of the methoxy group on their structure has been evaluated using density functional theory (DFT) calculations with Becke's 3-parameter hybrid functional and 6-31+G (d,p) basis set. DFT calculations have been carried out in the gas phase and in a solvent (water and methanol). A good agreement between DFT-predicted and experimentally measured bond lengths and angles of the aroylhydrazones has been found.

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2-P6. Host-guest interactions between IIA/IIB group metal cations and cyclodextrins: a DFT/CDM study

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Although a considerable amount of information about the complexing properties of cyclodextrins has been accumulated, many aspects of their coordination chemistry remain unknown. For example, there are no systematic studies on the main factors controlling the processes of metal binding and selectivity in these systems. Many questions still remain: (i) to what extent the properties of the metal cation influence the metal-cyclodextrin recognition process?; (ii) which structural zone of cyclodextrin host exhibits the greatest affinity for the metal guest?; (iii) whether and to what extent the dielectric properties of the environment are crucial for the processes of metal binding and selectivity in these systems?; (iv) the cyclodextrin can act as a ligand of the first or second coordination sphere of the metal cation and which type of coordination favours to a greater extent the complexation process in the host-guest system? Herewith we address these questions by employing a combination of DFT/CDM calculations.

Acknowledgment: The calculations were performed on a computer system at Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, purchased by financial support of the Bulgarian Science Fund through Madara project (RNF01/0110, contract No. DO02-52/2008).

2-P7. Synergistic effects of antioxidant compositions during inhibited lipid autoxidation

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Biologically active compounds with antioxidant potential, i.e. bio-antioxidants (natural and their synthetic analogues) have a wide range of applications. They are important drugs, antibiotics, agrochemical substitutes, and food preservatives. Many of the drugs today are synthetic modifications of naturally obtained substances with both activities: biological and antioxidant. Nowadays bio-antioxidants play an important role in prevention of human diseases as components of food additives and for treatment of different diseases as monotherapy or in complex therapy with drugs.

Twenty antioxidant compositions, containing mono-, bi-, and polyphenols, were selected for this study. Various kinetic parameters and theoretical descriptors were applied to explain the effects observed and mechanisms of action of these antioxidant compositions. It was proved that the synergism observed between components in the studied mixtures is due to a significant effect of TOH regeneration.

If two or more antioxidants are added to the oxidizing lipid substrate their combined inhibitory effect can be additive, antagonistic (negative) or synergistic (positive). Different effects of various antioxidant compositions were compared and discussed. Synergism can be observed when the combined inhibiting effect of the mixture ($IP_{AOH+TOH}$) is higher than the sum of inhibiting effects ($IP_{AOH} + IP_{TOH}$) of the individual components, i.e. $IP_{AOH+TOH} > IP_{AOH} + IP_{TOH}$. There is additivity when the antioxidant mixture ensured the same inhibiting effect as the sum of the inhibiting effects of the individual components, i.e. $IP_{AOH+TOH} = IP_{AOH} + IP_{TOH}$. When the combined inhibiting effects of the antioxidant mixtures is weaker than the sum of the individual components, antagonism can be observed, i.e. $IP_{AOH+TOH} < IP_{AOH} + IP_{TOH}$.

New equations for determination of the different observed effects (synergism and antagonism) and calculation (as %) were proposed.

2-P8. Synthesis and photophysical properties of a novel benzanthrone pH sensor based on internal charge transfer

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A novel fluorescence sensing derivative of 3-aminobenzanthrone configured as a 'fluorophore-receptor' system was synthesised by nucleophilic substitution of 3-aminobenzanthrone with benzoyl chloride. The synthesised compound was isolated, characterised, and identified by TLC, UV-vis, IR, and ^{1}H NMR spectroscopy. Due to internal charge transfer, the designed fluorophore was able to act as a pH-probe via an 'off-on' fluorescence sensing mechanism. The sensor activity toward protons as cations in solution of DMF/water (1:1) and on cellulose paper was studied by monitoring the changes of the fluorescence intensity. The fluorescence changes indicated that the compound would be able to act as an efficient 'off-on-off' switch for pH determination, for monitoring aggressive environment, e.g., in concrete and industrial pollutants.

2-P9. Synergistic effects of α-tocopherol/ascorbyl palmitate binary mixtures of different ratios

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DL-α-tocopherol (TOH) and L(+)-ascorbic acid (AscAH) are known as one of the most important lipid- and water-soluble antioxidants, respectively. Their mechanisms of action against free radicals have been widely studied due to their potential as individual compounds as well as in mixtures. Despite numerous studies in this field, there are many contradictory results in the literature due to the different conditions and particularly to the medium being applied. Both could be used for development of multi-component bio-antioxidant compositions with potential applications (as food additives and in cosmetics). However, it is not clear yet what ratios between the components in the mixtures are effective.

The aim of this work was to study binary mixtures of DL-α-tocopherol (TOH) and ascorbylpalmitate (AscPH, the lipid soluble analogue of AscAH) at different ratios (from 1:1 to 1:10) during bulk phase lipid autoxidation. It was proved that AscAH and AscPH demonstrated the same lipid autoxidation kinetics and no inhibiting effect was observed. The latter proved that during the lipid autoxidation they are not antioxidants, but only synergists. Significant synergism was obtained for all the studied ratios: (i) 1:1, i.e. equimolar binary mixtures (concentrations of 0.1 mM, 38.1% and 1.0 mM, 42.4%); (ii) 1:5 (1.0 mM TOH and 5.0 mM AscPH, 47.6%); and (iii) 1:10 (1.0 mM TOH and 10.0 mM AscPH, 60%). It is seen that the synergistic effects are higher (over 40%) for the binary mixtures, in which TOH is added as 1.0-mM concentration. The new results obtained could be explained by reduction of a side reaction of TOH at a higher concentration (1.0 mM) and they are important for practice and proved a significant role of TOH regeneration.

2-P10. Production and investigation of biodiesel fuels from spent coffee ground

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In search of cheaper raw materials in recent years, investigations related to the use of waste materials to produce biodiesel pay more and more attention. Coffee is one of the most consumed beverages in the world, resulting in large amounts of waste. It was found that oil derived from coffee is of high quality and a cost effective raw material for biodiesel production. Oil content in the coffee source varies from 11 to 20 wt.% and is a function of the extraction conditions: solvent and duration of extraction.

We have previously developed a method for oil extracting of spent coffee ground as a potential low cost alternative feedstock for biodiesel production. A combination of factors like temperature, contact time, microwave irradiation of raw material, and varying solvent system was used to prepare eleven samples. The yield and fatty acid composition of the oil fractions from spent coffee ground were investigated. Optimum conditions of the process were established by applying multi optimisation techniques.

The aim of this study was to produce and investigate biodiesel fuels from oil fractions of spent coffee ground. Oil fractions, extracted under different conditions from spent coffee grounds, were used to produce and investigate biodiesel fuels. For fuel production, esterification and transesterification with homogeneous catalysts were applied. Investigation of ester composition (FAME) in biodiesel was carried out by applying the EN 14103 modified and validated gas chromatographic method. Individual ester content was calculated using the method of internal standard. Results of total and individual FAME content in all studied objects are reported that provide information about biodiesel properties.

2-P11. Thermal stability of *Helix aspersa maxima* hemocyanin

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Hemocyanins are complex oxygen-transport proteins found in the haemolymph of many arthropods and molluscs. Thermal stability is an important characteristic of proteins having potential therapeutic applications. In the present study, the thermal unfolding of the hemocyanin, isolated from garden snails *Helix aspersa maxima* (HaH), has been investigated by differential scanning calorimetry and UV-VIS absorption spectroscopy. The thermal denaturation of HaH is an irreversible process. One transition, with an apparent transition temperature at 79.8°C, was detected in the thermogram of HaH in 20 mM HEPES buffer, containing 0.1 M NaCl, 5 mM $CaCl_2$, and 5 mM $MgCl_2$, pH 7.2, using a heating rate of 1.0 $Kmin^{-1}$. The scan rate dependence of the calorimetric profiles indicates that the thermal unfolding of the investigated hemocyanin is kinetically controlled. The apparent transition temperature and specific enthalpy values (ΔH_{cal}) for the thermal denaturation of HaH were found to be independent of the protein concentration indicating that the dissociation of the hemocyanin into subunits does not take place before the rate-determining step of the started process of thermal unfolding. A two-state irreversible model described the thermal denaturation of HaH. Based on this model the parameters of the Arrhenius equation were calculated. By UV-VIS spectroscopy a reversible change in the tertiary structure of the hemocyanin, affecting copper sites activity, was found to precede the irreversible unfolding of the protein.

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2-P12. Hemocyanin from *Rapana thomasiana*: structure and anti-breast cancer activity in the presence of cholinium amino acid ionic liquids

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The focus of the research is a hemocyanin, isolated from the marine snails *Rapana thomasiana* (RtH), and its interactions with ionic liquids based on a cholinium cation and a nonpolar amino acid as anion [Chol][AA]. Six RtH-[Chol][AA] complexes were obtained. Fragmentation and structural changes in the protein even at low protein to ionic liquid ratios were observed using dynamic light scattering and fluorescence spectroscopy. The effect of RtH-[Chol][AA] on cell viability of fibroblast (3T3) and two breast cancer cell lines (MCF-7 and MDA-MB-231) were tested and compared to the effect of pure RtH. Modification of the RtH resulted in a significant inhibition of MCF-7 cell growth and had no effect on 3T3 cell viability. At the same time the effect of RtH-[Chol][AA] on MDA-MB-231 cell viability was moderate and comparable with those estimated for the pure [Chol][AA]. The obtained results testified the cell specific effect of RtH, which could be explored in treatment of different tumours.

2-P13. Synthesis and SAR evaluation of the phytochemical activity of new N-pyrrolyl carboxylic acids

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Two new N-pyrrolyl carboxylic acids were synthesized via Paal-Knorr cyclisation by condensation of γ-aminobutyric acid and 1,4-dicarbonyl compounds. The obtained structures were elucidated by IR and ^{1}H-NMR spectroscopy and their purity was proven by TLC and melting points. The corresponding phytochemical activity of the obtained compounds on wheat and cucumber cultivars in three concentrations was studied. Both molecules were tested at four concentrations for herbicidal activity. No concentration dependence of the herbicidal effects was established. The inhibition of growth factors of the aerial parts and roots within 0.001 and 1 mM concentration range was comparable.

In addition, a number of structural parameters were calculated for the target compounds and some analogues thereof. A second-degree polynomial structure-activity dependence on the herbicidal effects from the corresponding miLogP was observed with R^2 in the range of 0.796 to 0.894.

3-P1. Distribution coefficients of ion exchange resin in acetic acid solutions

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Ion exchange resins are used in diverse areas of chemistry, biology, medicine, and as a solution for different technological applications. The behaviour of a large number of elements in acetic acid aqueous solutions in the high concentration range has been previously observed on ion exchange. So far, many sorption studies of a significant number of elements have been published. However, it appears that for some elements (e.g., Th, Hf, Zr, Ti, Ac, and Ra) the sorption data for ion exchange resins with acetate is very scarce. In the present study, the concentration limits of acetic acid were expanded and the distribution coefficients of ion exchange resin for elements of 2nd to 6th oxidation state were determined. We also studied elution distribution coefficients with different mixtures of acetic acid and ammonium acetate. The acquired information from this study is important for better separation and purification of elements.

3-P2. Behaviour of rare earth elements and actinides in a UTEVA-acid solution system

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Separation of rare-earth elements (REE) from actinides (An) like Th and U presents interest; therefore, it is an object of growing number of investigations. The extraction chromatographic resin UTEVA (Uranium and TEtraValent Actinides) has demonstrated high retention coefficients for tetravalent An and U(VI). In this work, by using different acid media we determined the distribution coefficients of some REE for UTEVA resin. In our study we confirm the low sorption of all REE in the range of 1–5 M HNO_3, which presents a possibility to separate REE from tetravalent An and U(VI). Data on high concentration HNO_3 shows a gradual increase of the distribution coefficients (K_d) on increasing the atomic number of REE as well as for Y and Sc. We also examined the UTEVA-CCl_3COOH system, which manifested a higher selectivity for Eu. Chromatographic separation was carried out in order to confirm the K_d values obtained for both systems.

3-P3. Trace metals pollution of natural water-soil systems in Kardzhali region (Bulgaria): modelling of chemical species and self-cleaning ability

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Trace metals pollution of waters and soils in Kardzhali region was assessed in September 2014 by monitoring studies and chemical speciation modelling by thermodynamics. The self-cleaning ability of the studied systems was also predicted by thermodynamic modelling.

In the waters Zn was found to be the biggest pollutant followed by Cu and Mn. Cadmium was at the level of the allowed concentrations, while Al, Fe, Co, Ni, and Pb were below this level. The dominating chemical species were free Co^{2+}, Ni^{2+}, Cd^{2+} ions, MnO_4^- species, Al/Zn-hydroxy species, Fe/Cu-hydroxy organic species with bidentate bonds, and Pb organic species with bidentate bonds.

The highest concentration of the trace metals in the soils was found for Cd, followed by Pb and Zn that exceeded significantly the maximum allowed levels. The dominating chemical species of mobile ions were free Mn^{2+} ions, Mn/Co organic species with electrostatic bonds, Co/Ni/Zn/Cd organic species with monodentate bonds, Cu/Pb organic species with bidentate bonds, and Fe/Al-hydroxy organic species with bidentate bonds.

Different self-cleaning ability of the trace metals was calculated in waters and soil solutions. It was deeper for Mn, followed by Fe and Al. Zn was self-cleaning only in waters and Pb only in soil solutions. No self-cleaning ability of Co, Ni, Cu, and Cd was calculated.

3-P4. Synthesis of blödite- and kröhnkite-type solid solutions, $Na_2Zn_{1-x}Cu_x(SO_4)_2\cdot 4H_2O$ and $Na_2Cu_{1-x}Zn_x(SO_4)_2\cdot 2H_2O$: structural, thermal, and spectroscopic investigations

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Two methods were used to prepare the title solid solutions, $Na_2Zn_{1-x}Cu_x(SO_4)_2\cdot 4H_2O$ (blödite-type structure) and $Na_2Cu_{1-x}Zn_x(SO_4)_2\cdot 2H_2O$ (kröhnkite-type structure): by crystallisation from ternary solutions and by precipitating the ternary solutions of sulphates in ethanol. Due to the cooperative Jahn-Teller effect the interruption in the solid solution series occurs at a comparatively low concentration of Cu^{2+} ions (about 14 mol.%).

It has been established that the inclusion of copper ions in the structure of $Na_2Zn(SO_4)_2\cdot 4H_2O$ and of zinc ions in the structure of $Na_2Cu(SO_4)_2\cdot 2H_2O$ does not change the lattice parameters of the host compounds as deduced from X-ray powder diffraction data.

Vibrational spectra of the double neat compounds as well as those of the solid solutions are interpreted in the light of their crystal structures. The strength of the hydrogen bonds as deduced from the frequencies of ν_{OH} and ν_{OD} of matrix-isolated HDO molecules is discussed. The method of double matrix-infrared spectroscopy was used to analyse the influence of the synergetic effect on the hydrogen bond strength in the solid solutions.

The phase transitions of the neat compounds and the solid solutions were studied by TG, DTA, and DSC techniques. Experiments show that the inclusion of guest ions (copper ions in $Na_2Zn(SO_4)_2\cdot 4H_2O$ and zinc ions in $Na_2Cu(SO_4)_2\cdot 2H_2O$) leads to a considerable increase of the values of ΔH_{deh} of the solid solutions.

3-P5. Crystal structures and infrared spectra of the $Rb(Cs)_2Mg(CrO_4)_2\cdot 6H_2O$ and $Rb_2Mg(SO_4)_2\cdot 6H_2O$ Tutton compounds, and of $Rb_2Mg(Cr_{1-x}S_xO_4)_2\cdot 6H_2O$ solid solutions

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The crystal structures of $Rb_2Mg(CrO_4)_2\cdot 6H_2O$ and $Cs_2Mg(CrO_4)_2\cdot 6H_2O$ as well as those of solid solutions as $Rb_2Mg(Cr_{1-x}S_xO_4)_2\cdot 6H_2O$ (0 > x < 1) were determined from single crystal X-ray diffraction data. They belong to the group of Tutton salts, crystallising isotypic to the respective sulphate and selenates in a monoclinic structure, which is characterised by isolated $Mg(H_2O)_6$ octahedra and CrO_4 tetrahedra interlinked by hydrogen bonds and Rb^+ and Cs^+ cations.

Infrared spectra of the title Tutton compounds are discussed with respect to both the normal modes of the tetrahedral ions and the water molecules. The extent of energetic distortion of the isomorphously included sulphate ions as deduced from the values of ν_3 (site group splitting) and $\Delta\nu_3/\nu_c$ (where ν_c is the centro-frequency value of the asymmetric stretches) is commented. The hydrogen bonds in the rubidium and cesium magnesium chromates are stronger than those in the respective selenates and sulphates as deduced from both the wavenumbers of ν_{OD} of matrix-isolated HDO molecules and the wavenumbers of ν_{OH}. Based on the spectroscopic experiments a conclusion was drawn that the chromate anions are stronger proton acceptors than the selenate and sulphate ions in the case of magnesium Tutton salts.

3-P6. Influence of the reaction medium on the physicochemical and morphological characteristics of double-doped amorphous calcium phosphates

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The influence of chemical composition and rheology of the reaction medium on the chemical and phase composition and morphology of ion-doped amorphous calcium phosphates precipitated by biomimetic synthesis was evaluated. The samples were synthesised from electrolyte solutions of modified simulated body fluids containing K^+, Na^+, Cl^-, HCO_3^-, SO_4^{2-}, and HPO_4^{2-} and were enriched with $CaCl_2$, $MgCl_2$, $ZnCl_2$ or K_2HPO_4. The method of continuous precipitation at constant pH 8 by using 1 M KOH was applied. Two buffer media, ammonia and glycine, differing in the type of ligands that could participate in the complex formation around Ca, Mg and Zn ions, were examined. The rheology of the glycine buffer was modified by a non-ionic surfactant (PEG-7 glyceryl cocoate), or by a polysaccharide hydrogel (xanthan gum). Chemical analysis, XRD, TEM, DTA, IR, and BET were applied.

It was found that the reaction medium does not influence the phase composition of the precipitate while the biomimetic electrolyte solution influences its chemical composition. The buffer medium provides for the formation of different chemical species and thus influences Mg^{2+} and Zn^{2+} ion incorporation into the precipitates. The reaction medium influences the shape, size and pore distribution but not the specific surface area of the particles.

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3-P7. Ceramic with high density from tungstate solid solutions Cr^{3+}–$Sc_{2-x}In_x(WO_4)_3$ as a new matrix for tunable lasers applications

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Indium tungstate $In_2(WO_4)_3$ and scandium tungstate $Sc_2(WO_4)_3$ belong to a class of compounds with general formula $Me_2(WO_4)_3$, (Me = Y, Sc, In, Al or lanthanides with small ionic radii: Ho, Er, Tm, Yb, and Lu). Doped by Cr^{3+} they are potential laser active media with a wide range of emission between 700–1000 nm.

The aim of our investigation was to obtain solid solutions of nanosized $Sc_{2-x}In_x(WO_4)_3$, (x=0÷2) doped with Cr^{3+} of controlled particle size and particle size distribution that are suitable to obtain high density ceramics.

The tungstates were obtained by co-precipitation technique from aqueous solutions of $Na_2WO_4.2H_2O$ and $Me(NO_3)_3.xH_2O$ nitrates, where Me is In, Sc, and Cr. The temperature ranges of crystallization of amorphous samples were determined by DTA analysis. These results were used to establish the optimal conditions for further sample thermal treatment. Structural and phase investigations of the nanosized powders were performed. Pure phases of investigated tungstates were characterised by X-ray analysis. The average particle size was in the range of 20–100 nm depending on temperature and thermal treatment period. The main structural units were determined using IR spectroscopy.

High-density samples from these powders will be obtained and used to determine fundamental applied characteristics (absorption and emission, lifetime, etc.). The main advantage of these tungstates is the possibility of varying laser properties in a wide range by changing the chemical composition.

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3-P8. Study on the electrochemical performance of $Na_{0.67}Ni_{0.5}Mn_{0.5}O_2$ used as a cathode in lithium-ion batteries

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Sodium-ion batteries have been considered promising candidates for medium and large-scale stationary energy storage in recent years. There are still a lot of challenges in sodium chemistry; however, the main one is to find appropriate sodium compounds with characteristics competitive to that of lithium electrode materials. Recently we have demonstrated that sodium deficient nickel manganese oxides with a $Na_{0.67}Ni_{0.5}Mn_{0.5}O_2$ composition and a *P*3-type of structure are attractive as electrode materials for both sodium and lithium-ion batteries. The electrochemical performance of the layered oxide $Na_{0.67}Ni_{0.5}Mn_{0.5}O_2$ has been shown to depend on the method of oxide synthesis and the potential range of cell cycling, etc.

In this contribution, we extend our study by exploring the effect of the electrolyte composition and the start mode of charging on the electrochemical performance of layered $Na_{0.67}Ni_{0.5}Mn_{0.5}O_2$ oxide used as a cathode in model lithium-ion cell. The electrochemical tests were carried out in model two-electrode lithium cells of the type $Li|LiR(EC:DMC)|Na_xNi_{0.5}Mn_{0.5}O_2$, where LiR= $LiPF_6$, $LiBF_4$. The cells were started in discharge or charge mode to intercalate lithium in oxides or to deintercalate sodium from them, respectively.

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3-P9. Stabilisation of olivine-type structure of $NaMnPO_4$ by Mg doping as a route for enhancement of its electrochemical performance in alkali-ion batteries

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Sodium-ion batteries are regarded as a ‘green’ and cheaper alternative of the lithium-ion batteries. Very recently, olivine-type $NaMnPO_4$ became a very attractive positive electrode material for high-power batteries owing to its high energy density, cyclic stability, and low cost. However, $NaMnPO_4$ exhibits a limited rate capability mainly associated with the instability of the desodiated phase $MnPO_4$ (Jahn-Teller effect of Mn^{3+}) and interfacial strain due to the large volume change in the phase boundary $NaMnPO_4/MnPO_4$.

The present work is a first report on the increase of the structural stability of $NaMnPO_4$ in both charged and discharged state by partial replacement of Mn by Mg ions. This approach ensures: (i) reduction and dilution in the crystal lattice of the Mn^{3+} ions that are responsible for the structure instability of $MnPO_4$; (ii) a decrease in the volume change across the two-phase interface during the electrochemical cycling; and (iii) improved electronic conductivity owing to the presence of the dopant Mg ions. All this causes improved electrochemical kinetics without compromising the energy density significantly. To achieve the desired positive effect of the Mg doping, $NaMn_{1-x}Mg_xPO_4$ was prepared by an innovative topochemical method that assures the necessary cation distribution of Na, Mn, and Mg ions in the olivine structure. Rietveld method, IR spectroscopy, and SEM were used to study $NaMn_{1-x}MgxPO_4$ structure and morphology. The reversible intercalation/deintercalation activity of the $NaMn_{1-x}Mg_xPO_4/C$ composites was examined in two- and three-electrode electrochemical cells.

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3-P10. Hydrogen sorption kinetics of magnesium-based composites with activated carbon additive obtained by ball milling

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Hydrogen absorption-desorption features of composites containing 95 wt.% Mg and 5 wt.% activated carbon were investigated. The activated carbon was synthesised from polyolefin wax, a waste product of polyethylene production at low pressure (POW) or apricot stones (AS), by ball milling under argon atmosphere. The hydrogen absorption- desorption properties of the composites were determined by volumetric or Sievert’s type apparatus. The phase composition of the samples before and after hydriding was characterised by X-ray diffraction analysis. The Mg-POW and Mg-AS composites were subjected to 80 cycles of hydriding-dehydriding. At the 2nd cycle the Mg-POW system reached 7.1-wt.% hydrogen absorption capacity and 6.4 wt.% at 80th cycle. The composite of AS-activated carbon required some activation cycles and reached 6.9-wt.% absorption capacity at 80th cycle. The Mg-POW and Mg-AS composites showed fast sorption kinetics and addition of activated carbons derived from POW and AS had a positive effect on their hydrogen absorption/desorption properties leading to an enhanced rate of hydriding reaction and high absorption capacity during manifold cycling.

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3-P11. Hydrogen sorption properties of 90 wt.% MgH_2-10 wt.% $CrSi_2$, CrSi, Cr_3Si, and Cr_5Si_3

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The hydriding-dehydriding characteristics of 90 wt.% MgH_2-10 wt.% $CrSi_2$, CrSi, Cr_3Si, and Cr_5Si_3 composites obtained by ball milling under argon atmosphere were studied. $CrSi_2$, CrSi, Cr_3Si, and Cr_5Si_3 single crystals were grown by chemical vapour transport with halogens as transport medium. MgH_2 of 98% purity was used to prepare above-mentioned composites. The composites were obtained by mechanical grinding in a planetary ball mill under argon for 60 min. The hydrogen absorption-desorption characteristics of the composites were determined by a Sievert's-type volumetric apparatus. Hydrogen absorption proceeded at temperatures of 623, 573, and 473 K and a pressure of 1 MPa. Desorption was carried out at 623 and 573 K and pressure of 0.15 MPa. The 90 wt.% MgH_2-10 wt.% $CrSi_2$ composite reached the highest absorption capacity of 6.2 wt.% H_2 at a temperature of 573 K and a pressure of 1 MPa. The phase composition of the starting $CrSi_2$, Cr_5Si_3, Cr_3Si, and CrSi and ball-milled composites before and after hydriding was controlled by X-ray phase analysis. The specific surface area of the composites after ball milling was measured through nitrogen adsorption-desorption isotherms. The hydrogen absorption capacity and the rate of absorption reaction decreased with diminution of silicon content in the additives. All composites demonstrated improved hydrogen sorption properties during multiple hydriding and dehydriding cycles.

4-K1. A novel hybrid flow system for the online fractionation and speciation of bioaccessible inorganic and organic mercury in environmental solid samples

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A hybrid sequential injection system integrating dynamic sequential extraction, online digestion, and atomic fluorescence spectrometric detection for the assessment of bioaccessible inorganic (In-Hg) and organic (Org-Hg) mercury in environmental solid samples has been developed. Four extractants (i.e. deionised water, HNO_3 solution, KOH solution, and solution containing both Na_2S and KOH) are applied sequentially to a solid sample, packed in a column, to release four Hg fractions (i.e. water soluble, exchangeable, organic matter associated, and sulphide-bound mercury). The concentrations of In-Hg and total mercury (T-Hg) in the extracts are determined prior and after sample digestion, respectively, and the Org-Hg concentration is calculated as the difference between T-Hg and In-Hg. The concentration of residual Hg in the solid sample after sequential extraction is determined after acid digestion. The newly developed method has been validated by applying it to two reference materials (river sediment and biosoil). The most important advantages of the online method in comparison to its batch-wise counterpart include: (i) significant reduction in the time for acquisition of the dynamic extraction data; (ii) minimization of matrix interferences; and (iii) elimination of readsorption or chemical transformation of the extracted Hg species. An additional significant advantage of the newly developed method compared to existing manual and online methods is its speciation capabilities.

4-O1. Spectral interferences in the determination of rhenium in molybdenum and copper concentrates by inductively coupled plasma optical emission spectrometry

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Possibilities of high resolution radial viewing 40.68 MHz inductively coupled plasma optical emission spectrometry (ICP-OES) for determination of rhenium in a complex matrix containing Mo, Al, Ti, Fe, Mg, Ca, and Cu were studied. The hyperfine structure (HFS) of the most prominent lines of rhenium (Re II 197.248 nm, Re II 221.426 nm, and Re II 227.525 nm) was registered. The HFS components under high-resolution conditions were used as separate prominent lines in order to circumvent the spectral interferences. The Q-concept was applied for quantification of the spectral interferences. Quantitative databases of the type and magnitude of the spectral interferences in the presence of the above-mentioned matrix constituents were obtained by using a radial viewing 40.68 MHz ICP at high resolution and an axial viewing 27.12 MHz ICP at middle resolution. Data on both ICP-OES systems were collected chiefly with a view to spectrochemical analysis to compare the line intensity and wing (background) spectral interference, and the true detection limits with spectroscopic apparatus of different spectral resolution. The sample pretreatment methods by sintering with magnesium oxide and oxidising agents as well as a microwave acid digestion were applied. Certified reference materials experimentally demonstrated the feasibility, accuracy, and precision of the analytical results.

4-O2. Supramolecular bioinorganic chemistry: an interdisciplinary challenge for the Faculty of Chemistry and Pharmacy at Sofia University

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Metallosupramolecules gain increasing popularity as both molecular containers with various analytical and catalytic applications, and anticancer agents. Here we aim to present the implementation of state-of-the-art spectroscopic and microscopic techniques, such as TEM and fluorescence microscopic imaging of tumour cells that have been achieved at the Faculty of Chemistry and Pharmacy in collaboration with specialists from the Bulgarian Academy of Sciences, Faculty of Biology at Sofia University, and Sofia Medical University. Significant cytotoxicity of Pt(II)- and Pd(II)-linked M_2L_4 coordination capsules against human cancer cells was observed. Mechanistic insights into the anticancer activity were obtained by fluorescence microscopy of tumour cells treated with the capsules, and complemented by TEM images, electrophoretic, enzymological, immunochemical tests.

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4-O3. A comparative study of the effects of salinomycin, monensin, and DMSA on the biodistribution of cadmium, calcium, copper, iron, and zinc in Cd-intoxicated mice

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To treat acute and chronic metal intoxications, a therapy with chelating agents was applied. The FDA-approved chelating agents ($CaNa_2EDTA$, DMSA) for the treatment of toxic metal intoxications are not effective antidotes to Cd poisoning. $CaNa_2EDTA$ has poor absorption by gastrointestinal tract and can be administered only by i.v. injections, which is one of the disadvantages of this chelating agent for the treatment of toxic metal intoxications. DMSA and its metal complexes are hydrophilic and might cause renal dysfunction.

Our studies have shown that monensin, administered p.os. as tetraethylammonium salt, decreased the Cd concentration in all of the organs of Cd-treated mice. The observed effect was in the range 90% for heart and 50% for liver compared to the untreated control animals. Furthermore, the antibiotic inhibited the Cd-induced toxicity and did not affect the homeostasis of Cu and Zn. These results provoked us to examine in detail the potential application of other natural polyether ionophorous antibiotics as chelating agents for the treatment of Cd intoxications. Among the polyether ionophorous antibiotics salinomycin exhibits the lowest *in vivo* toxicity. In 2012, the antibiotic was approved for clinical trials in patients diagnosed with invasive triple negative breast cancer. Herein we present novel information about the potential application of salinomycin as chelating agent for the treatment of Cd intoxications. The effect of the antibiotic on Cd, Ca, Cu, Fe, and Zn biodistributions in Cd-treated mice was compared with the effects of monensin and DMSA.

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4-O4. Chromate-imprinted sorbent supported on silica spheres for preconcentration and determination of Cr(VI) in textiles

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It is well known that Cr species have totally contrasting physiological effects: Cr(III) is identified as an essential nutrient for humans, required for glucose and fats metabolism, while Cr(VI) and its compounds are definitely recognised as carcinogenic and mutagenic substances. Furthermore, Cr(VI) is a strong dermal irritant, which can easily be released from fabrics, especially when the clothes are in direct contact with the human skin. As a result of perspiration, the soluble Cr(VI) species is able to migrate onto the skin, which can be a dangerous route of absorption, promoting severe dermatitis and skin ulcers.

This work is focused on the synthesis of a chromate surface-imprinted sorbent prepared by grafting of 3-methyl-1-trimethoxysilylpropylimidazole, preliminarily coordinated to CrO_4^{2-} as a template ion, onto the surface of silica spheres and its further application for preconcentration and determination of the extractable Cr(VI) in textile samples. Sorption and desorption characteristics of the surface-imprinted sorbent toward Cr(III) and Cr(VI) were examined by batch solid phase extraction. Excellent separation of Cr(VI)/ was achieved at pH 2–3 for 20 min. Cr(VI) ions were selectively retained on the sorbent, while Cr(III) remained in solution. A freshly prepared mixture of ascorbic acid and nitric acid was selected as the most efficient eluent for quantitative desorption of the retained Cr(VI). In order to evaluate a possible migration of Cr(VI), several types of fabrics were placed in 50-ml solution of artificial sweat, prepared by dissolving sodium chloride, sodium dihydrogen phosphate, and histidine in doubly distilled water at pH 4.2 and then shaken at room temperature for 12 h. After that, the textiles were removed and the artificial sweat solution was filtered and mixed with 100 mg of the sorbent. Solid phase extraction was carried out under the optimal conditions defined and Cr(VI) concentration in eluate was measured by ICP-MS.

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4-P1. Comparison of ISO 21748 and ISO 11352 standards for measurement uncertainty estimation in water analysis

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Two different approaches based on ISO standards: ISO 21748:2010 and ISO 11352:2012 for estimation of measurement uncertainty in the field of water analysis were compared. Several certified reference materials (CRMs) with certified values for different water quality parameters were measured and measurement uncertainties were evaluated for each of them according to the above-mentioned ISO standards. Results show an excellent agreement for chemical oxygen demand (COD), total organic carbon (TOC), ammonium nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N), total phosphorus (PO_4^{3-}-P), and chloride (Cl^-).

Based on the results obtained and the experimental design, the use of ISO11352:2012 for measurement uncertainty estimation is recommended. This international standard employs fewer determinations (a minimum number of eight measurements is required, compared to fifteen when using ISO 21748:2010, fewer working days (one compared to five), easier measurement uncertainty components' calculations and even gives opportunity for routine laboratories to use standard solutions over the more expensive CRMs for the measurement uncertainty estimation during method validation.

4-P2. Impact of sharp warming and freezing on the geochemical fractionation of americium in different soil types

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Sharp variations of environmental temperature might have a great impact on the geochemical behaviour of the radionuclides released in the soils after nuclear accident. The changes of soil characteristics because of rapid warming or freezing can influence the distribution and bioaccumulation of radioactive contaminants. This paper presents the effects of warming and freezing on the binding of ^{241}Am to the different soil phases one month after radioactive contamination. The investigation aimed to identify the main soil characteristics, that determine the geochemical behaviour of ^{241}Am at sharp temperature variations. The study was carried out by using ten different soil types from Bulgaria. The soil samples were contaminated with aqueous solution of $^{241}Am^{3+}$ and conditioned at −18°C (freezer) and 18 and 40°C (climate chamber) for a period of one month. Geochemical forms of ^{241}Am in the soils were studied by a sequential extraction procedure recommended for actinides. A Canberra 7221 HP Ge detector coupled to a 16000-channel DSA-1000 analyser was used to determine ^{241}Am by its gamma peak at 59.5 keV. The general characteristics of the studied soils, including pH, cation exchange capacity (CEC), soil texture, humus, and mineral composition of the crystal phase of the soil samples, determined by X-ray diffraction analysis were considered. The results showed that the sharp warming or freezing causes significant changes of the geochemical behaviour of ^{241}Am and increased its mobility up to six times in the soils of low CEC or loamy sand texture. The soils with normal range of CEC and loam or clay loam textures were found to be more resistant to sharp temperature variations and the changes in the fractionation of ^{241}Am did not exceed 30%.

4-P3. Total reflection X-ray fluorescence analysis of bottom ashes from Bulgarian coal-fired power plants

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Coal-fired power plants supply more than 40% of the electricity in Bulgaria and generate annually about 5.5–6.5 million tons of wastes (bottom and fly ashes). The analytical characterisation of these by-products is important for their evaluation, processing, and utilisation, because their chemical and physical properties vary widely depending on the kind of coal fired, boiler type, and burning regime.

In the present study the element composition of raw coal bottom ashes from four Bulgarian power plants were investigated. The elements Fe, K, Ca, Cu, Ni, Zn, Mn, Ti, Pb, Cr, V, Sr, Ba, and Rb were determined by total reflection X-ray fluorescence (TXRF) analysis using gallium as internal standard. The samples were analysed as suspensions in Triton X-114. The TXRF procedure was optimised and validated. The precision of the RSD determinations was within 4–12%. Hence, TXRF proved to be a fast and simple method for simultaneous determination of a large number of elements in bottom ash samples at concentrations ranging several orders of magnitude.

4-P4. Copper mining and phytoaccumulation of heavy metals

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The accumulation of Cd, Cr, Cu, Fe, Mn, Ni, and Zn by grasses, mushrooms, and *Taraxacum officinale* thriving in copper mine tailings in Bulgaria was investigated. The translocation factors of soil to aboveground tissues of plants were evaluated for aqua regia and EDTA soluble parts of soil metals. The lowest translocation factors were registered for grasses. Mushrooms were found to accumulate more cadmium, copper, and zinc than grasses and *Taraxacum officinale*. Iron accumulation was observed only for *Taraxacum officinale*. The difference in the accumulation of Cr, Mn, and Pb by the studied plants was statistically not significant. To assess the environmental impact of copper mining, the bio-concentration factors were also estimated. They were the highest for Cu followed by Cd and Pb.

4-P5. Problems and possibilities of inductively coupled plasma optical emission spectrometry in the determination of toxic elements in environmental samples

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The determination of toxic elements in environmental samples is of great interest in terms of their harmful health effects. The problems and possibilities of high resolution radial viewing 40.68 MHz inductively coupled plasma optical emission spectrometry (HR-ICP-OES) in determining As, Zn, Hg, Cd, Tl, and U in soils and Zn, Cd, Cu, Mn, Pb, Cr, and U in waters are shown.

Considerable systematic errors in ICP-OES may arise from spectral interferences. Environmental samples normally contain Al, Ca, Fe, Mg, and Ti as complex matrix. Quantitative databases for the type and magnitude of the spectral interferences in the presence of above-mentioned complex matrix were obtained chiefly with a view to the spectrochemical analysis.

Improvement of the true detection limits was achieved by optimum line selection and optimisation of the plasma operating conditions. The lowest detection limits were derived under robust plasma operating conditions (excitation temperature ~7200 K). The accuracy and precision of the analytical results were experimentally demonstrated by certified reference materials. The detection limits for the elements of interest satisfy the requirements for their maximum permissible concentrations of soils and natural water.

4-P6. Use of descriptor fingerprints for clustering of red wines according to their quality

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Descriptor fingerprints have been proposed and developed in a series of own papers for application to QSAR and QSPR studies. In contrast to structural fingerprints, they contain information on physical properties (descriptors) of the studied objects. Descriptor fingerprints have been used in the present investigation for clustering of red wines. The present investigation was performed to test the potentials of the fingerprint clustering algorithm for a set of 1599 red wines in relation to wine properties,

A large dataset of laboratory analytical test values for a set of 1599 red wines was taken from literature and the clustering procedure of Butina by using the descriptor fingerprints was carried out. Descriptor fingerprints were generated based on physicochemical laboratory data routinely used for wine characterisation (fixed and volatile acidity; residual sugar, total and free sulphur dioxide, citric acid, chlorides, sulphates, density, pH and alcohol content). The next step was a similarity search followed by the clustering procedure. As a result, we have obtained a distribution of the wines in 303 different clusters. A correlation between the quality of wines and the physicochemical descriptors was observed. Each cluster was composed of objects with similar values of laboratory parameters and with a wine quality certificate. The quality of the wine is characterised by a 10-point system (point 0 means very bad wine quality; point 10 is equal to excellent quality) and is perceived subjectively by a flavour and taste sense perception. In our case, some wines of the same quality but fallen in different clusters show different values of the laboratory descriptor parameters and vice versa, the wines falling in the same cluster clearly show either the same or closely similar laboratory descriptor parameters. Thus, a clustering based on descriptor fingerprints of descriptors taken from laboratory tests can be conducive to a certification of wines without any sensory tests.

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4-P7. Occurrence of triazine pesticides in Bulgarian drinking water

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Triazines are widely used herbicides that can be detected in the drinking and environmental water at trace level. The maximal permissible level of individual pesticides in drinking water including triazines is 0.1 μgl^{-1}.

The methodical part of the study is about analytical recovery of solid phase extraction of triazines by two type C_{18} cartridges. High analytical recovery of 70–80 % for Oasis HLB, 500 mg, 6 cm^3 (Waters) and Cleanert PEP-2, 500 mg, 6 cm^3 (Agela) makes them appropriate for determination of triazines. However, the price of Cleanert PEP-2 is two times lower and this makes it more economical for laboratory use.

The investigation has been performed for the 2008–2016 period. HPLC-DAD method was used for determination of total 1843 samples. Positive results were detected in 22 samples. Atrazine was found in 20 of them in amount 0.01 to 0.3 μgl^{-1}. In three samples, atrazine was above the maximal permissible level and atrazine and simazine were detected in trace concentrations in 4 samples. The positive samples were evenly distributed throughout the country: 9 in South Bulgaria and 11 in North Bulgaria.

Bearing in mind that triazines are not permitted for use, but our results show that there are residues in Bulgarian drinking water mainly in trace concentrations.

5-K1. Design of novel catalysts for CO and VOCs abatement

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Environmental catalysis represents one of the most important applications of solid catalysts worldwide. In spite of the ongoing efforts in developing environmentally benign routes to chemicals and the reduction of environmental impact of non-chemical processes, the abatement of air pollutants is still of increasing relevance. The design of novel catalytic materials with improved efficiency in the removal of air polluting substances is a subject of appreciable research. Gold, long regarded as poorly active catalyst, attracts significant attention in recent years due to the high activity of gold nanoparticles supported on metal oxides for catalysing various oxidation reactions at low temperatures. Catalytic performance depends on many factors, such as role of support, Au particle size and shape, electronic state of gold, influence of the preparation method, and catalyst pretreatment conditions. Although the possibility of a co-operative synergistic effect between some of these factors could exist, the nature of support could not only influence the amount of gold deposited on the surface, the size and shape of gold particles, but to directly participate in the reaction pathway when reducible oxides are used.

Here, we report recent results of our work on the effect of support composition on the CO, CH_3OH, and $(CH_3)_2O$ oxidation activity of gold catalysts. The catalytic performance of ceria-supported gold catalysts doped by different metal oxides (Me=Fe, Mn, and Co) in CO and VOCs oxidation was studied and a strong influence of dopant nature was observed. A superior low-temperature CO oxidation activity was demonstrated by Au/Co-doped ceria sample over which a 100% conversion degree at 25°C was obtained. Characterisation by XRD and HRTEM evidenced differences in average size and gold particle distribution. The highest hydrogen consumption (e.g. highest oxygen mobility) was registered by TPR measurements over gold catalyst on ceria doped by Co_3O_4. A high defectivity of exposed ceria faces, presence of gold particles of the smallest size and a highly reducible CoO_x phase resulted in a larger enhancement of the mobility/reactivity of surface ceria oxygen and led to a high oxidation activity. Investigation of the effect of quantitative modification of ceria with Co_3O_4 (5, 10, and 15 wt.%) showed that the support with 90 wt.% CeO_2–10 wt.% Co_3O_4 composition appeared beneficial for nucleation and growth of highly dispersed gold particles. A structure-reactivity relationship in Co_3O_4-promoted Au/CeO_2 catalysts for CH_3OH oxidation was studied by *in situ* FTIR and operando EXAFS. The results indicated that oxidised gold species are involved in the methanol oxidation reaction. In addition, EXAFS analysis of the catalyst under working conditions suggested that the active sites present on the most active sample (10 wt.% Co_3O_4) are those where the gold sites are strongly interacting with cobalt. On these active sites reactive oxygen species, possibly close to Co sites, can be activated and participate firstly in the oxidative dehydrogenation reaction of methanol to formate species and then in the complete methanol oxidation to carbonate species.

Further, we focus on the development of catalytically efficient formulations by promotion of alumina-supported mixed transition metal oxides with gold. The role of gold on the structural and catalytic properties of Cu-Mn/Al_2O_3 catalysts for simultaneous elimination of different types of air pollutants: CH_3OH, $(CH_3)_2O$, and CO in waste gases from formaldehyde production will be considered. The effect of Au can be related to the appearance of new active sites able to interact with CO as well as to improvement of the redox properties of Cu-Mn spinel that influences the mobility of lattice oxygen. Catalytic tests related to the simultaneous oxidation of CO, CH_3OH, and $(CH_3)_2O$ put in evidence the promising behaviour of the Au-promoted samples. A combination of the favourable features of Cu-Mn mixed oxides with those of gold nanoparticles represents an advantageous approach to developing new catalytic formulations of high effectiveness to eliminate different types of pollutants in waste gases. The use of a high surface area support is favourable to stabilise gold particles in a highly dispersed state. Additionally, the composition of this catalytic system, which is mostly composed of alumina (80%), is beneficial in case of practical applications because of its economic viability.

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5-K2. Impact of magnesium dopant on the properties and performance of nickel-based catalysts

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Nickel is one of the non-noble metals showing attractive performance as catalyst in various industrial processes. Depending on the operating conditions, destructive effects such as sintering would decrease its catalytic activity. It is well known that alkaline earth ions often are used as a textural promoter in commercial nickel catalysts. Dilution of the transition metal may affect the resistance to the thermal sintering, phase transformation, and Ni species reducibility. Alkaline earth ions as additive can improve catalyst surface basicity.

The effect of Mg dopant on the physicochemical and catalytic properties of Ni-based catalysts derived from two types of layered systems: Ni-Al layered double hydroxides (LDH) with takovite-like structure, and nickel phyllosilicates was examined through various characterisation methods.

Ni-Al LDH with Ni^{2+}/Al^{3+} molar ratios of 1.5 and 3.0 have been synthesised by co-precipitation, then modified by introduction of various amount of Mg^{2+} ions into the layered system, and investigated as catalyst precursors for purification of CO-containing gaseous mixtures by means of CO conversion by water vapour. The modification was accompanied by partial amorphisation of the crystal structure, a decrease in nanosize of the takovite-like particles, an increase of the specific surface area, and a decrease of the surface acidity. It was established that the Mg-doped NiAl samples, as an alternative to traditional water-gas shift (WGS) catalysts, showed a considerable catalytic activity in the 200–300°C temperature range if compared with undoped catalysts. CO removal was enhanced by Mg presence, thus the promoting effect of the alkaline-earth additive in the WGS reaction was proved. The increased basicity of the NiMgAl catalysts facilitated the decomposition of the intermediate surface formate species to CO_2 and H_2 in the medium-temperature WGS reaction.

The effect of Mg on the structure and activity of co-precipitated Ni-Al LDH as catalyst precursors for purification of hydrogen-rich streams from CO_2 by methanation was examined. Various M^{2+}/Al^{3+} molar ratios ($M^{2+}/Al^{3+} = 1.5$ and 3.0, where $M^{2+} = Ni^{2+}$ or $M^{2+} = Ni^{2+} + Mg^{2+}$), reduction and reaction temperatures as well as gas hourly space velocities (GHSV) were applied. Mg content was identical (at the expense of Ni) in both doped samples. All catalysts prepared by reduction at 400, 450, 530, or 600°C hydrogenated CO_2 successfully to 0–10 ppm levels at reaction temperatures in the range 400–320°C and GHSV from 3000 to 22000 h^{-1}. Highly Ni-loaded catalysts (3.0NiAl and 3.0NiMgAl) manifested a tendency to be more active than low Ni-loaded samples (1.5NiAl and 1.5NiMgAl). The activity of Mg-free NiAl catalysts at lower reaction temperatures (280 and 260°C) after reduction at 400 and 450°C was attributed to a larger metal Ni specific surface area and smaller metal Ni particles (higher Ni dispersion). Further treatment of the catalysts at 530 and 600°C induced sintering of the metal Ni particles, thus leading to a decrease of the methanation activity. The advantage of the Mg-containing Ni-Al catalysts is to keep metal nickel dispersion after reduction above 500°C due to a retarding effect of Mg on the Ni^0 sintering. Bearing in mind that the lower temperatures are thermodynamically and economically favourable for the reaction, the Mg-doped high-loaded Ni composition (3.0NiMgAl) is a promising catalyst for low-temperature (220 and 240°C) deep CO_2 removal from H_2-rich gas streams through the methanation reaction.

The effects of Mg additive on the structure, reduction process, and activity of silica gel (SIG) supported Ni catalyst in sunflower oil hydrogenation were examined. Two types of commercial SIG, named SIG-A and SIG-C, being different in their texture characteristics, were applied as supports to synthesise precipitated undoped Ni/SIG and Mg-doped precursors ($SiO_2/Ni=1.0$ and $Mg/Ni=0.1$). Catalyst activation by reduction was conducted at 430°C. A higher hydrogenation activity of MgNi/SIG-C was observed that can be related not only to the presence of readily reducible Ni^{2+} species at a temperature up to 430°C, which generates sufficient number of accessible Ni^0 active surface sites, but also to a larger average pore diameter of the MgNi/SIG-C precursor (15 nm) compared to MgNi/SIG-A (9 nm). A larger pore diameter allows faster diffusion of the triacylglycerol molecules through the pore system of the catalyst, reflecting on a higher reaction rate and a higher hydrogenation activity.

It can be concluded that Mg-doped Ni-based catalysts are a promising candidate for global and topical catalytic processes that are associated principally with environmental protection, hydrogen energy production, carbon emissions abatement as well as human health protection and improved quality of life.

5-K3. Guest molecules in metal-organic frameworks: FTIR spectroscopic studies

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The continuously growing interest in metal organic framework (MOF) materials is due to their unique adsorption properties. Although their applications in catalysis have not yet been commercialised, their high surface area, tunable porosity, and wide variety of functional groups make them especially attractive as potential catalysts. Therefore, gaining knowledge into the nature of the adsorption sites and the adsorption geometry is of great importance. In this respect, FTIR spectroscopy is one of the most suitable techniques to study in detail the adsorption process.

The adsorption sites in MOFs could be coordinatively unsaturated metal cations or hydroxyl groups. A representative of the former group is CPO-27-Ni. Coadsorption of CO and water on this material revealed an unprecedented behaviour of the Ni^{2+} sites: CO replaces water molecules from the Ni^{2+} sites in order to form carbonyls. The released water is then adsorbed onto other water forming a second adsorption layer. The results evidence that, when in the MOF structure, cations are characterised by enhanced ability of back donating electrons.

From the MOF materials possessing OH groups as active sites, MIL-53(Al) and NH_2-MIL-53(Al) were studied using different probe molecules. It is noteworthy that adsorption of carbon dioxide revealed vibrational interaction between two CO_2 molecules forming a highly symmetric dimeric structure connected to two structural OH groups. Upon formation of these dimers, a transition from large pore to the narrow pore forms of the MOF occurs.

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5-P1. Effect of ceria on the CO and VOCs oxidation over alumina-supported Cu-Mn catalysts

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Catalytic oxidation is considered one of the most promising and environmentally friendly technologies for the abatement of CO and VOCs. The aim of this work was to study the modification of alumina-supported Cu-Mn mixed oxides with ceria and to follow the effect on the activity and selectivity for simultaneous elimination of CO, methanol, and DME in waste gases from formaldehyde production. Copper-rich and manganese-rich samples having Cu/Mn molar ratio of 2:1 and 1:5, respectively, were modified by partial replacement of manganese with Ce. The samples were characterised by BET, TG/DTA, XRD, and TPR. Then catalytic measurements were performed. Added ceria improved the activity toward CO oxidation of both type of catalytic systems. The best effect was achieved after complete replacement of Mn. A slight influence on CH_3OH oxidation was registered only with 20-wt.% Ce samples. Ceria modification of Cu/Mn samples had an opposite impact in the oxidation of DME. An enhanced activity was measured over a Cu/Mn (1:5) sample modified with 20 wt.% Ce. Ceria had no positive effect in copper-rich samples. Structure-reactivity relationships will be analysed in order to explain the role of ceria.

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5-P2. Nanosized ZnO photocatalyst prepared by effective solution-solid process

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In this study, we report optimised conditions of effective solution-solid process for starch-mediated preparation of ZnO photocatalyst with excellent photocatalytic performance. The solution-solid route included first formation of starch-Zn precursor constituted by Zn(II) ions in starch framework (solution phase stage) and subsequent heat treatment of the precursor to obtain spatially separated ZnO nanocrystals (solid phase stage). Controlled solvent-exchange, further isolation of solid product by microfiltration, and drying prior to the thermal removal of template backbone were found to be important steps in this approach. Optimal conditions, such as a starch-Zn source ratio at different molar Zn(II) concentrations in solution phase and calcination temperature, were established. The samples prepared were characterised by XRD, SEM/EDX, and TEM/SAED observations, BET surface area measurements, TG/DTA analysis, UV-Vis, and PL spectra. It should be noted that ZnO nanoparticles could be prepared on large scale through this optimised solution-solid process. In addition, the results of photocatalytic tests indicate that this material exhibits a superior photocatalytic activity referring to the photodegradation of organic dye methylene blue (MB). The data obtained were compared with commercial TiO_2 (P25).

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5-P3. Ferrite modified with gold nanoparticles as photocatalyst for decomposition of organic water pollutants

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In order to improve the photocatalytic properties of ferrites modification with gold nanoparticles was applied. The sol-gel method was used for synthesis of $CoFe_2O_4$ nanoparticles where propylene oxide was the gelating agent. The ferrite prepared was modified with gold nanoparticles using solutions of various Au concentrations. Samples were characterised by XRD, transmission electron microscopy, and UV/Vis spectroscopy. The samples obtained were tested for decomposition of the organic pollutant malachite green in model solutions under irradiation with UV light. Tested samples CFO-0.08, CFO-0.28, and CFO-0.33 showed a photocatalytic activity that is dependent on Au nanoparticle concentration. Rate constant values increased on increasing gold nanoparticle content in the samples: 3.1×10^{-3}, 4.4×10^{-3}, and 5.2×10^{-3} min^{-1}, respectively. It was observed that a non-modified pure cobalt ferrite synthesised by the same procedure exhibited a lower photocatalytic activity. The results for the photocatalytic activity of the samples synthesised by the sol-gel method were compared with samples, synthesised by high-temperature solid phase reaction combined with mechanoactivation. The results are interesting taking into account recently established positive impact of precious metal nanoparticles on the semiconductor conductivity zone [1].

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5-P4. Selective synthesis of biogenic lepidocrocite by cultivation of *Leptothrix sp.* in Lieske medium

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A challenge to catalyst preparation applying the Leptothrix genus bacteria cultivation process is to select experimental conditions so that γ-FeOOH is predominant compound in the composition of the produced biogenic material. An attempt to use a selected support as part of the growth medium that could promote the synthesis of targeted compound was made. Samples were obtained by deposition of material obtained during cultivation in Lieske medium on aluminium foil one-sided covered by anodic Al_2O_3. A lamella support was preliminary submerged in the solution. The samples were studied by the methods of infrared and Mössbauer spectroscopy. They were compared to materials synthesised in media of Adler, Lieske, and Fedorov without use of support. A predominant formation of γ-FeOOH and γ-Fe_2O_3 was found in the absence of support. Further thermal treatment at 250°C resulted in systems that contained about 60–70% γ-Fe_2O_3 but the materials remained multicomponent. Part of the material obtained in Lieske medium, which was deposited on the submerged in the solution anodic Al_2O_3/Al lamella, showed formation of γ-FeOOH only. This result can be attributed to the composition of anodic Al_2O_3 layer containing a mixture of γ-Al_2O_3 (amorphous and crystal), γ-AlOOH, α-$Al(OH)_3$, and γ-$Al(OH)_3$. Most probably, a γ-AlOOH component helps and directs the formation of γ-FeOOH during the cultivation because γ-AlOOH and γ-FeOOH are isomorphous.

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5-P5. Effectiveness of TiO_2-doped catalysts in ozone-assisted photocatalytic degradation of adipic acid under UV irradiation

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Palladium and gold modified titania (Degussa P25) in the presence of oxygen and ozone containing mixture upon UV-A and UV-C irradiation were examined for catalytic activity toward photodegradation of adipic acid at 20°C and atmospheric pressure. The samples were synthesised by extractive-pyrolytic method with 0.5% loading of the active metal having particle size from 7 to 12 nm. XRD, XPS, TEM, and BET were employed for sample structural and chemical characterisation. In the presence of oxygen under UV-A light the apparent first-order rate constants of palladium- and gold-modified TiO_2 samples were respectively 1.7 and 2.3 times higher than that of the pure TiO_2 under the same conditions. Further, catalyst effectiveness regarding photooxidation of adipic acid in the presence of ozone was higher under both UV-C and UV-A light for all samples tested. The reaction rate constants under 254-nm irradiation were about 4 times higher relative to those with 365-nm light. This may be due to additional generation of $HO^{\bullet}$ radicals by the ozone on the conduction band of the TiO_2 photocatalysts and because of O_3 photolysis under irradiation with UV-C light. The higher rate constants of adipic acid decomposition under UV light irradiation over the Au/TiO_2 and $Pd//TiO_2$ catalysts are due to more efficient separation of the electron-hole charges generated upon irradiation.

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5-P6. Gas phase ozone decomposition over nickel catalysts supported on alumina

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Ozone is widely used in industrial and environmental processes, such as semiconductor manufacturing, deodorisation, disinfection, and water treatment. Ozone in the atmosphere protects the Earth's surface against UV radiation, however, on the ground level it is an air contaminant. Heterogeneous catalytic decomposition is an effective method for purification of toxic gases containing ozone. The catalytic decomposition of ozone to molecular oxygen was investigated over a range of deposited nickel catalysts. Catalytic samples containing nickel, copper, silver, and aluminium oxides were synthesised by coprecipitation method. The catalytic activity of the metal oxide catalysts in the reaction of ozone decomposition was measured by monitoring the inlet and outlet ozone concentrations and calculating the conversion of ozone to molecular oxygen. A maximum conversion degree of about 90% was achieved on the surface of catalytic sample bearing 3% silver oxide, 10% nickel oxide, 5% copper oxide, and 82% aluminium oxide. Kinetic experiments on dry and humid ozone decomposition over carbon-supported nickel samples were performed at O_3/O_2 GHSV of 12 000–48 000 h^{-1}. The catalytic activity decreased in humid medium (18% H_2O) and this might be a result of thin film formation of water molecules on the catalyst surface thus making ozone diffusion to the catalytic sites more difficult. The catalysts were characterised by various physical methods: BET, XRD, TEM, and XPS.

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5-P7. Nanostructured mesoporous TiO_2-ZrO_2 catalysts for methanol decomposition and total oxidation of ethyl acetate

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The synthesis and design of nanostructured metal oxides with crystalline framework of high surface area and thermal stability have attracted considerable interest due to their potential application in various areas, including catalysis, sorption, electronics, drug delivery, etc. Titania doping with different metal oxides could improve its dispersion, thermal stability, and textural and surface characteristics. ZrO_2-TiO_2 binary materials are very attractive due to their outstanding electrical, chemical, and mechanical properties that make them useful materials in the fields of ceramics, solid electrolytes, gas sensors, and catalysis. The aim of current investigation is to prepare nanostructured mesoporous ZrO_2-TiO_2 materials with different composition and to test them as catalysts in various processes, which are important for environmental protection, such as total oxidation of ethyl acetate and methanol decomposition. A template-assisted hydrothermal method was used for sample preparation and characterisation by physicochemical methods, such as nitrogen physisorption, XRD, UV-Vis, FTIR, and Raman spectroscopies. All bicomponent materials demonstrated higher dispersion and improved porous characteristics in comparison with the monocomponent oxides. XRD and spectroscopic studies revealed formation of a solid metal oxide solution in all bicomponent systems. These features promoted a higher catalytic activity and selectivity of the bicomponent samples in methanol decomposition to syngas and in the complete oxidation of ethyl acetate.

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5-P8. Promoting the oxidative removal rate of 4-chlorophenol on gold-doped TiO_2/graphene photocatalysts under UV light irradiation

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The photooxidation of 4-chlorophenol, catalysed by nanosized TiO_2, Au/TiO_2, and by the corresponding composite materials with reduced graphene oxide (GR) has been studied upon irradiation with UV light. XPS, SEM, and TEM methods have been applied to characterise prepared photocatalysts. The average size of the TiO_2 nanoparticles prepared by using the sol-gel method was 18 nm. The TiO_2 or Au/TiO_2 particles were randomly distributed on the surface of the graphene nanosheets. The average size of the Au nanoparticles in the modified TiO_2 photocatalyst was about 7 nm. XPS measurements confirmed graphene oxide thermal or photoreduction to graphene. The rate constants of 4-chlorophenol photooxidation catalysed by the studied samples follow the order: Au/TiO_2/GR > Au/TiO_2 > TiO_2/GR > TiO_2. The photocatalytic activity of the TiO_2/GR composite was by 40% higher than that of the unmodified sample. The increase of the photocatalytic activity of Au/TiO_2/GR, Au/TiO_2, and TiO_2/GR photocatalysts is the result of more efficient charge carrier separation of the light generated electron-hole pairs in the TiO_2 semiconductor. This favours additional generation of $HO^{\bullet}$ radicals on the TiO_2 valence band.

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5-P9. The effect of CeO_2 on the properties of Ni-based catalysts for hydrogen production

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Today hydrogen is an ideal carrier for energy production. During the last years, reforming processes of methane and ethanol to hydrogen have been intensively investigated for hydrogen production. However, a limitation of these technologies is catalyst deactivation due to carbon deposition during the high temperature processes. Therefore, the development of catalysts resistant to coke deposition is one of the main issues of these technologies. Carbon deposition is strongly dependent on the kind of used carrier and metal. Ni-based catalysts have been extensively studied due to their low price and wide availability. They are very active, but deactivate very fast. Due to the high oxygen storage capacity of CeO_2, the latter can be used as support or additive to reforming catalysts. The aim of the present work is to study the effect of CeO_2 on the structure, surface and catalytic properties of Ni catalysts supported on mixed CeO_2-Al_2O_3 oxides of different ceria content (1–12 wt.%). Various techniques such as XRD, XPS, Raman, HRTEM, and TPO were used for physicochemical characterisation. The highest CH_4 and CO_2 conversion values as well as the highest H_2 and CO yields were obtained for catalyst with 6 wt.% CeO_2. A fast deactivation was observed for alumina-supported Ni catalyst, whereas CeO_2-containing catalysts were stable with time on stream. Two kinds of carbon materials were detected in spent Ni catalysts: disordered carbon species like amorphous and carbon species as nanofibres. Spent CeO_2-containing catalysts were characterised by smaller particles and more homogeneous particle size distribution as particles below 8-nm size dominated. This explains the higher carbon resistance of ceria-containing Ni catalysts during the catalytic reaction of dry methane reforming since a noticeably lower amount of deposited carbon was registered by TPO in relation to that observed for alumina-supported Ni catalyst.

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6-K1. A new approach to modelling the mass transfer processes in industrial column apparatuses

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Modelling and simulation are the main approach to quantitative description of the mass transfer processes in the chemical, power, biotechnological, and other industries. The models of the mass transfer processes are possible to be realised based on physical approximations of the mechanics of continua. The mathematical point is equivalent to an elementary physical volume, which is sufficiently small with respect to the apparatus volume, but at the same time sufficiently large regarding the intermolecular volumes in the medium.

As a whole the industrial mass transfer processes are realised in one, two or three phase systems as a result of volume (homogeneous) and surface (heterogeneous) reactions, i.e. mass appearance (disappearance) of the reagents (phase components) in the elementary volumes in the phases or on its interphase surfaces. As a result, the reactions are mass sources (sinks) in the volume (homogeneous chemical reactions) and on the surface (catalytic reactions, interphase mass transfer, adsorption) of the elementary physical volumes.

The volume reactions lead to different concentrations of the reagents in the phase volumes and as a result two mass transfer processes are realised: convective transfer (caused by the movement of the phases) and diffusion transfer (caused by the concentration gradients in the phases). The mass transfer models are a mass balance in the phases, where components are convective transfer, diffusion transfer, and volume reactions (volume mass sources or sinks). The surface reactions participate as mass sources or sinks in the boundary conditions of the model equations.

Theoretical analysis of the mass transfer theories shows that the predictions of the diffusion boundary layer theories are more accurate than the model theories conclusions, but they are useful for modelling of the interphase mass transfer processes (absorption, adsorption, and catalytic reactions) in column apparatuses, where the faces of the phases are unknown.

The use of physical approximations of the mechanics of continua for the interphase mass transfer process modelling in industrial column apparatuses is possible if the mass appearance (disappearance) of the reagents on the interphase surfaces of the elementary physical volumes (as a result of the heterogeneous reactions) are replaced by the mass appearance (disappearance) of the reagents in the same elementary physical volumes (as a result of the equivalent homogenous reactions). So, the surface mass sources (sinks) caused by absorption, adsorption or catalytic reactions must be replaced by equivalent volume mass sources (sinks).

The new approach to modelling the mass transfer processes in industrial column apparatuses is the creation of the convection-diffusion and average-concentration models.

6-K2. Sol-gel hydrothermal synthesis of titanium dioxide nanoparticles

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Titanium dioxide (TiO_2) has the advantages of its high chemical stability, nontoxicity, and relatively low price, so it is widely used to be a photocatalytic material [2]. There are many methods to synthesise TiO_2 such as co-precipitation, solvothermal, sol-gel, combustion synthesis, microwave, and sol-hydrothermal techniques [3–4]. Hydrothermal technique is one of the most commonly used and effective methods for the processing of a great variety of materials. Hydrothermal synthesis is a prospective mode to obtain nanostructures where polymorphism, particle size, crystallinity, and morphology could be very well controlled as required compared to any other technique because of highly controlled diffusion in the crystallisation medium [1].

In this study, highly crystallised anatase TiO_2 nanoparticles were synthesised by hydrothermally treating the titania sol after peptisation with titanium isopropoxide at 200°C for 2 h. Sample phase structure and morphology were characterised by using X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The average crystallite size was 10 nm estimated from the peak broadening of XRD spectra.

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6-O1. Ultrasound-assisted extraction and nanofiltration of bioactive compounds from *Sideritis*

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This study is focused on a sequential process using ultrasound-assisted extraction and nanofiltration for separation and concentration of bioactive compounds (polyhenols and flavonoids) from *Sideritis* extracts. The effect of solvent, temperature, and ultrasonication is discussed in terms of phenolics yield and extraction kinetics. Permeate flux and rejection data during nanofiltration in a tangential module are given, using Duramem membranes with molecular weight cut-off 300 and 500 Da. Membrane fouling is investigated through the flux vs time decrease and predicted by Hermia's models. The highest yield with phenolics was obtained under 1-h extraction with 96% ethanol and ultrasound power of 100 W followed by concentration through nanofiltration by Duramem 500 membrane.

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6-O2. Study of the energy potential of vinasse

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The by-product remaining after distillation during the production of wine brandies is called vinasse. It is characterised mainly by a high content of organic matter (proteins, VFA, amino acids) and its typically balanced composition. The aim of this study is to determine the energy potential of organic waste from the production of wine brandy, i.e. vinasse, and to optimise the process of vinasse biomethanation. Process thermal stability was also investigated. The main characteristics of vinasse as a substrate for biomethanation (pH = 3.17, free protein = 6.34 g l^{-1}, COD= 29 gO_2 l^{-1}, etc.) were determined. A high specific yield of methane was reached by appropriate adapted methanogenic consortium. Biochemical methane potential (BMP) of vinasse was determined at a value of 0.39 lmethane $gCOD^{-1}$. A BMP assay provides a measure of the anaerobic digestibility of a given substrate. The BMP test was carried out in batch mode at a mesophilic temperature (35°C). The information provided by BMPs is valuable when evaluating potential anaerobic substrates and for optimising the design and operation of an anaerobic digester. Biomethanation process was optimised by adding appropriate microelements in the medium as the production of methane increased significantly. In a study of thermal stability of the process it was found that biomethanation takes place also under psychrophilic conditions (20°C), but the period for methane production is extended.

The results showed that the vinasse is a valuable substrate for biomethanation and the process is successfully optimised by adding appropriate microelements in the medium.

6-O3. Magnetically assisted fluidised bed bioreactor for bioethanol production

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Ethanol can be produced by fermentation of sugars from agricultural products as wheat and corn after milling and hydrolysis. The mash after dry mill contains up to 25% reducing sugars and suspended solids and it is very viscous. In this study, the effect of a magnetic field on ethanol fermentation with fluidised bed biofilm reactor (MAFBR) was investigated. Magnetically loaded polyurethane foam cubes (3×3×3 mm) were used as support material for biofilm formation in a fluidised bed reactor. The magnetite content was 1:1 (wt/wt) with density of 1050 kg m^{-3} and immobilised biomass of 200 mg g^{-1} (dry support). The polyurethane carriers were stable and exhibited high ethanol fermentation activity. The reticulated structure of the polyurethane foam enabled adherence as well as entrapment of biomass. Magnetically assisted fluidised bed experiments were performed in a glass column (50 mm ID) and total volume of 0.5 L surrounded by a pair of Helmholtz coils with 200 mm ID.

The performance of ethanol fermentation of mash in the MAFBR was affected by feed sugar concentration, dilution rate, and magnetic field intensity. Ethanol productivity reached 36 g $l^{-1}h^{-1}$ at a feed dilution rate of 0.4 h^{-1} with a reducing sugars concentration of 225 g L when the magnetic field intensity was kept in the range of 0 (zero field) to 10 kA m^{-1}. In order to use this developed MAFBR system for ethanol production from cheap agricultural materials, mash was used as the main fermentation substrate for continuous ethanol fermentation with the immobilised *S. cerevisiae* cells in the reactor system.

Ethanol fermentation of complex substrate by immobilized *Saccharomyces cerevisiae* cells in magnetic particles was successfully carried out in a magnetically assisted fluidized bed reactor (MAFBR) and the higher ethanol production was observed in the MAFBR than in a fluidized bed reactor without a magnetic field.

6-P1. New models of industrial column chemical reactors

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A new approach to modelling industrial column chemical reactors is presented. A theoretical analysis of the effect of the radial non-uniformity of the axial velocity component in industrial column chemical reactors is presented. Numerical analysis shows that an average concentration model, where the radial velocity component is equal to zero (in cases of constant velocity radial non-uniformity along the column height), is possible to be used in the case of axial modification of the radial non-uniformity of the axial velocity component. The use of experimental data on the average concentration at the column end for a concrete process and column permits to obtain model parameters related with the radial non-uniformity of the velocity. These parameter values permit to apply the average concentration model to modelling of different processes.

6-P2. New models of industrial column absorbers. Co-current absorption processes

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A new approach to modelling industrial column absorbers is presented. A theoretical analysis of the effect of the velocity radial non-uniformity on the co-current absorption processes in the column apparatuses is presented. The average concentration model, where the radial velocity component is equal to zero (in cases of constant velocity radial non-uniformity along the column height), is used in the case of axial modification of the radial non-uniformity of the axial velocity components in the gas and liquid phases. The use of experimental data on the average concentration in the gas and liquid phases at the column end for a concrete process (absorption of average soluble gas), permits to obtain gas and liquid phase model parameters related with the radial non-uniformity of the velocities. These parameter values permit to apply the average concentration models for different absorption process modelling in co-current columns.

6-P3. Kinetic studies on starch enzyme hydrolysis

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In order to study the condition of starch hydrolysis with thermostable α-amylase the influence of the substrate concentration, temperature, and pH were investigated. The kinetics parameters – K_m and V_{max} were determined using Michaelis-Menten equation and other modifications of it: Lineweaver-Burk, Hanes-Woolf, and Eadie-Hofstee. It was found that the reaction rate has a maximum value at pH 5.8 and temperature of 75°C. The values of K_m are within 60.42–65.72 μg ml^{-1}, while V_{max} has values between 108.9 and 113.5 μg ml^{-1} min^{-1}.

6-P4. Kinetics and mechanism of ozone reaction with cyclohexane

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The peculiarities of ozone absorption during the cyclohexane ozonolysis have been studied by continuous monitoring of ozone concentration at the bubbling reactor outlet under conditions of constant value of ozone concentration at the reactor inlet. Ozone solubility under various temperatures has been characterised. It was found that the rate constant of the reaction in the liquid phase at 20°C was 0.008 $l\ mol^{-1}\ s^{-1}$. An activation energy of 56.5 kJ mol^{-1} was also determined. The formation of reaction products were studied iodometrically and by gas chromatography. Dicyclohexyl was identified as a side product of the reaction. The kinetics of formation of cyclohexanol, cyclohexanone, and dicyclohexyl were investigated in detail by GC/MSD. A revised scheme of cyclohexane ozonolysis has been proposed.

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6-P5. Operating conditions of a fuel cell for sulphites oxidation

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Sulphite-contaminated wastewater treatment is a complex and expensive technological process. In own previous works, we have proposed an effective and cheap method of oxidising different sulphur ions contaminating wastewaters. This is done in a fuel cell of own design which allows harvesting and use of electrical energy. The aim of the current study is to identify the working conditions of the fuel cell operating with such wastewaters as fuel. The influence of the initial concentration, type of ion-exchange membrane as well as conductivity of the solution is shown.

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6-P6. Extraction of elements from coal fly ash using a thermal hydrometallurgical method

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Solid industrial wastes generated from thermal power plants (TPP) can be considered renewable secondary sources for recovery of valuable metals. The aim of the present research is to investigate the removal of metals and other valuable elements from TPP fly ash using combined extraction techniques. The investigations integrated thermal and hydrometallurgical methods for fly ash treatment collected from TPP in Bulgaria. The first stage of the autoclave treatment of the proposed process using sulphuric acid with concentration of 20 and 30 wt.% at a thermal treatment temperature of 100, 120, and 140°C for 60, 90, 120, 240, 360, and 480 min was studied. At the second stage, the obtained samples were dissolved with water at a constant temperature and time. Based on results from chemical analysis the extraction of 12 elements was determined. Experimental results indicate that this method is not selective for Al extraction as other elements like Fe, Ca, Mg, Na, Ni, Mn, Cu, and Zn are generally extracted with aluminium. The data obtained show that the method used provided yields of 88.8% for Al, 88.5% for Fe, over 80% for Ca, Cu, and Mn, over 70% for Mg, Cr, and Mo, and nearly 100% for Na, Zn, and Ni. The extraction behaviour depended on all studied parameters. Obviously stable minerals, like orthoclase, albite, anorthite, and plagioclase which contain fly ash can be decomposed and thus the mobility of the elements increased. The most of the valuable elements can nearly be completely extracted.

6-P7. Comparative study of biodegradation of 1,2-dichloroethane and 1,2-dibromoethane by *Xanthobacter autotrophicus* GJ 10 cells

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Chemical industry produces large amounts of short-chain halogenated hydrocarbons that are toxic and carcinogenic. 1,2-Dichloroethane (1,2 DCE) and 1,2-dibromoethane (1,2 DBE) are among the most dangerous pollutants throughout the world. This work presents a comparative study of 1,2-DCE and 1,2-DBE dehalogenation processes by cells of the strain *Xanthobacter autotrophicus* GJ 10. Full degradation was observed at low and moderate initial concentrations like 0.08, 0.14, 0.16, and 0.2 g l^{-1} for 1,2 DCE and 0.05 g l^{-1} for 1,2 DBE, respectively. Chlorine and bromide ions are released in two steps of substrate biodegradation. When only one halogen ion is removed, the degradation stopped only to the formation of acetaldehydes and halogenated acids at end of the process. Complete degradation was attained along with the release of stoichiometric quantity of chlorine and bromide.

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6-P8. Denitrification of crude cell-free extracts at high concentration of the substrate

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Nowadays nitrates are one of the main problems related to the environment, especially for the pollution of natural waters, rivers, and lakes. The reasons for the presence of nitrates in these waters are oxidation of NH_4^+ due to biodegradation of nitrogen-containing organic compounds and increased use of nitrogen fertilizers.

Enzyme reduction of nitrate ions by immobilised and crude cell-free extracts from microbial cells of strain *Pseudomonas denitrificans* was studied. After disintegration and filtration the cells were tested for reduction activity. It was established that there was no denitrification activity.

A comparative study was performed of the denitrification process between immobilised crude cell-free extract from bacteria *Pseudomonas denitrificans* and intact cells. The experiments were carried out at different temperatures, between 10 and 30°C. It was established that the denitrification rate is higher for immobilised cell-free extracts.

6-P9. Limited coalescence and Ostwald ripening in emulsions stabilised by hydrophobin HFBII and milk proteins

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Hydrophobins are proteins isolated from filamentous fungi, which, unlike most of proteins, are excellent foam stabilisers. In the present study, we demonstrate that hydrophobin HFBII is also an excellent emulsion stabiliser. The HFBII adsorption layers at the oil/water interface solidify similarly to those at the air/water interface. Thinning of aqueous films sandwiched between two oil phases ends with the formation of a 6-nm thick protein bilayer just as in the case of foam films. The drop-size distribution in HFBII-stabilised emulsions was investigated at various HFBII concentrations and oil volume fractions. The analysis of the obtained data indicated that depending on the experimental conditions the emulsification occurs either in the Kolmogorov's regime or in the regime of limited coalescence. The emulsions with HFBII are very stable: no changes in the drop-size distributions were observed after storage for one month. However, aged emulsions became unstable upon stirring because of the breakage of the solidified HFBII adsorption layers. This instability could be overcome if the emulsions were produced from mixed solutions of HFBII and β-lactoglobulin. Both these proteins were able to suppress the Ostwald ripening in the case when the disperse phase is oil that exhibits a pronounced solubility in water. Hence, the hydrophobin can be used to stabilise microcapsules of fragrances due to its dense adsorption layers that block the transport of oil molecules.

6-P10. Modelling and optimisation of absorptive ability to water and biological fluids of polyacrylonitrile fibres

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New highly absorptive polyacrylonitrile fibrous materials have been developed by chemical modification of polyacrylonitrile fibres with alkali and formaldehyde. A model-based approach to the Taguchi method of quality improvement was used on research and development stage. Three performance characteristics of product were studied: water absorption capacity, retention capacity, loss of fibres depending on five parameters of product/ process. Our objective was to select values of product parameters, which ensure maximal values of water absorption or retention capacity while minimising their variances due to random variations in mass production. This optimisation problem was resolved caring out the following steps:

(i) The models of performance characteristics were obtained based on an experiment without errors in product parameters. In model estimation we took into account that some of experimental runs failed. A boundary was defined between two regions of successful and unsuccessful experimental outputs.

(ii) Modelling the mean and variance of performance characteristics in mass production. They are used to find the optimal operating point of the process.

(iii) A confirmatory experiment was run at optimal point to verify predicted results. Medical assessments of fibres confirmed that the new material has high absorptive and retention capacity of biological fluids and is suitable for medical practice.

6-P11. Determination of the solubility products of silver, calcium, and zinc carboxylates: temperature and paraffin chain length dependencies

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Here, we report a conductivity-based procedure for accurate determination of the solubility products of silver, calcium, and zinc carboxylates. They were synthesised using water-soluble Ag^+, Ca^{2+}, and Zn^{2+} salts and sodium carboxylates such as octanoate (NaC8), decanoate (NaC10), and dodecanoate (NaC12). The obtained soap precipitates were purified by either using centrifugation-sonication cycles or filtration and abundant washing with deionised water. The purification step was crucial for the removal of any residual reagents and by-products, e.g., sodium nitrate and chloride. By atomic absorption spectroscopy (AAS) analysis, we confirmed that the synthesised Ag, Ca, and Zn carboxylates were pure and their metal content corresponded to that of neutral soaps. To determine the solubility product of each soap, the respective precipitate was dispersed in water and equilibrated at a fixed temperature for at least 24 hours. Successively, the electrolytic conductivity of the saturated aqueous phase was measured and the soap solubility was calculated for various temperatures in the range 25–45°C. Knowing soap solubility and stoichiometry, the solubility product constant, K_{sp}, was evaluated as a function of temperature, T, and paraffin chain length, n. As an independent validation of our results, we carried out turbidity measurements to determine the onset of soap precipitation, i.e., the soap solubility limit. For all the studied carboxylates studied it turned out that $pK_{sp} = -\log_{10}K_{sp}$ depended linearly on both n and $1/T$, which can be applied to estimate K_{sp} for long-chain metal soaps at various temperatures.

6-P12. Sulphonated methyl esters of fatty acids: interfacial and micellar properties

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The interest to sulphonated methyl esters (SME) of fatty acids has been growing during the last decade because these surfactants are considered an environmentally friendly and renewable alternative to the linear alkylbenzene sulphonates (LAS). Here, we present a quantitative study on the properties of aqueous SME solutions, and especially on their surface tension isotherms, critical micelle concentration (CMC), and its dependence on the concentration of added NaCl. It is demonstrated that the CMC of an ionic surfactant determined by electrical conductivity is insensitive to the presence of a small non-ionic admixture, so that the CMC values determined by conductivity represent the CMC of the pure surfactant. We have demonstrated the application of a new and powerful method for determining the physicochemical parameters of the pure ionic surfactant by theoretical data analysis (‘computer purification’) if the used surfactant sample contains non-ionic admixtures, which are present as a rule. This method involves fits of the experimental data for surface tension and conductivity by a physicochemical model based on a system of mass-balance, chemical equilibrium, and electric double layer equations, which allows to determine the adsorption and micellisation parameters of C12-, C14-, C16-, and C18-SME as well as the fraction of non-ionic admixtures. Having determined these parameters, we can further predict the interfacial and micellisation properties of the surfactant solutions, such as surface tension, adsorption, degree of counter ion binding, and surface electric potential at each surfactant, salt, and co-surfactant concentration.

7-K1. Co-assembly of block copolymers: a strategy toward multifunctional nanocarriers

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Block copolymer aggregates like micelles, vesicles, etc. have received remarkable interest due to their current and potential applications in the fields of biomaterials science, nanotechnology, and pharmaceutical industry. The successful exploitation of copolymer aggregates in these fields depends on the ability to fabricate precisely functional systems with tailored properties and desired size for specific applications. Recent efforts have been focused on developing systems of more diverse functions required for better performance at cellular and subcellular levels. Thus, the research on polymer aggregates based on ABC triblock terpolymers or binary mixtures of AB and CD diblock copolymers have received increasing attention. Compared to AB-type copolymers, the ABC-type systems are worth investigating because the aggregates then combine the intrinsic properties of three components rather than two, which increases their functionality and versatility.

The present contribution is focused on a strategy for preparation of multifunctional nanocarriers based on the cooperative self-assembly of two block copolymer partners. The formation of various nanocarriers combining the properties of different temperature- and pH-responsive, biodegradable and biocompatible polymers is described. Co-assembly of well-defined block copolymers under optimal conditions can obtain uniform aggregates comprising a mixed hydrophobic core and/or a mixed hydrated corona. Such systems are foreseen as an advanced drug carrier of at least two different drugs, since the hydrophobic core can be loaded with poorly water-soluble active substances, while the polyion chains in the corona can coordinate drugs like cisplatin or proteins.

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7-K2. Functionalisation of propylene and ethylene oxide copolymers for the synthesis of polymer-drug conjugates

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Copolymers consisting of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) blocks are extensively used as drug carriers due to their biocompatibility and amphiphilicity. The amphiphilicity of this kind of copolymers allows transformation of hydrophobic drugs in water-soluble compounds by means of micelle formation. This way, we are improving the hydrophobic drugs absorbability and bioavailability.

In this work, tailor-made copolymers have been synthesised through a three-step nucleophilic ring-opening polymerisation of ethylene oxide (EO), propylene oxide (PO), and glycidyl-propargyl ether (GPE), using two different initiators (water and ethanol). Potassium hydroxide has been used as catalyst since it is compatible for both EO and PO and its activity and purification is well established. However, organocatalysts such as N-heterocyclic carbenes (NHCs) and N-heterocyclic olefins (NHOs) as well as phosphazene bases will be considered. The developed method allowed achieving PEO-PPO copolymers functionalised with alkynyl groups, with low polydispersity index and suitable molecular weights for a further polymer-drug conjugates synthesis. Once, the copolymers were obtained the influence of the initiator and of the EO/PO proportion in the micelle formation and the drug incorporation into the copolymer structure were studied.

The influence of the initiator and of the EO/PO proportion on the micelle formation was studied by determining the critical micellar concentration (CMC) of the different copolymers in water. The CMC was determined by a tensiometer and was further checked by means of differential scanning calorimeter. As expected, the higher the EO/PO ratio, the higher the CMC, since the EO is more hydrophilic. On the other hand, the use of water or ethanol as initiator does not exhibit a significant influence.

For the polymer-drug conjugates, the zidovudine (AZT) drug, with an azide group, was selected to be attached to the polyether chain. Drug and copolymer conjugation was performed by the copper-catalysed azide-alkyne cycloaddition (CuAAC) reaction (click reaction). The success of the AZT incorporation in the copolymer chain was confirmed by means of ^{1}H-NMR.

7-K3. Thermoresponsive nanocarriers of active species

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Over the past several decades, remarkable progress has been made in the development of polymeric nanocarriers to increase solubility, improve biodistribution, reduce the immunogenicity, and prolong circulation half-life of their payloads. The phenomenon of thermally induced self-aggregation of thermoresponsive macromolecules was explored to obtain nanocarriers of active species. In dilute solutions above temperature of phase transition, thermoresponsive polymers may aggregate to nanoparticles (mesoglobules). This process can be controlled by polymer concentration, heating procedure, and the presence of low molecular additives.

Model hydrophilic pentapeptide was conjugated with thermoresponsive blocks of PNIPAM and PDEGMA. The thermally controlled self-assembly of the bioconjugates led to nanosize aggregates with peptide enriched surfaces. The presence of peptide at particle surface was evidenced by detecting products of enzymatic hydrolysis of nanoparticles by mass spectrometry. So obtained particles disaggregated below phase transition temperature. Two routes to stabilise thermally self-assembled carriers are discussed: nanocarriers stabilised by crosslinked shell and nanocarriers stabilised by click reaction.

Thermal aggregation was used to obtain nanocarriers of one of the most important clinically relevant peptide: met-enkephalin. Biocojugate met-enkephalin-co(oligoethylene glycol methacrylate) was synthesised by AGET ATRP with met-enkephalin macroinitiator. Met-enkephalin caused the decrease of phase transition temperature of bioconjugate compared to neat copolymer. Nanoparticles formed by the bioconjugate were stabilised by a particle shell of crosslinked poly(N-izopropylacrylamide) using nucleated radical polymerisation. During the coating procedure RGD targeting ligand was linked to the outer surface of the carrier.

For preparing nanocarrier of oncological therapeutics, the advantage of previously described aggregation in a system of mixed thermoresponsive polymers was taken. The starting thermoresponsive terpolymer was equipped with azide groups. Part of these groups served for conjugation of therapeutics by a degradable bond. The aggregation took place in the mixture of the bioconjugate and a suitable partner with alkynes leading to mixed mesoglobules. Their crosslinking was performed in click reaction. Resulting particles were degradable and contained therapeutics could be detached from the chain under the same conditions.

The methodology of preparing nanocarriers of thermoresponsive bioconjugates is universal and can be used for encapsulation of various active species.

7-K4. Novel NMR methods in polymer science in Bulgaria: diffusion NMR and magic angle spinning (MAS) NMR for investigation of structure, dynamics and interactions in polymer hydrogels

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During the last decade, the significant progress in NMR hardware development has opened prospects for the investigation of increasingly challenging samples, with high compositional and morphological complexity including complex fluids, soft matter, and solid materials. Within the wide toolbox of NMR techniques, diffusion NMR and MAS NMR have attracted the attention of researchers as novel and useful NMR methods in materials research. While diffusion NMR has proven its power as a valuable method for the investigation of molecular interactions and aggregation phenomena in liquid and solution-swollen samples, MAS has widened the applications of NMR to more detailed investigation of structure and interactions in soft and solid materials and phenomena at solid-liquid interfaces.

Considering polymer research in Bulgaria, the potentials of these novel NMR methods are exemplified on polysulphobetaine (PSB) hydrogels for elucidation of their structure and dynamics. PSB hydrogels are a class of polymers containing a covalently bound positively charged quaternary ammonium group and a negatively charged sulpho group (zwitterionic dipoles) in each monomeric unit. They possess very good biocompatibility due to their very low non-specific protein adsorption. In addition, PSBs swell better in a low molecular weight salt (LMS) aqueous solution than in water (antipolyelectrolyte effect). This effect is explained by the specific polyzwitterionic (PZI) structure of PSB hydrogels formed via interactions between the zwitterionic dipoles in the PSB side chains.

The aim of the present study was to investigate changes of the structural mobility of PSB networks as a function of LMS (NaCl) concentration in swollen and dry state. For this purpose solid phase NMR and high resolution MAS NMR in combination with diffusion NMR were applied. T_1 and T_2 relaxation times of $^{23}Na^+$, water, and selected structural fragments from PSB hydrogels swollen in $NaCl/D_2O$ solutions showed a characteristic dependence as a function of increased electrolyte concentration. The NMR data revealed two types of water of different relaxation and diffusion behaviour. An overall analysis of the NMR results evidenced that when LMS solution penetrates into the PZI network the LMS ions interact with charged PSB groups thus shielding the interaction between the zwitterionic dipoles of the PSB side chains. This causes disintegration of the PZI clusters between the PSB side chains thus leading to enchanced fragmental mobility of PSB structural inits. The higher mobility of PSB chains is also reflected in lower intensity of the PSB signals in the $^1H \rightarrow ^{13}C$ and $^1H \rightarrow ^{15}N$ cross polarisation MAS spectra of dry PSB networks in the presence of different amounts of NaCl as compared to the signal intensity of pure dry PSB hydrogel. The NMR observations are in agreement with the results obtained by differential scanning calorimetry and swelling kinetics measurements.

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7-K5. Synthesis, characterisation, and behaviour of polymer-stabilised silver nanoparticles for biomedical applications

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Recently, there has been an increasing interest for the direct synthesis of metal nanoparticles stabilised in a polymer matrix having the potential for their application in biotechnologies and biomedicine. With increasing number of infectious diseases caused by different pathogenic bacteria and the enhanced resistance toward different type of antibiotics, the investigations are orientated toward finding new and more effective antibacterial agents [1]. National health services worldwide have been spending a vast proportion of their annual budget in fighting infections caused by such pathogenic bacteria. Among different metal nanoparticles, considerable attention is focused on silver nanoparticles, because of their unique chemical and physical properties and pronounced antibacterial activity, which provide one of the most cost effective alternatives to the development of new antibacterial agents [1]. It is well known that silver and silver ions are effective antimicrobial agents showing an activity against bacteria, viruses, and fungi [2]. Nevertheless, numerous practical applications of silver nanoparticles require their entrapment in various substrates and matrices. From this point of view, polymers are materials of first choice because of their specific morphology, chemical and structural nature with long polymeric chains allowing incorporation and fine dispersion of nanoparticles. Additionally, the suitable functional groups of polymers can be used as targeted reactive sites for the controlled one-step synthesis of nanoparticles [3]. In order to fully exploit the properties of silver nanocomposites, they should be well dispersed within the polymer matrix without formation of large aggregates, which otherwise dramatically could reduce the antimicrobial effect of silver.

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7-K6. Bottom-up methods for nanostructured functional polymers and composites

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Top down methods, as best illustrated by lithography and electronic miniaturisation, have exquisite control over defining special features and layering of multiple materials. Their downside is low throughput and expensive infrastructure. Bottom up methods can be very energy and material-efficient, but often lack the precision and complexity that could be achieved in top-down methods. We combine naturally occurring structuring on the micro- and nano-level to design hybrid syntheses, with bottom-up approaches and their typically high efficiencies and scalability, yet with patterning resolution approaching and sometimes even exceeding that achievable by top-down lithographic methods. This is done by various confinements of the chemical reactions.

We show examples of engineering the symmetry breaking and dynamics for multiple structures and processes, on multiple length scales: from nanometres to centimetres. We demonstrate the formation of Janus and other asymmetric particles, which form as a result of coupling of chemical reactions to non-linear mechanical properties of materials [1,2]. We also demonstrate the opposite effects: how mechanical deformations and molecular interactions can help one simplify chemical syntheses [3]. Finally, we describe how we synthesise conductive polymers in the 1-nm confinement of the pores of metal-organic frameworks (MOFs) [4]. Thus, we achieve one of the first conductive MOF-polymer hybrids. We also for the first time remove the MOF from such a composite to reveal a nanostructured conductive polymer (nano-PEDOT) with macroscopic dimensions and nanoscale structure and ordering. We characterise these with a battery of techniques to show the nature of the synthesised polymer. We believe such extreme templating methods hold high promise for supercapacitors, electrochemical catalysis, and sensitive chemical detectors.

One particular consequence of confining chemical reactions to different spatial domains is the promise of easier design of multifunctional materials. Instead of designing all the desired functions in a single molecule, we use controlled internal phase separation in a material to introduce existing materials with already optimised functions, and interweave them into one [5]. With this combinatorial approach, we show how spatial separation of just 3 phases and 20 functions would lead to over 8000 trifunctional materials. We demonstrate such interpenetrating networks with the separate and synergistic emerging functions. One of the most exciting developments is recent materials capable of both sensing and actuation. Such proprioceptive combinations could lead to autonomous material robotics [6].

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7-K7. From solid-state postcondensation of neat polymers to mutifunctional nanofibrillar polymer composites: a tribute to Professor Stoyko Fakirov on the occasion of his 80th birthday*

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The present lecture illustrates how the molecular and morphological structure of polymeric materials can be influenced by different physical techniques in order to make them suitable for higher stiffness, strength and/or toughness applications. The particular focus is put on polycondensates, such as polyethyleneterephthalate (PET) or polyamide (PA), which allow a solid state postcondensation (SSP) through different thermal treatments, resulting in a controlled enhancement of their molecular weight and/or their degree of crystallinity [1]. This process is especially interesting for recycling of PET bottles and their reuse in high strength fibre applications or injection or blow-molded products, for which a higher molecular weight is usually required.

The unique attribute of SSP can also be used for blends of incompatible polycondensates with different melting temperatures in order to produce so-called microfibrillar composites (MFC). The latter consist of stretched microfibrils of the higher melting component in an isotropic matrix of the lower melting component. The SSP can in this case build-up chemical bonds along the interface of the reinforcing polymer microfibrils and the isotropic polymer matrix, thus enhancing the interfacial shear strength of the composite [2]. Although this mechanism does not work if one of the components is a polyolefin (e.g. low density polyethylene, LDPE), the manufacturing principle of MFCs is also possible, whereby in this case a good adhesion between the PET microfibrils and the LDPE matrix is achieved by a transcrystallisation process of LDPE lamellae on the surface of the fibrils [3].

Quite recently, a new technique was developed by which composites can be produced from just a single polymer (so-called ‘single polymer composites’, SPC). The latter are formed by a three-step process: (i) melt blending followed by stretching (or spinning) of a two component system (as in the MFC process); (ii) dissolving the lower melting matrix material; and (iii) hot compaction of the remaining micro- or nanosized fibrils of the higher melting polymer at a temperature approximately by 10°C lower than the peak melting temperature of this polymer. During this process, a significant premelting of the surfaces of the fibrils takes place resulting in the formation of a thin continuous film in which the micro- or nanofibrils are still preserved. Within the films, a certain degree of nanoporosity still remains. On the other hand, due to the same chemical composition of the matrix and the reinforcement, a good adhesion quality is guaranteed [4].

To all of the activities described, Professor Stoyko Fakirov has made very significant contributions during his more than 60 years scientific career. This led to many research papers and internationally well recognised books, and it brought him as an invited speaker and guest scientist from Bulgaria to many places in the world. This contribution is therefore meant as an appraisal of his scientific and personal achievements on the occasion of his 80th birthday which took place on 19th January 2016.

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7-K8. Advanced separation and characterisation of multifunctional polymer systems

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The application area of functional materials is growing rapidly following new directions, in which precisely tuned molecular properties are needed. This trend is based on the versatility, tenability, and high functionality of soft materials like highly branched [1], responsive or dynamic polymer systems [2] and their well-defined nanometre-sized structure. The understanding of these materials on a molecular level as well as how to tune their scaling parameters is crucial for their design for advanced applications. The development of in-situ and multidimensional separation of complex macromolecular systems is in the focus of our research.

Dendritic macromolecular architectures are of great industrial interest due to their high functionality and advantageous rheological features. Hyperbranched polymers as a particular example are product of simple statistical polymerisation, which results in multiple distributions making their physicochemical characterisation challenging but highly needed. We combine portfolio of model polymers with advanced characterisation techniques to get an insight into structure-property relationships and to find new ways for a general description of the scaling theory [3,4]. Light scattering, viscosity, hyphenated chromatographic separations, molecular dynamics (MD) simulations and, last but not least, small-angle neutron scattering help us to understand and describe self-similarity, fractal dimensions as well as local molecular structure. Finally, this extensive dendritic study enables us to find new approaches to a robust, multidimensional separation of dendritic macromolecules.

The question of interaction of dendritic biomacromolecules and biohybrid systems is highly relevant for biological applications. Functionalised amphiphilic, core-shell or dendronised polymers lead to complex host-guest systems, bioconjugate, and bioaggregate distributions which need in-situ characterisation of the scaling parameters depending on pH or concentration [5]. Alternative, smooth separation approaches as field flow fractionation (asymmetrical flow, AF4) with a variety of hyphenation possibilities are appropriate for this purpose. Using AF4 coupled to static light scattering, dynamic light scattering as well as using complementary methods such as AFM, cryo TEM, and MD simulations we can shed light on the interaction profile of these dendritic structures.

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7-O1. Functionalised hydrophilic polymers for modification of biomacromolecules or nanocarriers

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Various polymer nanoparticulate systems have been designed as nanovehicles to deliver specific bioactive load to the target site in the organism at relevant times and doses. Nevertheless, the engineered polymer nanoparticles, circulating through the body, interact with cells and the extracellular environment and can trigger a sequence of biological effects or undergo metabolic degradation. Therefore, size, shape, and surface characteristics are important factors for the fate of the nanocarrier in the biological environment. Modification with hydrophilic polymer chains, i.e. poly(ethylene glycol), polyzwitterions, etc., via covalent binding, non-covalent entrapment or adsorption of the shell forming chains onto an object, is a widely used approach to enhance surface biocompatibility. The design of polymer-protein nanoparticles is considered an advanced approach to integrate a broad spectrum of properties and biofunctions into a single device. The combination of proteins and synthetic polymers increases the diversity of the biomaterials and affords a variety of structures and applications. In this context, synthesis of functionalised hydrophilic polymers designed for modification of biomacromolecules or other active species under mild reaction conditions is a key step in the development of a carrier platform.

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7-O2. Star nanocarriers of nucleic acids

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Star polymer-based vectors are nowadays one of the promising carriers since some of them exhibit better transfection efficiency in comparison with linear counterparts. The binding ability of cationic stars to nucleic acids is known but the relation between the star size and chemical composition versus transfection efficiency is not obvious and requires further studies. Star polymers with arms made of N,N'-dimethylaminoethyl methacrylate (DMAEMA) homopolymer and copolymers of DMAEMA and di(ethylene glycol) methyl ether methacrylate (DEGMA) as well as with hydroxy terminated oligo(ethylene glycol) methacrylate (OEGMA-OH) were synthesised via ATRP. The introduction of DEGMA or OEGMA-OH into the star structure caused the decrease of the cytotoxicity in comparison with DMAEMA homopolymer stars. The synthesised stars were able to bind DNA and RNA to polyplex nanoparticles. Polyplexes sizes were dependent on the comonomer, the solvent and the ratio of star amine groups to phosphorus groups of nucleic acid (N/P ratio). The hydrodynamic diameter of the polyplexes were in the range of 100–260 nm and zeta potentials of 10–20 mV, which was desirable for interaction with negatively charged cell membranes. The high transfection efficiency of obtained polyplexes tested using HT-1080 cells showed that the studied systems are prospective gene delivery agents.

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7-O3. Polymer-based gene-delivery vector systems with entrapped gold nanoparticles

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In this study, we report on preparation of novel non-viral vector systems for gene delivery. These new systems are based on cationic poly(vinyl benzyl trimethylammonium chloride) homopolymers and block copolymers with poly[oligo(ethylene glycol) metacrylate]. The polyplexes were prepared via electrostatic interactions between polycations and DNA at a wide range of amine to phosphate (N/P) group ratios. They are additionally loaded with gold nanoparticles in order to combine the beneficial properties of polymer and gold vectors. The resulting vector systems exhibit good colloidal stability. Dynamic light scattering measurements revealed formation of nanoparticles with narrow size distribution and hydrodynamic radii below 75 nm. The zeta potential varied from positive to negative values depending on the N/P ratio. Quenching of ethidium bromide fluorescence is used to monitor the polyplex formation, whereas hybrid vectors were visualised by transmission electron microscopy. In general, these multifunctional hybrid nanostructures may be utilised for combined gene therapy and bioimaging or photothermal therapy, and theranostics applications.

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7-O4. Numerical analysis of controlled/living radical polymerisation

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Based on the common reversible-deactivation mechanism of three general methods for controlled/living radical polymerisation (atom transfer radical polymerisation, nitroxide mediated polymerisation, and reversible addition fragmentation chain transfer polymerisation, RAFT) an original algorithm has been developed for calculating the conversion evolution of molecular weight characteristics of polymers produced. Conversion relationships were deduced for the concentration of monomer (M), initiator (I) and active propagation chains (A) as functions of probability (γ_i) for transformation of the A chains to dead (T) ones at the i-th conversion step. From them, the recurrent relationships for the number degree of polymerisation for monodisperse 'living' (L) (active, A, and dormant, D) propagation chains and polydisperse T macromolecules are deduced for each conversion step. Polymer polydispersity is defined mainly by the polydispersity of T chains. On this basis, the relationships for total number average and weight average degrees of polymerisation were deduced. An expression for polydispersity index (PDI_i) was obtained which shows that it increases with γ_i because of the larger contribution of polydisperse T macromolecules. The specific possibilities for γ_i decrease for the three methods discussed are outlined. The calculations for the RAFT polymerisation were more complex due to participation of two different D states (dithiobenzoate-propagating radical adduct and stable intermediate adduct radical). The calculations allowed distinguishing the pre-equilibrium and main equilibrium RAFT kinetics. Two versions of the algorithm were developed: by instantaneous and continuous initiation. According to the literature, the algorithm developed allows following the I, M, A, D, and T concentration kinetics, but also to introduce the reasonable corrections mentioned above after comparison of the calculated and experimental conversion curves.

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7-O5. Hybrid polymer/silica materials based on poly(N,N-dimethylacrylamide) copolymers: synthesis, properties and potential application

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Polymer/inorganic hybrids obtained by applying the sol-gel chemistry approach have recently become one of the most rapidly developing fields of materials science. Synthesis of such hybrids facilitates the design of new engineering materials with exciting properties for a wide range of applications, including separation media, immobilization matrixes, protective coatings, and bioactive compounds for prostheses or implants.

In this paper the synthesis of hydroxyl-functionalised copolymers of N,N-dimethylacrylamide (DMAA) and the development of novel polymer/silica hybrid materials on their basis are presented. Double hydrophilic di- and triblock PDMAA/poly(ethylene glycol) (PEG) copolymers were synthesised using cerium ion initiated redox polymerisation and PEG as initiating moiety. In addition, pH-responsive PDMAA copolymers were prepared by using 2-(acryloyloxy)ethyl trimethyl ammonium chlorides as a cationic comonomer. The chemical structure and copolymer composition were investigated by spectroscopic methods (NMR, FTIR) and size exclusion chromatography. Solution properties and aggregation in aqueous media were followed by DLS and ζ-potential measurements. Polymer/silica hybrid materials were formed by in situ sol-gel reaction of tetraethoxysilane in aqueous solutions of the copolymers at room temperature. The polymer/silica hybrid particles obtained were tested by using LS and TEM. A significant dependence of properties such as particle size, homogeneity, and optical transparency on the reaction conditions of the sol-gel process (e.g. the pH value) as well as on the copolymer structure and composition was observed.

7-O6. Polymer surfaces for biomedical application

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This work deals with the preparation of polymer surfaces based on biocompatible polyglycidol and its derivatives, polyoxazolines and poly(oligo(ethylene glycol) methacrylate)s that have potential biomedical applications. Two main areas are considered: coatings for protein-repellent implants and polymer thin films for tissue engineering. The 'grafting-to' and 'grafting-from' methods were used to covalently immobilise polymers onto glass or silica support. The use of controlled polymerisations (atom transfer radical or ionic) allowed to design the structure and molar mass of the tethered polymers. The composition, thickness, philicity, and morphology of polymer layers were investigated by XPS, ellipsometry, contact angle measurements, and AFM. It was established that the protein adsorption was reduced by 45–90% on the polyglycidol-coated surfaces, as compared to the bare support, depending on the molar mass of the polymer, polymer layer thickness, type of polymer bonding with the surface and type of modification of the outer surface layer. The surfaces based on polyoxazolines and poly(oligo(ethylene glycol) methacrylate)s were successfully used for human skin cells cultures and detachment regulated by the environment temperature alteration. The influence of the type of immobilised polymer, polymer layer thickness, and affinity to water was studied.

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7-O7. Polybenzimidazole-based anion conductive polymer electrolyte membranes for AEM fuel cells and electrolysers

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Polymer electrolyte membrane fuel cells (PEM FCs) generate electricity from an electrochemical reaction in which oxygen from air and hydrogen combine to form water. After doping of the polymer membrane with alkaline electrolyte (e.g. KOH) it becomes a solid anion exchanger (anion exchange membranes, AEM) with good OH^- conductivity. In the AEM electrolyser, water is split into hydrogen and oxygen. In order to operate at temperatures above 100°C the AEM fuel cell or electrolyser requires the use of membranes of improved chemical and mechanical stability.

The objective of this study was to prepare different polybenzimidazole-based membranes doped with KOH (PBI/KOH membranes) of improved mechanical properties. Two routes for mechanical stabilisation of m-, p-, and AB-PBI membranes were used: crosslinking of the membrane followed by doping with potassium hydroxyde (up to 50%) and preparation of KOH-doped PBI composite membranes containing an inorganic layered silicate filler (montmorillonite, MMT). An easy and efficient procedure for cross-linking of m-, p-, and AB-PBI membranes has been developed. The KOH-doped cross-linked membranes, depending on the PBI used, exhibit greatly improved mechanical properties and stability as well as excellent anion conductivity: 300–890 mS cm^{-1} at 110°C and relative humidity (RH) of 100%. The same effect was observed for the composite membranes containing MMT. For cross-linked AB-PBI membranes containing 50 wt.% MMT and doped with 50 wt.% KOH an extremely high conductivity of 1245 mS cm^{-1} (110°C, RH 100%) was measured.

7-O8. Mechanical and tribological behaviour and biomineralisation ability of hydroxyapatite-modified hydrogels

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The present work is focused on the investigation of natural polymer hybridised hydrogels based on poly(acrylamide) (PAAm) and poly(N,N-dimethylmethacryloyl oxyethyl propane sulphonate) (PDMAPS) reinforced with hydroxyapatite (HA). In this study, the influence of the PDMAPS content in HA-modified natural polymer hybrid gels on their water capacity and mechanical and tribological behaviour as well as their biocompatibility and biomineralisation ability was investigated.

Investigation of cytotoxicity of gel release was performed by MTS tests and showed insignificant depression of cell growth (L929) after 3 days of incubation. After 7 days of culturing, however, cell viability notably increased and was unexpectedly higher than that of the reference samples. Results of the dynamic biomineralisation ability of hydrogels immersed in simulation body fluid (SBF) showed a decrease of the Ca ions concentration in solution after 7 days of immersion. This indicates that there was no release of apatite from the gels. Moreover, HA on the gel surface worked as a nucleation agent for the HA crystal growth from SBF. This was accompanied by the reduction in concentration of phosphate ions in SBF for hydrogels without PDMAPS. Despite the decrease of Ca ion concentration for PDMAPS containing samples an increase of the phosphate ion concentration in SBF was observed. This makes such composites promising objects for further investigations.

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7-O9. Polymer-containing photovoltaics: current state and new perspectives

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The best reproducible power conversion efficiency of polymer-containing photovoltaics (PVs) present bulk heterojunction (BHJ) solar cells comprising an active layer of mixture of semiconducting polymer, i.e. poly(3-hexylthiophene) as electron donor, and a fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) as electron acceptor. Donor copolymers are poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and poly(4,8-bis-substituted-benzo[1,2-b:4,5-b']dithiophene-alt-4-substituted-thieno[3,4-b]thiophene) (PBDTTT), and fullerene acceptor derivative are [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$), respectively. Usually, the active layer of conventional polymer-containing PVs was sandwiched between transparent anode of indium tin oxide (ITO), a layer of poly(ethylene dioxythiophene)/ polystyrenesulphonate (PEDOT/PSS) or recently introduced more stable molybdenum trioxide (MoO_3) and various combinations of metal cathodes (Al, Ag or Ca). In order to control the active layer morphology, the films were subjected to different post-deposition treatments (annealing) by varying temperature and solvent atmosphere. Optical properties, film thickness, Raman, photoluminescence and AFM spectroscopy were used to characterise the active layer. Test devices of different bulk heterojunction architecture were prepared using magnetron-sputtered or thermally evaporated metal contacts. Current-voltage (I-V) characteristics and power conversion efficiency of the constructed polymer-containing PVs were measured under AM 1.5G illumination.

7-O10. Functionalisation of self-assembling copolymers for nanoencapsulation of phase changing materials

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The present work is aimed at chemical functionalisation of nanoshell building polymers containing maleic units in the main chain structure for nanoencapsulation of phase change materials (PCMs) for potential application in thermal comfort textiles and garments. Incorporation of additional functional groups in the structure of polymers is required for both improved graft-ability of nanocapsules (NCs) to textiles and the creation of reaction centres for dense crosslinking of the nanoshell. The latter is required to create chemically stable, laundry, and abrasion resistant nanocapsules with more or less ‘no-release’ profile.

Different amounts of urea and lactamide were used to chemically modify three copolymers representing anhydrous, acidic, and partial alkylester types of maleic units in the main chain. Modifications were carried out at 90, 170, or 180°C depending on polymer type and modification. The modified polymers were self-assembled in NCs using the new in situ self-assembly nanotechnology. These NCs were then characterised by the dynamic light scattering technique in terms of particle size and distribution, and the results were compared to that of the reference polymer having an average diameter (d) of 130 nm and polydispersity index (PDI) of about 0.12.

The most promising result (d~140 nm, PDI~0.08) was achieved by modification of alkylester containing polymer with lactamide at 90°C. This modification was also successfully applied for nanoencapsulation of a PCM. Compared to the same encapsulated in the reference polymer (d~170 nm, PDI~0.26), the resulting NCs showed a larger average diameter (d~225 nm) and, however, a broader size distribution (PDI~0.42).

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7-O11. Polymer nanocrystals in aqueous dispersions

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Water-soluble polymerisation catalysts enable the generation of defined colloidal polyethylene particle dispersions. Unprecedentedly small, hexagonally shaped nanoparticles of linear polyethylene of about 6 nm thicknesses and 25 nm lateral extensions were obtained via catalytic ethylene polymerisation at 15°C with water-soluble salicylaldiminato Ni(II) complexes. The single crystal nature and unique single lamellar structure of the particles was illustrated by cryo-TEM and SAXS analysis. Modifications of the catalyst complexes and their activity and prolongation of the polymerisation time resulted in evolution of the particle shape from hexagons via truncated lozenges to the classical diamond shape of PE single crystals. By precise placement of bulky branches, which are excluded from the crystalline areas, the lamellar thickness can be significantly influenced, while the chemical character of the branching groups regulates surface properties. In this fashion, methyl-branched polyethylenes (carrying methyl side groups on every 21st backbone carbon atom) were synthesised and dispersed in aqueous media to yield anisotropic oblate shaped nanoparticles stabilised by added surfactants. However, the methyl groups can change the lamellae thickness only to some extent.

A novel concept based on the direct encoding of the crystal thickness via the polymer molecular structure was considered. A precise placement of hydrophilic groups at constant distances along the polymer chain can induce regular arrangement of the hydrocarbon chain segments. Carboxylic acid groups were chosen as branching groups, since these groups are bulky enough to be completely excluded from the crystalline segments and furthermore enable self-stabilisation of nanoparticles in aqueous dispersions, when deprotonated with a base. A thicknesses of 5–6 nm and ca. 3-nm size of the obtained nanoparticles with platelet-like shape correspond well with the defined distances of 44 and 20 methylene units between carboxy branches in the corresponding precisely functionalised polymers. Shape and thickness of the particles were evaluated from cryo-TEM images.

7-O12. Polyacrylate and polymethacrylate based interpenetrating polymer networks as drug delivery systems

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Interpenetrating polymer networks (IPN) are special class of polymeric materials in which the combination of two or more polymer networks results in the formation of new materials with structure and properties combining those of the single ones. Many properties of IPN such as controllable porosity, swelling capacity and their ‘smart’ response to external stimulus (change in pH, temperature, ionic strength, etc.) are favourable for their abilities as controllable drug delivery systems, but their potential in this area is still not fully disclosed.

The aim of this study is focused at the synthesis of hydrogels and microparticles based on IPN of poly(acrylic acid)/polyacrylamide and poly(methacrylic acid)/polyacrylamide and at revealing their potential as drug delivery systems for cationic drugs. The synthesized IPNs hydrogels were characterized in terms of their swelling ability, morphology and smart behaviour (pH and temperature responsiveness. IPN microgels were characterised in terms of their zeta potential (ZP) and hydrodynamic radius under pH titration conditions. The drug entrapment efficiency as well as the drug release profiles of thus developed new polymeric materials were studied utilizing verapamil hydrochloride (VPH) as model drug.

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7-P1. Degradable mesoglobules as delivery systems of anticancer drug

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A wide range of nanomaterials based on synthetic polymers has been applied for the development of new anticancer therapeutics. This work deals with the preparation of particles of potential use as carrier of an anticancer drug. The applied method to obtain the particles is based on the thermoresponsiveness of polymer materials. The selected polymers are based on methacrylates: di(ethylene glycol) and oligo(ethylene glycol) methyl ether methacrylates providing thermoresponsiveness and (2-aminoethyl) methacrylate comonomer to generate the units for chains crosslinking. SET LRP conditions were used for copolymerisation. Amine functions in copolymers were modified to introduce clickable groups: azide [P(D-co-O-co-A_Az)] and 2-propyn-1-yl carbamate groups [P(D-co-O-co-A_Pr)] in reaction with 2-azido-1,3-dimethylimidazolinium hexafluorophosphate and propargyl chloroformate, respectively. Obtained modified copolymers exhibited a transition point in water solutions at 47°C for P(D-co-O-co-A_Az) and 39°C for P(D-co-O-co-A_Pr). In dilute aqueous solutions, they aggregated above phase transition temperature to spherical particles as mesoglobules. An anticancer drug with degradable 2-propyn-1-yl carbamate bond was conjugated to [P(D-co-O-co-A_Az)] in Huisgen reaction forming triazole rings [P(D-co-O-co-A_Az_Drug)]. A polymeric drug carrier was formulated in a solution containing P(D-co-O-co-A_Az_Drug) and P(D-co-O-co-A_Pr). Mixed mesoglobules formed above phase transition temperatures of both components were stabilised in Huisgen reaction. An anticancer drug linked with P(D-co-O-co-A_Az) by triazole ring can be released from the polymer chains.

7-P2. Thermoresponsive conjugate of therapeutic peptide

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This study describes a novel approach to polymeric nanocarriers of therapeutic peptides based on the aggregation of thermoresponsive polymers. Thermresponsive copolymers of di(ethylene glycol) monomethyl ether methacrylate (DEGMA) and oligo(ethylene glycol) monomethyl ether metacrylate (OEGMA_{300}) were conjugated using grafted entity from approach with peptide met-enkefalin (sequence Tyr-Gly-Gly-Phe-Met), Opioid Growth Factor (OGF). Transmittance of aqueous solution of the copolymer and its bioconjugate were observed using UV-vis spectroscopy during gradual heating and cooling of the samples. The process of controlled thermal aggregation of P(DEGMA-ran-OEGMA) and met-enkephalin conjugates was studied by light scattering. Sizes and size distribution of particles formed by bioconjugate in solution during gradual and abrupt heating were measured by dynamic light scattering. Mesoglobules were stabilised by constructing two-layer outer shell using seeded radical polymerisation of NIPAM with addition of biodegradable crosslinking agent: N,N'-bis(acryoyl) cystamine. During second coating, the targeting peptide RGD with fluorescence marker was coupled with the shell. RGD presence was confirmed by fluorescence. The obtained particles were stable and retained their thermoresponsiveness. Biodegradation of particles was performed with glutathione as reducing agent at pH~8.0 to test the release of therapeutic peptide. Nanoparticles were visualised by atomic force microscopy.

7-P3. Preparation, properties and application of waterborne polyurethane acrylate oligomer as a matrix in UV-curing fibreglasses

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A waterborne polyurethane-acrylate oligomer (WPUA) was prepared via in-situ anionic self-emulsifying method from hexamethylene diisocyanate, polyether polyol, dimethylol butanoic acid, and capped by 2-hydroxyethyl methacrylate. Then ultraviolet curable fiberglass was obtained from WPUA oligomer, 2- hydroxyethyl acrylate as reactive diluent, Irgacure 500 as photoinitiator and different weight of glass fabric (81, 163, 660 $g\,m^{-2}$). The WPUA oligomer was characterised by Fourier transform infrared spectroscopy, particle size, and apparent viscosity. Some mechanical properties of UV-cured fibreglass, such as tensile strength, elongation at break as well as thermal properties via differential scanning calorimetry were measured. The specific UV-WPUA was selected as a material with many applications. The results indicate that the prepared UV-WPUA is a possible matrix for UV-curable fiberglass.

7-P4. Electroless deposition of silver on poly(3,4-ethylenedioxythiophene) obtained in the presence of polystyrene sulphonate or dodecyl sulphate ions: effect of polymer layer thickness

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The aim of the present work is to study the electroless deposition of silver on poly(3,4-ethylenedioxy thiophene) (PEDOT) layers produced in the presence of perchlorate ions with the addition of two organic dopants: dodecyl sulphate (DDS) or polystyrene sulphonate (PSS). PEDOT/ClO_4^- without organic dopants were also studied as reference layers. PEDOT layers of three different thicknesses (*d*) were synthesised in each polymerisation solution. The electroless deposition of silver was followed by monitoring the open circuit potential at PEDOT-coated working electrodes. The amount of deposited silver was determined by voltammetric stripping in 0.4 M $HClO_4$. Data on the size and dispersion of the silver crystals at the PEDOT surface were obtained by SEM.

It was found that the doping ions used for PEDOT synthesis had a marked effect on the amount of deposited silver (m_{Ag}) for a given thickness of the layers. Furthermore, depending on the type of anions used in the course of synthesis, *d* affects the values of m_{Ag} in different way.). PEDOT/ClO_4^- layers accommodate the smallest amounts of silver with weak dependence on *d*. On the contrary, PEDOT/SDS layers provide the largest quantities of deposited silver and increasing m_{Ag} on increasing *d*. PEDOT/PSS showed opposite thickness dependence trends for silver deposition from Ag^+ and $[AgEDTA]^{3-}$ solutions. The plating from the two silver ionic species shows a stronger dependence of m_{Ag} on *d* when using $[AgEDTA]^{3-}$ as a source for metal reduction. In the latter case, better dispersion of the metallic phase was also observed.

The obtained results are discussed in terms of the organic anion-imparted characteristics of the PEDOT layers and the opportunities for ionic transport of silver species in the bulk of the polymer layers.

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7-P5. Poly(zwitterion)s for modification of bioactive agents

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Poly(zwitterion)s involved in biomedical applications are widely studied due to their hydrophilicity, biocompatibility, and superior resistance to nonspecific protein adsorption. They can be applied as PEG alternatives to modification of bioactive substances and delivery of biomacromolecules, such as nucleic acids and proteins. Therefore, the design of functionalised poly(zwitterion)s capable of conjugation to biomacromolecules or other active species under mild reaction conditions is a prerequisite for successful development of a delivery system.

This communication is reporting the preparation and characterisation of polysulphobetaines bearing end-functional groups able to react selectively with amines in aqueous media. They were used for modification of poly(ethyleneimine) and conjugation to human serum albumin as model bioactive molecules. The conjugation reactions were studied by NMR spectroscopy. The effect of poly(zwitterion) modification on the solubility and biological properties was evaluaed.

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7-P6. Complexes of transition metals ions with block copolymers

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Complexes of block copolymers (BC) were prepared by interaction with transition metal salts such as $Na_2MoO_4.2H_2O$, $VOSO_4.5H_2O$, $FeCl_2.4H_2O$, $CoCl_2.6H_2O$, and $CuCl_2.2H_2O$ in aqueous solution at room temperature. The metal complexes are formed by coordinatively bonding the polymer ligands with the metal ions through a reaction between the BC-containing donor atoms (in this case, N or O atoms) and the different metal ions. These complexes were characterised by elemental analysis, FTIR spectroscopy, and thermal analysis. Geometric optimisation of monomer fragments of transition metal ions complexes was carried out by the semi-empirical quantum method ZINDO/1 from HyperChem software package. The latter study of the complexes enabled us to suggest the probable stereo structures of the monomer fragments.

The catalytic epoxidation of cyclohexene in the presence of *tert*- butyl hydroperoxide as oxidant and toluene solvent was investigated in presence of the complexes. The reaction products were analysed by gas chromatography with flame ionisation detection. The catalytic activity of Mo(VI) complexes in the epoxidation reaction was generally higher than that of the V(IV), Cu(II), Co(II), and Fe(II) coordination compounds. Reaction by-products were 2-cyclohexene-1-ol and 2-cyclohexene-1-on.

7-P7. Synthesis of non-phthalic plasticisers for PVC plastisols: reaction kinetics and characterisation

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In the present work, the esterification process of adipic acid (AA) and 2-ethylhexan-1-ol (EH) in the presence of acidic type homogeneous catalysts, CH_3SO_3H, p-$CH_3C_6H_4SO_3H$, and H_2SO_4 was studied. Catalyst content was 5, 7, and 10 mass% with respect to the adipic acid and the reaction temperature was in the range of 80–120°C. Results showed that the reaction rate attained the highest values at 80°C with 7% H_2SO_4 catalyst. Activation energy and pre-exponential factor values were 40.5 kJ mol^{-1} and 4.56 min^{-1}, respectively. This factor corresponds to a first-order reaction.

Molding effect of mixtures containing emulsion of polyvinyl chloride and bis-2-ethylhexyladipate (mass ratio 70:30) was investigated in the range of 120–190°C. It was found that both tensile strength and elongation at break increase with temperature.

The highest values of tensile strength (19.41 MPa) and elongation (339.89%) were achieved at a temperature of 170°C. However, on increasing the temperature to 180–190° C both tensile strength and elongation values were decreased.

For investigation of both tensile strength and elongation at break of the plastisols, mixtures of polyvinyl chloride to plasticizer at 75:25, 70:30, 65:35, 60:40, and 55:45 ratios were prepared. It was observed that increasing the plasticizer content caused a decrease and an increase in tensile strength and elongation values, respectively.

7-P8. Synthesis and characterisation of a series of copolymers based on poly(N-isopropylacrylamide)-g-poly(ethylene glycol)-b-poly(-L-lysine)

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It is known that the stability of biological macromolecules in solution is limited by degradation and denaturation processes as well as by difficulties to penetrate through the cytoplasmic membrane. Therefore, the new tendency in the development of diagnostics, target drug delivery, and regenerative medicine are focused to find carries for efficient storage and transport of biological macromolecules. Polymeric nanoparticles are promising candidates due to their low toxicity, high biocompatibility, and possibilities to impart biodegradability, functionality, and control of their properties. This motivated our research to prepare new copolymers with potential application to medicine and pharmacy.

The synthesis of novel hybrid copolymers comprising a poly(N-isopropylacrylamide) (PNIPAm) block with short poly(ethylene glycol) (PEG) side chains and a cationic block of poly(L-lysine) (PLLys) is described. The copolymers were synthesised in a two-step procedure. At the first step, a thermally sensitive PNIPAm-g-PEG macroinitiator with a terminal ammonium hydrochloride group was prepared. The macroinitiator was characterised by ^{1}H NMR and UV spectroscopy. PLLys blocks of different degrees of polymerisation were obtained at the second step involving controlled ring-opening polymerisation of Z-L-lysine N-carboxyanhydride initiated by the macroinitiator. PLLys is positively charged and it is capable to form complexes with various oppositely charged biomacromolecules such as DNA or RNA, which is a good precondition for gene-delivery applications of the prepared copolymer-based carriers.

7-P9. Diblock copolymers of poly(allyl glycidyl ether) and polyglycidol bearing a hydrophobic residue: synthesis and aqueous solution properties

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Well-defined poly(allyl glycidyl ether)-polyglycidol (PAGE-PG) diblock copolymers bearing a higher aliphatic residue were prepared applying a three-step synthetic procedure: (i) ring-opening anionic polymerisation of allyl glycidyl ether (AGE) initiated by dodecanol followed by (ii) anionic polymerisation of ethoxyethyl glycidyl ether (EEGE, protected glycidol) and, eventually, (iii) cleavage of the protective ethoxyethyl groups. The copolymers differ in their overall molecular weight and ratio of the constituent blocks. Polymerisations of both AGE and EEGE were carried out in bulk and found to proceed in a controllable and predictable way. After successful cleavage of the protective groups, PAGE-PG copolymers with fixed molar mass of the PAGE block and increasing from 25 to 70 mol.% PG contents were prepared. The block copolymers were characterised by means of ^{1}H NMR spectroscopy and GPC. The process of self-assembly of the copolymers in aqueous solution was investigated. Copolymer ability to form particles of various size and morphologies depending on molecular weight, polymer concentration, ratio between constituent blocks, etc. was studied using light scattering and transmission electron microscopy.

7-P10. Evaluation of the hydrogen bonds network impact on the membrane properties of polyglycidol containing hybrid liposomes

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Liposomes are artificial structures that are formed spontaneously in aqueous media. They are composed of phospholipid molecules assembled in a self-enclosed bilayer surrounding a water compartment. Liposomes can easily be loaded with both hydrophilic and hydrophobic drug molecules located in the inner water domain and in the phospholipid membrane, respectively. However, plain liposomes are characterised by short lifetime, when applied *in vivo*, due to fast recognition by the mononuclear phagocyte system cells, which is preceded by opsonisation by different blood native molecules, mostly lipoproteins and burst leakage of the loaded therapeutic agent. An elegant approach to reduce opsonisation is grafting the liposome membrane with hydrophilic polymer chains, thus creating a repulsive barrier that prevents liposome-lipoproteins interactions. The aim of the present contribution is to evaluate the potential of linear polyglycidol as a hydrophilic, flexible, and biocompatible polymer to provide stabilisation properties to liposomes based on dipalmitoyl phosphatidylcholine. To achieve the aim, a series of polyglycidol-derived lipids having polymerisation degree of the polyglycidol chains in the 23–110 range were synthesised. Liposome formulations of varying copolymer type and content were prepared by film hydration technique followed by extrusion. The hybrid structures were studied by means of dynamic and electrophoretic light scattering, cryogenic transmission electron microscopy, and fluorescence spectroscopy. Cytotoxicity toward OPM-2 and EJ cell lines was assessed as well.

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7-P11. Determination of minimum PPO/GPE ratio that can be incorporated into PPO-PEO block copolymers according to the initiator

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Block copolymers are those in which the monomers come together in a sequence consisting of long stretches of one monomer followed by a long stretch of the other one, thus the structure is well known. On the other hand, in random copolymers monomer distribution is unknown and does not follow an established pattern.

In this study, a polypropylene oxide-polyethylene oxide (PPO-PEO) block copolymer functionalised with glycidyl propargyl ether (GPE) and initiated by two different initiators (water and ethanol) was synthesised. Introduction of a known amount of commercially available GPE in a controlled way during the synthesis process allows one to obtain an alkynyl polyether prepared for future click attachment. In order to find the maximum amount of GPE that can be incorporated into the chain, different PPO/GPE ratios were used.

According to our results for polyols initiated with water, the maximum allowable PPO/GPE ratio by a polymer chain is 0.4, which is equivalent to 17.74 mass% of GPE added. For all PPO/GPE ratios studied, it could be seen that increasing the GPE concentration caused higher polydispersity index values, so an optimal balance between polydispersity and PPO/GPE should be found. When ethanol was the initiator, the maximum allowable ratio was 0.5, so the amount of GPE incorporated was smaller than in the case of water. In addition, two size distributions were obtained and the polydispersity increased with GPE to a greater extent than in the previous case.

Since the aim of these copolymers is the production of polymer-drug conjugates, a monodisperse polymer is preferred. Thus, water is better initiator than ethanol, because besides the best polydispersity index, it also allows adding a larger amount of GPE to the polymer chain.

7-P12. Advanced electrospun hybrid materials for photodegradation of organic pollutants

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Hybrid polymer nanomaterials showing photocatalytic properties are efficient materials for remediation of polluted air and water. Therefore, the aim of the work is to find appropriate conditions for preparation of novel photocatalytic materials by electrospinning. The first step in the development of these advanced materials was the synthesis of CuS/ZnS core/shell nanocrystals. Further, hybrid materials of ‘in’ and ‘on’ types were fabricated by electrospinning of PAN-CuS/ZnS mixture and simultaneous electrospinning of PAN and electrospraying of CuS/ZnS dispersion, respectively. It was found that electrospinning performed in conjunction with electrospraying of CuS/ZnS dispersion resulted in uniform distribution of aggregates of nanocrystals along fibre length. Photocatalytic activity tests under visible light of the hybrid materials were carried out using a model organic pollutant, Rhodamine B. Discoloration was monitored spectrophotometrically in the presence of the two types of hybrid materials. It was demonstrated that the hybrid materials of different design displayed excellent photocatalytic activity under visible light even after threefold use of the materials. Therefore, the prepared electrospun hybrid materials are very promising for wastewater treatment using photoreactors.

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7-P13. Curcumin-loaded cellulose acetate/polyvinylpyrrolidone fibrous materials: design, preparation, characterisation, and antibacterial activity

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Curcumin is a naturally occurring polyphenolic compound with remarkable biological activity. Incorporation of curcumin in polymer matrix by electrospinning was shown to be an effective route to obtain materials suitable for diverse biomedical applications [1,2]. In the present study, novel electrospun materials from cellulose acetate (CA) and polyvinylpyrrolidone (PVP) for curcumin delivery were obtained. The possibility to modulate curcumin release by appropriate selection of the composition of the polymer matrix and by the preparation technique (one-pot electrospinning or dual spinneret electrospinning) was shown. Incorporation of PVP resulted in increased hydrophilicity of the fibres and faster curcumin release. Curcumin was found in the amorphous state in the curcumin-containing fibres and these mats exhibited antibacterial activity against *S. aureus*. The results show that the obtained new antibacterial materials are suitable for wound dressing applications, which necessitate diverse release behaviour of the bioactive compound.

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7-P14. Preparation and characterization of dextran cryogels

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Polymeric cryogels are formed via cryogenic treatment (moderate freezing-crosslinking-thawing) of solutions or colloidal dispersions of appropriate precursors. Moderately frozen solutions are heterophase systems containing both solids (i.e. polycrystals of frozen solvent) and some unfrozen fraction called ‘liquid microphase’, where the solutes are concentrated. In this study, we report the synthesis of novel super-macroporous cryogels based on dextran by UV irradiation. The advantages of UV irradiation are extremely short time for efficient gel formation and low capital outlay. Photocrosslinking of dextran was done using water-soluble photoinitiator (4-benzoylbenzyl)trimethyl-ammonium chloride and the crosslinking agent N,N′-methylenebis(acrylamide). The study aimed to determine the effect of polymer and crosslinking agent concentrations on the crosslinking efficiency. It was found that the amount of dextran and crosslinking agent in the initial solution strongly influenced both the gel fraction yield and degree of swelling of the resulting cryogels. The highest gel fraction yield (over 90%) was reached at dextran concentration of 3 wt.%. The optimal content of N,N′-methylenebis(acrylamide) required for preparation of cryogels with high gel fraction was 10 wt.% with respect to polymer. The beta-blocker metoprolol was successfully loaded in dextran cryogels and the drug release profile was studied.

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7-P15. Numerical analysis of atom transfer radical polymerisation

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Original algorithm has been developed for calculating the conversion evolution of molecular weight characteristics of polymers produced by ATRP. Conversion relationships were deduced for the concentration of monomer M, initiator I and active propagation chains A as functions of the probability γ_i for transformation of the A chains to dead (T) ones at the i^{th} conversion step. Recurrent relationships for the number degree of polymerization for monodisperse 'living' (L): active (A) and dormant (D) propagation chains and polydisperse T macromolecules were deduced for each conversion step. Then, the total number average and weight average degrees of polymerization were deduced. Using them, an expression for polydispersity index ($\chi_i = PDI_i$) was obtained which showed that χ_i increases with γ_i because of the larger contribution of polydisperse T macromolecules. Decreasing γ_i is possible by increasing k_{-1} and $C_{Cu(II)}$ and reducing of the K_e value. These requirements are satisfied via suitable change of the reaction media, temperature, and nature of the ligand for copper cations. The acceleration at AGET ATRP is a result of the decrease of $C_{Cu(II)}$: a shift of the activation-deactivation equilibrium to the active state of the propagation chains. However, it became clear from the equations derived that in this way γ_i increases and so does χ_i. An original approach was developed in the present work predicting simultaneous ATRP acceleration and χ_i decrease through the participation of M in both right and reverse reactions of the activation-deactivation equilibrium. The acceleration is a result of the addition of two new chain propagation reactions. It is noteworthy that by this method it is possible to explain the considerable ATRP acceleration in aqueous media, the preservation of the L chains after the monomer depletion (condition for the synthesis of block copolymers) and the difference between conventional and ATRP monomer reactivity ratios. In addition, it became possible to reduce the generally accepted great difference between the k_1 and k_{-1} rate constant values.

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7-P16. Electrospun fibrous materials containing natural phenolic compounds with antibacterial and *in vitro* antitumour activity

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Novel curcumin (Curc) or caffeic acid (CA)-loaded fibrous materials from polyesters (polylactide or poly (3-hydroxybutyrate) or non-inogenic polymer (polyvinylpyrrolidone) were obtained by one-pot electrospinning. Morphology and surface composition of the obtained fibrous materials were studied by means of scanning electron microscopy and X-ray photoelectron spectroscopy. The thermal properties of the prepared mats were evaluated by differential scanning calorimetry. Curc and CA incorporated in the fibrous materials were in the amorphous state. *In vitro* release of Curc or CA was modulated by controlling the composition of the fibrous mats. Performed microbiological screening revealed that in contrast to the bare mats, the Curc- or CA-containing fibrous materials were effective in suppressing the growth of the Gram-positive bacteria *Staphylococcus aureus*. The obtained materials exhibited high cytotoxicity toward human cervical HeLa tumour cells. The observed strong antiproliferative effect of the mats was mainly due to induction of cell apoptosis.

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7-P17. Functional block and star copolyelectrolytes of potential biomedical application: synthesis and detailed structural characterisation

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Polyelectrolytes are unique class of polymers well known to play an important role in living systems and find manifold application in industrial processes, biotechnology, and medicine. Recently considerable attention has been focused on the design of complex polyelectrolyte topologies: block, graft, comb, star, etc., due to their special properties determined by the chemical structure and electrochemical and macromolecular parameters.

In this work, linear as well as tri-arm star copolymers were investigated comprising cationic poly{[2-(methacryloyloxy)ethyl]trimethylammonium chloride} (MAETMAC) segments. Series of copolymers were synthesised via redox polymerisation of MAETMAC in aqueous media when using low molar mass or oligomeric alcohols as initiating moiety and N,N-dimethyl acrylamide as comonomer. A detailed structural characterisation of the obtained functionalised copolymers was performed by using FTIR, NMR, and electrospray MS (ESI-MS). Elucidation of the copolymer composition and complex macromolecular structure of the studied new functional polyelectrolytes is important in view of their potential application as sustained drug delivery carriers.

7-P18. Synthesis of poly(oxyethylene phosphoramidate)s and their glycoconjugates via Staudinger reaction

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Glycopolymers are synthetic polymers with carbohydrate residues attached to their backbone. They are important oligosaccharide mimics that can be utilised for drug and gene delivery, nanomedicines, and biotechnology sensors. Phosphorus-nitrogen compounds play a substantial role in the biological and pharmacological research. Due to their unique properties and biological activity, P-N compounds are applied as catalysts in biological transformations or as inhibitors for treatment of various diseases.

This work reports a new route to obtain glycopolymers containing P-N motifs, i.e. poly(phosphoramidate)s with pendant carbohydrate residues. Poly(oxyethylene H-phosphonate), which is a biodegradable, biocompatible and low toxic polymer, was converted into tri-coordinated phosphorus species, poly(oxyethylene trimethylsilyl phosphite), and then reacted with different azides, including sugar azides (glucose- and mannose-containing azides), via Staudinger reaction to furnish the desired poly(oxyethylene phosphoramidate)s and their glycoconjugates. ^{31}P NMR spectroscopy was applied as a powerful tool for determination of the conversion and structure of the reaction products. The obtained poly(phosphoramidate)-glycoconjugates were characterised using dynamic light scattering and analytical ultracentrifugation techniques. The cytotoxic effects of the precursor poly(oxyethylene H-phosphonate) and the glucoconjugate on viability of Human Embryonic Kidney 293 cell line were assessed.

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7-P19. Novel water-soluble fluorescent nanomicelles as a tool for biomedical investigations

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Fluorescent probes for sensing and reporting of chemical species are currently of great interest due to the increasing need of fast and reliable detecting of chemical species in many areas of human activity. In recent years, most attention has been paid to development of fluorescent sensing systems for ions under physiological conditions. The biggest disadvantage of most organic probes is their hydrophobicity and work in organic solvents, which significantly restricts their practical applications. Fluorescent polymeric nanoassemblies have become a focus of intensive investigations during the past few decades due to combined advantages: improved biocompatibility, water dispersibility, stimuli-responsiveness, facile integration into optical detection devices, and ability of functionalisation. One approach to prepare such a structure consists of the use of amphiphilic diblock copolymers that can self-assemble in solution forming nanosized morphologies. In many cases, spherical micelles consisting of core formed by hydrophobic block and shell arising from the hydrophilic block can be obtained in an aqueous solution. Based on this consideration different organic fluorophores can be incorporated into the hydrophobic core of the micelles which can provide their water solubility. Herein, we report on the synthesis of novel water-soluble fluorescence micelles with embedded Dyad or PDI fluorescent probes. The prepared nanomicellar architectures show high cell-permeability and low cytotoxicity suggesting a high potential of the prepared micelles for future biomedical applications.

7-P20. Polyzwitterionic hydrogels for immobilisation of alkaline protease

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The interest towards zwitterionic polymers has grown significantly in recent years due to their exceptional biocompatibility. It is believed that the origin of their biocompatibility lies in their structural similarity with natural patterns, e.g. the betaine structure of the amino acids, the zwitterionic phospholipid head as a building block of cell membranes, etc.

This study deals with the synthesis and characterisation of zwitterionic polymers networks (PZI) and their application as hydrogel wound dressings. PZI could provide several advantages in this role as they swell more in salt solution, i.e. wound excudate, than in water (so-called antipolyelectrolyte effect). In order to functionalise the PZI hydrogels, alkaline protease was immobilised therein with the aim to impart cleaning ability of necrotis tissues, which is necessary for faster wound healing. The alkaline protease is already used as an agent in several products for wound healing (creams, ointments, etc.) that are available on the Bulgarian market.

To achieve this goal two types of monomers were used: (i) carboxybetaine methacrylate and (ii) sulphobetaine methacrylate. The resulting polymer networks were characterised in terms of their swelling ability and were then loaded with alkaline protease. The enzyme activity of the loaded protease in PZI materials was evaluated and related to PZI crosslinking density. Thus, the proteases immobilisation in PZI resulted in a new functional hydrogel wound dressing.

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7-P21. Water transport and behaviour in polysulphobetaine hydrogels

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Polysulphobetaines (PSBs) are a class of polymers containing a covalently bound positively charged quaternary ammonium group and a negatively charged sulpho group in each monomeric unit. These polymers provoke very low non-specific protein adsorption and thus possess very good haemo- and biocompatibility. The excellent performance of PSBs as biomaterials is explained by their ability to swell better in a low molecular weight salt (LMS) aqueous solution than in water (antipolyelectrolyte effect). This behaviour of PSBs is explained by cluster formation due to dipole-dipole interactions between PSB monomeric units. These clusters are stable in water but destroyed by LMS. Thus, the interactions in PSB-LMS aqueous solutions are interesting in view to understanding their properties and should reveal details about the PSB performance *in vivo* as the LMS aqueous solution resembles the body fluids.

The aim of the present study was to investigate the dynamic swelling and the structural mobility of PSBs networks in aqueous solutions as a function of LMS concentrations. LMS concentration increase resulted in enhanced PSB-water interactions when PSB hydrogels are swollen in LMS aqueous solutions as revealed by the dynamic swelling. DSC data confirmed this conclusion as the fraction of bound water in PSBs hydrogels increases with LME concentration. These results are in agreement with data obtained by HR MAS NMR spectroscopy.

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7-P22. Creep and deswelling peculiarities of the polyzwitterionic ‘straight’ and ‘reverse’ poly(dimethylmethacryloyl propanesulphonate)-poly(acrylamide) double networks

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Double network (DN) hydrogels with cross-linked poly(dimethylmethacryloyl propanesulphonate) as a high density single network (HDSN) and poly(acrylamide) as a low density single network (LDSN) were synthesised and the characteristics of their creep and deswelling curves (stationary levels and initial rates of displacement and deswelling) were determined. It was shown that the values of these characteristics depend on the monomer 1 to monomer 2 concentration ratios, monomer/cross-linking agent, duration of cross-linking polymerisation, and order of HDSN and LDSN formation. When the first SN is a polyzwitterionic (HDSN), the DN is called ‘straight’ DN, whereas in the opposite case the DN is called ‘reverse’. It was established that by transition from ‘straight’ to ‘reverse’ DN, the network density decreases, the elasticity increases, and the weight fraction of the bound water rises. The results are explained by the formation of dipole-dipole clusters between the opposite oriented zwitterion groups in the side groups of the polyzwitterionic macromolecules.

7-P23. Composite films and fibres based on polybenzimidazoles

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Polybenzimidazoles (PBIs) are a class of high performance polymers, which have found applications as thermally stable and inflammable textile fibres, high temperature matrix resins, adhesives, and foams. As a glassy thermoplastic of exceptional thermal stability (T_g 427°C), broad chemical resistance, and ability to function as a proton-acceptor or proton-donor, PBIs are uniquely suited for moving protons, hydrogen, and water. For these reasons, PBIs are highly suited for fuel cell proton exchange membranes and organic chemical pervaporation dehydration membranes, both types for use at high temperatures. In the present work, we demonstrate further applications of PBIs. Due to excellent thermal and mechanical properties, the PBIs have great potential for use as firefighter's turnout coats, astronaut space suits and gloves, and in the metalworking industries.

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8-O1. Efficient drug delivery: characterisation of peptide-based complex of doxorubicin

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The clinical use of doxorubicin (DOX), the latter being a member of the anthracycline antibiotics family with broad application in chemotherapy, is limited by adverse effects that follow its administration. A promising approach to decreasing its toxicity is the attachment of the drug to various carriers. As a first step of constructing a more complex system for its delivery to neoplastic cells, non-covalent interactions between DOX and a tailored drug-binding peptide (DBP) are explored. Classical molecular dynamics (MD) was used to determine the structural characteristics of the drug-peptide complex in aqueous solution at room and body temperature. The interactions were analysed and the π-stacking between the conjugated fragments of DBP and DOX could be considered dominant. The binding energy (BE) in the gas phase was evaluated at DFT level of theory for the representative geometries from the MD trajectories. The interactions were mainly attractive and covered a broad range of values. The effect of the first solvation shell on the BE was investigated via an ONIOM model but binding was mildly influenced by its presence. Models with multiple DOX molecules were used to explore the self-assembly process of such complexes. The drug-binding capacity of DBP was confirmed and the affinity of the drug towards the peptide was apparent. This outlines the complex as a prospective drug-carrying unit.

8-O2. Transfer of a drug-peptide complex through model cell membranes

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In order to improve the effectiveness of drugs used in chemotherapeutics, different molecular carriers are tested to facilitate the passage of active substances across the cell membrane. Cell-penetrating peptides (CPP) can be used as building blocks of new systems for enhanced drug delivery. More specifically, CPPs can aid the transfer of doxorubicin (DOX), one of the most potent chemotherapeutic antibiotics, to the cell cytosol [1]. To characterise the interaction of such a drug-peptide complex with molecules from the cell membrane, we considered a model system of a lipid bilayer and a DOX-CPP conjugate in water. Two types of bilayers were analysed: one composed solely of DPPC and another one, a mixed lipid bilayer with a lipid ratio reproducing that in human erythrocytes. From atomistic molecular dynamics simulations we obtained some basic structural characteristics of the bilayers and the complex. The energetics of the transfer process was quantified. It was found that near the membrane the secondary structure of the drug-peptide complex retained random coil conformation. At the initial transfer stages, DOX-CPP was located mainly among the lipid heads and formed pronounced curvature in the lipid layer. This study represents a first step toward understanding the mechanism by which the complex enters the cell.

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8-O3. Micellar solubilisation of hydrophobic drugs

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Over 50% of the new drug candidates are characterised by low water solubility, which leads to low oral bioavailability and limited practical application. We studied the increased solubility of hydrophobic drugs in micellar surfactant solutions, with the aim to determine the influence of drug and surfactant molecular structure on micellar solubilisation capacity.

18 different surfactants were studied for their effect on the solubility of five hydrophobic drugs. We studied nonionic, anionic, and cationic surfactants with different hydrophobic chain length (C-10 to C-16). Equilibrium drug solubility in surfactant solutions was determined by high-performance liquid chromatography.

The micellar solubilisation capacity increased with the increase of surfactant hydrophobic chain length for all studied drugs regardless of surfactant charge. The hydrophilic surfactant head had a strong effect on the solubilisation capacity, which depends on the type and charge of drug. The solubility of charged drug molecules increased very strongly in micellar solutions of oppositely charged surfactants. The latter gave evidence for the formation of mixed micelles due to electrostatic interactions.

The obtained results demonstrate that one of the major parameters controlling drug solubilisation in surfactant micelles is the drug molecular volume: when the molecular volume is higher than 300 $Å^3$ the mole fraction of drug in the micelles is low (< 0.11). Drug solubilisation increased linearly with the increase of surfactant hydrophobic chain length, when the length of drug molecule was smaller than that of the surfactant.

8-P1. New class of heterocyclic ring systems: synthesis of benzo[b]imidazo[1,5-d][1,4]oxazepines

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Benzoxazepine ring systems are common pharmacophores, which can be found in many structures with biological activity. A number of compounds with benzoxazepine scaffold have been described as potent antiviral, anticonvulsant and neuroleptic agents.

As a part of our research on the design and synthesis of novel heterocyclic systems with potential biomedical application, we developed a convenient five-step approach to the preparation of tricyclic benzoxazepines containing a fused imidazolone ring. In this report, we present a useful method for the synthesis of target compounds, which involves the use of benzoxazolones as easy available starting reagents. The key points of our approach are the ring transformation of 3-(2-oxopropyl)-2(3H)-benzoxazolones to the corresponding phenoxyacetic acids following by reaction of intramolecular acylation in PPA, leading to the formation of a seven-membered oxazepine ring.

The target compounds were obtained in good yields and their structures were established by spectroscopic methods (IR, NMR). Based on the structural analogy with compounds from PBOX group, we expected an interesting pharmacological profile for the tricyclic benzoxazepines with fused imidazolone ring. The biological experiments concerning their cytotoxicity on different cancer cell lines are in progress.

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8-P2. Sulphurbioisosteres of benzoxazolone allelochemicals: synthesis and crystal structure of 4-acetyl-2(3*H*)-benzothiazolone

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Allelochemicals are plant secondary metabolites, which can be released into the environment by roots, stems, bark, flowers, or seeds in the case of microbial infections or plant competitions for limited light, water, and nutrients. Benzoxazolones are group of plant secondary metabolites mainly presented in cereals such as corn, rye, and wheat. Their role as defence compounds toward pests, like bacteria, fungi, and insects, is well documented. One of the most important member is 4-acethyl-2(3*H*)-benzoxazolone (4-AcBOA) isolated from the kernels of the Fusarium-resistant corn hybrid. Several studies indicated that 4-AcBOA inhibits the biosynthesis of the mycotoxin deoxynivalenol produced by certain Fusarium species, which caused gibberella ear rot in corn. Following the classical concept of bioisosterism, we designed a new biomemic analogue of 4-acethyl-2(3*H*)-benzoxazolone by oxygen-sulphur interchange in benzazole ring. Therefore, in this work we report the synthesis and structural characterisation of the sulphur bioisoster of 4-AcBOA. Starting from commercially available and inexpensive 2-aminotoluene, we developed a multi-step synthetic approach to 4-acethyl-2(3*H*)-benzothiazolone in 23% overall yield. The structure of the target compound was unambiguously confirmed by NMR spectroscopy as well as by X-ray crystallography.

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8-P3. Thermoresponsive copolymer network films for transdermal Galantamine hydrobromide delivery

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Galantamine, an alkaloid obtained from the bulbs and flowers of *Galanthus caucasicus* or synthetically is widely used for the treatment of Alzheimer's disease and various other memory impairments, in particular those of vascular origin. Galantamine hydrobromide (GH) is available as fast-release tablets, extended-release capsules, and in oral solution. However, oral delivery of GH can cause severe side effects, such as nausea, vomiting, and gastrointestinal disturbance. Transdermal delivery of GH could avoid these unwanted side effects. Besides, the patch can be removed easily and immediately if any side effects are detected. Transdermal delivery is also patient friendly, especially for unconscious patients, patients with swallowing difficulties, and patients with mental disturbances.

In this work, thermoresponsive copolymer networks based on N-isopropylacrylamide were studied as new platforms for transdermal GH delivery. Series of networks of varied structure and composition were synthesised and investigated by applying swelling kinetics in different media as well as different spectroscopic and thermal methods. The network films were drug loaded in GH aqueous solution and the main characteristics of the obtained GH delivery systems were evaluated by using various spectroscopic and microscopic methods. The GH release kinetics profiles in BS at pH 6.8 and 37°C were established and discussed.

8-P4. Bigels as promising vehicles for ketoprofen-loaded polymer nanoparticles

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The purpose of this study was to investigate the stability and biopharmaceutical characteristics of ketoprofen, loaded in a homopolymer of vinyl acetate, a copolymer of vinyl acetate and dimethylaminoethyl methacrylate and mixtures of poly(vinyl acetate) with chitosan, Carbopol®, and hydroxypropyl cellulose which were included into bigels as semisolid dosage forms.

The polymer carriers of ketoprofen were obtained by emulsifier-free emulsion polymerisation of the monomers in aqueous media or in a solution of polymer chitosan, Carbopol®, and hydroxypropyl cellulose. The morphological characteristics of the carriers and *in vitro* release of the drug at pH 5.5 were estimated. The photochemical stability of the ketoprofen included in the carriers was also evaluated. Models with optimal characteristics were included in bigels, which consist of hydrophilic phase: Carbopol® hydrogel, and a nonpolar phase: almond oil and sorbitan monostearate. The bigels were characterised in terms of pH, rheological behaviour, spreadability, and *in vitro* drug release.

The carriers of ketoprofen were characterised by high yield and drug loading. The particle size distribution varied widely according to the polymer used and a sustained release was provided up to 24 h. The polymer carrier, alone or included into a bigel composition, had a better photostability of the drug compared to unprotected ketoprofen. Bigels with ketoprofen-loaded particles provided sustained release of the drug and showed optimal rheological parameters.

Poly(vinyl acetate) carriers of ketoprofen and the bigels in which they were included provide an enhanced photostability and sustained drug release.

9-K1. Industry 4.0 for batch cooking process at Mondi Stambolijski

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Batch digester technology for pulp delignification is one of the oldest processes in the pulp and paper industry. The connection of discontinuous and continuous production is burdened with an extremely long inertia of cooking process. Regular sequencing suffers under disorders of connected continual processes and, vice versa, an efficiency-decreasing effect in turbine house due to fast changes in the steam flows toward digester house.

Industry 4.0 opens quite a new approach to control this complex of conflicting requirements. Digitalisation of batch cooking process (virtual digester house as a mathematical copy of physical, technical, and technological properties and functions of the real plant) enables forecasting of the steam flow more than 1 hour ahead. The forecasting software is synchronised with interval of 1 min in order to clarify trend of steam consumption 60 min forward continuously. This information simplifies control task in turbine house, which increases efficiency of power production significantly.

At the beginning of each heating sequence, the digester specific heat parameters are automatically calculated using available instrumentation and digester-heating recipe is maintained significantly precise compared to the former temperature control. The steam consumption is smoothed, which again simplifies control task in turbine house.

The most decisive task for mill data communication is a balancing of production rate between paper machine and digester house. This function controls digester sequencing as a superior function including pulp storages and its availability in connection with production plan on paper machine. The purposeful usage of pulp storages reduces inefficient time in digester house to minimum and maximises production capacity of the paper machine.

9-O1. Modern approach applied in the process of structural and graphic design of consumer packaging for cosmetics

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This communication presents a modern strategic approach to workflow design packaging tentatively called ‘inside out’. Project approach is applied in a series of individual consumer packaging group and a ‘gift’ family pack for natural cosmetics ‘Plantifolia’: shampoo, conditioner, spray, hair mask, and soap. The main design here is consumer packaging production from class sheet material (semi hard).

All packages are made of cardboard and are classified as second layer packaging, except packaging for soap classified as first packaging layer. Accordingly, standard polypropylene (PP) and the one glass packaging used in the cosmetics industry are taken as the first layer packaging: tube, bottle, and glass jar of cream are designed series of self-adhesive labels. The design here is done at two stages: a first stage structural packaging design from ground zero level and a second stage, namely, author graphic design of the exterior appearance of the packaging.

The main objective of this publication is to inform the audience with the modern best practices in work processes applied in the packaging industry under the conditions of a difficult, complex, and time-consuming design in this class consumer packages carried by one of the best in its class professional CAD/CAM systems: EngView Package Designer.

9-O2. New deinking technology for digital printed paper

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In recent years, the digital printing share of the total print market is growing steadily and projections are that it will be a lasting trend for the future: from 9 to 20.6% in the period 2008–2018. Effective nanotechnologies are used in digital printing, but problems in paper recycling still emerge. Nanoparticle inks in waste digital printed paper cannot be removed. For the first time, the INGEDE association alerted to problems in deinking of digital prints. Current liquid toner (Indigo) prints fail to pass INGEDE`s deinkability test. The best current achievement is deinking of a mixture-recovered paper containing 5% of digital prints (France).

Pearson has formulated a general principle based on experimental observations according to which hard acids prefer to coordinate with hard bases and soft acids prefer to coordinate with soft bases. Klopman has developed this principle using a quantum chemistry approach. It is based on a polyelectronic perturbation theory involving both reactants and solvents.

Using this modern approach allows the selection and experimentation with catalyst additives that improve charge-controlled interaction between nanoparticle inks and surface-active agents in water.

Laboratory tests for deinking of digital printed paper were carried out using a flotation cell type PTS. It was established that the deinking rate increases by 17% for 4% higher ISO brightness values in the presence of additives catalysing charge-controlled reactions with nanoparticles inks.

The advantage of the new technology is better nanoparticle removal, a double increase in the share of digital prints in recovered paper mixture, and a higher deinking rate.

9-O3. Lignosulphonate and waste technical hydrolysis lignin as adhesives for eco-friendly fibreboard

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Formaldehyde emission from wood-based composites is a serious problem for research. At present adhesives such as urea, formaldehyde and phenol formaldehyde are used as the binder. The main problem with these adhesives is continuous emission of formaldehyde vapour that is carcinogenic in nature. The possibility of using replacement materials for formaldehyde-based resins and excluding synthetic resins from wood composites are the most effective solutions to this problem. In this regard, many studies have investigated the production of binderless boards. The results of these studies have shown that the lignin from the lignocellulosic materials plays an important role in binderless board performance.

The object of this study was to investigate the use of lignosulphonate product and waste technical hydrolysis lignin as adhesives for eco-friendly fibreboard. The effect of the pressing temperature and lignin ranging up to 20% on the properties of medium-density fibreboard was studied. All samples were tested according to EN 310 standards.

Results show that the waste technical hydrolysis lignin is more like an active additive than as a binder. By proper technique, ensuring the accurate mixing of lignin and fibres with resin is possible reduction of the phenolic resin charge. However, the fibreboards obtained by addition of lignosulphonate as a natural adhesive have good mechanical and water resistance properties that completely satisfy relevant standard specifications.

9-O4. Comparative analysis of topochemical kinetic equations applied to cellulase hydrolysis of lignocellulosic biomass

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Biomass from plantations of fast-growing tree species represents a large renewable resource for bioconversion. The enzymatic hydrolysis of lignocellulosic biomass to glucose by cellulases is one of the major steps involved in the conversion. Optimisation of this process requires good knowledge of the reaction kinetics.

The aim of the present study is to compare topochemical kinetic equations, which describe cellulase hydrolysis of pretreated fast-growing tree species. The samples have been analysed and comparison has been made of their chemical composition and density. The steam explosion method was used for substrate pretreatment. The cellulase NS22086 complex and the NS22118 β-glucosidase were used for the enzymatic conversion. The applicability of different kinetic equations referring to diffusion, topochemical and other heterogeneous catalytic processes was examined.

It was found that the cellulasic hydrolysis is best described by the modified Prout-Tompkins and Avrami-Erofeev equations. According to these kinetic models, the hydrolysis rate depends on the amount of substrate left and the inhibition of the enzyme by the product formed and on a combination of chemical interaction and diffusion processes. It was established that both the activation energy and the preexponential factor increase simultaneously on increasing the conversion degree. A new rate equation has been proposed.

9-O5. Dyeing of offset printing paper with new reactive dyes: influence on paper properties and ageing

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According to Smithers Pira, paper and board demand in the region of Central and East Europe is expected to increase by about 2 million tons from 2014 to 2019. A significant part of it is coloured paper mainly due to the increased consumption of corrugated board papers, but also because of the increased consumption of specially coloured printing papers for the new digital technology for the printing and publishing industry. Therefore, dyeing of offset paper is reasonable and the use of reactive dyes would have benefits. Reactive dyes for cellulose resemble acid dyes in their basic structure, but additionally possess one or more reactive groups. Dyes containing a dichlorotriazinyl reactive group are capable of reacting with cellulosic fibre in the presence of alkali to form a covalent bond between the dye and the fibre.

The aim of this study was to investigate the influence of three new reactive dyes over the main strength and hydrophobic properties of the coloured offset printing paper and colour stability during ageing.

In the present study three reactive dyes were used, two of them were laboratory-synthesised monochlorotriazine reactive orange and red dyes containing a stabiliser fragment and another one was a commercial reactive red dye product from the Levacell range of Kemira. Dyes were used at consumption of 0.2, 0.4, and 0.6% of o.d.f. in the composition of offset printing paper with a fibre content of bleached softwood and hardwood pulp at a ratio of 1:1. For fixing the reactive dyes, a cationic polymer based on epichlorhydrin dimethylamine copolymer was used. The paper was sized with alkyl ketene dimer and calcium carbonate was used as filler. Modified polyacrylamide was used as retention additive. The main strength and hydrophobic properties of the coloured papers were been examined. The optical properties and colour stability of the paper samples were also examined before and after thermal and light-accelerated ageing of the resulting paper samples.

9-O6. Reuse of sludge from wastewater treatment in production of recycled paper for corrugated packaging solutions

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The corrugated segment of the packaging industry is growing rapidly. The demand for corrugated packaging material is expected to increase by an average of more than 4% annually over the next five years, and will amount to almost 115 million tonnes of converted material by 2019. The development of innovative designs and reductions in paper weight is being driven by increasingly demanding environmental and sustainability requirements. Producers are making significant investments in environmental protection and energy optimisation programmes in addition to other activities aimed at reducing water consumption and improving logistics and transportation. Paper producers face the need to improve efficiencies and reduce costs to meet their customers' high expectations. On the other hand, the sludge from wastewater treatment system causes additional costs for dewatering and thickening before final disposal or landfill.

In this study, we are exploring how the sludge can be used in paper production to decrease fibre losses. The main purpose is to find optimal amount sludge, which will keep the same paper performance. During the study, we observed how sludge affects qualitative indicators such as physicomechanical parameters, surface structure, and optical parameters. Potential issues in real production were considered.

9-O7. Bentonite as a cleaning agent for pitch deposition on paper machine

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Lipophilic extractives from woody plants cause significant problems in pulp and paper manufacturing industrial processes. They form the so-called pitch deposits in mill circuits, equipment, and final product. These compounds may deposit alone or with other components such as inorganic salts, defoamers, and coating binders present in the pulping and papermaking process. Trends toward a higher degree of system closure in pulping and bleaching plants to fulfil environmental demands are aggravating these problems. The deposition of organic substances is considered a major problem in multiple stages of pulp and paper processing. Some of the undesired effects involve an increase in downtime, costs to replace paper machine clothing, frequent paper breaks, reduction of product quality, reduced operational efficiency, and losses in productivity of converting and printing operations, etc. The tendency of fatty and resin acids to form films and micelles have been elucidated by studies of mono- and multimolecular films.

In this study, the potential of using bentonite as a cleaning agent was investigated. The bentonite has the same behaviour like the talcum, but bearing a high active surface area it is more attractive for use as an agent for cleaning and deposit prevention. Before experiments with bentonite, a program for pitch deposit removal was used applying a combination of dispersant, blocking polymer pitch from agglomeration and deposition, and an enzyme for fatty and resin acid destruction. Laboratory measurements with flow cytometer showed 25 to 50% less sticky materials, which means that they are sorbed at the active surface of the bentonite slides. From these results, we may conclude that the bentonite reduces the tendency of deposition, protects the equipment, and increases the efficiency of paper production by reducing downtime for cleaning.

9-P1. Foam-formed cellulose-based composite materials for use in cushioning and insulation applications

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In recent years, efforts have been made to develop alternative materials from renewable resources, which are biodegradable and biocompatible under well-defined environmental conditions facilitating waste management by biological processes. Such materials have applications in economical fields where renewability and biodegradability are desired features. Cushion and insulation are examples of such domains, where the materials that are widely used are mainly made from plastic and polyurethane foam or expanded and extruded polystyrene. These materials are not biodegradable and makes disposal in soil or composting operations untenable. To reduce the impact on the environment, the use of bio-based polymeric foams with inclusion of cellulose fibres, can be one viable green alternative, which can also cut the costs of the recycling process for many industries.

This type of low-density composite materials is a porous material produced in foam laid media. There are many potential applications of high-porosity foam-formed composite materials, including thermal and acoustic insulating or kinetic energy absorber networks and, due to biocompatibility, foam-formed materials can also be utilised in scaffolding, tissue engineering, and as biocomposites in pharmaceutical and biomedical applications.

This paper presents a methodology for producing low-density cellulose composite materials based on foam laid media. This is realised by combining a surfactant with cellulose fibres (from virgin pulp and recovered papers), mixing at high shear velocity to entrain air, dewatering on Buchner funnel under vacuum, and air-drying in non-restrained conditions. These foam-formed composite materials were tested for acoustic properties using an experimental impedance tube. The effect of different parameters (thickness, density, air content) on the acoustic and mechanical properties of the foam-formed composites was investigated. Based on the obtained results and high level of porosity (approx. 98–99%), this type of materials can be applied as a porous sound absorber as well as for cushioning in different packaging systems.

9-P2. Study of the possibilities of using silver nanoparticles in packaging paper

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Nanotechnology offers new opportunity for innovations in food packaging, which can benefit both consumers and industry. The application of nanotechnology shows significant advantages for improving the quality of packaging materials. Innovations related with the use of nanotechnology in food packaging and quality control is a core focus in the modern food industry. Packaging can be made to be 'smart', which means that it can ensure conditions of safe environment or to send a signal in case of pollution and pathogens. Silver nanoparticles have become the dependable antimicrobial material with a variety of applications. Packaging materials with nanoparticles of silver or related cationic silver nanocomposites provide a possibility for effective and safe antimicrobial packaging.

In the present study, the opportunities for using silver nanoparticles in the composition of packaging paper were examined. The physicomechanical properties of laboratory-obtained packaging papers with and without silver nanoparticles were studied. Microbiological tests of the paper samples were also performed. The results indicated a bacteriostatic effect of the silver nanoparticles on packaging paper properties.

9-P3. Designing and creation of display and packaging for souvenir

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Packaging originated in antiquity and the original purpose was for protection and storage of transported items. Nowadays, packaging performs more and more diverse functions. It has become a powerful tool for marketing and advertising to help rapid and successful implementation of products on the market.

This project aims to study the basic processes of design and manufacture of corrugated display and consumer packaging from folding cardboard to the stage of their approved real sample. This project is focused on young children. The structural and graphic design should be interesting and attractive to the attention of children and should enhance their ability to recognise and remember animal variety.

For the structural design of display and package, EngView Package Designer was used as well-known software in the packaging industry. It is a CAD/CAM program, which enables creation of every stage of the design and production process by starting from conceptual design to its three-dimensional representation and to the final arrangement of graphic design and management of machines for cutting the finished product.

The process from the idea to inception of the packaging is a workflow that should be conformable to the materials, technology, market, and consumer needs and even more. The modern design of packaging and its appropriate commercial realisation involves the usage of a large number of software products that repeatedly shortens steps in the design but requires a specific knowledge of the exact materials of which packaging should be produced and specific technologies that enable successful implementation of the original idea.

9-P4. Investigation on the influence of new reactive dyes on the colour stability of offset printing paper during ageing

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Contrary to the general belief that coloured papers are mainly used for hygiene and tissue papers, nowadays some of the specialists in the new digital printing technology and publishing industry prefer to produce special books and journals with specifically coloured paper. Therefore, dyeing of offset paper is reasonable and the use of reactive dyes would have benefits, both for the properties and for the colour stability during paper ageing. Generally, paper is coloured by dyes of different chemical nature: inorganic pigments; synthetic organic pigments; basic, acid, direct dyes, etc. The reactive dyes are well known mainly as textile dyes and they have only limited use in paper production. They are capable of forming covalent dye-polymer bonds, for instance, with the hydroxyl groups of cellulose.

The purpose of this study was to investigate the influence of new laboratory-synthesised reactive orange dyes on the colour stability during accelerated ageing of the paper, which involved drying at 105°C and exposure to light (765±75 W m^{-2}, 290–800 nm).

In these experiments, two laboratory-synthesised reactive orange dyes were used, being derivatives of chlorotriazine and one of them containing a stabiliser fragment. Dyes were used in the composition of offset printing paper with a fibre content of bleached softwood and hardwood pulp at a ratio of 1:1. The paper was sized with alkyl ketene dimer and calcium carbonate was used as a filler. The L*C*h* optical properties from the CIE Lab colour space were examined before and after the accelerated ageing of the resulting paper samples.

It was found that both reactive dyes were used to obtain paper samples with similar colour shades and uniform colouring. According to the colour stability, both reactive dyes gave paper with stable colour that is stable under thermal and light-accelerated ageing.

9-P5. New methods of protection during book conservation

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The libraries storing paper funds often withdraw from circulation a series of books that have become unusable due to biodegradation. Usually destroyed materials are weakened, pigmented, and crumbled, covered with barnacles with colourful spots and often with tight-glued pages. Species compositions of microorganisms that break down the cellulose component of the paper in terms of libraries are not adequately studied and it is of interest both in theoretical and practical terms. In conservation libraries, new worldwide environmental technologies are being implemented. New specific methods of treatment without toxic substances and chemicals have been designed to disinfect bibliographical and museum cultural heritages. Anoxia is a non-toxic disinfection method using controlled oxygen-free environment and embedded control pest insects without any risk to the literary heritage of people and the environment. This method involves an artificial pretreatment to oxygen to levels below 0.5% and inert gas (99.5%), nitrogen in most cases. At the same time, temperature and relative humidity are kept within certain parameters method efficiency. The Anoxia method eliminates parasites by dehydration and suffocation. Pest mortality was 100% irrespective of development stage.

The Anoxia method was applied at the regional library in Rousse (Bulgaria).

9-P6. Conservation and restoration of documents from the National History Museum fund through appropriate methods

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Libraries and museums keep in their funds millions of written pages that contain the wealth of Bulgarian cultural and scientific heritage. The conservation and restoration of the written materials is associated with preservation, rehabilitation, and bringing objects to their original overall condition. To apply the restorative processes it is necessary to have knowledge of the essential changes of the materials forming written cultural monuments under their long-term preservation, to suspend destructive factors causing accelerated ageing of the paper and the inks, and to develop reliable restoration methods. Each object received for restoration and conservation has its own specific value: historical, technical, and artistic. The primary task of restoration and conservation of written documents is not only mechanical adhesion of the detached places of separate pages and restoration of missing parts of the documents with new material but also stabilisation of material basis of the paper, manuscript or document and termination of further destructive processes aiming preservation for a maximum possible period of time.

The purpose of the current study is survey and application of appropriate methods of document restoration and conservation. Various documents restored at the laboratory of conservation and restoration at the National History Museum will be presented.

9-P7. The ageing kinetics of books

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A typical sign of paper ageing is lowering the degree of brightness and deterioration of physical and mechanical properties of the paper. For examination of the resulting changes, an artificially accelerated thermal ageing is conducted. The examination of regularities in the ageing process of printed and unprinted samples of paper that compose the individual elements of the book is also of interest. The result of ageing is primarily associated with the presence of carbonyl groups formed due to oxidation of the hydroxyl groups of the second and third carbon atoms in the elementary unit of the cellulose macromolecule and the presence of both aldehyde and carboxyl groups in the cellulose materials. The reduction in the degree of paper whiteness can be associated with the presence of lignin, hemicelluloses, metals, and type of sizing.

Paper, as an elasto-plastic and capillary porous material, can rapidly be destroyed by increasing the temperature. The heat accelerates the chemical reactions in the paper, such as ageing. The depth of the changes in the paper depends not only of the temperature but also on impact duration. The rate of the chemical reactions can be described by the Arrhenius equation.

An artificial thermal ageing at three different temperatures (90, 105, and 120°C) for 6, 12, 18, 36, and 48 hours was conducted in the present study. The level of whiteness was defined to examine the kinetics of the process.

9-P8. Preparation of microcrystalline cellulose from bleached hardwood pulp

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Cellulose nanocrystals and microfibrillated cellulose are renewable biopolymer nanomaterials with novel applications. Many of these unique attributes arise because of their nanoscale morphology. Depending on the composition, cellulose nanomaterials can be biodegradable to provide an environmentally friendly alternative to plastics. Acid hydrolysis is the main process in the traditional manufacture of microcrystalline cellulose. Mechanical methods such as those discussed previously precede acid digestion and improve fibre solubility and dispersion. The processing requirements, and therefore energy costs, can be reduced by combining mechanical processing techniques with additional treatments such as TEMPO oxidation. Enzyme production of microcrystalline cellulose does not require harsh chemicals, has lower energy requirements, and is environmentally sustainable.

The object of this study was to investigate the possibilities of obtaining microcrystalline cellulose from bleached hardwood pulp produced at Svilocell EAD. The influence of the cooking and bleaching conditions was studied as well as various methods of subsequent hydrolysis on the degree of polymerisation of the obtained microcrystalline cellulose. Microcrystalline cellulose showing lower values of the degree of polymerisation was achieved by hydrolysis with hydrochloric acid compared to hydrolysis with sulphuric acid and upon a cellulase treatment. The conditions of hydrolysis process and the additional peroxide treatment had a minor effect on the degree of polymerisation.

9-P9. Fast growing paulownia wood: a perspective raw material for production of fibrous materials

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The present paper is intended to make a comparative kinetic analysis of the effect of bleaching pretreatment and temperature increase on thermal ageing of fibre material derived from fast growth Paulownia wood. The brightness reversion of bleached and unbleached samples was followed within an interval of 6 to 72 h. The temperature values applied refer to 90, 105, and 120°C.

An exponential kinetic equation was applied for description of the ageing process kinetics by means of which initial and current rates of the process were calculated. Both activation energy and preexponential factor values in the Arrhenius equation were increased in the course of the process. A linear relationship between them indicated a compensation effect.

9-P10. Printing quality of chitosan and rice starch coated packaging paper

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Biopolymers used as coatings on packaging paper can provide sufficient barriers (water, gas, etc.). However, increased environmental concerns, synthetic packaging, and coatings are nowadays being replaced by bio-based materials. Therefore, thermoplastic starch and chitosan can be a good substitute of petroleum-based products in packaging industry.

In this research chitosan and rice starch were used as coatings on packaging paper. The aim of the research was to determine printing quality on coated paper, which could be used for further applications. The influence of coated thickness on the printing quality was also investigated.

Paper was coated with two different coating mixtures. The first was only chitosan coating and the other one was a mixture of chitosan and rice starch at a ratio of 1:1. Coating was applied by two different bars to achieve two different thickness values: 40 and 80 μm. The ink rub test was performed by using a rub tester and the procedure was made according to TAPPI T830 standard. The dry rub test showed that all coated samples achieved better results (optical density) in comparison with uncoated paper. In this research, two rubbing times were determined: 25 and 50 cycles, at a rubbing speed of 106 cpm. After 25 cycles, sample paper coated by chitosan and rice starch achieved the best quality with respect to uncoated and chitosan coated paper. After 50 cycles, the chitosan and rice starch coating still had better abrasion resistance, but it could not be sufficient for further use. The study proved a higher printing quality of the coated paper especially using a coating with mixture of chitosan and rice starch.

9-P11. Adhesive-based or recycling polyurethane foam for wood materials

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Adhesives based on polyurethanes (PUR) are used in a wide range of applications. Recycling polyethylene terephthalate (PET) based PUR wood composites and adhesives are object of current industrial interest to avoid environmentalal pollution problems and cost effectiveness. PET recycling to polyols is an important way to reduce the cost of raw materials used to produce PUR adhesives.

Another source to produce polyols that is suitable as a basic raw material of adhesives is the recycling of PUR foams. Generally, there are two ways to recycle PUR foams: physical and chemical.

In this paper, we describe an attempt to synthesise polyether polyols out of PUR foams to form the basis of adhesives for gluing wood products. This is a continuation of previous work to develop wood composite materials using polyurethane recycling polyols in prepolymers as a binder. The process used was glycolysis of PUR foam using dipropylene glycol and di-*n*-butylamine as cleavage reagents and solvent. The oligomers obtained and polymeric methylene diphenylisocyanate (PMDI) were utilised to formulate the PUR adhesives. The synthesised adhesives were used for wood to wood bonding system. The bond strength and the delamination strength were measured by shear strength and water resistance delamination tests.

9-P12. The effect of ultrasound treatment on soy protein and chitosan coating solution for packaging paper

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Natural polymers are already used as barrier coatings on packaging materials and in recent years, there has been a focus on renewable polymers, mostly as edible films and coatings. Bio-based coatings, such as starch (rice, corn, potato, etc.), proteins (soybean), polysaccharides (chitosan and chitin) and lipids are extracted directly from the biomass. Their advantage is that they are non-toxic, environmentally friendly and have great grease, gas, and aroma barrier properties.

From the presented research, bio-based polymers (soy protein and chitosan) were used as coatings on packaging paper. Ultrasound treatment was used for the preparation of the coating solution. Paper sheets were solution-coated using a hand coater. The study was carried out using uncoated paper, untreated coated paper, and coated paper using ultrasound as pretreatment. The coating solution consisted of chitosan and soy protein at a ratio of 1:1. The goal of the research was to make a paper coating, which will be biodegradable, will have an improved mechanical and barrier (grease, antimicrobial) properties. Ultrasound was used to reduce the production costs and to make paper with better barrier properties, compared to uncoated and coated paper, which solution was not pretreated. The tensile properties (tensile stress and strain) of pretreated, solution-coated paper were improved. Due to protein addition in the coating, the strength and toughness of the paper (pretreated and not pretreated solution) compared to uncoated enhanced. As expected, the surface of treated coated paper was more even without many defects, pinholes, or cracks. It was observed that the surface of untreated coated paper is less smooth. Grease resistance of coated paper was determined using a modified TAPPI test. The results showed that grease migration was detected, the stained percentage area of untreated and coated paper detected being about 1%. The detected stained percentage area for ultrasound treated coated paper was less, about 0.5%. The results of grease migration are probably due to very small pinholes, cracks, and thin portions, where grease could permeate through. Ultrasound treatment has great effect on mechanical properties, surface and grease barrier properties of coated soy protein-chitosan coating solution on packaging paper.

9-P13. Evaluation of changes in the optical properties of high yield fibrous material under thermal treatment

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Plants raw materials are a huge source with good stock and annually renewable origin of fibres, which are needed for different kinds of industries. Wood is one of most important and easy for processing and treatment raw material for humanity. The wood is consisted of non-homogenous organic matter, which after chemical and mechanical treatment is converted to fibrous materials. Cellulose is one of most important component obtained from fibrous materials. Another one, which is actual material at present, is a high yield fibrous material. This material is suitable and perspective for using in the composition of packing papers and corrugated boards.

Except the well-known and usable wood species like *Populus* in the last years in many regions like South-East Europe, there is a big demand and interest for the *Paulownia.* The *Paulownia* is belonging to a group of fast growing hardwood species, which makes it one of the perspective sources of high yield fibrous materials.

In this study, chemical mechanical pulp (CMP) from both *Populus* and *Paulownia* woods was obtained. Then it was bleached at two stages by hydrogen peroxide and Rongalyt C.

An artificial thermal ageing was carried out. Measuring, tracing, and evaluation of the optical properties of the obtained CMP were performed before and after artificial ageing at a temperature of 90°C at 0, 6, 12, 24, 36, 48, and 72 h.

The aim of this work was to obtain chemical mechanical masses of *Populus* wood and *Paulownia* wood, bleaching, ageing at 90°C, and evaluation of optical and colour characteristics.

9-P14. Investigation of quality of offset images printed on Bopp with UV inks

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Quality and cost value of printing on polymer materials for manufacturing packages and other type of printing products is very important for all printing house customers. The main technique for this activity is a flexographic printing method. In recent years, the manufacturers of printing equipment have produced a new generation of offset presses, which can print with excellent quality on polymer materials. The results are high quality prints of low price, which are very suitable for low and medium runs. In this study comprehensive analysis of print quality by methods especially for the experiment were performed. Experimental runs with modern printing press and curing equipment under real working conditions were performed. The results are very important from practical point of view and they could be used to find optimal conditions for quality work and production of excellent quality packages.

9-P15. Investigation of colour characteristics changes of semichemical pulp samples in ageing process

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Fibrous species are the main raw material needed for production of the various types of papers for printing and graphic industry, corrugated boards, and packaging papers. Because of increasing demands, lack of materials, high value of raw fibre resources and ecological reasons there is substantial and increasing necessity of wood processing to manufacture high yield fibrous material.

In this study, semichemical pulp was utilised, which was obtained from hardwood fibrous material. The semichemical pulp used for experiments was bleached at two stages. Changes in the optical properties of bleached and unbleached type of fibrous materials before and after artificial thermal ageing at 105°C for 0, 6, 12, 24, and 36 h were followed.

A complete characterisation and estimation of colour parameters and differences in CIE Lab system was performed for all tested materials during entire processing and ageing. Changes in the optical properties and colours before and after ageing were observed.

Experimental results and sample properties show that the tested semichemical hardwood pulp could be used for producing corrugated boards and addition to packing paper compositions. Cellulose replacement by semichemical pulp leads to cheaper ecological products for printing and packing industry.

9-P16. Study of colour characteristic changes of printed images under artificial ageing on different papers

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A comprehensive study of colour characteristic changes of offset printed images under artificial ageing has been performed. A specialised printing test form designed for this research was used. Under working conditions in printing houses on different papers, the test form was printed using a great number of control strips and elements for colour measurements. The optical and colour characteristics properties of different combinations of inks, paper, and printing presses were evaluated before and after artificial ageing periods. The main goal of this work is to estimate and evaluate the impact of artificial ageing of inks and papers under real working printing conditions on most used papers.

9-P17. Obtaining of high yield fibrous material from hardwood and evaluation of its optical properties during thermal treatment

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The main fibrous materials used in the pulp and paper industry are cellulose, semichemical pulp, high yield fibrous materials, and second fibres, all of them being of plant origin. They are obtained mainly from wood and annual plants.

Poplar wood species of the *Populus deltoids cultivar Hunnegem* type with density of 504 kg m^{-3} was used in this study. Two types of chemical mechanical pulps (CMP) were obtained. CMP of type 1 was obtained by 7% NaOH and 5% Na_2SO_3 while CMP of type 2 was prepared by means of 7% NaOH, 5% Na_2SO_3, and 2% H_2O_2. Types 1 and 2 CMP were received under the same conditions of temperature, hydromodule ratio, process duration, etc.

Both chemical mechanical pulps had a low degree of brightness, and therefore they were bleached at two stages. The initial process of bleaching was conducted by hydrogen peroxide whereas the second stage was performed by means of Rongalyt C. Samples of both CMP pulps were exposed to artificial thermal ageing at 105°C. Changes of brightness and yellowness in the process of thermal ageing at 105°C for 0, 6, 12, 24, 36, and 48 h were found.

The main goal of this research was to obtain, bleach at two stages, thermally age, and evaluate the brightness and yellowness properties of CMP hardwood.

Experimental results of this study show that the obtained CMP hardwoods can be added to papers for printing, graphic, and packaging industry to increase printing properties (printability), adhesion of inks and varnishes, and optical properties (opacity) of papers.

9-P18. Overview of security printing types and trends for future development

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In this study, we will describe various ways to protect secure documents, labels, and packages, and the different security printing techniques applied today and the way they will develop in the future.

Security products constitute a wide variety of different types of documents, packages, labels, and cards. The degree to which these need protection from counterfeiters, forgers, and terrorists depends upon how deleterious their illegal procurement and misuse is to human welfare and financial stability.

In order to reduce forgery and counterfeiting, the printing industry uses a big range of variable security methods, and via different combinations a high security document is achieved. Security printing devices are often categorised as either ‘overt’ or ‘covert’.

Another advantage that the security printer has today is the ability to produce security documents on non-traditional, nonporous substrates such as plastic and polymer biaxially oriented polypropylene. Due to this complexity in its chemical structure, documents and banknotes have a greater abrasion resistance and lower rate of tampering.

By this research, we aim to give a broad view of the industry of security printing and its complexities.

9-P19. Improvement of physicomechanical and optical properties of the packaging production trough coating with aqueous polymer dispersions complied with the environmental requirements

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The nowadays-growing demands toward sustainable development and environmental protection have led to increased interest in biodegradable materials from renewable sources.

Aqueous polymer dispersions are used for surface coating of paper and cardboard in the packaging industry in order to improve the physicomechanical and optical properties of the production.

This article highlights the main parameters in the preparation, processing, and utilisation of aqueous dispersions based on synthetic and biodegradable polymers that are used in print finishing.

9-P20. Studies of technologies for exposing photopolymer plates in a controlled atmosphere and their application to a corrugated post print

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The new technologies for digital plate production proved a key to achieving a higher quality of corrugated post print.

The goal of the present study was to examine the technologies of exposing photopolymer plates in a controlled atmosphere and their optimal use in flexo corrugated post print.

The main problems with the flexo corrugated post print are the dashboard effect on the printed image. It is created by the difference in the impression corresponding the waves of corrugated board, forming an unstable dot gain in half tone areas of the image and generating visible stripes. The purpose of these studies will be to determine whether and to what extent the technology for exposing photopolymer plates with a flat top dot in a controlled atmosphere can reduce or eliminate these problems.

9-P21. The effect of washing temperature and number of washing cycles on the quality of screen-printed textiles materials

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Life standards growth has led to the fact that buyers of textile materials, beside functionality, expect aesthetic value as well. The aesthetic characteristics of the textile materials are often promoted by the printing process of these materials. Printed textile materials, as well as printed surfaces itself, are exposed to various effects during exploitation. These materials are often exposed to washing process. The washing process causes changes of textile fibres as well as changes of the colour reproduction on these materials, where, as a result, the overall print quality is changed. The aim of this research was to determine the effects of the washing process on colour changes in the CIE L*a*b* colour space as well as the effects of the washing process on water retention value changes of screen printed cotton textile materials using black ink. The study included an analysis of two different parameters related to the washing process: temperature and number of washings. Experimental results indicate that the washing temperature increase leads to major colour reproduction changes, where the number of washing cycles has a certain influence on the colour reproduction of printed textile materials exposed to washing tests as well. The investigation revealed that the washing process caused washing-out of ink particles, which increases the water retention value of the tested printed materials. The results show that the quality of printed textiles, besides the washing process parameters, affects its material characteristics.

9-P22. Ink-jet imprints in just noticeable colour difference evaluation

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In this paper, we investigated the possibility of using ink-jet printing technique for the purpose of just noticeable colour difference evaluation (JND). When performing colour difference evaluations with printed samples, it is expected that specimens should be reproduced in a manner that at least differ in colour from the target values defined in the prepress. The uniformity of printed area and consistency in colorimetric values is also necessary. The printing technique used may significantly influence the colour reproduction, thus altering the targeted colour difference. In order to evaluate the level of colour uniformity influenced by the chosen printing technique, we have selected five initial colour centres, varied their lightness and hue in a way that we have created a range of patches for each colour with colour difference starting from 0.25 to 1.5. The colour difference between neighbouring entities was kept at the level of 0.25. The created test charts were printed on uncoated 120-g m^{-2} paper using ink-jet printing technique (Epson Stylus Pro 7800). For accurate quantification of colour difference, we used CIELAB colour difference formula as well as MCDM formula. We found that the expected colour differences were not obtained in all cases and for all colours used. In addition, it was shown that the variability is dependent on whether the colour difference was effected by initial variations in colour lightness or hue. The study that should perform colour difference evaluations on ink-jet printed samples at the level of 0.25 will be strongly influenced by printing inconsistency.

9-P23. Surface roughness of flexo and letterpress printing plates by indirect SEM image-based profilometry

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In this paper, an indirect image-based approach to the characterisation of surface structure and roughness of flexographic and letterpress printing plates was investigated. In a previous research, we have shown that a direct stylus profilometric method, when used in flexographic and letterpress printing plates surface roughness characterisation, resulted in certain problems even in result inconsistency (repeatability, accuracy, and dissipation). Being a polymeric structure, the surface of plates was scratched by stylus diamond tip and the measuring device has shown drift in performance. The solution of such a problem lies in indirect and non-contact profilometry approach. According to literature, SEM micrographs can be used for non-contact surface topography characterisation, since they are an excellent tool for visualisation and qualitative description of surface topography. The indirect approach was based on the use of Gwyddion software functions for analysis of SEM images and calculation of standard profilometric parameters. The results of the study have shown that it is possible to obtain profilometric parameters from the analysis of SEM micrographs.

This study also involves analysis of the influence of different magnifications and calibrations of grey scale intensity distributions on final surface roughness results. It is shown that by properly calibrated grey scale intensity distributions, an optimal agreement with expected Ra value was achieved using the indirect profilometric method. Statistical analysis indicated that the magnification level had no significant influence on obtained results (based on a p-value of 0.05). Overall, the results showed that the proposed indirect image-based profilometry is a useful tool for the characterisation of surface topographies of flexo and letterpress printing plates.

9-P24. Comparative study of offset plate-tone value reproduction using different measuring and image processing tools

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The quality of tone values on offset printing plate is one of the crucial factors affecting the printed product. In particular, when producing printing plates, a rigorous quality control is necessary, since any bulk and surface imperfection can have a detrimental effect on tone value reproduction and thus on print sharpness, contrast, non-uniformity, and other print properties.

The aim of this paper was to analyse results of two different measuring instruments and two different image processing software determined by two different assessment methods. For direct analysis of tone value parameters on the printing plate, we have used a Techkon spectroplate measuring device with built-in software for image analysis. For indirect analysis, we have used a Vitiny VT-300 digital microscope for image recording and microDot software (CC dot) for image analysis. Tools independent software-based image analysis, on all recorded images from both measuring devices, was accomplished using ImageJ, a public domain Java image-processing program. This study has shown that indirect and independent image analysis-based evaluation methods proved to be a viable alternative to the established ones on built-in software method with a Techkon spectroplate measuring device, providing a reliable tool to monitor tone value reproduction parameters of offset printing plate.

9-P25. Colorimetric and microscopic analysis of colourfastness to rubbing process caused by different compositions of screen print inks

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Screen-printing is a dominant method for textile printing. Wide verity of textile products and their applications demand also printing inks of different composition. These differences among inks cause various exploitation characteristics. Having in mind that textile products are printed mainly in order to achieve aesthetic effect it is important to maintain constant colour values throughout the products exploitation period. Among other influencing factors, rubbing process is very important factor in colour changes of textile products during its exploitation period. This paper aims to conduct colorimetric and microscopic analysis of colourfastness to rubbing process caused by different compositions of the oil- and water-based screen print inks. Beside ink composition, mesh count variation of the screen was also used (45 and 100 threads cm^{-1}). A 100% cotton-based textile material was used as a substrate. Results indicate that oil-based inks and lower mesh count of the screen can produce better colourfastness, thus resulting in longer lasting printed products.

10-O1. Student's attitudes related to science and scientists: stereotypes, peculiarities, implications

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This work presents two studies of science-related attitudes with participation of 642 Bulgarian students aged 14–17 years from different types of schools. The attitude is a complex concept that involves three components: cognitive (beliefs, thoughts, opinions), affective (feeling, evaluation), and behavioural (past behaviours or behavioural intentions) toward science-related objects. The first survey aims to obtain an overall picture of student attitudes and perceptions related to scientists and science in society, in and out school (n = 249). The results outline some stereotypes and bias toward science and scientists. Peculiarities are observed, such as polarisation of perceptions of scientists and attitudes toward science at school, very low interest in science-related education and career, and insufficient use of learning in informal settings. The second survey measured and compared the attitudes of 10th grade students from high schools specialising in mathematics and science and general (comprehensive) high schools (n = 393). It used a 40-item Attitude toward Science Questionnaire (ATSQ) and Mann-Whitney U Test. The results show that regardless of type of school a large majority of students has a positive attitude toward science social implications. Significant differences between groups are observed mainly on the level of student's self-concept, interest in science subjects, and science-related careers. These studies lay a foundation for future educational research in youth's attitudes and factors that influence them.

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10-O2. Bulgarian university ranking system: indicators for student motivation to choose university education in the chemical sciences professional field

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This presentation reports a study aimed at analysing and assessing those individual indicators of the Bulgarian university ranking system, which are related to students' motivation to choose university education in the chemical sciences professional field. University rankings give important information for the choice of the right university and the right field. The Bulgarian ranking system is compared as a whole with several other international rankings of higher education institutions. The Bulgarian university system uses over 80 different indicators grouped into six categories against which universities can be compared in a particular field. The results are based on statistical data collected from different sources including sociological surveys and national institutions. A few indicators, which could affect student motivation to choose chemical sciences field at St. Kliment Ohridski University of Sofia, have been selected and commented: satisfaction with teaching and learning process, satisfaction with teaching and learning environment, prestige among students, employers and professors, unemployment among graduates, applicability of degree acquired, and realisation by vocation. The scores on individual indicators are discussed and some suggestions for a more comprehensive study are made.

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10-O3. Key set of skills of the successful science teacher in constructivist learning environment

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In modern education worldwide, there is a tendency to give central role to students in the school processes. The basic requirements are to focus on forming key competencies, preparation of the students for real life and lifelong learning, and learning that happens in modern and challenging environment. Constructivist ideas and their development in the problem-based learning, inquiry-based learning, and project-based learning are considered opportunities to meet these requirements and efficiently implement them in the schools. However, in the dynamic environment of constant changes in education, for the success of the whole system the essential role is that of teachers. In order to implement the constructivist ideas and the mentioned methods successfully, teachers need certain attitudes and motivation to accept changes for reflection and self-development as well as a set of skills that differs from that of the teachers in the past.

The questions addressed by the researchers are the following: what is the impact of the philosophy of the constructivist ideas on modern science teacher training, what are the key skills that the successful science teacher needs to develop and how they can be formed? In the report, a set of skills for the constructivist science teachers is proposed, where they are divided into three groups: technical skills, interpersonal skills, and contextual skills. The detailed view on these required skills will have an impact on the future training of science teachers.

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10-O4. Results of an international study on constructivist practices in chemistry education

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A survey has been carried out to assess the learning environment with 2322 students from 47 high schools and their science teachers in Austria, Albania, Bulgaria, Kosovo, Poland, Romania, Turkey, and the Netherlands. A choice of suitable tools for students and teachers is made for the study of learning environment from the perspective of constructivist learning. Data collection methods for students were three surveys: What is happening in this class? (WIHIC), Constructivist Learning Environment Survey (CLES), and Modified Attitude Scale Modelled on Test of Science Related Attitudes (TOSRA) and for teachers: Teacher Pedagogical Philosophy Interview (TPPI). Data from the questionnaires, observations, and interviews has been processed and the particular learning environment has been described in terms of constructivist type of learning. In all surveyed European countries a traditional, clearly structured and transmission approach, where the leading role is played by the teacher, and the constructivist approach, in which students are the active side, are compatible. The learning environment in all international schools that are participants in the study is predominantly constructivist. Least constructivist characteristics manifested learning environment in public schools with national programs, in particular those in Bulgaria, Poland, and Turkey. The nature of the school environment impact on the student attitudes towards science in international school classrooms is discussed, which reveal themselves as the most constructivist, the student interest in science being greatest.

10-O5. A study of the floral migration and floral specialisation of worker bees

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This study is aimed at estimating the impact of the degree of parasitemia by the Varroa destructor on the floral migration and floral specialisation of worker bees. The investigation was carried out in August and September 2015 by a group of students from the apicultural club at Asen Zlatarov Secondary School in the town of Parvomay. The students examined two honeybee colonies. A basic treatment against the Varroa mite was conducted with *Varotom* strips placed simultaneously in both beehives. Counting took place three times every seven days. The hives were outfitted with a screened bottom board made by the students-beekeepers to collect the bee pollen. Floral migration and floral specialisation were determined based on the colour of the pollen granules. The relationship between floral migration and floral specialisation of the worker bees on the one hand and the degree of Varroa destructor parasitemia, on the other hand, draw to the conclusion that a higher level of parasitemia can reduce the amount of the collected bee pollen.

Discussion

Novel materials for clean environment

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Traditional chemical technology is resource demanding and wasteful, and often involves the use of hazardous substances. That is why modern trends in the chemical science are concentrated on the development of new technologies involving waste-free and less energy-demanding methods. Many of them are called green chemistry and clean technology with a focus on resource efficiency and on the design of environmentally friendly chemical products and processes. Green chemistry and clean technology can be seen as tools by which sustainable development can be achieved.

In the majority of cases, these new methods require new materials, their production being also a task of chemistry. Some of these new materials are:

- Catalysts for oil and natural gas derivatives;
- Catalysts for one-pot or short-cut organic synthesis leading to saving of energy, raw materials, and waste;
- Catalysts for organic synthesis based on renewable raw materials;
- New materials and catalysts for fuel cell applications;
- New materials for microelectronic applications;
- Adsorbents for hydrogen storage;
- Specific sorbents for waste water treatment;
- New polymers with new applications;
- Nanotechnologies based on new materials.

This list is not completed. The main philosophy is to increase process efficiency in order to save energy, raw materials, and time.

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Notes

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