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Studium elektrochemického chování sekundárních struktur oligonukleotidů adsorbovaných na povrchu elektrody z pyrolytického grafitu

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Nukleové kyseliny mohou vytvářet různé sekundární struktury. Kromě obecně známé dvoušroubovice mohou úseky deoxyribonukleové (DNA) nebo ribonukleové kyseliny (RNA) o vhodné nukleotidové sekvenci zaujmout tzv. alternativní struktury, např. křížové formy, triplexy nebo guaninové (G4) či cytosinové kvadruplexy (tzv. I-motivy). Jsou-li tyto struktury vytvářeny v určitých místech genomové DNA (např. v promotorových oblastech genů), mohou ovlivňovat důležité procesy (expresi příslušných genů). Díky moderním elektroanalytickým metodám, je možné nukleové kyseliny citlivě detekovat pomocí běžně používané rtuťové kapkové elektrody nebo nově využitím elektrody z pyrolytického grafitu (PGE)[1]. Ta díky svému širokému rozsahu využitelného potenciálu (−2,0 V až 1,6 V) umožňuje detekci jednotlivých bází nukleových kyselin i jejich produktů elektrochemické přeměny. Ověření možnosti jejího využití pro detekci sekundárních G4 struktur DNA pomocí PGE bylo podstatou této práce. Byl studován vliv podmínek (složení elektrolytu a velikost potenciálového okna) na detekci vybraných oligodeoxynukleotidů (ODN) pomocí cyklické voltametrie v prostředí 0,2 mol.l^{-1} acetátu sodného nebo amonného pufru pH 5,0. Pro následná měření byl zvolen 0,2 mol.l^{-1} amonno-acetátový pufr pH 5,0, ve kterém ODN poskytovaly nevyšší redoxní signál guaninu[2]. V tomto pufru byly dále zkoumány výšky všech dostupných redoxních signálů ODN adsorbovaných na PGE ve vztahu k jejich předpokládané sekundární formě, které v roztoku za vhodně zvolených podmínek tvoří. Výsledky této práce dokazují nemožnost rozlišení mezi jedno-vláknovou, dvou-vláknovou a G4 formou ODN využitím voltametrického měření na PGE. Důvodem může být nedostatečná stabilita sekundárních struktur po jejich adsorpci na povrchu elektrody nebo rozpad sekundární struktury vlivem vloženého potenciálu. Podrobnější studium bude součástí navazující práce.

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Poděkování

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Fluorescenční spektroskopie ve výzkumu modelových systémů pro cílenou distribuci léčiv

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Tato práce se snaží objasnit alespoň částečně základy výzkumu cílených nosičů léčiv, které je možno využít například při léčbě rakoviny. Jednou z metod léčení rakoviny je například chemoterapie. Tento typ léčby zasahuje celé tělo a dochází k celkovému oslabení organismu. Chemoterapie je pro tělo mnohdy větší zátěží než nemoc sama. Cílené nosiče nepůsobí na celé tělo, ale účinkují pouze v oblastech zasažených rakovinným bujením. Na vyvinutí léčby pomocí cílených nosičů léčiv pracují výzkumníci na celém světě, protože by měla eliminovat nežádoucí účinky chemoterapie na lidský organismus.

Zaměřily jsme se tedy na metodu fluorescenční sondy v oblasti vývoje cílených nosičů léčiv. Fluorescence je zde využita hlavně k charakterizaci modelů pro cílenou distribuci léčiv. Zkoumané modelové nosiče léčiv jsou založeny na elektrostatické interakci kladně nabitých agregátů tenzidu a opačně nabité hyaluronové kostry.

Součástí této práce je seznámení se s výzkumem pomocí fluorescenční sondy. Dále jsou zde měřena fluorescenční spektra pyrenu ve vybraných modelových systémech. Cílem je práce zjistit různá chování tenzidu a vytvořených micel v určitých simulovaných prostředích.

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Poděkování

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SEKCE STUDENTŮ BAKALÁŘSKÝCH A MAGISTERSKÝCH PROGRAMŮ

Má lignín antibakteriálne vlastnosti?

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Ligníny sú aromatické biopolyméry s amorfnou štruktúrou zložené z fenylpropánových jednotiek s rôznymi funkčnými skupinami. Základná funkcia lignínu v rastlinách je ochranná a stužujúca funkcia cievneho systému. Antibakteriálna aktivita extraktov z rozličných lignocelulózových rastlín je všeobecne akceptovateľná [1]. Avšak lignίny sú heterogénne a po izolácii z rastlín majú fyzikálne a chemické vlastnosti odlišné od „natívneho lignínu“ prítomného v bunkových stenách rastlín. Jednoznačná štruktúra lignínu doposiaľ nebola popísaná.

V tejto práci bola skúmaná hypotéza, že sóda lignín izolovaný z hroznových výliskov by mohol mať antimikrobiálne vlastnosti [2]. Izolácia lignínu prebiehala pomocou tzv. sódového rozvlákňovania (soda pulping) [3], prebiehala dvoma spôsobmi a to za použitia laboratórnej aparatúry za atmosferického tlaku a pomocou hydrotermálneho autoklávu, vyrobeného pre túto prácu. Následne bola porovnaná efektivita týchto metód, pričom efektívnejšia bola izolácia lignínu v hydrotermálnom autokláve, s výťažnosťou 36,35 g lignínu na 100 g hroznových výliskov. Zároveň bola pomocou FTIR preukázaná vyš-

šia čistota takto izolovanej vzorky. Lignín izolovaný oboma spôsobmi nemal antimikrobiálne vlastosti, čo bolo preukázané pomocou jamkovej difúznej metódy. Následnou modifikácou lignínu časticami striebra bola dosiahnutá antibakteriálna aktivita, avšak žiadna zo vzoriek nepôsobila proti kvasinkám. Antimikrobiálna aktivita bola testovaná na baktériách *Bacillus subtilis, Escherichia coli, Micrococcus luteus, Serratia marcescens* a kvasinkách *Saccharomyces cerevisiae* a *Candida glabrata*, pričom najvyššia aktibakteriálna aktivita bola zaznamenaná pri *Micrococcus luteus*.
V tejto práci bolo zistené, že lignín izolovaný z hroznových výliskov je možné modifikovať naviazaním častíc striebra a tým dosiahnuť jeho antibakteriálne vlastnosti voči gram-pozitívnym aj gram-negatívnym baktériám.

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Poďakovanie

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Konstrukce jednoduchého syntetického bakteriálního konsorcia s dělbou práce

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Mikrobiální konsorcium je soužití dvou nebo více odlišných mikroorganismů, které spolu nějakým způsobem interagují. Téměř každý volně žijící mikroorganismus na planetě žije v nějakém druhu mikrobiální komunity. Díky této životní strategii se může člen konsorcia odprostit od náročného života samotáře a specializovat se na jeden daný úkol. Toto označujeme jako princip dělby práce. V posledních letech rapidně roste zájem o mikrobiální konsorcia v oblastech biotechnologií a syntetické biologie. Ve srovnaní s klasickým využitím pouze jednoho kmene dělba práce teoreticky zvyšuje výtěžek koncového produktu a odolnost buněk vůči stresu. [1]

Cílem prezentovaného projektu je vytvořit jednoduché mikrobiální konsorcium složené ze dvou rekombinantních kmenů biotechnologicky atraktivní bakterie *Pseudomonas putida*. Konsorcium bude využívat principu dělby práce. Je navržené tak, aby jako zdroj uhlíku bylo schopné zpracovat modelový polymerní substrát karboxymetyl celulózu (CMC), která simuluje odpadní rostlinou biomasu, a z ní generovalo cílový produkt s vyšší přidanou hodnotou. První kmen produkuje celulolytické enzymy, které jsou do prostředí vypuštěny indukovanou buněčnou lyzí. Enzymy následně začnou štěpit přítomný polymerní substrát. Druhý kmen roste na uvolněných monosacharidech a oligosacharidech a tvoří požadovaný produkt.

U mikrobiálních systémů s indukovanou buněčnou smrtí je často problém s bazální expresí smrtícího genu. Proto je v této diplomové práci vyzkoušen nový systém řídící expresi genu, takzvaný digitalizační modul. Modul zajišťuje, aby k expresi toxického genu docházelo jen a pouze v přítomnosti specifického induktoru. [2]

Zatím se nám podařilo metodami genetického inženýrství připravit základ pro plánované konsorcium – dva kmeny *P. putida* označené zeleným a červeným fluorescenčním proteinem. Do kmene s červeným fluoroforem byl vložen plasmid s digitalizačním modulem a lytickým genem a byla testována jeho funkce. Buněčné kultury jsou analyzovány spektrofotometricky v mikrotitračních destičkách a pomocí průtokové cytometrie.

Dalším krokem je dokončení přípravy rekombinantních kmenů a otestování jejich funkcí samostatně. Následně budou kmeny skombinovány v syntetickém konsorciu, jehož chování bude detailně analyzováno a srovnáno s kmenem, který bude všechny funkce konsorcia zajišťovat sám. Toto srovnání potvrdí či vyvrátí hypotézu o výhodnosti dělby práce u tohoto konsorcia.

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Poděkování

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Degradace biopolyesterů v simulovaných tělních tekutinách

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Povědomí o enviromentální zátěži petrochemickými polymerů vede k celosvětové snaze vyvíjet materiály s podobnými fyzikálně-chemickými vlastnostmi, které budou získávány z obnovitelných zdrojů a zároveň budou plně biologicky rozložitelné, a tudíž šetrné k životnímu prostředí. Budování trhu takovýchto biopolymerů vede k úvahám využívat tyto materiály nejen jako náhradu petrochemických polymerů pro průmyslové aplikace. Řada výzkumů jasně ukazuje, že jsou tyto materiály velmi vhodným kandidátem také pro aplikace biomedicínské.

Tradičně využívané materiály pro lékařské implantáty, jako jsou kovy, keramika nebo syntetické polymery, mohou v těle interagovat a projevovat se negativními imunologickými reakcemi. Často je nutnost provést druhou operaci pro jejich odstranění z těla pacienta. Biopolyestery, kterým se věnuje tato práce, jsou biokompatibilní, necytotoxické a podléhají biodegradaci, při níž dochází z rozkladu na tělu vlastní látky, které jsou v organismu dále metabolizovány nebo přirozeně vyloučeny z organismu ven, tudíž zde odpadá nutnost opětovně operativně zasahovat do těla pacienta pro odstranění podpůrného materiálu.

V této práci byla studována *in vitro* biodegradace dvanácti vzorků různých typů biopolyesterů – polykyseliny mléčné, polyhydroxyalkanoátů a poly(butylen adipát-*co*-tereftalátu). Tenké filmy, jež byly využity pro samotný experiment, byly připraveny rozpouštěním polymeru v chloroformu, vylitím do formy a následným odpařením rozpouštědla. Dle typu polyesteru a jeho stupně krystalinity se měnily vlastnosti připravených filmů, jejich vzhled byl v škále od transparentních do mléčně zakalených a mechanické vlastnosti se lišily především v elasticitě.

Studium degradace probíhalo ve dvou simulovaných tělních tekutinách, a to v syntetické žaludeční šťávě a ve fyziologickém roztoku pufrovaném fosfáty s lipázou při teplotě 37 °C po dobu 81 dní. Během degradace docházelo k viditelné změně morfologie filmů a studované vzorky získávaly vyšší stupeň křehkosti a nižší kompatibilitu.

Ze získaných výsledků lze potvrdit, že biodegradace u těchto biopolyesterů opravdu probíhá. Její průběh je ale závislý na mnoha proměnných faktorech, díky nímž je možno rychlost biodegradace korigovat a měnit, a tedy je možné předpokládat široké využití v mnohých biomedicínských aplikacích.

Poděkování

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Polymerní systémy s kolchicinem pro cílené dodávání léčiv

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Vývoj systémů pro dodávání léčiv založený na polymerních nanočásticích může řešit jednu z hlavních výzev při bojích s rakovinou, a to zlepšení biologické dostupnosti léčiva v těle. Hlavním cílem tedy je vytvoření takového systému, který podpoří cílení léčiva a umožní mu kontrolované uvolňování. Zároveň musíme myslet na velkou toxicitu cytostatických léčiv a na možnosti ochrany zdravých buněk.

Kopolymer kyseliny glykolové a kyseliny mléčné (poly(lactide-*co*-glycolide) - PLGA) patří k nejpoužívanějším biologicky odbouratelným polymerům pro jeho dobrou biologickou kompatibilitu a možnost kontrolovatelné degradace hydrolýzou. Další výhodou je možná úprava povrchu PLGA na požadované vlastnosti (např. zvýšení rozpustnosti). Uzavření kolchicinu do polymerního systému má potenciál z důvodu cytostatických účinků kolchicinu, ale zároveň pro snížení jeho vysoké toxicity.

Provoz, optimalizace a využití kapacitní deionizační jednotky

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1 Úvod

V České republice je zásobováno 30 % obyvatel tvrdou vodou a 6 % obyvatel velmi tvrdou vodou [1], která může způsobovat problémy ve spotřebičích. Například v Brně máme přibližnou tvrdost 2,85 mmol/l [2]. K ničení spotřebičů dochází z důvodu tvorby nánosu v potrubí nebo vyloučením například uhličitanu vápenatého při varu vody [3].

Existuje více technologických řešení na změkčování pitné vody, mezi které nejčastěji řadíme membrány, iontoměniče [3] nebo námi studovanou kapacitní deionizaci. Kapacitní deionizace má v porovnání s membránovými procesy podstatně menší tlakové nároky, tím i nižší náklady na provoz. V porovnání s iontoměniči není potřeba používat žádné další provozní chemikálie.

Další praktické využití nalézá kapacitní deionizace při odsolování brakických vod, zejména při adsorpci alkalických kovů, kovů alkalických zemin a amoniaku. Z aniontů dochází nejčastěji k adsorpci halogenidů, dusičnanů, dusitanů a fosforečnanů. Rovněž se uplatňuje v hybridním systému s reverzní osmózou (RO), kdy lze kapacitní deionizaci použít pro úpravu permeátu na odseparování zbylých iontů [4].

Kapacitní deionizace (CDI) je založená na separaci nabitých iontů z roztoku elektrostatickými silami. Mezi dvě elektrody se aplikuje napětí a disociované ionty v roztoku jsou nuceny migrovat k sobě opačně nabitým elektrodám. Z protékajícího elektrolytu se vlivem elektrosorpce ukládají ionty do elektrické dvojvrstvy v mikropórech a makropórech. Kationty jsou přitahovány k záporně nabité elektrodě a anionty jsou přitahovány ke kladně nabité elektrodě. Ionty jsou adsorbovány na povrchu elektrod, a tím je snížena jejich koncentrace ve výstupním roztoku. Při naplnění kapacity elektrosorpce jsou elektrody zkratovány nebo je na elektrody vložen opačný potenciál. Nastává desorpce iontů z povrchu zpět do roztoku a na výstupu dostáváme zvýšenou koncentraci roztoku. Výsledkem je střídavě vytékající diluát a koncentrát z elektrochemického článku [6].

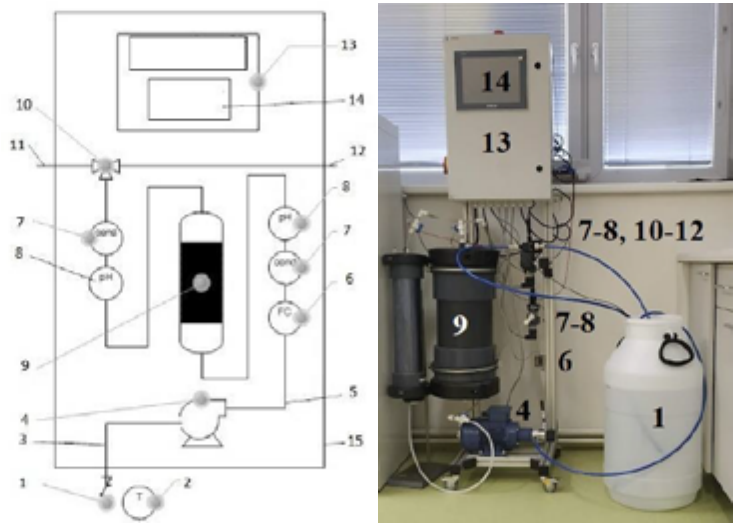
Na článcích kapacitní deionizace probíhají faradaické a nefaradaické reakce, přičemž faradaické reakce jsou v kapacitní deionizaci nežádoucí, z důvodu oxidace elektrody, což snižuje účinnost separace [8, 10]. Za faradaický proces považujeme takový proces, když na povrchu elektrod probíhají redoxní reakce [8, 12]. V případě uhlíkových elektrod se na anodě oxiduje uhlík na karboxylovou skupinu, dále se oxiduje voda na samotný dikyslík. V případě, že roztok obsahuje i chlorid, dochází k jeho oxidaci až na chlorečnan. Přes peroxid vodíku dochází na katodě k redukci dikyslíku na vodu. Rovněž dochází k redukci uhlíku, kdy probíhá hydrogenace a vzniká C-H skupina. Za nefaradaický proces označujeme to, když oxidační stav látky zůstává zachován, ale vlivem náboje je přitahován k povrchu elektrody. Ionty jsou vázány elektrostatickými a adsorpčními silami v elektrodové dvojvrstvě [6, 8, 12].

V této práci byly použity uhlíkaté elektrody, které jsou vyráběné z levných materiálů a mají vysokou měrnou povrchovou plochu pro adsorpci. Rovněž materiál elektrod musí mít vhodnou distribuci pórů, aby dokázal zachytit veškeré typy iontů. Cílem práce je vyzkoušet optimální nastavení faktorů ovlivňující sorpci a poté provedení experimentů na modelové vodě.

2 Experimentální část

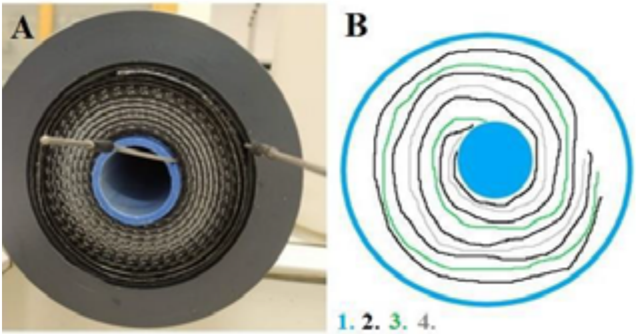
2.1 Popis přístroje

Na Obrázku 1 je bodově popsána jednotka CDI. Surová voda určená k odsolení (1) je čerpána čerpadlem (4), jehož výkon je regulován frekvenčním měničem podle požadavku na průtok. Poloprovozní jednotka kontinuálně měří následující parametry: průtok, vodivost, pH a teplotu. Po nasátí čerpadlem (4) proudí kapalina přes první vodivostní (7) a pH (8) sondu. Kapalina vtéká do elektrodového prostoru (9) a pokračuje na druhou pH (8) a vodivostní (7) sondu. Na konci je třícestný elektromagnetický ventil (10), který určuje směr proudu kapaliny na diluát (11) nebo koncentrát (12). Měření teploty probíhá teplotním čidlem (2) mimo uzavřený systém. Toto čidlo lze umístit do jedné z provozních kapalin. Celý systém je řízen centrálním rozvaděčem (13), jenž je napojen na dotykový displej (14) s možností připojení externího zařízení skrze ethernetový kabel.



Obrázek 1: Schéma CDI a laboratorní jednotka CDI, 1 zdroj surové vody, 2 teplotní čidlo, 3 sání čerpadla, 4 čerpadlo, 5 výtlak čerpadla, 6 průtokoměr, 7 vodivostní čidlo, 8 pH sonda, 9 elektrodový prostor, 10 trojcestný ventil, 11 potrubí diluát, 12 potrubí konce

Elektroda je spirálovitě vinutá, viz Obrázek 2, aby se v malém prostoru docílilo co nejvíce aktivně využitelného měrného povrchu elektrody. Je umístěna v plášti se středovou trubicí (1). A je vyrobená ze směsi komerčního aktivního uhlí. Jako pojivo pro aktivní uhlí je použit polymer polyvinylidenfluorid (PVDF). Tloušťka porézní uhlíkové vrstvy (2) je cca 200 µm. Po dvojici elektrod je izolační fólie (3). Prostor mezi elektrodami je oddělen polypropylenovou (PP) mřížkou (tzv. spacer) (4), kde proudí surová voda.



Obrázek 2: Vrchní pohled na elektrodu (A) a schematické znázornění vynutí elektrody (B), kde 1. je středová trubice, 2. porézní uhlíková vrstva, 3. izolační fólie a 4. spacer

2.2 Odsolování modelové vody

Na jednotce kapacitní deionizace lze nastavit tři hodnoty napětí a průtok v rozmezí 0,2 – 1,2 l/min. Na průběh sorpce mají vliv ionty obsažené v roztoku, počáteční koncentrace iontů, typ a stáří elektrodového materiálu. Na optimalizaci byl použit roztok chloridu sodného c(NaCl) = 38 mg/l a chloridu vápenatého c($CaCl_2$) = 298 mg/l. Jejich koncentrace byla připravena tak, aby se vodivost pohybovala okolo 500 µS/cm. Pracovní roztok byl cirkulován po dobu 20 hodin. To odpovídá 6 cyklům, přičemž jeden cyklus se skládá ze 2 hodin adsorpce a jedné hodiny a dvaceti minut desorpce včetně postupných změn napětí.

Pro separaci vybraných iontů byly připraveny pracovní roztoky 1. Ca, c(Ca^{2+}) = 150 mg/l, 2. Mg, c(Mg^{2+}) = 50 mg/l, 3. Ca + Mg, c(Ca^{2+}) = 125 mg/l, c(Mg^{2+}) = 25 mg/l, 4. NH_4NO_3, c(NH_4NO_3) = 150 mg/l, 5. Cl^-, c(Cl^-) = 250 mg/l. Tyto pracovní roztoky byly použity na zkoušku účinnosti odstranění vápníku, hořčíku, celkové tvrdosti, dusičnanů a chloridů. Byly měřeny tři cykly. Při prvním cyklu docházelo k homogenizaci roztoku a do vyhodnocení byl použit druhý cyklus.

2.3 Analytické metody

Výsledkem optimalizace faktorů je vyhodnocení ze všech šesti cyklů. Vyhodnocení bylo provedeno tak, že byla odečtena průměrná maximální hodnota vstupu pracovního roztoku a průměrná minimální hodnota výstupu pracovního roztoku. Z těchto dvou hodnot byl vypočten rozdíl vstupu a výstupu, který představoval adsorbované množství iontů. Při porovnávání majoritní adsorpce jednomocných nebo dvojmocných iontů byl stanoven Na^+ pomocí plamenového fotometru PFP7 (JENWAY, Velká Británie) a Ca^{2+} pomocí titrace chelatonu 3 (LACHEMA, Česká republika) s indikátorem murexid (LACHEMA, Česká republika).

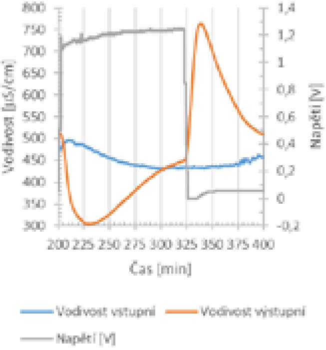
V experimentech se separací vybraných iontů byly použity metody: stanovení vápníku odměrnou metodou se směsí metalochromních indikátorů (ISO 5975: 1983), stanovení hořčíku diferenční metodou (ISO 5975: 1983), stanovení vápníku a hořčíku volumetricky s indikátorem v pevném stavu (ISO 5975: 1983), stanovení dusičnanů pomocí setu mobilní analytiky Spectroquant Nitrate Test (Merck spol. s.r.o., Česká republika) a stanovení chloridů odměrným argentometrickým stanovením podle Mohra (ISO 9297: 1989).

3 Výsledky a diskuse

3.1 Optimalizace

3.1.1 Napětí

Napětí bylo testováno při třech hodnotách, a to: 0,9 V; 1,0 V a 1,2 V. Nejúčinnější adsorpce byla jednoznačně při napětí 1,2 V, kdy došlo k poklesu vodivosti o 144 µS/cm. Na Obrázku 3 je znázorněn druhý cyklus při nejúčinnější hodnotě použitého napětí. Stejných výsledků bylo dosaženo v práci autora Oladunni [5].



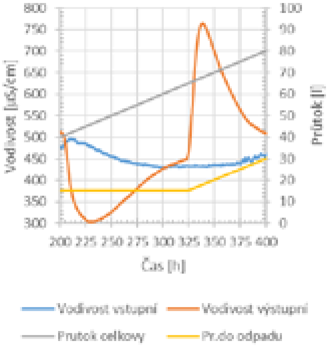
Obrázek 3: Graf závislosti vodivosti a napětí na čase, při 1,2 V, 0,2 l/min v roztoku NaCl, 2. cyklus

3.1.2 Vliv ostatních iontů

Byl testován vliv sodného a vápenatého kationtu. V obou případech se jednalo o chlorid. Byla testována sorpce jednotlivých iontů a směsi iontů v poměru 1:1. V roztoku s jednou látkou byla více adsorbována látka NaCl. Vodivost klesla o 144 µS/cm. Iont Na^+ má menší hydratovaný obal než Ca^{2+}, a tak byl adsorbován ve větší míře, zatímco elektrostatické síly ovlivnily adsorpci ve směsi iontů. Ve směsi došlo k adsorpci sodných iontů $c(Na^+) = 14$ mg/l, zatímco vápenatých iontů bylo adsorbováno $c(Ca^{2+}) = 44$ mg/l. Na Obrázku 3 je druhý cyklus látky s největším poklesem vodivosti. Ve směsi jsou dvojmocné ionty upřednostňovány před adsorpcí jednomocných iontů. Podobných výsledků bylo dosaženo v práci autora Oladunni [5].

3.1.3 Průtok

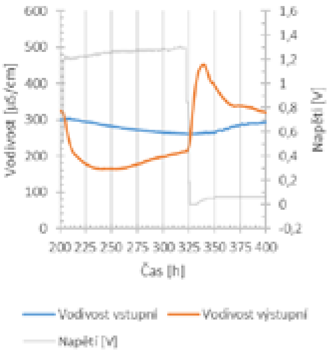
Průtok byl testován na minimální možné nastavitelné hodnotě a posléze i u dvou větších hodnot pro ověření účinnosti. Měření bylo prováděno při průtoku: 0,2 l/min; 0,3 l/min a 0,5 l/min. Dále byl měřen procentuální podíl koncentrátu při daném průtoku. Nejúčinnější adsorpce byla jednoznačně při nejnižším průtoku (0,2 l/min), kdy došlo k poklesu vodivosti o 144 µS/cm a současně byl nejmenší procentuální podíl koncentrátu 37,8 %. Na Obrázku 4 je znázorněn druhý cyklus při nejúčinnější hodnotě průtoku. Podobných výsledků bylo dosaženo v práci autora Mossad [7].



Obrázek 4: Graf závislosti vodivosti a průtoku na čase, při 0,2 l/min, 2. cyklus

3.1.4 Vliv počáteční koncentrace

Byly zvoleny čtyři počáteční koncentrace. První testovaná koncentrace byla v předcházejících měřeních připravena tak, aby odpovídala přibližně 500 µS/cm = 0,238 g/l NaCl, což byla doporučená vodivost pracovního roztoku od firmy ASIO, spol. s r. o. Následující měřená počáteční koncentrace byla dvojnásobná (0,476 g/l NaCl), trojnásobná (0,714 g/l NaCl) a poloviční (0,119 g/l NaCl). Na Obrázku 5 je znázorněn druhý cyklus při optimální hodnotě počáteční koncentrace. K největšímu poklesu vodivosti došlo při počáteční koncentraci 0,119 g/l, ale pokles byl téměř totožný s koncentrací 0,238 g/l. Došlo k poklesu vodivosti o 145 µS/cm a 144 µS/cm. Při takto nízkých koncentracích již není velký rozdíl v adsorbovatelném množství. Podobných výsledků bylo dosaženo v práci autora Mossad [7].



Obrázek 5: Graf závislosti vodivosti a napětí na čase, při 0,119 g/l NaCl, 2. cyklus

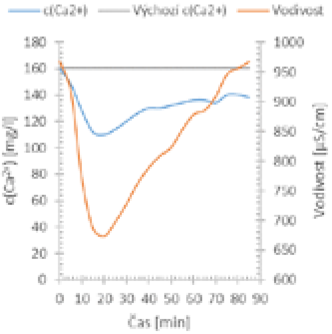
3.1.5 Elektrodový materiál

Při experimentech byly k dispozici celkem čtyři elektrody. Při separaci vybraných iontů byla použita elektroda č. 2. Sorpční kapacita byla změřena před samotnými experimenty a po experimentech. Došlo k poklesu absorpční kapacity o 30 µS/cm. To bylo způsobeno částečnou degradací elektrody v průběhu měření.

3.2 Separace vybraných iontu v laboratorních podmínkách

3.2.1 Vápenatý kationt (Ca^{2+})

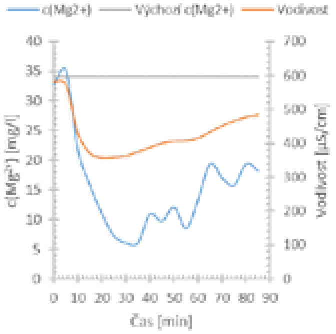
Výchozí koncentrace byla zvolena na základě informací ze zdroj [3, 9]. Na Obrázku 6 je znázorněn pokles koncentrace a vodivosti v čase druhého cyklu. Z grafu je patrné, že aktuální vodivost v daném čase koresponduje s aktuální koncentrací vápníku. Skutečná koncentrace připraveného pracovního roztoku byla 160,32 mg/l Ca^{2+}. Za druhý cyklus bylo vyprodukováno 16 litrů diluátu s průměrnou koncentrací 131,82 mg/l, což odpovídá poklesu o 17,8 %.



Obrázek 6: Graf závislosti koncentrace vápníku a vodivosti na čase, snižování koncentrace vápníku ve vodě, 2. cyklus

3.2.2 Hořečnatý kationt (Mg^{2+})

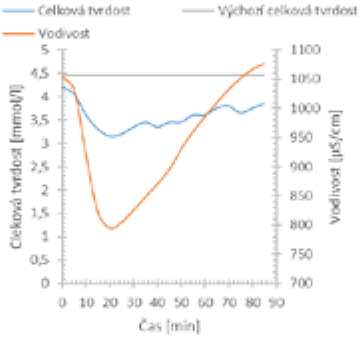
Výchozí koncentrace byla zvolena na základě informací ze zdroje [3, 9]. Na Obrázku 7 je znázorněno, že při experimentu s hořčíkem byla počáteční vodivost vyšší z důvodu nedostatečného proplachu před měřením. V důsledku toho se zpětně do roztoku uvolňoval vápník z předchozího měření. Skutečná koncentrace připraveného pracovního roztoku byla 34,03 mg/l Mg^{2+} U hořčíku došlo ke snížení koncentrace o 54,2 %. Během cyklů bylo vyprodukováno 16 litrů s průměrnou koncentrací hořčíku 15,59 mg/l.



Obrázek 7: Graf závislosti koncentrace hořčíku a vodivosti na čase, snižování koncentrace hořčíku ve vodě, 2. cyklus

3.2.3 Celková tvrdost

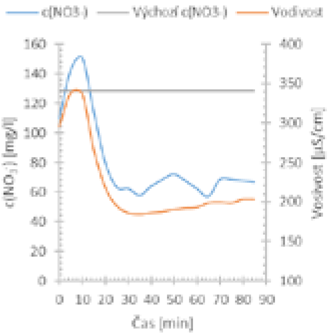
Na Obrázku 8 je znázorněno, že výchozí tvrdost byla 4,45 mmol/l a jednalo se o velmi tvrdou vodu. Průměrná tvrdost ve 2. cyklu byla 3,59 mmol/l a během sorpce bylo vyprodukováno 16 litrů diluátu. Jednalo se stále o tvrdou vodu, avšak se tvrdost blížila k hodnotně legislativně doporučené pro pitnou vodu, tedy do rozmezí 2-3,5 mmol/l [11]. Celkem tedy došlo ke snížení tvrdosti o 19,3 %.



Obrázek 8: Graf závislosti celkové tvrdosti a vodivosti na čase, změkčování vody, 2. cyklus

3.2.4 Dusičnany (NO_3^-)

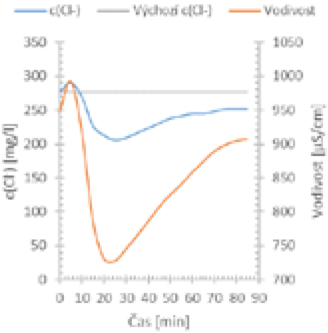
Na obrázku 9 je znázorněn 2. cyklus sorpce, kde nejprve docházelo ke zvýšení a poté k poklesu koncentrace a vodivosti v čase. Zvýšení na začátku sorpce je způsobeno degradací elektrody. Pokud se zanedbá degradace a průměrná koncentrace se vypočítá až od 15. minuty sorpce, kdy došlo k faktickému snižování koncentrace dusičnanů, výsledkem je průměrná hodnota 69,06 mg/l. To odpovídá výrobě diluátu se sníženou koncentrací dusičnanů téměř o 46,2 %.



Obrázek 9: Graf závislosti koncentrace dusičnanů a vodivosti na čase, snižování koncentrace dusičnanů, 2. cyklus

3.2.5 Chloridy (Cl^-)

Obrázek 10 znázorňuje graf závislosti koncentrace chloridů a vodivosti na čase při 2. cyklu. Z počáteční koncentrace 276,53 mg/l chloridů bylo vyprodukováno v 2. cyklu 16 l diluátu s koncentrací 240,04 mg/l. Pokud se zanedbá počáteční nárůst koncentrace, a průměrná koncentrace se vypočítá až od 15. minuty sorpce, výsledkem je hodnota 231,71 mg/l. Jedná se však o pokles pouze o 16,2 %. Tento malý pokles koncentrace je pravděpodobně způsoben vysokou počáteční koncentrací chloridů a také z důvodu degradace elektrody.



Obrázek 10: Graf závislosti koncentrace chloridů a vodivosti na čase, snižování koncentrace chloridů 2. cyklus

4 Závěr

V této práci byla použita jednotka kapacitní deionizace, kterou vyvinula firma ASIO, spol. s r.o. a cílem bylo optimalizovat vybrané faktory (napětí, průtok, vliv iontů obsažených v roztoku, vliv počáteční koncentrace iontů v roztoku a stáří elektrodového materiálu) a odzkoušet její účinnost na vybraných ukazatelích (vápenaté ionty, hořečnaté ionty, celková tvrdost, dusičnany, chloridy).

Bylo zjištěno že, optimálním nastavením je napětí 1,2 V, průtok 0,2 l/min. Z hlediska mocnosti iontů probíhala nejúčinnější adsorpce v roztoku s jednomocným iontem. Při experimentech, kdy byly ionty testovány ve směsi, převládaly elektrostatické síly. Z naměřených dat vyplývá, že dvojmocné ionty jsou upřednostňovány před adsorpcí jednomocných iontů. Při separaci vybraných iontů byla použita elektroda č. 2. Sorpční kapacita byla změřena před samotnými experimenty a po experimentech. Došlo k poklesu absorpční kapacity o 30 µS/cm. To bylo způsobeno částečnou degradací elektrody v průběhu měření.

Práce byla zaměřena na selektivní účinnost odstranění iontů při procesu změkčování vody. Při experimentech u vybraných iontů došlo ke snížení koncentrace vápníku o 17,8 %, hořčíku o 54,2 % a u celkové tvrdosti vody došlo ke změkčení o 19,3 %. U aniontů došlo k poklesu obsahu dusičnanů o 46,2 % a u chloridů pouze o 16,2 %. Z výsledků je patrné, že metodu kapacitní deionizace lze použít pro separaci všech sledovaných iontů.

Z naměřených dat vyplývá že kapacitní deionizace má velký potenciál využití na místech s nedostatkem energie, protože v porovnání s ostatními separačními metodami, má CDI několik výhod: malá energetická náročnost, bez nutnosti dávkování chemikálií, produkce malého množství koncentrátu, nenáročné provozní podmínky. Některé ze studií poukazují na případnou možnost kombinace s RO. Lze očekávat, že výzkum se bude mimo jiné v budoucnu také věnovat vývoji nových materiálů elektrod a inovovaným konfiguracím modelů.

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Poděkování

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Príprava a charakterizácia spin crossover polymérnych systémov Hofmannovho typu s fotoizomerizovateľnými molekulami

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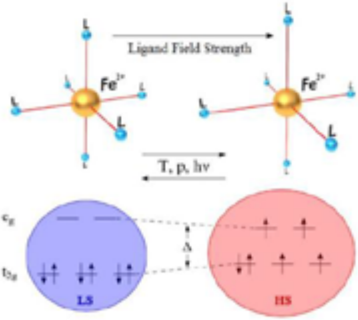
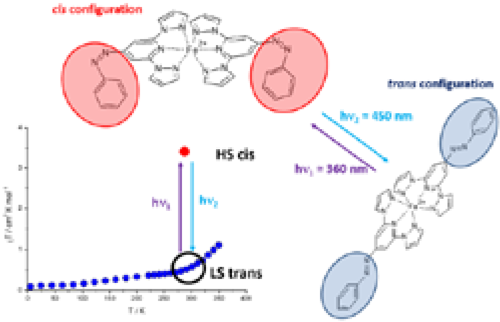
Už od svojho objavenia boli zlúčeniny vykazujúce spinový prechod (ďalej už len SCO, z angl. „Spin Crossover“) intenzívne skúmané pre ich unikátne optické, magnetické, elektrické a štruktúrne vlastnosti. Koordinačné zlúčeniny iónov prechodných kovov s valenčnou konfiguráciou 3d4 -3d7 môžu za určitých okolností vykazovať SCO, pri ktorom ión kovu vratne mení svoj spinový stav v dôsledku zmeny teploty, pôsobenia tlaku, vplyvom magnetického poľa či pri ožiarení viditeľným alebo IR žiarením. 1 Keď je ión kovu v oktaedrickom usporiadaní vystavený pôsobeniu kryštálového poľa ligandov, dochádza k štiepeniu degenerovaných 3d orbitálov na nižšiu, trojnásobne degenerovanú hladinu (t2g) a vyššiu, dvojnásobne degenerovanú hladinu (eg). Oktaedrické komplexy môžu byť vysokospinové (ďalej už len HS, z angl. „High Spin“) alebo nízkospinové (ďalej už len LS, z angl. „Low Spin“), v závislosti od veľkosti sily ligandového poľa a energie spárovania spinov. 1 Zmena spinového stavu je spojená so zmenou dĺžky väzby medzi centrálnym atómom a ligandom (Obr. 1), čo má za následok zmenu fyzikálno-chemických vlastností materiálu (napr. farba, termodynamické, štruktúrne a magnetické vlastnosti).



Obrázok 1 Schematické znázornenie SCO prechodu pre centrálny atóm Fe^{2+} s konfiguráciou valenčnej vrstvy 3d6 . T, p, hu predstavujú teplotu, tlak a svetlo, ktoré sa používajú na indukciu SCO.

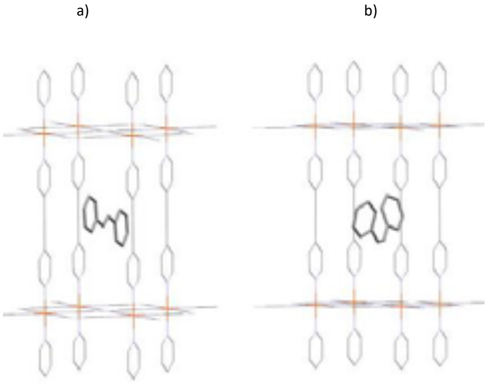
Schopnosť SCO molekúl meniť svoje fyzikálne vlastnosti vplyvom vonkajších podmienok sa stala základom pre ich potenciálne využitie v technológiách, napríklad v rôznych senzoroch, ovládacích komponentoch a zariadeniach na spracovanie informácií. Oproti teplotne indukovanému spinovému prechodu sa ožarovanie svetlom javí ako vhodný nástroj na prepínanie spinových stavov SCO materiálov.2 Je známe, že ožarovanie SCO materiálu špecifickou vlnovou dĺžkou dokáže vratne meniť jeho spinový stav (viditeľné svetlo pre LS→HS prechod a IR žiarenie pre spätný HS→LS prechod). Tento jav, známy ako priamy alebo spätný LIESST efekt (z angl. Light-Induced Excited Spin-State Trapping), je založený na priamej excitácii elektrónov koordinačného centra a bol zdokumentovaný na viacerých železnatých a železitých SCO komplexoch.4 Avšak nízke teploty, ktoré podmieňujú existenciu metastabilného HS alebo LS stavu pri LIESST efekte, predstavujú veľkú nevýhodou pre aplikáciu týchto materiálov.

Druhou alternatívou, pomocou ktorej vieme svetlom zmeniť spinový stav, je použitie fotocitlivých ligandov schopných reverzibilnej transformácie medzi dvoma izomérnymi formami (napr. cis-trans alebo fotocyklizačné izomerizácie). Opäť aj v tomto prípade sa jednotlivé izomérne konfigurácie dajú „prepínať“ ožiarením selektívnou vlnovou dĺžkou, pričom táto fotokonverzia vedie k modifikáciám ligandového poľa, teda aj ku zmene spinového stav centrálneho iónu kovu (Obr. 2). Tento ligandom riadený fotoindukovaný SCO (LD - LISC; z angl. Ligand-Driven Light-Induced Spin Crossover), ktorý bol prvý krát popísaný Zarembowitchom a kol.[5] je fascinujúcim objavom, pretože zmenu spinového stavu môžeme riadiť aj pri izbovej teplote. [6]



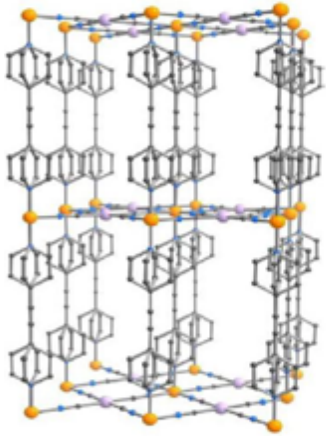
Obrázok 2 Reprezentácia LD – LISC efektu na jednojadrovom železnatom SCO komplexe s ligandami funkcionalizovanými azobenzénovými substituentami, ktoré sú schopné vratnej cis-trans fotoizomerizácie. Zmena spinového stavu sa zvyčajne deteguje magnetickými meraniami (funkcia χT vs T).

Výskumná skupina Dr. Bousseksoua a doc. Šalitroša len nedávno predstavila koncept fotoindukovaného SCO, ktorý je riadený prítomnosťou alebo neprítomnosťou hosťujúcich molekúl (GD – LISC fenomén; z angl. Guest-Driven Light-Induced Spin Crossover).[7] Tento koncept využíva porézne trojrozmerné koordinačné polyméry (MOF; z angl. Metal-Organic Frameworks), ktoré vykazujú SCO efekt. Za posledné dve desaťročia bolo syntetizovaných niekoľko SCO – MOF molekúl, pričom najznámejšie sú SCO klatráty Hofmannovho typu, pripravené výskumnou skupinou vedenou J. A. Realom[8] so štruktúrou {Fe(L)[M(CN]4} (M = Ni, Pt, Pd; L = pyrazín, 4,4´-bipyridín, 4,4´-azopyridín, 1,2- bis(4-pyridyl)etylén, 1,2-bis(4-pyridyl)acetylén (bpac).9 V prípade 3D MOF molekúl je Fe^{2+} v ekvatoriálnej rovine koordinovaný cez diamagnetický metalokyanitový ligand a na túto 2D rovinu je kolmo orientovaný ďalší mostíkujúci ligand L dotvárajúci hexakoordináciu Fe^{2+} (Obr. 3). Takto sa vlastne vytvorí 3D koordinačný polymér, ktorý vykazuje SCO prechod a vo svojej štruktúre obsahuje 3D dutiny do ktorých je možné implementovať hosťujúce molekuly. Spinový stav železnatých centrálnych atómov v takýchto koordinačných polyméroch možno ovplyvňovať povahou a množstvom hosťujúcich molekúl.[10-13] Skupina Dr. Bousseksoua a doc. Šalitroša si pre túto prácu zvolila klatrát $\{Fe(bpac)[Pt(CN)_4]\}$. u ktorého bola potvrdená prítomnosť SCO efektu so širokou termálnou hysteréziou pri izbovej teplote.[7] Veľké rozmery pórov v tejto zlúčenine (cca 300 Å 3 v LS stave) umožňujú prijatie objemnejších molekúl, napríklad fotoizomerizovateľných molekúl azobenzénu a stilbénu, ktorých rozmery zodpovedajú rozmerom dutín (Obr. 3). Azobenzén, stilbén a ich deriváty sú dobre známe fotochromatické molekuly so širokou škálou využitia, a sú schopné reverzibilnej interkonverzie medzi trans a cis formou aktivovanej svetlom (Obr.2).



Obrázok 3 Schematické znázornenie pravdepodobného umiestnenia (a)trans - stilbénu a (b) cis - stilbénu v hostiteľskej molekule $\{Fe(bpac)[Pt(CN)_4]\}$. [7]

V úvode môjho výskumu som sa venovala príprave prázdnych MOF systémov systémov (neprítomnosť hostí v kavitách) konkrétne $\{Fe(bpac)[Pt(CN)_4]\}$ a $\{Fe(bpac)[Ni(CN)_4]\}$ (**bpac** = 1,2-bis(4-pyridyl)acetylén (**Obr. 1**). V prípade prvého klatrátu, bola dokázaná prítomnosť širokej termálnej hysterézie pri izbovej teplote, čo je veľmi žiadúce pri SCO materiáloch, a preto sme sa rozhodli nadviazať na predchádzajúcu prácu a modifikovať kryštálové pole pomocou rôznych hosťovských molekúl. Pri príprave sme použili priamu syntézu ako aj kryštalizáciu pomocou H-trubice. Druhá, časovo náročnejšia metóda viedla k získaniu kryštálu, ktorý sa podrobil monokryštálovej RTG difrakčnej analýze, čo viedlo k poznaniu absolútnej štruktúry klatrátu. Spin crossover vlastnosti boli skúmané pomocou merania reflektivity a magnetické vlastnosti pomocou MPMS SQUID magnetometra. Takto pripravené a pomocou nepriamych analytických techník ocharakterizované klatráty (elementárna analýza, teplotne závislá infračervená spektroskopia s Fourierovou transformáciou, termogravimetrická analýza) sme použili ako hosťovský polymér, do ktorého sme implementovali rôzne molekuly.

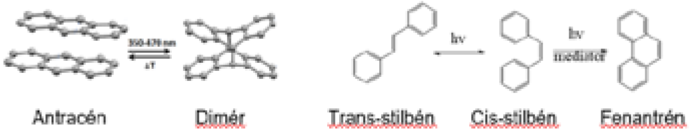


Obrázok4 Molekulová štruktúra MOF systému

V druhej polovici sme sa sústredili na prípravu MOF klatrátov s hosťovskou molekulou vo vnútri, pričom sme sa sústredili na:

1. organické fotoaktívne molekuly, ktoré podliehajú vratnej izomerizácii prostredníctvom elektromagnetického žiarenia (cis/trans stilbén) a pomocou oxidačného činidla dávajú vznik fenantrénu (**Obr. 5**)
2. organická molekula, ktorá podlieha vratnej fotodimerizácii (antracén/diantracén) (**Obr. 5**)

Dôvodom, prečo sme sa zamerali práve na tieto molekuly, je skutočnosť, že magnetické vlastnosti vieme ovplyvňovať pomocou žiarenia, a v prípade slabej priepustnosti klatrátu pre svetlo, pomocou teploty. Rozdielne SCO vlastnosti pripravených zlúčenín sú dôsledkom interakcií hosť-hostiteľ čo súvisí so stérickými efektmi a medzimolekulovými interakciami.



Obrázok 5 Schematické znázornenie použitých hosťovských molekúl a možnosti ich modifikácie

Metódou priamej syntézy, sublimáciou za zníženého tlaku a zmiešaním hosťovských molekúl s MOF polymérom v roztoku, sa nám podarilo pripraviť zlúčeniny požadovaného zloženia, a to: ({Fe(bpac)[**M**$(CN)_4$]}).antracén, ({Fe(bpac)[**M**$(CN)_4$]}).trans-stilbén, ({Fe(bpac)[**M**$(CN)_4$]}).cis-stilbén, ({Fe(bpac)[**M**$(CN)_4$]}).fenantrén (**M**=Pt, Ni). Všetky zlúčeniny sme ocharakterizovali pomocou elementárnej analýzy, termogravimetrického merania, teplotne závislej infračervenej spektroskopie s Fourierovou transformáciou a práškovej difrakčnej analýzy. Spin crossover vlastnosti sme zisťovali pomocou merania reflektivity a magnetické vlastnosti pomocou MPMS SQUID magnetometra. Výsledky poukázali na to, že metóda prípravy úzko súvisí množstvom hostí vo vnútri klatrátu a teda priamo ovplyvňuje spinové vlastnosti. Ako najvhodnejšia metóda sa javí metóda priamej syntézy, pretože krivka závislosti magnetickej susceptibility od teploty je strmá s teplotnou hysteréziou, čo je žiadúce, ak takéto materiály majú byť využité v priemysle.

Posledným cieľom tohto výskumu bolo skúmanie GD-LISC efektu, teda vplyvu prítomnosti hosťa na hosťovský polymér a jeho fyzikálne vlastnosti. Tieto experimenty spočívali v ožiarení nami pripravených zlúčenín v roztoku za účelom „prepnutia“ trans-stilbénu na cis-stilbén, následne prídavkom oxidačného činidla získať fenantrén a sledovať zmeny magnetických vlastností. Druhý experiment bol založený na dimerizácii antracénu vo vnútri 3D polyméru použitím elektromagnetického žiarenia vlnovej dĺžky 350 – 470 nm. Bohužiaľ ani v jednom prípade sa nám nepodarilo preukázať že došlo k fotoizomerizácii, resp. dimerizácii, čo pripisujeme slabej priepustnosti MOF systému pre svetlo. Ďalšie experimenty budú zahrňovať práve pokusy s ožarovaním (použitie lámp s rôznou vlnovou dĺžkou) a optimalizáciou podmienok.

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Fyzikálno-chemická charakterizácia pyrolýznych materiálov na báze čistiarenských kalov

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1. Úvod

Čistiarenský (alebo aj splaškový) kal je definovaný ako tuhý, polotuhý alebo kvapalný zvyšok vznikajúci v procese čistenia v čistiarňach odpadových vôd (ČOV)[1]. Čistiarenský kal je vedľajším produktom v procese čistenia odpadových vôd, počas ktorého sa zo znečistenej vody oddeľujú kvapalné a tuhé kontaminanty. Voda je po procese čistenia vypustená do vodných recipientov (rieky, potoky) ako úžitková voda, zatiaľ čo tuhé látky sú po separácii ďalej upravované alebo pripravené na finálne skládkovanie. Zložky tuhých vedľajších produktov čistenia vody sú štrk, piesok, väčšie nečistoty (napr. kúsky jedla, dreva, plastov) a čistiarenské kaly. Zo zložiek odstránených čistením odpadových vôd je práve kal tou najobjemnejšou zložkou. Kal odstránený z odpadových vôd procesmi čistenia je zvyčajne kvapalného skupenstva alebo tvorí suspenziu s obsahom tuhých látok medzi 0,25% až 12% celkovej hmotnosti kalu[2]. Zloženie a vlastnosti kalov sa menia na základe rôznych faktorov, akými sú proces produkcie kalov, vek, environmentálne podmienky (teplo a vlhkosť) atď.

Kal je komplexná heterogénna zmes zložená z anorganických a organických látok a mikroorganizmov. Medzi organickými látkami nájdeme chlórované parafíny (CP), polycyklické aromatické uhľovodíky (PAU), polychlórované bifenyly (PCB), perfluorované zlúčeniny (PFZ), pentachlórfenoly (PCF), ropné uhľovodíky (RU), benzotriazoly, per- a polyfluoroalkylové zlúčeniny (PFAZ), pesticídy ako aj široké spektrum povrchovo aktívnych látok. Okrem vyššie uvedených sa v kaloch môže nachádzať aj zložitá zmes nedegradovaných organických zložiek pozostávajúcich z proteínov, peptidov, lipidov, polysacharidov, rastlinných makromolekúl s fenolovými štruktúrami alebo alifatických štruktúr spolu s organickými toxínmi.[3] Čistiarenský kal obsahuje pomerne vysoké koncentrácie nutrične dôležitých prevažne vo forme zlúčenín fosforu, dusíka a draslíka. Rovnako však v biomase kalu nájdeme zastúpené potenciálne toxické prvky ako ťažké kovy. Ťažké kovy ako Zn, Cu, Ni, Cd, Pb, Hg a Cr obmedzujú jeho použitie na poľnohospodárske účely.[4] Okrem nebezpečných chemických zlúčenín obsahuje čistiarenský kal aj patogény, ako sú vírusy (hepatitída A, rotavírus), baktérie (*Escherichia coli, Salmonela*), parazity (*Cryptosporidium, Giardia*) alebo parazitické červy (*Ascaris*)[1].

Metódy nakladania s kalmi z ČOV zahŕňajúce skladovanie sa v súčasnosti nahrádzajú metódami vedúcimi k jeho stabilizácii a bezpečnej recyklácii. Poľnohospodárske využitie sa stalo jednou z hlavných metód nakladania so splaškovými kalmi najmä v minulosti. Najnovšie trendy v oblasti kalového hospodárstva, teda spaľovanie, mokrá oxidácia, pyrolýza, splyňovanie, spoluspaľovanie splaškových kalov s inými materiálmi na ďalšie použitie ako zdroj energie, stabilizácia a použitie splaškových kalov alebo ich popola v stavebníctve, vzbudili značný vedecký záujem. Toxicita a stabilita znečisťujúcich látok, chemické a fyzikálne vlastnosti, môžu ovplyvňovať zmeny v technológii spracovania kalov s cieľom vyvinúť ďalšie spôsoby nakladania s kalmi. Preto je dôležité, aby v každej fáze spracovania tohto druhu odpadu bol výsledný materiál podrobený komplexnej fyzikálno-chemickej charakterizácii.

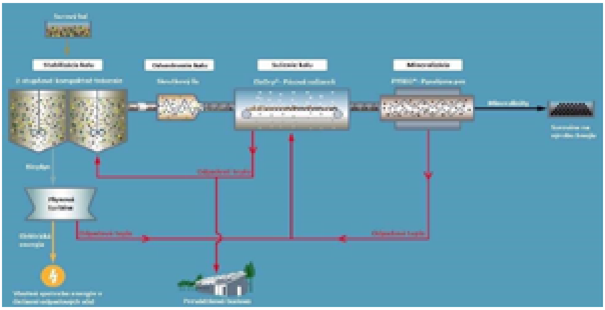
Pyrolýza je proces, pri ktorom sa vstupné organické látky tepelne rozkladajú v anoxickej atmosfére (s použitím N_2 alebo CO_2 ako inertného plynu) pri teplotách pohybujúcich sa v rozmedzí 300-700°C a atmosférickom tlaku[5]. Produktom pyrolýzy sú pyrolýzne oleje (bio-oleje), pyrolýzne plyny (syngas) a pevný uhlíkatý materiál (biouhlie). Podľa Európskeho certifikátu pre biouhlie EBC[6] je pomenovanie biouhlie viazané na obsah uhlíka >50%. Preto v prípade pyrolýzy kalov z ČOV sa využíva označenie pyrogénnych resp. pyrolýznych uhlíkatých materiálov. Pyrolýza čistiarenských kalov spočíva v ich zahrievaní v inertnej atmosfére a následnom uvoľňovaní organických látok. Táto technika sa javí ako menej znečisťujúca v porovnaní s bežnými metódami (spoluspaľovanie, spaľovanie), pretože produkuje minimálne emisie a koncentruje ťažké kovy v tuhom uhlíkatom zvyšku, takže ich extrakcia nie je taká zložitá, ako v prípade popola zo spaľovania[2]. Reakcie, ktoré prebiehajú v pyrolýznom reaktore predstavujú termické štiepenie a kondenzačné reakcie. V porovnaní so spaľovacím procesom, ktorý je vysoko exotermický, je pyrolýza skôr endotermický dej[7]. Medzi rôzne typy technológií pyrolýzy kalov patria pomalá pyrolýza, rýchla pyrolýza, vákuová pyrolýza a blesková (flash) pyrolýza. Kľúčovými parametrami, ktoré ovplyvňujú proces pyrolýzy, sú doba zdržania biomasy kalu v reaktore, pyrolýzna teplota a samotný charakter vstupnej suroviny. Pyrolýza sa používa na spracovanie najrôznejších surovín vrátane plastov, tuhého komunálneho odpadu, splaškových kalov a drevnej biomasy[8].

V prípade pyrolýzy kalov ide o termochemickú konverziu predsušeného uhlíkatého podielu kalu na stabilnejší a nutrične dôležité prvky bohatý produkt. Uplatnenie pyrolýznych materiálov na báze čistiarenských kalov spočíva v pôdnych aplikáciách ako aditív v poľnohospodárstve, záhradníctve, okrasných záhonoch ako aj substrátoch tzv. zelených striech. Na základe uvedeného je nutné podporiť vedecké myšlienky, ktoré smerujú k základnému i aplikovanému výskumu venujúcemu sa použitiu konvenčných technológií v pomerne nových využitiach úpravy kalov.

Hlavným cieľom tejto práce bolo zhodnotenie pyrolýzneho materiálu na báze komunálneho čistiarenského kalu z pohľadu ekotoxicity, biologickej prístupnosti fosforu ako aj samotnej materiálovej charakterizácie.

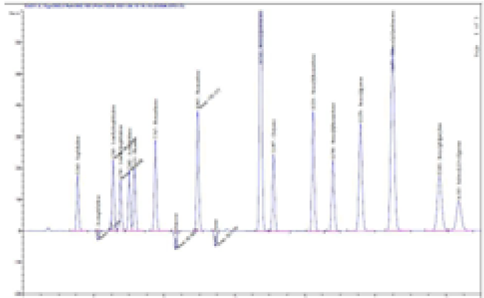
2. Experimentálna časť

Pyrolýzny materiál na báze čistiarenského kalu (BC) bol vyprodukovaný v spolupráci s ČOV Linz Unkel (Nemecko). Pre produkciu bol využitý veľkokapacitný kontinuálny pyrolýzny reaktor Pyreg (Obr.1) s teplotou pyrolýzy 603-615°C, striktne anoxickou atmosférou a priamym spaľovaním vznikajúcich plynov (FLOX-zariadenie). Pyrolýzny materiál bol zositovaný na frakciu 0,5-1 mm.



Obr. 1 Schéma produkcie pyrolýzneho materiálu z čistiarenských kalov v ČOV Linz-Unkel (Nemecko)

Pyrolýzny materiál bol charakterizovaný stanovením aktívneho a potenciálneho pH, hodnoty elektrickej vodivosti (EC) a obsahu popola. Obsah uhličitanov sme zisťovali vo vzorkách biouhlia volumetrickou metódou s aplikáciou Jankovho vápnometra. Jankov vápnomer funguje na princípe reakcie HCl s uhličitanmi za vzniku CO_2, ktorý vytláča vodu v kalibrovanej časti vápnometra. Pre stanovenie celkovej koncentrácie 18 štruktúr polycyklických aromatických uhľovodíkov (PAU) podľa USEPA (1995) konkrétne: naftalénu, acenaftylénu, acenaftalénu, fluorénu, fenantrénu, antracénu, fluoranténu, pyrénu, benzo(a)antracénu, chrysénu, benzo(b)fluoranténu, benzo(k)fluoranténu, benzo(a)pyrénu, dibenzo(a,h)antracénu, benzo(g,h,i)perylénu, ideno(1,2,3)pyrénu, 1-metylnaftalénu a 2metylnaftalénu (Obr.2) bola využitá modifikovaná extrakčná procedúra podľa Hilber a kol. (2012)[9]. Do extrakčných patrón sme navážili 5 g vzorky biouhlia. Patróny sme vložili do Soxhletovej extrakčnej aparatúry a do varnej banky sme pridali 125 ml extrakčného činidla – toluénu (p.a). Varnú banku sme zahrievali pri teplote <115°C na dosiahnutie varu extrakčného činidla. Extrakcia prebiehala po dobu 36 h. Získané extrakty boli zakoncentrované pomocou vákuovej odparky HEIDOLPH Hei-Vap (Nemecko) pri podmienkach 42°C, 140 rpm a tlaku 50 mbar. Na kvantifikáciu PAH látok bola použitá vysokoúčinná kvapalinová chromatografia (1260 Infinity, AGILENT Technologies) s využitím kolóny Restek C18 PAH (150 x 4.6 mm; 4 µm), mobilnej fázy acetonitril-voda a DAD detektora (λ = 280 nm). Objem vzorky 5 µL a teplota 30°C.



Obr. 2 HPLC chromatogram štandardov (10 mg/L) naftalénu, acenaftylénu, acenaftalénu, fluorénu, fenantrénu, antracénu, fluoranténu, pyrénu, benzo(a) antracénu, chrysénu, benzo(b)fluoranténu, benzo(k) fluoranténu, benzo(a)pyrénu, dibenzo(a,h)antracénu, benzo(g,h,i)perylénu, ideno(1,2,3)pyrénu, 1metylnaftalénu a 2-metylnaftalénu použitých pre kalibráciu metódy (R^2>0,999)

Na klíčivostné testy sme použili ako rastlinný model Žeruchu siatu (*Lepidium sativum*) z čelade kapustovité, kvôli jej rýchlemu klíčeniu, a vodné extrakty pyrolýzneho materiálu (BC) s hmotnostným pomerom materiál:voda – 1:10 a 1:100. Pre sledovanie vplyvu skúmaného pyrolýzneho materiálu na vodnú faunu bol využitý test akútnej toxicity s využitím Dafnie obyčajnej (*Daphnia pulex*) podľa Bastos a kol. (2014)[10]. Testovacie jedince boli získané z komerčne dostupného chovu, uskladnené v chladničke pri 5°C a bezprostredne po získaní aplikované v teste. Vek lariev bol odhadnutý na základe morfologických znakov na 3-4 dni. Vplyv prídavku pyrolýzneho materiálu BC (5% a 10% v/v) na rast a produkciu biomasy bol testovaný v kultivačnom experimente s využitím rastlinného modelu reďkovky siatej (*Raphanus sativum*). Anorganické formy fosforu vo vzorke biouhlia sme zisťovali pomocou kyslej extrakcie použitím 1 mol/L HCl v pomere 0,2g vzorky k 10 ml HCl, aby bol dodržaný pomer 1:50 w/v (vzorka : extrakčné činidlo). Suspenziu sme miešali po dobu 24 h pri 22°C a 45 rpm na laboratórnej trepačke (Orbital Shaker- Multi-RS 60, Biosan, Lotyšsko). Anorganický fosfor sme kvantifikovali na základe postupu STN EN ISO 6878 v supernatante, ktorý sme od suspenzie oddelili centrifugáciou pri 4000 rpm a 20 minút. Na základe odčítania hodnôt celkového P od anorganického P sme vypočítali podiel organického P vo vzorke biouhlia. Celkový fosfor bol stanovený podľa práce Frišták a kol. (2018) po predchádzajúcej mokrej oxidácii HNO_3 a H_2O_2. Väzbovosť fosforu vo vzorke biouhlia sme zisťovali pomocou sekvenčnej extrakcie podľa Quian a Jiang[11]. Ľahko rozpustné formy fosforu a jeho vápenatých zlúčenín sme zisťovali Calcium Acetate Lactate (CAL) metódou podľa Schüllera[12]. Fosfor sme vo vzorkách pyrolýzneho materiálu kvantitatívne stanovovali na základe postupu STN EN ISO 6878 pre stanovenie ortofosfátov vo vodných vzorkách s využitím UV-VIS spektrofotometrie (Cary 50, Varian). Podstatou stanovenia je reakcia kyslého roztoku obsahujúceho ióny antimónu a molybdénanu s ortofosforečnanovými iónmi za vzniku antimón-fosfomolybdnénanového komplexu. Redukciou komplexu kyselinou askorbovou vzniká sýto sfarbený komplex molybdénovej modrej. Koncentrácia prítomných ortofosforečnanov sa stanoví spektrofotometrickým meraním absorbancie komplexu pri 880 nm. Pracovný kalibračný mód bol 0,2-2 mg/L. Vnútorné a povrchové štruktúry boli zisťované pomocou skenovacej elektrónovej mikroskopie (SEM) a elektrónovo-disperznej röntgenovej analýzy (EDX) za použitia elektrónového mikroskopu JEOL JSM 7600F (Japonsko). Analýzy boli realizované pri tlaku vákua 9,0 x 10^{-4} Pa, napätí 20 kV a pri zväčšení 50x a 250x.

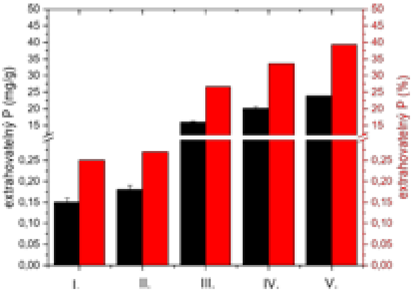
3. Výsledky

Zo základnej charakterizácie fyzikálno-chemických vlastností pyrolýzneho materiálu (Tab. 1) je možné usúdiť, že aktívne aj potenciálne pH je vzhľadom na podmienky prípravy a obsah uhlíka vo vzorke nízke, nakoľko pri teplote pyrolýzy ≥ 550°C by mali hodnoty pH stúpať do zásaditej oblasti pH. Zastúpenie uhlíka a dusíka vo vzorke pyrolýzneho materiálu je pomerne vysoké pri porovnaní s obdobnými materiálmi. Obsah dusíka v pyrolyzovanej vzorke je pomerne vysoký, čo môže značiť prítomnosť organického dusíka, ktorý zostal po pyrolýze vo vzorke a ktorý môže prispievať k nižšiemu pH vzorky materiálu. Elektrická vodivosť pyrolýznej vzorky nám naznačuje prítomnosť iónov, ktoré sa môžu zo vzorky uvoľniť počas lúhovania v rozpúšťadle. Ukazovateľ obsahu popola naznačuje prítomnosť pomerne veľkého množstva anorganických látok, ktoré môže byť väčšinovo tvorené ťažkými kovmi alebo minerálnymi zložkami. Obsah prchavých látok naznačuje, že po pyrolýze zostalo v štruktúrach alebo na povrchu pyrolýzneho materiálu málo prchavých látok ako aj vlhkosti v porovnaní s obsahom prchavých látok v sušených kaloch. CAL extrahovateľné formy fosforu vo vzorke, ktoré ako chemické nástroje charakterizujú množstvo biologicky prístupného fosforu pre rastliny, dosahovali koncentráciu 7,25 mg/g, čo je približne 12% celkového fosforu. Celkový obsah polycyklických aromatických uhľovodíkov vo vzorke pyrolýzneho materiálu bol 1,054 mg/g

Tabuľka 1 Fyzikálno-chemické charakteristiky vzorky BC

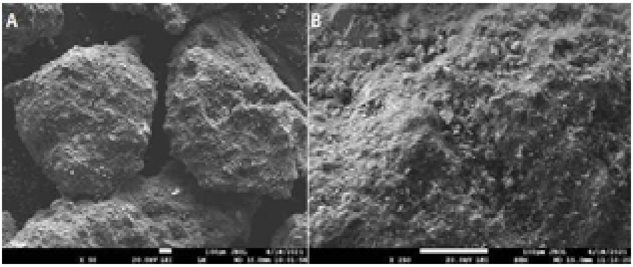
pH_{H2O}	6,40 ± 0,001
pH_{KCl}	5,73 ± 0,007
EC (µS/cm)	623,3 ± 2,6
Obsah popola (%)	27,09 ± 0,26
Obsah prchavých látok (%)	6,57 ± 0,06
CO_3 (%)	0,2 ± 0,001
C (%)	35,5
H (%)	0,95
N (%)	4,21
S (%)	0,72
18 PAU (mg/kg)	1,054
Celkový P (mg/g)	60,23 ± 2,40
CAL extrahovateľný P (mg/g)	7,25 ± 0,43

Vzorka pyrolýzneho produktu získaného z čistiarenského kalu (BC) obsahovala viac ako polovicu celkového fosforu v organickej forme (58,82%), čo môže byť následkom transformácie počas pyrolýznej úpravy. Zo sekvenčnej extrakcie sme zistili zastúpenie foriem fosforu prítomného vo vzorke pyrolýzneho materiálu (Obr.3). Na základe našich výsledkov môžeme usúdiť, že mobilné formy P, extrahovateľné vodou boli vo vzorke pomerne málo zastúpené, čo mohlo byť spôsobené pyrolýznou úpravou kalu, pri ktorej sa v pyrolýznom zvyšku fosfor transformoval na stabilnejšie formy. NaOH-extrahovateľný fosfor predstavuje ortofosforečnanové kompozity s Fe a Al, ktoré sa pomaly uvoľňujú do pôd a v prípade našej pyrolýznej vzorky predstavujú pomerne vysokú hodnotu (>27%). HCl extrahovateľný fosfor predstavuje formy stabilnejšieho fosforu a minerálov, ktoré sa do pôdy uvoľňujú veľmi pomaly, pričom hodnota HCl-extrahovateľného fosforu bola v našej pyrolýznej vzorke zastúpená v najvyššom podiely (>34%). Neextrahovateľný P ako reziduálny, ktorý nie je mobilizovateľný žiadnym z použitých extrakčných činidiel predstavoval 40%.



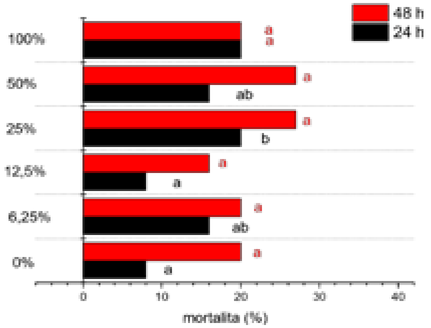
Obr. 3 Frakcionácia viazaného fosforu vo vzorke pyrolýzneho materiálu (BC), stanoveného sekvenčnou extrakciou s poradím krokov: H_2O-extrahovateľný (I.), $NaHCO_3$-extrahovateľný (II.), NaOH-extrahovateľný (III.), HCl-extrahovateľný P (IV.) a reziduálny (neextrahovateľný) P (V.).

Morfológiu povrchu pyrolýzneho materiálu na báze kalu (BC) sme skúmali pomocou SEM analýzy (Obr.12) so zväčšením 50x a 250x. Zo získaných mikrosnímkov je možné usúdiť, že morfológia kalu je pomerne kompaktná, resp. má minerálny charakter. V porovnaní s pyrolýznymi materiálmi pripravenými z konvenčných vstupných materiálov ako je drevná štiepka, orechové škrupiny, záhradný drevný odpad alebo poľnohospodárske odpady je zrejmé, že pórovitosť produktu je silne závislá na vlastnostiach a najmä štruktúre pôvodnej biomasy.



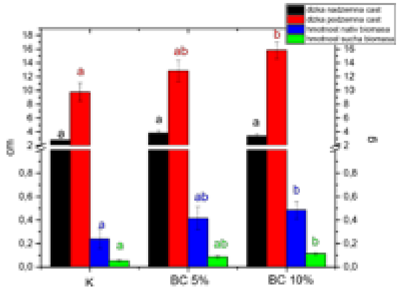
Obr. 4 SEM snímky povrchu pyrolýzneho materiálu (BC) so zväčšením 50x (A) a 250x (B)

EDX analýza preukázala prítomnosť P, O a Fe vo vzorke BC a na základe prekryvov týchto troch prvkov je možné usúdiť, že sú na seba chemicky viazané a to pravdepodobne vo forme fosforečnanových solí železa. Zo získaných výsledkov klíčivostných testov možno konštatovať, že pridané vodné extrakty pyrolýzneho materiálu nemajú negatívny vplyv na klíčivosť žeruchy siatej (*Lepidium sativum*), nakoľko sa už po 12h testu ukázalo, že vzorky s extraktmi z pyrolýzneho materiálu v pomeroch 1:10 a 1:100 mali rýchlejšiu klíčivosť ako kontrolná vzorka s destilovanou vodou. Na zistenie ekotoxicity vodou-extrahovateľných látok z pyrolýzneho materiálu sme realizovali test s využitím malých vodných kôrovcov konkrétne dafnie obyčajnej (*Daphnia pulex*). Získané výsledky (Obr.5) nepotvrdili štatisticky významný rozdiel medzi mortalitou jedincov po 48 h v 100% výluhu pyrolýzneho materiálu v porovnaní s kontrolnou vzorkou (s nulovou koncentráciou výluhu).



Obr. 5 Porovnanie vplyvu vodou extrahovateľných látok z BC na mortalitu jedincov dafnie obyčajnej (*Daphnia pulex*) s dobou expozície 24h a 48 h. Percentuálne hodnoty vyjadrujú podiel BC vodného extraktu v živnom médiu. Rozdielne písmená označujú štatistickú významnosť medzi jednotlivými prídavkami v danom parametri na základe Tukey post-hoc testu (p<0,001).

Na základe výsledkov kultivačného testu s reďkovkou siatou môžeme potvrdiť významnú štatistickú odchýlku pri porovnaní kontrolnej vzorky bez pyrolýzneho materiálu a vzorky s 10% prídavkom pyrolýzneho materiálu na rast podzemnej časti reďkovky siatej (Obr.6). Štatisticky významný rozdiel môžeme pozorovať aj v prípade nárastu natívnej (nevysušenej) a suchej biomasy.



Obr. 6 Porovnanie vplyvu 5% a 10% (V/V) prídavku BC na rastové charakteristiky (dĺžka podzemnej časti, dĺžka nadzemnej časti, hmotnosť vyprodukovanej biomasy pred a po vysušení do k.h.) reďkovky siatej po 6 týždňoch kultivácie s kontrolnou vzorkou (K) piesku bez prídavku BC. Rozdielne písmená označujú štatistickú významnosť medzi jednotlivými prídavkami v danom parametri na základe Tukey post-hoc testu (p<0,001).

4. Závery

Termochemická konverzia čistiarenských kalov sa s pribúdajúcimi výskumnými prácami ukazuje ako sľubná metóda na spracovanie týchto heterogénnych a značne komplikovaných odpadov.

Charakterizačné štúdie potvrdili nízku hodnotu celkového uhlíka v pyrolýznej vzorke, ako aj prítomnosť pomerne vysokého množstva fosforu. Sekvenčnou extrakciou boli zistené koncentrácie rôznych foriem fosforu, z ktorých dominovali pomaly uvoľniteľné formy fosforu (NaOH a HCl-extrahovateľné). Ekotoxikologické testy realizované s použitím žeruchy siatej a dafnie obyčajnej nepreukázali významné nebezpečenstvo pre tieto organizmy. Kultivačný test na reďkovke siatej potvrdil významnosť použitia pyrolýzneho materiálu z čistiarenského kalu zvýšeným rastom podzemnej časti rastliny, ako aj vyššou tvorbou biomasy. Na základe získaných výsledkov sa pyrolýzny materiál pripravený z komunálneho čistiarenského kalu zdá byť sľubným pôdnym aditívom a potenciálnou alternatívou konvenčných anorganických hnojív. Akokoľvek je veľmi dôležité poukázať na prítomnosť ťažkých kovov, ktoré sa v procese pyrolýzy multiplikujú vo výslednom produkte. Otázka ich biologickej prístupnosti a extrahovateľnosti si vyžaduje rozsiahlejšie skúmanie a ďalšie experimenty.

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Poďakovanie

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SEKCE STUDENTŮ DOKTORSKÝCH PROGRAMŮ

1) Life Science - Sekce organické, environmentální chemie a biochemie

Self encapsulation of plant growth--promoting bacteria Azotobacter vinelandii for their use as next--generation bioinoculants

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Azotobacter vinelandii is a plant-growth-promoting bacterium (PGPB), capable of synthesizing two different biopolymers with great application potential. Polyhydroxyalkanoates (PHA) are produced and stored in a form of intracellular granules, whereas alginate is produced extracellularly. Plant growth-promoting bacteria can be used as bio-inoculants to increase yields in agriculture. Encapsulation of bacteria into hydrogel-based carriers substantially improves the application potential of the bioinoculant as well as the viability and robustness of the bacterial culture. In this work, the alginate produced by the bacteria themselves was crosslinked with a calcium chloride solution to form a hydrogel carrier with encapsulated bacteria. This unconventional concept that we termed „self encapsulation" simplifies bacterial encapsulation and production of hydrogel carriers, reduces the cost, and expands its usability in numerous applications. Firstly, we screened five strains of *Azotobacter vinelandii* to select those with a sufficient production capacity concerning alginate and PHA and suitable gelation properties. Actually, the strain DSM 87 reached the highest concentration of the alginate (4.9 ± 0.6 g/l). The alginates produced by strains DSM 87 and DSM 720 demonstrated the best gelation properties. The bacterial entrapped in a gel matrix seemed to be viable and cultivatable. Hence, the preliminary results confirmed the feasibility and viability of the novel concept.

Development of a Multiplex PCR Assay for Simultaneous Detection of Closely Related Fruit Species in Food

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Food adulteration is a long-standing problem. As new ways of adulteration develop, new methods for food authenticity checking, including DNA-based ones, should be developed, too. In this work we focused on multiplex real-time PCR-HRM and its possible use in simultaneous detection of various fruit species in food. New apricot-specific primers were also designed as a part of this work. Peach and apricot were chosen as the fruit species of interest because they occur as both the adulterant and the adulterated commodity [1], and because certain foodstuffs (such as infant food) contain both of these fruits. We analyzed three fruit purees, two of which contained approximately 70 % of apple and 30 % of either apricot or peach. In these purees, neither apricot nor peach was detected. The third puree contained both apricot and peach, but not apple. Using multiplex PCR, we were able to detect apricot in the last puree by both HRM analysis and electrophoresis, and peach was detected by electrophoresis. From these results we conclude that while multiplex PCR can be used for simultaneous detection of peach and apricot in certain foodstuffs, further study focusing on the influence of matrix type on the results of this method would be appropriate.

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Environmental risk assessment of polyhydroxybutyrate micro-bioplastics – summary of project results

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Mankind invests significant amount of resources and effort to decrease micro-plastics production; one of the solutions is replacement the conventional plastics by biodegradable plastics. However, the conditions for biodegradation are not always met in real environment, thus the degradation of the bioplastics is slow or incomplete and paradoxically it leads to the micro-bioplastics formation [1]. The adverse ecotoxicological effects of conventional micro-plastics on living organisms are known, but the micro-bioplastics are almost overlooked [2]. There is also lack of articles describing the effect of both micro-plastics and micro-bioplastics on soil abiotic processes [3]. We tried to address this issue by analyzing the effect of polyhydroxybutyrate (PHB) micro-bioplastics and polyethyleneterephtalate (PET) microplastics. The aim was to assess I) the effects of PHB micro-bioplastics on soil structure, II) the effect of PHB on soil megafauna, and III) how the biodegradation of bioplastics effects the nutrient content, microbiological activity and thus the crops growth.

We used following setups. I) Influence of MPs on abiotic characteristics of soil was investigated in sapric histosol spiked with different concentrations of micro-plastics and micro-bioplastics exposed to the different relative humidity. The soil indicator describing the soil water retention and desiccation (water holding capacity and soil water evaporation enthalpy) and effects on soil structure were measured using DSC. II) The ecotoxicological adverse effects caused of PHB was tested according to the OECD acute, chronic and escape earthworm tests. The pot maize plant experiment was conducted to describe effects of PHB micro-bioplastics on the crops and agricultural soil. III) The maize seeds planted in pots were exposed to different concentrations of PHB. Subsequently the pots were kept in the growth chamber for 90 days and then the plants were harvested. The plant biomass, soil microbial activity and soil microorganisms were analyzed.

Results: We have found out that contamination of micro-plastics and micro-bioplastics results in changes in the soil organic matter structure and accelerated desiccation of soil. The presence of micro-bioplastics also leads to microbial activity boost, the mineral soil nutrient depletion, and significantly lower yields of biomass.

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Synthetic approaches towards novel vitamin B_2-inspired derivatives for organic (bio)electronics

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The family of yellow pigments flavins includes nature-inspired molecules derived from the tricyclic heterocycle isoalloxazine. The omnipresent biological source, riboflavin, is an important segment of redox cofactors serving as electron shuttles within the cellular metabolism. Both natural and synthesised flavins share unique properties attributed to the isoalloxazine core, defining the redox and optical properties.

Our research group has recently studied the synthesizability of flavin derivatives resulting in the preparation of NH-free molecules with prolonged conjugation of the aromatic system [1]. In addition, we focused on the solubility of the molecules in common organic solvents and enhanced it by N,N'-alkylation, leading to better processability and consequent complex evaluation of the physicochemical properties [2].

The initial research served as a springboard towards constructing novel branched flavins with donor-π-donor (D-π-D) character. Thus, corresponding nature-inspired D-π-D systems are auspicious for the use in organic electronic and bioelectronic devices in terms of their biocompatibility, non-toxicity with a potential low-cost production. Herein, our current progress in synthesis is presented. The approach requires elaboration of a reliable method for preparing the responding 1,2-diketones to form the isoalloxazine core of the flavin by condensation reaction with 5,6-diaminouracil.

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Biosource materials for coatings

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Abstract

The work is focused on the chemical processes leading to the production of polymerizable material precursors made out of the natural sources with the potential for the coatings applications. There are various biosource substrates which can be transformed into the potential coating materials such as vegetable oils, sorbitol or lactic acid. The modification of these reactants via acrylic acid, methacrylic acid and methacrylic anhydride has been studied. Modified vegetable oil structure contains a significant amount of biosource carbon. Sorbitol material precursor derivatives show high glass transition temperature numbers (T_g > 100 °C) after their polymerization and ethyl lactate methacrylate as a polymerizable derivative of lactic acid reached the highest conversion level of 99.9 %. There is a possibility that the fatty acids together with sorbitol derivatives such as isosorbide in the form of an ester can combine their properties. These materials are supposed to be an alternative to the materials used currently for the coating applications like pure acrylates or artificial polyurethanes.

Keywords: Biosource material, coating, vegetable oil, sorbitol, ethyl lactate

1 Introduction

Vegetable oils are one of the appropriate substrate for a biopolymer coating material. The biggest motivation for using these molecules is probably their high bio-source carbon content. There is also a big variety of the oil kinds such as soybean, sunflower, palm, rapeseed, linseed etc. which leads to a usage of a regional sort of vegetable source. Oils particularly are used because of their liquid phase form. Although this kind of a potential polymer substrate is liquid, it is not volatile enough to negatively affect the environment, that's also one of the reasons for considering them for coatings application. When oils are unmodified there is few opportunities of how to prepare a polymer material out of them. Alkydes can be prepared from a crude oil for example. However if oils undergo the epoxidation reaction in order to modify the double bonds occurring in the structure of triacylglycerol, the epoxy functional groups are formed out of them. Epoxy groups may be cross-linked via diamines or dicarboxylic acids according the nucleophile substitution reaction mechanism. There is a possibility to modify the epoxidized triacylglyceroles further by the polymerizable carboxylic acids. Acrylic acid and methacrylic acid are members of this group of organic acids. If we use them with a suitable catalyst, we'll obtain acrylated or methacrylated oils. These derivatives can be polymerized by thermo of photo initiators. Since there is always more than one double bond triacylglycerol structure (further epoxidized and acrylated) a resin is a product of the polymerization. Therefore these materials are insoluble due to the 3D molecular network [1,2].

Lactic acid is a naturally occurring carboxylic acid containing one hydroxyl functional group. This compound is produced via numerous biotechnological processes and it is used in the food industry as an additive or pH regulator. The presence of hydroxyl group provides specific properties such as the possibility to generate H-bonds, it also leads to a higher polarity of the compound and it also enriches the acidity due to the inductive effect [3]. Lactic acid is used for the production of poly(lactic acid), which can be synthesized by various ways. This carboxylic acid is also a substrate for esterification reactions and namely ethyl lactate. Ethyl lactate is one of the most promising organic solvents due to many factors. This ester does not negatively affect health conditions, it is not teratogenic and can be metabolized in the living organism via the hydrolysis mechanism to produce ethanol and lactic acid, which are not dangerous compounds either and can be metabolized as well. Ethyl lactate is considered to be a renewable and sustainable solvent at the same time [4]. The presence of a hydroxyl functional group in the structure of ethyl lactate has the potential to be modified by acrylic or methacrylic functional groups which can provide an opportunity of the radical polymerization. The resulting polymers might stay polar enough to interact with polar solvents (water) and their potential for hydrolysis could be promising towards the biodegradability. Lactic acid and its esters are optically active and L-lactic acid (and its derivatives) is the save enantiomer for the human metabolism. This leads to another application of acrylated/methacrylated ethyl lactate polymers such as enantioselective catalysts [5,6].

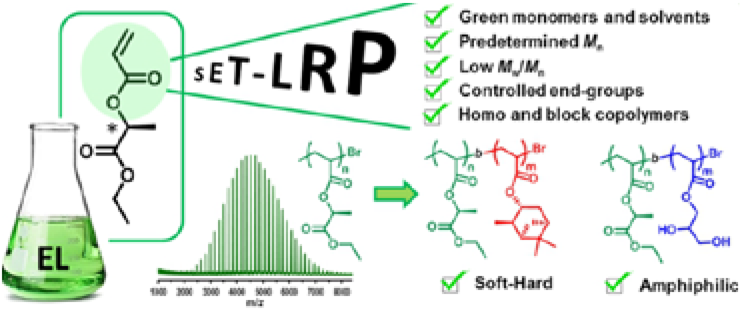

Figure 1: *Ilustration of the structure of modified ethyl lactate polymers and the list of their properties [6].*

Sorbitol as a product of the reduction reaction of the carbonyl compounds such as glucose or fructose contains in total six hydroxyl functional groups. They can undergo intramolecular etherification which leads to the formation of various anhydrohexitols or one particular dianhydrohexitol – isosorbide (1.4:3.6-dianhydrohexitol). This compound contains only two hydroxyl functional groups while one of them creates H-bond inside of its own structure therefore this particular hydroxyl group is more stabilized against nucleophile substitutions for example. This property can be used for selective reactivity of isosorbide. The molecule of isosorbide is crystalline with the melting point around 60-64 °C and its interesting property is a high glass transition temperature of particular its derivatives (T_g > 100 °C). This is caused by the rigid bicycle structure of the compound [7]. One of the most well known groups of isosorbide derivatives are their methacrylates. If methacrylic acid and an appropriate catalyst are used and the forming water is separated from the mixture by azeotropic distillation, for example monomethacrylated isosorbide can be prepared. Both hydroxyl groups can be modified by methacrylic anhydride since this functional derivative of a methacrylic acid is sufficiently reactive. According to the functionality of the modified isosorbide a thermoplastic polymer in the case of polymerization of the monomethacrylated isosorbide and a reactoplastic polymer (resin) via the polymerization of the dimethacrylated isosorbide can be prepared [7,8].

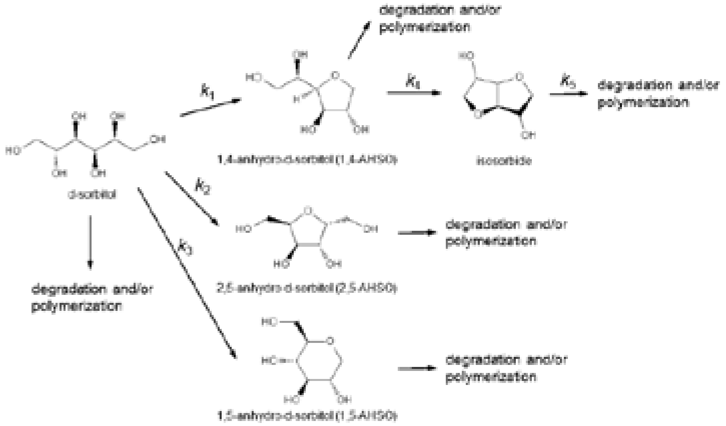

Figure 2: *The reaction pathway of sorbitol dehydration [9].*

These three mentioned groups of polymerizable compounds were already synthesized and characterized in order to get information necessary for their possible applications in a field of coating technologies. Properties important for this kind of usage are viscosity, boiling point or the rate of polymerization. Besides of obtaining some of these properties there have been made particular analyses to obtain structural information in order to confirm the structures of prepared compounds. These analyses involve FTIR spectrometry, volumetric analysis, the refractometry or the polarimetry.

2 Experimental

2.1 *Materials and methods*

For the experimental work sunflower oil (triacylglycerol, I.V. = 121.8 g I_2/100 g purity > 99 %, Fichema s.r.o.); sorbitol (D-glucitol, purity > 90 %, Fichema s.r.o.) as a substrate for the synthesis of isosorbide; and ethyl lactate (ethyl 2-hydroxypropionic acid, purity > 99 %, Sigma-Aldrich) which was used for the preparation of ethyl lactate methacrylate (ethyl 2-(methacryloyl)oxypropionate) were used. Chemicals used for the modification purposes were hydrogen peroxide (concentration 35 % by weight, Fichema s.r.o.), formic acid (concentration 85 % by weight, PENTA s.r.o.), acrylic acid (prop-2-enoic acid, purity > 99 %, Sigma-Aldrich), methacrylic anhydride (2-methylprop-2-enoyl 2-methylprop-2-enoate, purity > 94 %, Sigma-Aldrich). Catalysts used for syntheses were triethylamine (TEA, *N*,*N*-diethylethanamine, purity > 99.5 %, Sigma-Aldrich) and DMAP (4-(Dimethylamino)pyridine, purity > 99 %, Sigma-Aldrich). To prevent a spontaneous polymerization, 4-(Methoxy)phenol (hydroquinone monomethyl ether, purity > 99 %, Sigma-Aldrich) was used as a stabilizer.

The sunflower oil was epoxidized by molar ratio 1:1.4:0.2 (double bonds of oil, H_2O_2 solution, formic acid solution) in order to be further modified. The epoxidation was realized in stirred 2 dm^3 reactor and the conditions were the temperature of 62 °C and the time of reaction 10 hours. After the epoxidation process the mixture was centrifuged, the organic phase containing epoxidized oil was transferred into a round bottom flask (1 dm^3) and the remaining water was distilled. After this process, a pure anhydrous epoxidized oil was added into the solution of acrylic acid, a stabilizer and the catalyst (TEA) in a molar ratio 1:1.5:0.005:0.026 (epoxy groups, acrylic acid, 4-(Methoxy)phenol, triethylamine). This mixture was tempered for 8 hours at 80 °C. After the reaction the remaining acid was neutralized and dissolved into a water phase and separated along with the stabilizer and the catalyst. The remaining water from the organic phase was distilled.

Isosorbide was prepared via the dehydration. Sorbitol was mixed with sulphuric acid (96 % by weight) by the mass ratio 1:0.001 (sorbitol, sulphuric acid). This mixture was kept for 10 hours in a reactor with the temperature of 120 °C. After the dehydration process the acid was neutralized by sodium hydroxide solution (equimolar ratio to the acid) and all formed water was distilled. The prepared crude isosorbide was recrystallized in a methanol twice and the pure product was characterized. The coating precursor material – isosorbide dimethacrylate – was synthesized via the acylation reaction. The reaction mixture consisted of isosorbide and methycrylic anhydride in a molar ratio 1:2 and the stabilizer (0.5 mol. %) with the catalyst (DMAP, 3 mol. %) were added into the mixture. The mixture was aerated during the reaction for an optimal stabilization. The temperature of the reaction was kept at 70 °C. The mixture was neutralized after approximately 48 hours to separate the formed methacrylic acid. After this step, the solution was extracted via water to separate secondary reaction products, the stabilizer and the catalyst. The remaining water was distilled from isosorbide dimethacrylate.

Ethyl lactate methacrylate was synthesized out of ethyl lactate and methacrylic anhydride according to molar ratio 1.6:1.5. The mixture contained the same molar percentage of either the catalyst (DMAP, 3 mol. %) and stabilizer (4-(Methoxy)phenol, 0,5 mol. %) as the methacrylation mixture producing isosorbide dimethacrylate. The temperature of the reaction remained the same as well (70 °C). After approximately 48 hours the formed methacrylic acid was neutralized and the remaining ethyl lactate, the methacrylic salt, the catalyst and the stabilizer were extracted. The product was centrifuged and the remaining water distilled.

2.2 *Results and characterization of the products*

The epoxidation of the sunflower oil was monitored via the volumetric methods such as the acidity value, the iodine value, the saponification value. All these titrations are often used to analyze particularly fats and oils. The selective volumetric method to determine the level of the epoxidation is the oxirane oxygen content (OOC), which is giving the information of the number of epoxy functional group in the analyzed sample. All these parameters have been measured and the results are shown in table 1.

Table 1: *The results of the volumetric analyses of the process of the epoxidation.*

Epoxidation of the sunflower oil			
Parameter	**Unit**	**Oil**	**Epoxidized oil**
Iodine value	[g I_2/100 g]	121.8	17.6
Number of double bonds	[-]	4.2	0.6
Theoretical OOC	[% oxirane oxygen]	7.12	6.3
Acidity value	[mg KOH/g]	0.5	0.5
Saponification value	[mg KOH/g]	191.5	–
M_n	[g/mol]	878.8	937.9

The calculated conversion according to the iodine value and the OOC is above 85 %. The FTIR characterization is shown in the fig. 3.

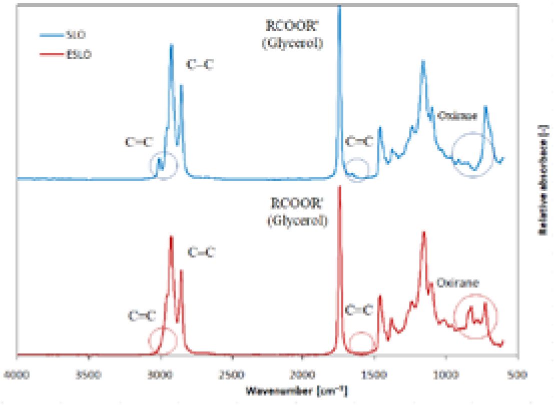

Figure 3: *The comparison of the FTIR spectra of the sunflower oil (SLO) and the epoxidized sunflower oil (ESLO). There are evident the changes in the areas of double bonds signals and the area of the finger print part showing the formation of epoxy functional groups (oxirane) [10].*

The acrylation process modifying the structure of triacylglycerol was monitored by measuring the acidity value and the OOC while both of these values decreased since the epoxy functional groups were substituted by the attacking acidic nucleophiles. The results of the preparation process are summarized in the table 2.

Table 2: *The results of the volumetric analyses of the epoxidized oil's acrylation.*

Acrylation of the epoxidized suflower oil			
Parameter	**Unit**	**Epoxidized oil**	**Acrylated oil**
OOC	[% oxirane oxygen]	6.3	0.7
Acidity value (acid mixture)	[mg KOH/g]	217.8	91.3

The calculated conversion according to the acidity value and OOC is around 90 % considering the theoretical 100 % value of the acidity number being 72.6 mg KOH/g. The FTIR characterization of the product is shown in the fig. 4.

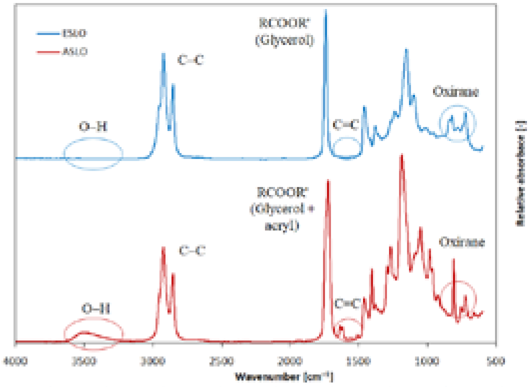

***Figure** 4: The comparison of the FTIR spectra of the epoxidized sunflower oil (ESLO) and the acrylated sunflower oil (ASLO). There are evident changes in the areas of double bonds signals, in the area of the finger print part showing the disappearing of epoxy functional groups and it is also evident the forming of a signal proving the presence of hydroxyl functional groups resulting out of the acrylation process [10].*

The synthesis of isosorbide from sorbitol was also analysed via the volumetric method. The hydroxyl functional groups were reduced tremendously during this reaction due to the formation of intramolecular ether bonds. Also an equimolar amount of the reaction water which was measured via the gravimetric method was formed. The results of the dehydration are shown in table 3.

Table 3: *The results of the volumetric and gravimetric analyses of the process of the sorbitol's dehydration.*

Isosorbide synthesis				
Parameter	**Unit**	**Sorbitol**	**Isosorbide (theoretical)**	**Isosorbide (measured)**
Weight of the water content	[g]	–	433.9	446.5
Hydroxyl value	[mg KOH/g]	1847.8	767.7	768.5

The structure of the reaction's product was verified via FTIR analysis. A comparison of the standard isosorbide sample (99 % purity, Sigma-Aldrich) and the synthesis' product was made. The results are summarized in fig. 5.

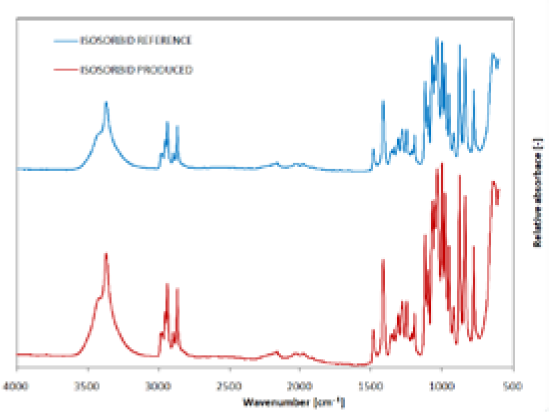

Figure 5: *The comparison of the FTIR spectra of standard and synthesized isosorbide [10].*

The process of methacrylation of the prepared isosorbide was analysed by the measurement of the hydroxyl value. The product was also characterized via FTIR spectrometry. Both results are shown in table 4 and fig. 6. The calculated conversion according to the hydroxyl value is around 80 %.

Table 4: *The volumetric analysis of the methacrylation of the isosorbide.*

Isosorbide methacrylation			
Parameter	**Unit**	**Isosorbide**	**Isosorbide dimethacrylate**
Hydroxyl value	[mg KOH/g]	768.5	167.3

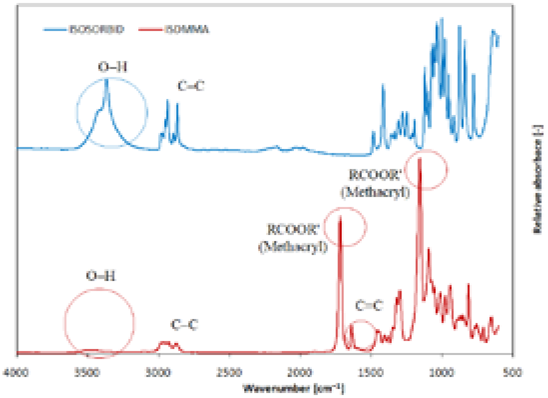

Figure 6: *FTIR spectra of isosorbide and isosorbide dimethacrylate (ISDMMA). There are evident differences in the areas of hydroxyl groups and the double bonds [10].*

Last prepared polymerization precursor was ethyl lactate methacrylate. The methacrylation process was realized by the same way as the one with isosorbide as a substrate. The analyses describing the product were volumetric analysis and the refractometry. The calculated conversion of the reaction from the hydroxyl number is closing to 99.9 %. The results are shown in the table 5.

Table 5: *The results of the analyses of the synthesized ethyl lactate methacrylate and ethyl lactate.*

Synthesis of ethyl lactate methacrylate			
Parameter	**Unit**	**Ethyl lactate**	**Ethyl lactate methacrylate**
Hydroxyl value	[mg KOH/g]	470.5	0.5
Refraction index	[-]	1.4110	1.4336

All the synthesized products were analyzed via the viscometry. The reason for this characterization comes from the fact, that the value of an apparent viscosity is very important for the coating technologies. The results of the viscometry are summarized in the table 6.

Table 6: *The results of the viscometry of synthesized materials.*

Viscometry of the synthesized materials	
Product	**Apparent viscosity at 22 °C [mPa·s]**
Epoxidized oil	426
Acrylated oil	10 600
Isosorbide	*(Solid)*
Isosorbide dimethacrylate	182
Ethyl lactate methacrylate	3

3 Conclusion

Various polymer precursors were prepared from the various renewable biosource materials. The conversion of each product was calculated and the highest conversion close to 99.9 % was reached in the case of ethyl lactate methacrylate. The lowest viscosity, as the main factor for the coating applications, was also measured for ethyl lactate methacrylate (3 mPa·s). However ethyl lactate methacrylate doesn't contain the highest amount of the naturally occurring carbon and the percentage in its case is 55.5 % (of a bio source carbon). The other products reached either lower amount (isosorbide has 42.9 % of bio source carbon) or a higher value (acrylated sunflower oil has 86.4 % of bio source carbon). Acrylated oil reached the highest viscosity out of all products resulting in 10 600 mPa·s.

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Determination of carotenoids in vegetables by HPLC-DAD

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Carotenoids are bioactive compounds that are widely found in nature as natural pigments, synthesised mostly by plants, algae and microorganisms. The main dietary sources of carotenoids are vegetables and fruits. Analysis of these compounds can be challenging because carotenoids are usually structural isomers or differ just in the number of hydroxyl groups. Liquid chromatography coupled with diode array detector or mass spectrometer are the most popular analytical techniques combinations used for the analysis [1,2].

Presented study focuses on quantitative determination of three major carotenoids – lutein, lycopene and β-carotene – using high performance liquid chromatography with diode array detection (HPLC-DAD). Overall, several varieties of fresh and frozen spinach, green peas, carrots, tomatoes and corn were analysed. These vegetables were chosen because they are rich in carotenoids. Analytes were extracted with and without hydrolysis. Separation was achieved using reverse phase C18 column with gradient elution. The eluent was further analysed at the characteristic detection wavelength for each carotenoid. The identification was based on comparison of the retention times and spectra of the measured samples with the standards. Quantification was done using external calibration. To ensure the precision of the method, certified reference material (CRM) was also analysed by the same method.

It was found that the crucial step was the alkaline hydrolysis as almost no free forms of carotenoids were detected. Also, there was nearly no difference between fresh and frozen vegetables in terms of carotenoids content. Such information can be important for food producers. The analysis of CRM showed that the method used is precise and reliable.

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Utilization of waste material from wine production as a binding agent in DGT technique for heavy metals analysis in aquatic systems

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The diffusive gradients in thin films technique (DGT) was first reported by Zhang and Davison in 1994 for determination of zinc in seawater. The DGT devices conventionally employs a diffusive layer consisting of polyacrylamide or agarose hydrogel, sorption layer consisting of appropriate binding agent immobilized in hydrogel and membrane filter as a protective layer. The principle of DGT technique is based on kinetic separation of metal ions, dissolved inorganic or small labile organic complexes from aquatic system according to Fick's First Law and their accumulation in sorption layer. A major advantage of DGT technique is the *in situ* deployment for metal bioavailability and time-integrated measurements. In addition, DGT preconcentrates metal solutes improving problems of contamination and method detection limits. Traditional DGT device for metal analysis comprise a Chelex-100 as binding agent, which can be used for the determination of 24 cationic metals. But for greater comprehensiveness of DGT, many other materials have been employed as adsorbents due to their availability or selectivity for specific chemical species. One way of the recent research progress of DGT technique is utilization of low-cost materials an agricultural by-products as binding agents considering an economic and green-technology approach. For example, banana peels, coffee grounds or baker's yeast have already been used in DGT technique for metal ions determination [1-3].

This study focuses on using of waste material from wine production as possible binding agent in DGT technique. High content of organic matter makes wine-processing waste material an excellent sorbent for removing metal ions from aquatic system because of high content of functional groups (such as carboxylic or phenolic compounds) present in the cell wall of the material. These compounds provide attractions forces to the metal causes their high-efficiency removal. First step of experimental part was preparation of material and its incorporation into agarose hydrogel to prepare binding layer. Wine waste and agarose-waste gel disks were characterized by Scanning Electron Microscopy, Energy Dispersive X-ray Spectrometry and IR spectroscopy. In order to study the binding kinetic and uptake efficiency of metal ions, the agarose-waste gel disks were deployed in 50 ml of a 1 $mg.l^{-1}$ of mixed metal solution (0.05M NaNO3 at pH 5,5±0,1) under constant stirring for 48 hours in triplicate, whereas in different time intervals subsamples were taken for ICP-OES analysis. To assess the elution efficiency the agarose-waste disks were put into 50 ml of a 1 $mg.l^{-1}$ of metal solution under the same conditions. 1M HNO_3 and 2M HCl were used as elution agents. This study has shown good selectivity of wine waste incorporated in agarose hydrogel for Al, Cr, Cu, Fe and Pb determination from aqueous solutions in laboratory deployment, so next experiments with bioadsorbents will be performed.

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ISOLATION OF FERULIC ACID FROM WHEAT BRAN HYDROLYZATE BY ADSORPTION

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Together with maize and rice, wheat accounts for about 90 % of the world's cereal production. Besides other valuable compounds such as wheat germ and endosperm parts, wheat bran remains a major by-product during the milling process [1]. Wheat processing mills can produce up to 50 tons of bran per day. This waste material is suitable for further processing, as it still contains a significant proportion of phenolic compounds, especially ferulic acid. Ferulic acid is contained in bran in the form of feruloylated oligosaccharides [2].

The aim of this work was to develop a method for the isolation of ferulic acid from wheat bran. The research was divided into several segments. The first part of this work was focused on the pre-treatment of wheat bran. Wheat bran was subjected to protein removal to increase the purity of the final product.

The next step in the process was to obtain the wheat bran hydrolysate to release ferulic acid into the solution. This step was realized by alkaline hydrolysis. This process was modified from the process described by Buranov [3]. Hydrolysis of bran was performed by 0,5 M NaOH in stirred, heated reactor with reaction time 4 hours at 50 °C with mixing at 180 rpm. After reaction, the solution was adjusted by the addition of 3M HCl to pH 3. A solid part of the mixture was separated by centrifugation.

Supernatant after hydrolysis was subjected to isolation of ferulic acid by adsorption on amberlite XAD-16. The ratio of adsorbent to supernatant was 1 g to 150 ml. Adsorption was performed at pH 3 for 50 minutes with continuous stirring. Supernatant and adsorbent were further separated by 0,1 mm sieve. The adsorbent was rinsed by a solution of HCl with pH 3.

Desorption of ferulic was the final step. It was made by mixing the adsorbent with 96% ethanol. Desorption was performed at laboratory temperature for 60 minutes with continued stirring at 150 rpm.

Analysis of isolate was carried out by reversed phase HPLC on Shimadzu SCL-10 A with Kinetex 2.6 µm; C18; 100 × 4.60 mm column with 10 % acetonitrile and 90 % acetic acid (1% v/v) mobile phase.

Based on the analyses, the efficiency of the whole process was evaluated. The amount of ferulic acid in the final isolate solution was 676 ± 57 mg/l. This is equal to yield 1,38 ± 0,27 g/kg ferulic acid from deproteinate wheat bran. The isolate does not contain only ferulic acid and solvent. The isolate can contain a variety of substances such as polysaccharides, proteins, salts or other phenolic substances. The main contaminant was identified as proteins (4,38 ± 1,16 g/l).

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Influence of Bioplastics' Biodegradation on Soil Quality

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Over the past decade, the society has brought attention to microplastics. They are produced by various industries and spread across the environment. As they are no longer considered inert (with no further effects on plants and other living organisms) many researchers including us are constantly working to address this situation. In this sense, bioplastics has been brought to a media spotlight. They are presented as an ecological alternative to solve generally plastic related problems, but what is often forgotten, their main advantage might also be their bottleneck.

Majority of scientific articles, focusing on their presence in the environment are limited only on marine and fresh waters [1] and therefore their behaviour in air and soil remains rather unclear. For that reason, a work mentioned in this contribution focuses on negative effects associated with presence of microplastics (specifically poly-(R)-3-hydroxybutyrate bioplastic) in soils as their common receptor. We consider soil to be a recycling facility - carbon is circulated to the atmosphere as carbon dioxide, nitrogen is made available as ammonium and nitrate, and the rest of the associated elements appear in forms required by higher plants [2]. In this sense, during microbial decomposition of carbon-rich compounds, only part of the carbon is released, and the rest remains in the form of soil organic matter. This matter is available to all living organisms and is being constantly reused. Addition of any substrate (in our case a bioplastic) to such an environment will cause an imbalance in this system, which can seriously endanger soil quality and thus plants and living organisms. Therefore, it is essential to focus on their transport and transformation in the environment.

To investigate physico-chemical changes in soil induced by the presence of bioplastic, we combined respirometry, elemental analysis, thermogravimetry and enzymatic assays. Our results suggested a negative effect on soil organic matter and water retention in soil. A phenomenon called „priming effect“ [3] was widely investigated as acceleration as well as retardation of soil organic matter decomposition took place. We registered different influence of selected concentrations of biopolymer on the soil system as well as an influence of soil properties on the course of degradation. Finally, increased enzymatic activities clearly suggested impact of biopolymer presence on the microbial community. Such findings let us conclude, that biopolymer addition leads to long-term impact on a range of soil ecosystem services.

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Contamination of Urban Forest Soils with Potentially Toxic Elements in Brno City, Czech Republic

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Urban forests are an important component of urban ecosystems, given many beneficial services they provide. The quality of the services, however, can be adversely affected by a soil contamination with potentially toxic elements. Despite the high research interest in the contamination of urban soils, the contamination of forest soils in cities remains on a fringe of a scientific interest. The aim of this study was to assess the contamination of urban forest topsoil (0–10 cm) with potentially toxic elements in Brno City, Czech Republic. A total of 50 soil samples were taken and analysed using the triple quadrupole inductively coupled plasma mass spectrometer (ICP-MS/MS) after a decomposition in *aqua regia*. Results were

compared with limits from the Czech Decree No. 153/2016 Coll. on agricultural soil quality. The median values for As, Cd, Cr, Cu, Ni, Pb and Zn were 7.98, 0.22, 30.1, 15.2, 12.3, 25.4 and 62.7 mg/kg, respectively. The limits were exceeded for Cd, Cu, Ni, Pb and Zn in 8, 6, 4, 2 and 16% of cases, respectively. The limits for As and Cr were not exceeded. The results suggested that the contamination of forest soils in Brno is predominantly low. However, the contamination found can potentially adversely affect quality of forest products, such as mushrooms, and local forest ecosystem services.

Assessment of the effect of pasteurization and filtration on the content of selected nutrients in beer

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Beer is a complex chemical matrix that consists of over 450 constituents [1]. Besides polysaccharides, proteins, lipids and organic acids beer also contains nutritionally important substances such as vitamins, phenolic compounds and elements [2]. Phenolic compounds affect the formation of beer haze, redox state, colour, flavour, foam stability and stability of the beer during aging [3]. Mineral content is significantly connected to sensory properties of beer, enzymatic activity during mashing and regulate processes during boiling, cooling and fermentation of wort [4]. B vitamins are water-soluble substances used by yeasts in many biochemical pathways as cofactors. Post-fermentation treatments (e.g. pasteurization, filtration) are important in brewing to achieve stability and durability of the final product and form desired organoleptic properties. However, these procedures may influence the chemical composition of beer [5].

In this study, a total of 28 samples of beer were analysed. They were divided into three groups according to their post-fermentation treatments – NPNF (non-pasteurized, non-filtered), NPF (non--pasteurized, filtered) and PF (pasteurized, filtered). The content of catechin, gallic acid, vanillic acid, coumaric acid, ferulic acid and B group vitamins (B2, B3, B6, B9 and B12) were determined using HPLC-DAD. Elemental analysis of beer was performed by ICP-OES. This research indicates that post-fermentation treatments affect the chemical composition of beer and its nutritional value. Pasteurization and filtration caused a decrease of phenolic compounds content. Filtration influenced concentration of riboflavin and niacin. Another statistically significant differences were identified in the content of elements, specifically Fe, K, Si and Mg.

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NUTRITION PROPERTIES OF WHEAT BRAN PROTEIN ISOLATES

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Proteins are one of the most important group of nutrients, they should contribute to about 10–35 % of the human diet. However, in modern lifestyles, people don't have enough time to intake a sufficient amount of proteins. Fortification of food by proteins is a solution to protein deficiency in the diet. The food can be fortified by animal or plant proteins, which differ in nutrition properties, but also in price. Plant sources of proteins are cheaper and, therefore, more available also for the ordinary people. Wheat bran is one of the significant plant source of proteins. It is a secondary product of wheat utilization and contains approximately 16 % of proteins. About 50 % of the wheat bran proteins are not digestible, as they are part of complicated polysaccharide structures.

Experiments were focused on the development of the protein isolation method. The digestible protein fraction was successfully isolated from wheat bran by pH-shift method. After an alkaline extraction and centrifugation of raw wheat bran, proteins were released to the supernatant. These proteins were then precipitated by adjustment to pH 4. The yield of the isolation process was about 8 % with 90% protein content. Dehydration of the product was performed by lyophilization.

Isolated protein material was subjected to chemical characterization. After lyophilization, the isolated material contained about 8 % of water. Based on the amino acid analysis, it was found, that the most abundant amino acid is arginine, which is important to e.g. for muscles growth and regeneration. Minor components of the isolated material are ferulic acid, which is a very good antioxidant, and glucose, whose content was up to 0,5 %. One of the important characteristics of this material is its mineral content. ICP-OES analysis of the isolated material has shown that it contains only 337 ± 3 mg/kg phosphorus. According to the phosphorus/protein ratio, this material seems to be suitable for the nutrition of people with kidney diseases.

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3D Scaffolds Based on Bacterial Cellulose

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Bacterial cellulose is an extracellular polysaccharide formed as a protective envelope around certain types of bacterial cells. The application of bacterial cellulose has been explored in many areas, such as the food industry, medicine, biotechnology, cosmetics, electronics, and textile industry. Several cultivation methods have been investigated to enhance bacterial cellulose production and decrease its cultivation costs [1].

This work involves optimizing bacterial cellulose by modifying the production medium and subsequently preparing 3D samples of bacterial cellulose to increase its mechanical stability.

It has been found that an increase in bacterial cellulose production can be achieved by modifying the surface of the gas-liquid interface, such as by aeration, the addition of acetate buffer, or oil. Active aeration increased bacterial cellulose production by 235%. Next, the effect of using fed-batch cultivation compared to static batch cultivation was also verified.

In this work, several cultivation strategies have been employed to produce stable mechanical 3D bacterial cellulose scaffolds in-situ during the cultivation of *Komagateibacter xylinus*. The most effective methodologies enabling bacterial cellulose production in the form of cylinders with a height of up to 2 cm were: 1) the static cultivation of *K. xylinus* inside the stable foam [2] or 2) cultivation in Hestrin-Scharmm medium with the addition of polyvinyl alcohol. The morphological investigations have shown that the bacterial cellulose's porosity varies significantly depending on the applied cultivation methodology.

It can be concluded that porosity is an important parameter that affects the absorption of water and the viscoelastic properties of bacterial cellulose scaffolds. The advantage of scaffolds with variable porosity based on bacterial cellulose is their non-toxicity, biocompatibility and the possibility of gradual release of the bioactive substance or drug.

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Wastewater preconcentration method for the determination of legislation limits of cadmium, arsenic, zinc, copper, nickel, chromium and lead employing portable ED-XRF

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Abstract

The chemical laboratories of the Fire Rescue Service of the Czech Republic (hereinafter referred to as CHL FRS) encounter the issue of determining hazardous metals in wastewater or surface water several times a year. The determination of hazardous metals such as arsenic, copper, lead, zinc, chromium, nickel or cadmium can be problematic, since not all CHL FRS have available instrumentation infrastructure such as ICP-OES or ICP-MS, for determination of trace amounts of heavy metals in samples. However, all CHL FRS have a mobile energy-dispersive X-ray fluorescence analyzer Delta X (hereinafter ED-XRF). The detection limits of ED-XRF for above-mentioned elements are at a concentration level of 10 mg/l. The limits for selected elements in the surface water and wastewater are specified in Government Regulation No. 401/2015 Coll. from tenths to several mg/l If CHL FRS are to achieve these values by ED-XRF, it is necessary to use an effective preconcentration technique.

Keywords

Cd, As, Zn, Cu, Ni, Cr, Pb, ED-XRF, preconcentration, wastewater.

Introduction

This study deals with the development and optimization of preconcentration technique, which uses agar as a preconcentration medium. It was found that using this technique, a preconcentration factor of around 400 could be achieved, depending on the analyte of interest. Thanks to this finding, it is possible to determine the concentrations of some hazardous metals at approximately 30 µg/l using the devices of CHL HZS. However, in practical verification, this concentration is around 100 µg/l for selected elements for an optimized workflow and method set in the ED-XRF instrument.

Materials and Methods

The Delta Profesional X mobile device was equipped with a 4 W Rhodium X-ray. Thanks to its good geometry, no vacuum is required inside the device. The device was equipped with an SDD detector (Silicon Drift Detector) equipped with an integrated full VGA camera and the possibility of narrowing the X-ray beam from 9 mm to 3 mm [1, 2].

Chemicals

Agar (Dorapis, Prague, Czech Republic), nitric acid (Penta, Chrudim, Czech Republic), distilled water, ICP multi standard solution IV (Supelco, Darmstadt, Germany) with a concentration of 1000 mg/l in 6,5% HNO_3, ICP multi standard solution VIII (Supelco, Darmstadt, Germany) with a concentration of 100 mg/l in 6% HNO_3, certified reference material (ASTASOL®, Prague, Czech Republic) with a concentration of 1000 mg/l in 2% HNO_3 for metals: cadmium, arsenic, zinc, copper, nickel, chromium and lead.

Optimized workflow

The method was inspired by a study of Kazuhiko Nakano and his team, who analyzed preconcentrated heavy metals in agar utilizing a Rigaku laboratory wave X-ray fluorescence instrument [3]. Their method used a basic pH range. On the contrary, our optimized method achieves very nice results in the acidic pH range of the analyzed solution, pH must be adjusted before analysis (see Figure 1). The sample is then mixed with 70 mg of agar in a double-sided open XRF cuvette. Further, the cuvette is heated on a hot plate at 90 ° C for 30 minutes. The cuvette containing gel was cooled freely to room temperature and then placed in an oven at 90 ° C for 2.5 hours. The gel is then ground for better homogenization of the sample. The measurement takes place directly in a double-sided open XRF cuvette by the ED-XRF Delta X instrument.

Figure 1: effect of pH on preconcentration factor.

Instrument setup

The ED-XRF Delta X settings were optimized for the most accurate identification of the monitored analytes. Thanks to the adjustment of measuring times and user calibration of the device, the detection limits and reproducibility of the obtained data were improved.

Figure 2: calibration for Cu.

Determination of preconcentration factors

Working solutions of 50 mg/l and 100 mg/l were prepared for chromium, nickel, copper, zinc, arsenic, cadmium and lead. These solutions were processed according to the above-stated optimized procedure and measured on a Delta X instrument. For each concentration and element, 5 samples were prepared, which were measured in three technical replicates. Preconcentration factors for the monitored heavy metals are listed in Table 1.

Table 1: Preconcentration factors for the monitored heavy metals.

	Cr	Ni	Cu	Zn	As	Cd	Pb
50 mg/l	317 ± 5	444 ± 7	397 ± 6	326 ± 7	243 ± 8	110 ± 5	90 ± 5
100 mg/l	315 ± 4	445 ± 6	395 ± 5	330 ± 4	249 ± 7	105 ± 5	94 ± 4

Limits of determination of metals

From the determined limits of detection of analytes on the Delta X instrument, it is possible to determine the limit of quantification (hereinafter LD) of these heavy metals, which can be determined by this method of preconcentration, based on previously measured preconcentration factors. To verify these values, solutions with concentrations of 10 µg/l, 50 µg/l, 100 µg/l, 200 µg/l and 500 µg/l were prepared according to the above-mentioned procedure. It has been found that chromium, nickel, copper, zinc and arsenic can be well determined from a concentration of 100 µg/l. In the case of lead and cadmium, it was at a concentration of 200 µg/l. Table 2 shows the comparison of the limit of quantification and the verification of the limit of quantification to the standard.

Table 2: comparison of the limit of quantification and the verification of the limit of quantification to the standard

	Cr	Ni	Cu	Zn	As	Cd	Pb
theoretical LD [µg/l]	31,6	22,5	25,3	30,5	40,7	93,0	108,7
real LD [µg/l]	100	100	100	100	100	200	200

Results and Discussion

Figure 1 shows that this method is applicable in the whole pH range, but does not always reach the maximum possible preconcentration factor. The best values of the preconcentration factor for all monitored metals were found in the acidic pH. The identified preconcentration factors helped to determine the theoretical limit of quantification. These theoretical values were validated as shown in Table 2. The advantage of this preconcentration method is that there is no loss of analytes due to pouring, since the entire preconcentration takes place in a bilaterally open XRF cuvette. Another advantage of this method is low cost of analysis.

Conclusions

Our results show that an optimized work procedure could be sufficient for the needs of the Fire Rescue Service of the Czech Republic. Without the use of preconcentration procedures, chemical laboratory units are not able to use Delta X to analyze low concentrations of metals such as chromium, nickel, copper, zinc, arsenic, cadmium and lead. The detection limits of the preconcentration procedure using agar easily reach the limits that need to be determined according to Government Decree No. 401/2015 Coll. as amended on the values of permissible surface water and wastewater pollution.

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The Effect of Feed Composition On the Metabolome of Edible Insects

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The world population is constantly growing thus the demands for food crops are increasing. [1] This puts enormous pressure on food systems. One of the solutions how to supply the population with enough nutrients and especially proteins is the production of edible insects. In comparison with the common livestock, insects grow faster and the conversion of the feed is fairly higher. Moreover, edible insects farming produces less greenhouse gas, leaves a smaller environmental footprint, and demands on water and space are also lower. [2] These advantages make edible insects a possible challenging sustainable alternative to traditional animal protein sources and make it a possible future common ingredient of food and feed. This potential usage of insects makes this commodity a growing concept and draws the attention of researchers who mainly focus on the impact of rearing conditions such as temperature on biomass gain, feed conversion, and nutritional properties. [3,4] However, there is still a lack of information on the effect of the feed composition on the content of bioactive substances, both desirable and undesirable, which affect the resulting safety and quality of edible insects.

This study we focused on the evaluation of the impact of rapeseed meal added to feed on the composition and quality of the Jamaican field cricket (*Gryllus assimillis)* biomass. For this purpose, metabolomic analysis using ultra-performance liquid chromatography with high-resolution tandem mass spectrometric detection (U-HPLC–HRMS/MS) was chosen as a suitable approach. Using the subsequent multivariate statistical analysis, it was possible to distinguish the tested groups of the Jamaican field crickets according to the composition of the feed. In addition to that, thiamine and sinapine were evaluated as possible markers of the presence of rapeseed meal in the feed fed to the crickets. In addition to that, screening of goitrin in tested samples was carried out. This antinutrient of the rapeseed meal was not detected in any of the analyzed samples.

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SEQUENTIAL CHEMICAL FRACTIONATION AS A TOOL FOR ACCESSING THE ORGANIC MATTER IN BIOCHAR

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This contribution is focused on utilization of a sequential chemical fractionation method for determination of organic matter content, its distribution in biochar and the possible use of biochar as a soil conditioner in agriculture. For these purposes the optimized chemical fractionation procedure was used to reveal the content of organic matter in different biochar samples with different properties (samples with European biochar certification for usage in agriculture) which depend significantly on the temperature used during a pyrolysis of biomass residues in the process of biochar production. In parallel, these samples were also fractionated by classic alkaline extraction to obtain the so-called extractable fraction of organic matter (NOM).

Biochar is one of the important soil conditioners, known for having positive effect on crop yield, soil quality, nutrient cycle and carbon sequestration due to the transfer of organic carbon from it to the soil. However, the effect depends on the properties of the biochar, its doses to the soil, but also on the properties of the soil itself. Surprisingly, some authors point to the fact that biochar does not always have a positive effect on soil, plants or microfauna. Therefore, it is necessary to perform its depth characterization to be able to predicts its role in soil and its optimal application dose [1].

Individual fractions obtained from sequential chemical fractionation as well as NOM samples were characterized by methods of elemental analysis (determination of organic elements content), thermogravimetry (contents of ash, organic matter and moisture). The results showed that the method of sequential chemical fractionation gives higher yields of organic matter compared to classical alkaline extraction. Moreover, the obtained fractions divided according to solubility and strength of binding to residual inorganic matter of biochar can be better characterized by physical-chemical methods, which provides more detailed information about organic matter in biochar and its possible effect on soil properties [2,3].

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SEKCE STUDENTŮ DOKTORSKÝCH PROGRAMŮ

2) Material Science - Sekce analytické, anorganické a materiálové chemie

Preparation and characterization of photocatalytic active thin layers of Tungsten Oxide via „Brick and Mortar“ method

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Water treatment and pollutant degradation became aim of research these days and photocatalytic reactions provides promising results for this application. Most common catalyst for these applications is titanium dioxide. This compound has bandgap varied about 3,2 eV [1] which corresponds to UV light wavelength.

As alternative tungsten trioxide can be used. In comparison with titanium dioxide, bandgap is lower, 2.6 eV [2] which correspond to visible light (≈466 nm).

Suspension of Tungsten Oxide was prepared using powder of tungsten oxide and alcohol solution of acetylperoxotungstic acid (APTA). APTA was used as functional binder „mortar“ for deposition on glass substrate or FTO glass plates. Nanoparticles of tungsten oxide served as „brick“.

Acetylperoxotungstic acid was synthetized by dissolving tungsten powder in 30% hydrogen peroxide solution to form solution of pero-

xotungstic acid. The solution was filtered and added to glacial acetic acid. Final mixture was refluxed and vacuum dried. Yellowish flake powder of acetylperoxotungstic acid was formed. [3]
Prepared precursor suspension was ink-jet printed on Na-Ca glass and FTO glass plates in 1-5 layers. Samples were calcined in various temperature 200 – 500 °C.
Profilometry measurement showed mostly linear increase of layer thickness depends on number of deposition layers varied between 250 – 900 nm thickness.
Dependence of thickness, resp. photocurrent generation on calcination temperature was measured using profilometry resp. chopped linear voltammetry method. Thickness of samples was not dependent on calcination temperature. Photocurrent increased slightly with higher temperature until 400 °C and then started to drop at temperature over 400 °C.
During voltammetry was observed change of color of samples between voltage of 0,25 – 0,75 V. Voltammetry data corresponds with that occurrence with wide curve in that region. In this region layer was reduced and change of color occurred. With increasing voltage over 0,8 V layer undergoes re-oxidation and starts to react to chopped irradiance of light and generate photocurrent. Maximum of generated photocurrent of 1 cm^2 sample (300 µA) was observed between 1,5 – 2 V.

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Perovskite Single Crystals for Energy Conversion of Solar Radiation

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Modern optoelectronic devices (solar cells, photodetectors, LED) are highly dependent on silicon manufacturing processes, which include significant energy consumption (up to 1 000 kWh/kg-Si) and several toxic, flammable and explosive chemicals (e.g. lead, brominated flame retardants, cadmium and chromium) [1].

Most of energy required for pure silicon production is generated from coal-fired plants in China. Environmental effects of such production are still unknown. Therefore, researchers switch focus from silicon-based optoelectronic towards more environmentally friendly and cheaper materials, one of which comes in form of organic-inorganic hybrid perovskites (OIHP). OIHP are solution-processable materials with intriguing optoelectronic properties: tunable bandgaps, large optical absorption coefficient, high electron and hole mobility, long carrier diffusion length and lifetime, low exciton binding energy [2].

These properties enable them to become the heart of various optoelectronic devices such as solar cells, photodetectors and light-emitting diodes. Low energetic demands of perovskite production and wide spectrum of possible applications put them on the hotspot of ever-evolving field of semiconductor physics. Perovskite solar cells are the best example of progress in this field. Their efficiency has been enhanced to over 25.6 % in just a decade, which has surpassed polycrystalline silicon solar cells and is comparable to the monocrystalline silicon solar cells [3].

Perovskites are studied in various dimensions: quantum dots (0D) as promising light emitting material, polycrystalline thin films (2D) as an active layer of perovskite solar cells, and single crystals (3D) as an active layer in both solar cells and photodetectors [4].

Previous studies point out that monocrystalline perovskites show better intrinsic properties than its polycrystalline counterpart. In particular, voids and defect present in polycrystalline materials lead to fast degradation and loss of their optoelectronic properties. In comparison, the monocrystalline perovskites (single crystals) have less defects and are therefore characterized with higher electron and hole mobility, longer carrier diffusion length, higher stability toward ambient erosion, high temperature and moisture [5]. Even though very promising materials, their commercialization is still hindered by the two major obstacles: poor stability compared to silicon semiconductors and presence of lead in their structure. Theoretical part of our work deals with the properties and frequently used synthetic routes of $MAPbX_3$-based perovskite single crystals (X= Cl, Br or I). Possible

future applications and problems which might slow down their commercialization are also discussed. Experimental part of our work describes $MAPbBr_3$ synthesis via inverse temperature crystallization (ITC) method, structural and optical properties of as-prepared single crystals and electrical characterization of Au/$MAPbBr_3$/Au light-sensitive assembly. Its parameters (responsivity, external quantum efficiency and specific detectivity) are calculated based on the spectral and switching (on/off) current responses. The material is further discussed as possible active component for photovoltaic panels and photodetectors.

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Assessment of Degradation of Alkali--Activated Blast Furnace Slag Progress Using the Mercury Intrusion Porosimetry

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Alkali-activated systems (AAS) represent a low-carbon inorganic binder as an alternative to Ordinary Portland cement. The main benefits of AAS are the lower carbon foot-print and economic demands along with the superior durability in aggressive environments contrary to the OPC. The techniques like the determination of compressive and flexural strength are usually used for characterization of degradation processes since their realization is accompanied by the deterioration of these properties. The phenolphthalein technique or advanced instrumental techniques (SEM, XRD) can be used as well. This paper study the possibility of utilization of the mercury Intrusion porosimetry (MIP) to characterize the degradation of alkali-activated blast furnace slag. The degradation processes are dependent on the porosity or permeability of the material, as the penetration of the aggressive media into the internal structure is a key for the reaction to take place. The MIP is a suitable method for the characterization of material porosity, thus it can indicate which material will be more susceptible to degradation than the others. Moreover, it can characterize the changes taking place since the reactions like the decalcification are associated by the increase of the total porosity. Various alkaline activators (sodium water glass, sodium hydroxide, sodium carbonate) were used for alkali-activation of blast furnace slag in the same activator dosage (6 % Na_2O by the slag weight). A binder based on common cement (CEM III) was also prepared for comparison. Water to binder ratio was kept the same (w/b = 0.45). After the initial 28 days of hydration in water the testing samples (mortars with 3 : 1 sand : binder ratio) were immersed in various aggressive environments (CH_3COOH, $MgSO_4$, Na_2SO_4, NaCl, NH_4NO_3 and water for 84 days). Then the changes in porosity were characterized with the dependence on the time of degradation. It was found out that immersion in solutions of acetic acid (pH = 3) and ammonium nitrate (6M) had the most significant effect to both total porosity and the pore size distribution. Immersion in other environments did not cause any relevant changes.

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Hot Humid Air Cooling by Shell and Tube Heat Exchangers

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The processes of cooling gasses by shell and tube heat exchangers for subsequent application in processes of removal of gaseous air contaminants via liquid absorber is the major topic of this work. The aim of the work is to verify both the theoretical computational relations and the theoretical convenience of silicon carbide as a better heat transfer surface material compared with traditional borosilicate glass material characterized by two orders of magnitude worse thermal conductivity. The theoretical computational model using the j factor, the correction factors for the baffles, and the correction for air humidity condensation have been used.
Heat transfer on semi-operating shell and tube heat exchangers with glass or carbide heat exchange surface and baffles is exami-

ned by cooling the air by 50% propylene glycol in tubes having an inlet temperature just above 0 °C. Unfortunately, the coolant inlet temperature cannot be precisely regulated. Coolant flow can be regulated in many steps (max 24 m^3/h), but only laminar flow rates are available. Three-way flow of coolant is used. Air flow can be regulated by frequency changer (max 280 kg/h). Air could be heated up to 90 °C and the humidity of air could be increased by water stream with intensity up to 2,7 kg/h.

In previous experiments, local air heat transfer coefficient was low due to low ventilator power, the potential of the exchanger was not used also because of low temperature, and low humidity. Contrary to the assumption, new experiments with higher inlet air temperature resulted in a higher value of the heat transfer coefficient. The outlet temperature was only slightly higher than when measured without heater. The increase in humidity has a barely measurable effect on the heat transfer from the dry air. The effect of coolant flow on transferred heat is almost negligible. The efficiency of exchangers is very high (91–94 % with carbide and 88–89 % with glass), at higher temperatures even higher (up to 98 % with carbide and 96 % with glass).

Experiments with higher local air heat transfer coefficient are planned. More powerful ventilator will be installed, and the air flow will increase as well as heat transfer coefficient. Although devices increasing the enthalpy of currents have been installed, the potential of the exchangers was still far from being exploited. So, the temperature will be measured directly in the exchanger and the heat exchange in the beginning of the exchanger will be verified. Then, cooling of air will be situated in front of the separation of gaseous impurities from gas into liquid using a scrubber, more effective at lower temperatures. Separation of some pollutants could also take place by condensation in the exchanger at very low temperatures, or high pressures.

Determination of heavy and platinum group metals in rains settling tanks near highway

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Rain settlement tanks which collect and capture rainwater from specified drainage section of a highway D1 (Czech Republic) and in case of an accident with a substance leak, serve to capture the relevant unwanted liquid. In the case of precipitation, the water flows out of it after settling by an overflow into the adjacent water recipient such as river, stream or lake.

Intensive automobile traffic in Czech Republic is the reason for the release platinum and palladium to the environment. These metals form active layer in the automobile catalysts but there is significant leakage into the surrounding atmosphere during their use. Were analyzed water and sludge from rain settlement tanks and soil matrix which is near to rain settlement tanks. In view of the simpler diagnostics and more precise determination of the content of platinum and palladium, it is shown that the soil matrix and sludge are more suitable for studies of metal contents. In the case of the water samples, the sensitivity of the

determination was lower [1].

As a sampling point were chosen based on provided coordinates from organization Transport research centrum in the Brno. Sampling points are placed nearby the dam Švihov lake with distance between points less than 10 km.

Platinum and palladium are moving to the environment due to using autocatalysts in cars. Platinum metals are immobilized on the surface of the catalyst, where they are exposed to changing chemical, physical, and redox conditions that result in wear of the catalysts. [2] This wear leads to a gradual release into the environment during car operation. The obtained results show that the highest accumulation of platinum, palladium and heavy metals occurs in the soil and sediments of the monitoring tanks. [3]

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Modification of Polyvinyl Alcohol to Increase Resistance to Moisture in MDF Composites

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A Macro defect free (MDF) composites are materials consisting of inorganic cement and organic polymer. These materials have extreme mechanical properties that far outperform other cementitious materials and can compete with both ceramic and metal materials. Their mechanical properties are given by the minimization of pores and macro defects in the material and at the same time by mechanical-chemical interactions between cement and polymer. However, it is the presence of the polymer phase that reduce the moisture resistance of MDF composites. The water molecules travel along the structure of the polymer chain to the internal structure of the MDF composite, where the polymer swells and the cement hydrates additionally. This creates internal stresses, secondary defects and loss of mechanical properties. This work aims to increase the resistance of MDF composites to moisture. This can be achieved by increasing the density of the polymer phase by crosslinking the polymer. Maleic anhydride was selected as the crosslinking agent and grafted onto the polyvinyl alcohol polymer chain (GOHSENOL KH-17) in various batches. The amount of grafted maleic anhydride was determined by UV-VIS spectrometry. The measured values were further verified by FTIR spectroscopy and XPS analysis, which confirmed the increasing amount of maleic anhydride in the polymer chain. The resistance of the prepared samples to moisture was analysed using rheology. When the polymeric films were prepared and left under the action of water for 24 hours. Subsequently, the viscosity of the aqueous medium was measured. The highest resistance to moisture was observed in the sample with the highest degree of grafted maleic anhydride. To determine the mechanical properties, test specimens containing aluminous cement, modified polyvinyl alcohol, water and glycerol were prepared by twin-roll mixer. Flexural tensile strength was measured after 7 days. Samples were stored in a dry environment, at 100% humidity and under water. Here, as expected, the highest strength was found for samples stored in a dry environment. The highest strengths (65 MPa) were achieved by test specimens prepared from polyvinyl alcohol grafted with 20% maleic anhydride. When stored in 100% humidity, the strengths decreased by a quarter and when stored in water decreased by almost two third.

Acknowledgement
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CHLORINATED PARAFFINS AS PRECURSORS OF CHLORINATED PROCESSING CONTAMINANTS IN REFINED OILS

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Ester bound 2- and 3-chloropropanediol (2- and 3-MCPD) with fatty acids represent one of the most important groups of processing contaminants, contained primarily in refined oils, fats and products thereof. In recent years, considerable efforts have been made to understand the mechanisms of their formation including identification of their precursors [1,2].

The International Agency for Research on Cancer (IARC) classifies free 3-MCPD as a potential human carcinogen (Group 2 B). Although most of the 3-MCPD present in foods occurs in ester (approximately 85% diester and 15% monoester) bound forms, free 3-MCPD has been shown to be effectively released *in vivo* by the activity of lipolytic enzymes in the gastrointestinal tract. On this basis, in 2016 the European Food Safety Authority (EFSA) established a tolerable daily intake of 2 µg/kg body weight for 3-MCPD and its fatty acid esters, expressed as 3-MCPD equivalent, and in 2020 new maximum levels for 3-MCPD and its esters in oil and fats have been established. The required toxicological data

for the risk assessment of 2-MCPD are not yet available [1-3].
A critical factor for MCPD formation is a chlorine source. Previous studies have shown that, besides inorganic chlorine compounds, organochlorine compounds (present in crude oils and fats mostly as exogenous contaminants), which might decompose under elevated temperatures. However, their structure, origin and potential contribution to MCPD formation is not yet fully understood [3-5].
The aim of this study was therefore to evaluate the potential of one group of lipophilic environmental contaminants - chlorinated paraffins (CPs) - to contribute to this process. These compounds were shown to be possible contaminants in crude oils and fats [6,7] and, therefore, potentially acting as chlorine donors for MCPD formation during oil refining process. For this purpose, laboratory scale model systems representing crude vegetable oil contaminated with CPs were designed and subjected to heat treatment to simulate the deodorization process. Varying degrees of MCPD formation and CPs decomposition were observed in crude palm oil samples. Nevertheless, these results could not yet be replicated in triolein systems and this topic requires further investigation as it uncovers more complex issues with each step.

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Cesium halide perovskite as a material for scintillator detectors

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The enormous research attention given to hybrid organic-inorganic perovskite materials, a result of the unprecedented increase in perovskite based solar cell efficiency, helped to uncover their additional properties such as luminescence. These properties together with the presence of heavy Pb atoms makes hybrid perovskites an interesting candidate materials for radiation detectors. Nevertheless, the research also uncovered some crucial limitations like the susceptibility to external influences (moisture, UV radiation). The conducted studies usually ascribed this to the organic cation in the perovskite structure [1]. This discovery led to an intensive search for inorganic cations which could be used instead of the organic one, for example cesium cation Cs^+. Cesium lead halide perovskites show excellent luminescent properties [2,3] and are interesting candidates for use as scintillators for high-energy radiation detection. Cs perovskites in form of nanocrystal were reported as scintillators for X-ray detection with results comparable or better than the currently commercially used materials [4].

In our work we study Cs perovskites as possible materials for scintillators for detection of electrons (i.e. in electron microscopy). The preparation of nanocrystals by straightforward reprecipitation method is shown as well as characterization of resulting nanocrystals and prepared thin films.

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Dual-focus fluorescence correlation spectroscopy in the study of hydrogel properties

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This contribution describes dependency of nanoparticles diffusion in the agarose hydrogel on the hydrogel concentration. The description of Brownian motion, in this case diffusion coefficient, can be measured by many techniques. Main disadvantage is the need to have a large amount of sample. For fluorescence correlation spectroscopy (FCS) techniques, it is necessary to have only few microliters of nanomolar concentration of the sample, also the confocal volume allows measurement of pretty small amount of the sample.

Unlike the single-FCS method, calibration is not required in dualfocus each time the temperature changes. Based on the optimization of the method and previous measurements, a suitable procedure for measuring the agarose samples was chosen. All data obtained from dual-focus FCS were compared with data measured using single-focus FCS. It was found, nanoparticles in water had very similar diffusion coefficient value. Significant differences were have been seen even at the lowest hydrogel concentration. Some of the autocorrelation curves had different shape compared with autocorrelation curves obtain form single-focus FCS.

For this type of measurement was chosen fluorescent labeled silica nanoparticles of suitable size for the selected hydrogel concentration.

Device for ionic exchange explanation: Organic electrochemical transistor in a fluorescence study

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The organic electrochemical transistor (OECT) is currently, among other things, a sought-after and researched device for its possible application in the field of bioelectronic devices, energy-harvesting technologies, sensing, etc. This transistor is based on the mixed ionic/electronic conductivity of organic semiconductors. These are referred to as supercapacitors. The development of such new organic semiconductors has a key role in expanding the portfolio of applications and especially in adapting their properties to the requirements of individual applications.
The organic electrochemical transistor is based on the principle of doping the entire volume of organic semiconductor with ions from the electrolyte. The degree of this doping is expressed by the value of transconductance, its equation is given by the channel parameters (width W, thickness d, and length L), volumetric capacitance C^*, mobility of charge carriers μ, and the magnitude of the applied voltage (V_G–V_{Th}), equation 1.

$$g_\mathrm{m} = \frac{Wd}{L}\mu C^*(V_\mathrm{Th} - V_\mathrm{G}) \qquad (1)$$

And it is the volumetric capacitance and mobility of charge carriers that are two key material parameters when comparing organic semiconductors from the perspective of electronic applications, and especially when designing these materials for use in OECT-based sensors. The volumetric capacitance of an organic semiconductor together with the mobility of charge carriers are the only two parameters of transconductance that cannot be influenced simply by changing geometric parameters or experimental conditions and govern the transconductance. However, the knowledge and ability to compare these values, especially the volumetric capacitance values, of individual organic semiconductors among themselves provide one of the possible ways to increase the overall sensitivity of OECT.

Although this is a figure-of-merit parameter, and there are a large number of publications, direct experimental determination of volumetric capacitance and understanding of its origin is still insufficient and is based primarily on various assumptions and theoretical models. This work deals with the possibility of studying the ion exchange between PEDOT:PSS and its environment (electrolyte) using two independent measurements (electrical detection using OECT and fluorescence detection using an ion-selective fluorescence probe).

By combining these two methods we would like to contribute to the understanding of the ionic exchange of organic semiconductors and for the most used one, poly(3,4-ethylene dioxythiophene):poly(styrene sulphonate), determine the amount of exchanged ions, thus the volumetric capacitance. The OECT was modified to enable fluorescence measurement, and the potassium ions exchange could be electrically and optically detected. We demonstrate that the fluorescence intensity decreases when the applied gate voltage is increased which corresponds to the assumptions (when is applied gate voltage potassium ions interact within the layer of organic semiconductor and the amount of ions in the electrolyte is decrease). This implies that the volumetric capacitance can be calculated using these two methods when the one calibrate these methods.

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Poly(3-hydroxybutyrate) chain extension in the solution using bi- and trifunctional additives

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For those, who are working with it, thermal degradation of poly(-3-hydroxybutyrate) (PHB) is a well-known phenomenon. What is not very clear is how to overcome this. Upon heating to the temperatures between 170 and 200 °C, which are the typical processing temperatures for PHB, the degradation is manifested by the change in molecular weight and viscosity of the system. Random scission is carried out by cis-elimination mechanism, also called McLafferty rearrangement [1-3]. One of the formed sub-molecules has an unsaturated crotonate end group and the other has carboxylate end group, which is theoretically prone to chain extension reaction which should lead to improvement of the thermal and mechanical performance of this polymer [4].

In this work, four functional groups reactive towards carboxyl group were studied: isocyanate, carbodiimide, hydroxyl and epoxy. Bifunctional reagents: hexamethylene diisocyanate, carbodiimide Stabaxol LF, diethylene glycol, and diglycidyl ether bisphenol A and trifunctional reagents: poly(hexamethylene diisocyanate), glycerol and trimethylol-propane triglycidyl ether were used. For the reactions, PHB was firstly pre-degraded in a laboratory hot press to mimic the degradation state obtained during processing. 5 wt% solution of

PHB in chloroform was prepared and after adding the reagent, the solution was kept under reflux for 6 hours. The reagent was added in two amounts corresponding to 2-fold and 100-fold overdose.

The effect of reagent addition was studied indirectly via change in the solution viscosity and directly by the change of molecular weight and thermal properties of the polymer.

For almost all the samples with bifunctional additives the solution viscosity was increased. The highest effect was observed in the case of diethylene glycol (+13.3 % in the case of 100-fold overdose). In the case of trifunctional additives, there was only slight rise for glycerol and trimethylol-propane triglycidyl ether for 2-fold overdose.

Similarly, the influence on molecular weight measured by gel permeation chromatography was more apparent for bifunctional additives. All trifunctional additives, together with some of the bifunctional successfully increased the number average molecular weight. The increase in weight average molecular weight was observed mainly in the case of 100-fold overdose of hexamethylene diisocyanate and carbodiimide samples, suggesting their potential use for chain extension of PHB during processing.

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Direct Potable Water Reuse through Pressure-driven Membrane Technology

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1. Introduction

The recent drought period from 2014 to 2018 in the Czech Republic have raised concerns about serious consequences of climate change for water availability in this region [1]. Municipal wastewater reuse among others could be a reliable and sustainable solution in cities and regions facing negative effects of drought [2]. In 2019 more than 790 million cubic meters of wastewater were treated, and then discharged into recipients across the Czech Republic [3]. On the other hand, this treated wastewater could be potentially returned to the urban water cycle [4]. This could result into diminished demand for freshwater resources, reduction of wastewater discharged into the environment and potential improvement on surface and ground water quality [5]. It also encloses the full cycle of urban wastewater management from the source through distribution, collection and treatment to its reuse which fully corresponds to the principles of the circular economy [6].

Direct potable reuse (DPR) comes with higher public health risks than indirect potable reuse. To reduce the risk associated with technology malfunction, a multiple barrier approach is needed [6]. The non-membrane multiple barrier approaches are not popular due to its complex maintenance and high operating costs [7]. Therefore pressure-driven membrane technology has an important role in wastewater reuse in several potable water reuse applications across the globe [8]. The dual membrane processes (DMP) show many advantages, e.g. modular installation, lower operating costs and high effectivity [9]. Placed after secondary stage of wastewater treatment plant (WWTP), DMP could be robust, sufficient and cost-effective DPR technology [10]. Microfiltration (MF) or ultrafiltration (UF) is commonly used in the first stage in DMP to remove suspended solids and colloids from the secondary stage effluent [11]. Nanofiltration (NF) or reverse osmosis (RO) is commonly used as a second stage to remove wide range of organic and inorganic contaminants found in urban wastewaters [12]. However it also removes most of dissolved minerals in the water which can have serious negative effects on human health [13], taste of produced water [14] and its corrosivity [15].

This study aimed to evaluate the quality of produced water from UF/RO prototype unit within the context of the Czech drinking water legislative as well as on the assessment of the prototype technological design and usability in the Czech Republic.

2. Materials and Methods

2.1. UF/RO prototype unit

For the needs of this study, an already existing pilot-scale ultrafiltration and reverse osmosis membrane unit developed by ASIO TECH l.t.d. (Brno, Czech Republic) was used. Membrane unit consists of two ISO containers placed directly at the municipal wastewater treatment plant (WWTP). A schematic diagram of UF/RO unit is shown in Figure 1.

In the first container, water from the WWTP effluent flows into 1 m^3 tank. From there, treated water is pumped through UF INGE XL-150 MB 40 (DuPont, USA) module with Multibore® 1.5 capillary membrane (DuPont, USA). Ferric sulphate coagulant is inline dosed in 150 mL/h (68-70 mL/m^3) rate.

Duration of dead-end filtration is 35 minutes, followed by 40 seconds of forward flushing and 50 seconds of backwash. After 40 cycles, chemical-enhanced backwash takes place. Inlet water flow is 2.2 m^3/h with transmembrane pressure difference 0,7/0,5 bar. Permeate flows into 1 m^3 collection tank and concentrate flows directly into sewerage.

UF permeate is pumped to the second ISO container where the reverse osmosis membrane unit is placed with UV pre-disinfection. Antiscalant Vitec 3000 (Avista technologies, UK) is inline dosed in 5 g/m^3 rate into CSM® 4040-BLF low pressure RO module (Lenntech, NL) with four spiral-wound polyamide thin-film composite membranes connected in series. Transmembrane pressure difference is set to 5,5/4,5 bar. Input UF permeate flow is set to 1 m^3/h, recirculation flow rate to 1.2 m^3/h, permeate flow rate to 0.5 m^3/h and concentration flow rate to 0.25 m^3/h. RO permeate is collected in 1.5 m^3 tank and concentrate flows into sewerage.

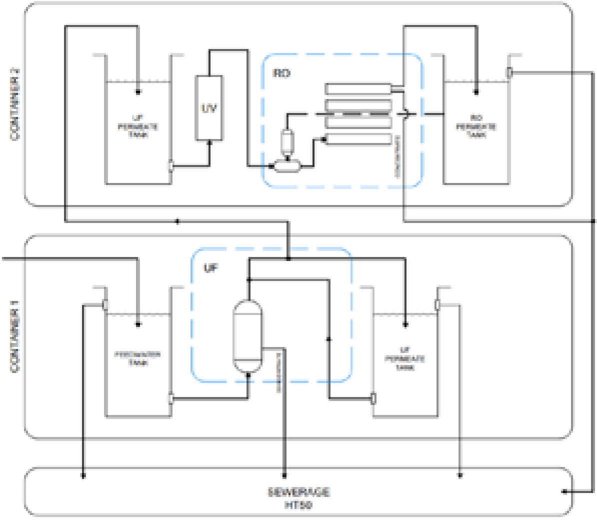

Figure 1 RO/UF prototype unit scheme (simplified)

2.2. Wastewater treatment plant effluent

Municipal WWTP with population equivalent approximately 500 000 has a biological secondary treatment stage designed as nitrification with pre-denitrification and chemical phosphorus removal via Fe(III) and/or Al(III) salts coagulation. Treated wastewater flow at the WWTP is more than 90 thousand cubic meters per day.

2.3. Sampling and sample preparation

Sampling took place across 2 months, from April to June 2021 in accordance with ISO 5667-5:2006, ISO 5667-3:2018 and ISO 5667-14:2014 standards. Samples of WWTP effluent and RO permeate were immediately filtered by a 0.45 µm membrane filter (Pragopor 5, Pragochema, CZ), stabilized by 1 mL of concentrated HNO_3 per 100 mL of the sample and refrigerated at 4 °C for the following analyses.

2.3. Analytical methods

There were 44 physical, chemical and microbiological parameters tested in input water (WWTP effluent) and RO permeate in accordance with the Decree 70/2018 Coll. [16] which determines hygienic requirements for drinking water in the Czech Republic. Parameters such as temperature, pH and conductivity have been measured on site during sampling using a mobile conductometer and a pH meter. Turbidity was measured in accordance with ISO 7027-2:2019, colour in accordance with ISO 7887:2011 and chemical oxygen demand (COD) in accordance with ISO 8467:1993.

Ionic composition of samples has been analysed using mobile analytical sets (Spectroquant®, Merck, CZ) for NH_4^+, NO_2^-, NO_3^-, F^-, Cl^-, SO_4^{2-}, PO_4^{3-}, CN^- ionic species.

For elemental analysis, inductively coupled plasma mass-spectrometry (ICP-MS) technique has been used. Agilent 7500ce was configured with carrier gas (Ar) flow at 1.08 L/min rate and collision gas (He) flow at 5 mL/min. Electron multiplier operated in both pulse and analogue modes, therefore, P/A factor have been calibrated. Both internal and external standards have been used for ICP-MS analysis. Internal standard consisted of 1 mg/L Li, Sc, Bi, Rh, In and a commercially available external standard (NIST SRM 1643f, NIST, USA) has been used.

Microbiological parameters have been analysed using standard cultivation techniques in accordance with ISO 6222:1999 and ISO 9308-1:2014. Nutrient Agar No.2 (HiMedia Laboratories, IN) was used to analyse plate counts at 22 °C and 36 °C. Chromocult® Coliform Agar (Merck, CZ) was used for coliform species.

3. Results and discussion

3.1. Bulkparameters

RO permeate temperature was dependent on weather, respectively on temperature of the feed water from the WWTP effluent. During monitored period, produced water temperature was between 18.0 °C to 24.3 °C. Such temperature is undesirable for the customer. Drinking water temperature is recommended to be from 8 °C to 12 °C [16]. However it is not a big technological issue to cool the produced water to the recommended temperature. Also pH of the produced water was not in the range of the Czech legislative limits (6.5-9.5) [16] but slightly lower between 5.7 to 6.7. It was observed that pH value tends to get lower after UF and RO. The same dependence applies as well for conductivity, when feed water was in the range between 1364 to 1036 µS/cm and the produced water had conductivity only between 65.8 to 108.2 µS/cm due to reverse osmosis treatment step. Organoleptic properties such as colour and turbidity were under limit of detection (LOD) 0.0 mg/L Pt for colour and 0 FNU for turbidity.

3.2. Nutrient's removal

Carbon, nitrogen and phosphorus are considered as essential and limiting elements for microbial regrowth in water [17]. The regrowth of opportunistic pathogens during drinking water distribution after the water treatment poses a significant health risk [18]. To evaluate the risk of microbial regrowth in produced water during its supply and storage, the concentration of nutrients is investigated.

Chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter in water that is oxidable by a strong chemical oxidant [19]. Most of organic matter can be oxidized by strong oxidants (potassium dichromate or potassium permanganate) [20-21]. It is commonly used for indirect measurement of the quantity of organic compounds in water [22]. COD for input water was in the range 5.89 – 7.83 mg O_2/L during monitored period. RO permeate had COD from 0.03 to 0.12 mg O_2/L. COD limit value according to Decree 70/2018 Coll. is 3.0 mg O_2/L [16]. Nitrogen is present in various forms in water, such as ammonia, cyanides, hydroxylamines, elemental, organic, nitrates and nitrites [23]. The EU and the Czech drinking water legislative set limits only for some of these forms, specifically, ammonia, cyanide, nitrates and nitrites [16,23-24]. During monitored period, WWTP effluent exhibited concentration of ammonia in the range from 0.05 to 0.66 mg/L. For RO permeate it was from 0.03 to 0.15 mg/L. The Czech legislative limit value is set to

0.50 mg/L [16]. The removal rates of NO_2^- and NO_3^- reached 26.4 % and 74.4 %. Cyanides had not been detected in monitored period. Phosphorus, as mentioned above, is considered as a limiting element for microbial regrowth, too. However it is not considered as a risk for human health in concentrations found in samples. The removal rate for PO_4^{3-} species was 54.8 % which is quite below the expected 95-98 % from the literature [25]. It may be caused by lower RO transmembrane pressure used during the experiment which on one hand declines the RO membrane performance but on the other hand reduces an operation costs for sufficient RO membrane performance.

3.3. Other ionic species

Concentrations of other ionic species specifically chlorides, fluorides and sulphates were determined regarding to their legislative limits. For chlorides the Czech legislative limit is set to 100 mg/L [16]. Observed concentrations in RO permeate were in the range from 9.50 to 15.90 mg/L with 93.2 % removal rate which corresponds to the values reported in the literature [25]. Fluorides, similarly to ammonia, had poor removal rate around 5.3 %. However, the legislative limit 1.5 mg/L [16] has not been exceeded during monitored period. Concentration ranged from 0.10 mg/L to 0.54 mg/L. Among monitored ionic species, sulphates have had the largest fluctuation in terms of the feed water concentration. Concentration range in feed water was observed from 121.0 to 772.0 mg/L with mean value 207.0 mg/L. Removal rate 84.0 % was lower than expected. Nevertheless, drinking water limit value 250.0 mg/L [16] has not been exceeded.

3.3. Macroelements removal

The first group of elements is macroelements. These are elements with high expected concentrations namely Na, Mg, Ca and K. These elements occur in water mostly in their ionic forms as singly charged ions such as Na^+ and K^+ or they occur in doubly charged ions such as Ca^{2+} and Mg^{2+}. Ionic charge pre-determines their removal rate – the bigger the charge is, the bigger is the removal rate. This assumption is based on dielectric exclusion model for NF and RO membranes [26-27]. Proof of this model has been clearly observed in our experiment, where removal rates of singly charged Na^+ and K^+ ions have been roundly 87 % for both ions and for doubly charged Ca^{2+} and Mg^{2+} were removal rates same as well, exactly 99.7 %. Observed concentrations were well below limit values. Although such low mean concentrations – 10.44 mg/L for Na, 3.37 mg/L for K, 0.26 mg/L for Ca and 0.04 for Mg are too low for the long-term human consumption, because of its potential health risks [13]. Therefore an adequate post-treatment remineralisation technique needs to be implemented to the unit technological design. Usually a carbon dioxide acidification of the permeate, followed by lime or limestone dissolution is used to enrich permeate with Ca^{2+}, Mg^{2+} and CO_3^- ions to required amount and mutual ratio [28]. This technique could possibly solve the slightly lower pH of permeate, too.

3.4. Microelements removal

The second group of the elements is metals and metalloids that occur in water in low concentrations, well below 1 mg/L. There were 19 microelements monitored, namely Be, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Pb and U. Legislative limits [16] are set for 15 of them, excluding V, Co, Zn and Mo. Observed concentrations of analysed microelements in feed water and RO permeate are shown in Figures 2, 3 and 4. None of analysed microelements surpassed legislative limits during the monitored period. Furthermore, some of the analysed elements were below the LOD in the RO permeate as shown in the Table 1.

Table 1 Analysed elements below the ICP-MS LOD

Element	LOD [μg/L]	Element	LOD [μg/L]
Be	0	As	0,012 1
Al	0,068 7	Se	0,076 1
V	0,001 91	Mo	0,002 61
Cr	0,029 0	Ag	0,005 59
Mn	0,060 0	Cd	0,000 159
Fe	0,051 0	Sb	0,002 83
Co	0,005 90	U	0,001 84

The worst retention has been observed for boron, only 4,0 %. Removal of boron is greatly dependent on the pH and operating pressure [29]. The lower the pH is, the lower is the retention. The same dependence applies to operating pressure. Boron occurs at the given pH mainly in nonionic form as $B(OH)_3$. Nevertheless, boron has been inside the legislative limit for the drinking water and it was even in concentrations similar to those in the Czech water supply network [23].

On the other hand, iron and manganese have been removed with 97,0 % and 99,1 % retention. Nickel, zinc, molybdenum, antimony, lead and uranium have been removed almost entirely. Retention coefficients could not be credibly calculated for elements with permeate concentrations below LOD, such as Co, Cu, As, Cd, Sb and U.

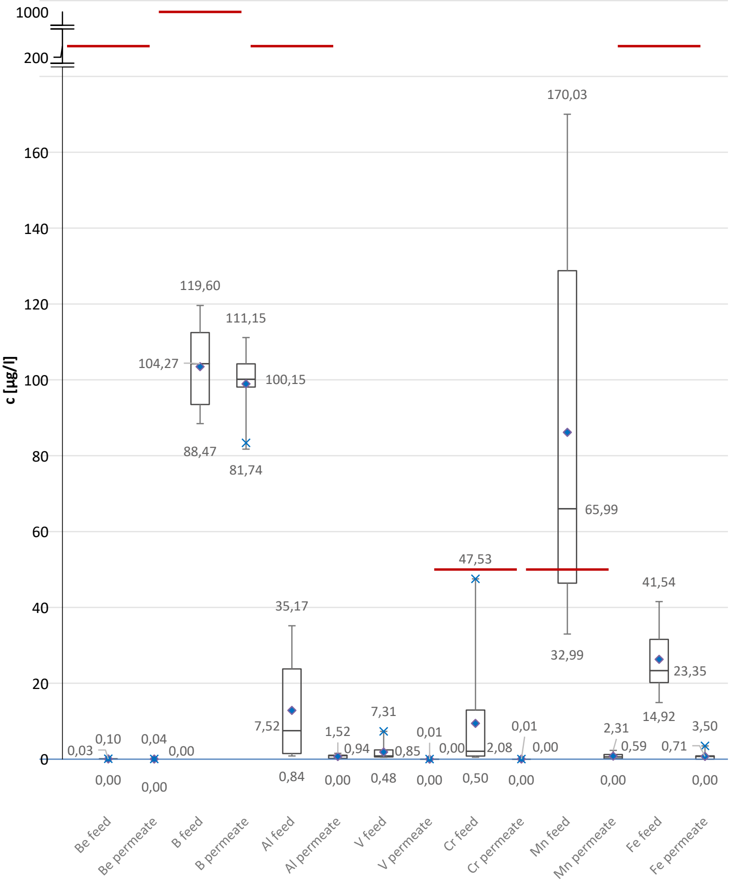

Figure 2 Observed concentrations of Be, B, Al, V, Cr, Mn and Fe in feed water and RO permeate with labelled minimum, maximum and median values. Red lines indicate legislative limit values according to Decree 70/2018 Coll. Blue crosses indicate outliers and blue squares indicates arithmetic mean.

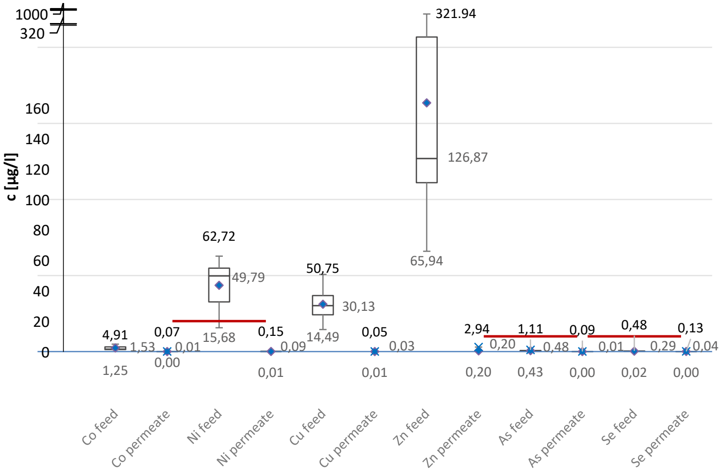

Figure 3 Observed concentrations of Co, Ni, Cu, Zn, As and Se in feed water and RO permeate with labelled minimum, maximum and median values. Red lines indicate legislative limit values according to Decree 70/2018 Coll. Blue crosses indicate outliers and blue squares indicates arithmetic mean.

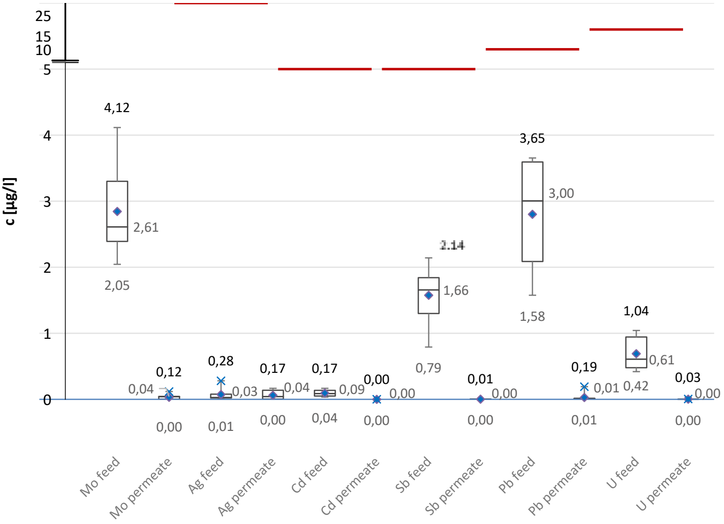

Figure 4 Observed concentrations of Mo, Ag, Cd, Sb, Pb and U in feed water and RO permeate with labelled minimum, maximum and median values. Red lines indicate legislative limit values according to Decree 70/2018 Coll. Blue crosses indicate outliers and blue squares indicates arithmetic mean.

3.5. Microbiological parameters of permeate

Number of viable bacteria in water is used to assess the health risks for human consumption [24]. Monitoring of these parameters is crucial for DPR technologies and tells us whether the multiple barrier approach could effectively prevent an entry of harmful microorganisms from highly polluted wastewaters to drinking water supply chain [30].

In the monitored period, these microbiological parameters were analysed: plate counts at 22 °C and 36 °C, overall coliforms including species such as *Klebsiella, Enterobacter, Citrobacter, E. Coli 0157:H7, E. coli*, Gram negative bacteria*, Salmonella, Shigella* and *Yersinia*. None of these parameters exceeded the Czech legislative limit values. Plate counts were in the range from 6 to 196 colonies per mL at 22 °C and from 3 to 17 colonies per mL at 36 °C, legislative limit is 200 colonies per mL at 22 °C and 40 colonies per mL at 36 °C. As you can see, RO permeate is not sterile and some of the bacteria could be transferred through RO membrane because of its compromised integrity [30].

Overall coliforms including named species were not detected in permeate. Feed water contained thousands or tens of thousands of colonies per millilitre of each analysed group of bacteria.

3.6. Applicability of DPR technologies in the Czech Republic

Fundamental question that needs to be raised is whether the use of DPR technologies is meaningful in medium-sized landlocked countries in temperate climate zones such as the Czech Republic. The quality of produced water is not going to be a hindrance, as shown by the results of physical, chemical and microbiological analyses.

Despite recent droughts, the Czech Republic ranks among the countries without any major shortages in drinking water supply [3]. Hence, there is no acute need for the use of DPR technologies nowadays. Despite that, DPR technologies are economically demanding [31] and compared to current potable water solutions economically disadvantageous. In addition, so-called ‘yuck factor’ [32] (a problem of public DPR acceptance) could cause loss of public trust in drinking water quality which tends to be fragile.

4. Conclusion

This study investigated the potential use of the pilot-scale UF/RO prototype for DPR in accordance with the Czech drinking water legislation. There were 44 physical, chemical and microbiological parameters monitored across 2 months period. The experiment showed that none of the analysed parameters exceeded legislative limits. However high temperature, low mineralisation and slightly lower pH of permeate may hinder the potential for prototype implementation into practice. Accordingly, minor technological improvements have been proposed, such as remineralisation technique. After the implementation of adequate remineralisation technique, RO permeate quality would not be an obstacle to its implementation into practice, as physical, chemical and microbiological analyses shown.

On the other hand, what actually hinders the implementation of the protype, are its economic demands and public DPR acceptance. In addition the Czech Republic has no major shortages in drinking water supply currently. Therefore there is no acute need for the use of DPR. Nevertheless the future can bring situations, when DPR could be relevant for the Czech Republic, too.

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Preparation and characterization of highly hydrophobic coatings on magnesium alloy AZ91

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Magnesium and its alloys have many interesting properties and thanks to them it can be used in many applications (transport industry, medicine etc.). Disadvantage of these materials is their high corrosion rate. For this reason, there is an effort to achieve high corrosion resistance through different modifications of magnesium and its alloys. In recent years the superhydrophobization of the surface seem to be an attractive solution for this question. This type surface modification minimalize contact between the surface and water.

In this diploma thesis the superhydrophobic surface was created on the magnesium alloy AZ91. The first step included pretreatment of AZ91 surface by etching in solution of $SnCl_2$ or $ZnCl_2$. Next step was superhydrophobization in the ethanolic solution of stearic acid.

The surface morphology and elemental analysis of the superhydrophobic coating were explored by use of scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS). The adhesion properties of the coating on the AZ91 were analysed by means of scratching test. Contact and sliding angles were measured for superhydrophobic coatings. Electrochemical characterization of the coatings was determined using potentiodynamic polarization (PD) and electrochemical impedance spectroscopy (EIS). Finally, the analysis of composition and the functional groups was made using Fourier-transform infrared spectroscopy (FTIR) and the phase composition analysis was performed using X-ray diffraction (XRD).

The results show that the coatings prepared by etching did not lead to good corrosion properties, even though the value of contact angle was about 150°. The reduction of corrosion resistance could be caused by not obtaining required surface morphology or insufficient binding of stearic acid in the form of stearate to the sample surface.

Characterization and Optimization of Novel Polymer Composite PEDOT:DBSA for Bioelectronic Applications

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Organic conducting materials represent a very promising alternative to traditionally used inorganic materials, especially in the fields of medicine and personalized treatment. Their unique properties give rise to many interesting next generation bioelectronic devices for various applications. PEDOT (poly(3,4-ethylenedioxythiophene)) doped with PSS (poly(styrenesulfonate)) is an organic polymer, which currently plays a main role in such applications, mainly because of its good processability and thermal and electrical stability. Nevertheless, recent research has shown minor cytotoxicity of the material attributed to the PSS moiety, whose sulfonate groups restrict cell adhesion. Therefore, the aim of this work was to introduce new conducting materials based on PEDOT, with improved properties compared with PEDOT:PSS. For this purpose, PEDOT doped with DBSA was studied.

This material proved its potential for bioelectronics, since it showed electrical properties comparable with PEDOT:PSS and other commonly used materials. However, two other key parameters limit the use of any material for such applications, stability in aqueous media and biocompatibility. In this study, PEDOT:DBSA has shown better long-term stability than PEDOT:PSS, which was further improved by cross-link. Cross-link also led to enhanced attachment of the material to the substrate and complete resistance against dissolution. Furthermore, the positive effect of the DBSA dopant on the materials biocompatibility was proven using standard MTT assay. Cells grown on pristine and also cross-linked material have shown almost twice as high relative viability compared with PEDOT:PSS and other commonly used organic semiconductors. This indicates that PEDOT:DBSA exceeds the properties of PEDOT:PSS and has a great potential for use in bioelectronic devices.

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Novel Highly Stable Conductive Polymer Composite PEDOT:DBSA for Bioelectronic Applications

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Organic bioelectronics presents a potential revolution in medicine as it holds the promise of personalised treatment. Conducting polymers have emerged as an excellent tool for bioelectronic devices due to their unique properties. Among them, PEDOT:PSS (poly (3, 4-ethylenedioxythiophene) doped with poly(styrenesulfonate)) has become increasingly selected as a material of choice for various applications thanks to its superior properties, especially excellent solution processability, electrical conductivity or stability. However, as recent research has shown, there are still limiting disadvantages of this material, light cytotoxicity and inadequate biocompatibility. These problems are attributed mainly to the presence of PSS moiety, which restricts the proper contact between material surface and living cells. Thus, the aim of this work was to propose a novel material with enhanced properties compared to PEDOT:PSS. To reach this, PEDOT doped with DBSA molecule was studied. It was proved that dopant DBSA itself has a positive effect on the biocompatibility of the polymer. Furthermore, the modification of material by cross-link provided excellent long-term stability. However, for bioelectronic applications, appropriate electrical properties present another key factor of essential importance. The electrical conductivity of pristine PEDOT:DBSA is of the same order as that of PEDOT:PSS. Even OECT based on this material showed behaviour typical for a p-channel transistor working in the depletion mode, with μC^* value comparable to other commonly used materials. But its cross-link had a significantly negative impact on electrical properties. This drawback was overcome using sulphuric acid post-treatment. The OECT based on such post-treated cross-linked material showed μC^* value even higher than pristine polymer. This shows the potential of PEDOT:DBSA, modified or not, for bioelectronic applications.

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SYNTHESIS OF NEW PARA-BIS(2-THIENYL)PHENYLENE DERIVATIVES AS MOLECULAR PHOTOSWITCHES CANDIDATES

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Light is a noninvasive exogenous stimulus with high spatiotemporal resolution and precise remote on demand regulation of wavelength and intensity. Moreover, it does not cause contamination of samples. Thanks to these abovementioned characteristics, light can be considered as ideal candidate for *in situ* chemical and biological manipulation; it can be for example used to control the activity of biomolecules inside living cells selectively and specifically [1]. Molecular photoswitches are promising to serve for the above purpose as they undergo a characteristic change of their chemical structure upon light irradiation and consecutive photon absorption causing change to their respected chemical, physical, electrical and optical properties. This unique character together with wide range of possibilities for structural modifications on molecular level enables design and synthesis of new advanced molecular photoswitches tuned for specific applications [2].

This work is focused on synthesis of new para-bis(2-thienyl)phenylene derivatives with dodecyl and adamantyl-ethyl side chains. The basic trimer was prepared by the means of Kumada and Stille cross-coupling reactions via both conventional and microwave-

-assisted way. Another important goal of the research was the incorporation of the carbonyl functional group into the structure of the prepared trimer. This procedure was optimized through several synthetic approaches in the form of nucleophilic aromatic substitutions and nucleophilic additions. The carbonyl compound is a perfect intermediate for preparation of series of new derivatives by the means of condensation reactions; in this study a condensation with selected group of amines – aniline, 1-naphthylamine and 2-aminobenzothiazole was chosen. The imine C=N double bond is presented in the structure of the final products, thanks to which they are able to undergo a reversible *trans* to *cis* photoisomerization upon irradiation with 365 nm light. With consecutive relaxation in the dark, this whole process can be repeated with no significant sign of photodegradation. With the respect to these characteristics, prepared molecules are promising candidates for the applications in the field of molecular photoswitches.

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Key words

Molecular photoswitches, photoisomerization, imines, condensation reactions, organic synthesis.

Hydrogels with Gradient Properties

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Hydrogels are widely implemented materials of current importance due to their tunable and well customized functionality, reversibility, flexibility and biocompatibility. Unfortunately, homogeneous hydrogels cannot always satisfy the sophisticated demands of material engineering. For this reason, recently, there is a growing necessity in developing the materials with gradient properties for different application fields such as water treatment, tissue engineering, pharmacy, cell biology etc. Particularly, the gradient hydrogel has a progressive change in structure and function [1], that enables not only to mimic complex and anisotropic structures and control targeted release of active molecules or cell interactions, but also leads to more precisely adjustable application properties (transport, mechanical, separation).

Gradient hydrogels can be generated via various methods, providing either sharp or continuous physical and chemical gradients. Nevertheless the range of existing preparation methods is not universal. Each method is suitable for specific materials, requires certain equipment and has its own advantages and shortcomings. It should be noted, that common techniques for soft-material characterization are designed to analyze homogeneous samples. Hence, in the case of gradients, they must be adapted not only to inhomogeneous structures, but also to the copresence of chemical components or physical properties that can differ in satisfying the requirements for the use of a specific analytical technique [2]. Therefore the aim of presented study is to optimize selected preparation methods and characterization techniques, intended for gradient materials, and to analyze the main factors affected the creation and spatial distribution of the final gradient.

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Synthon

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