BIONICS – INSPIRATION IN NATURE FOR NEW ADSORBENTS DESIGN AND THEIR POTENTIAL IN PHARMACEUTICALS REMOVAL

BIONIKA - INŠPIRÁCIA V PRÍRODE PRE NOVÉ ADSORBENTY A ICH POTENCIÁL V ODSTRAŇOVANÍ FARMACEUTICKÝCH LÁTOK

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Abstract: According to a new definition, zeolites are clathrates or inclusion compounds, able to host various guest substances in their versatile structure. The most industrially used natural zeolite is clinoptilolite. Materials designed using components derived from biological sources such as collagen, chitosan, three-dimensional polymeric hydrogels like surfactants, alginate, plant proteins and polysaccharides have been investigated thoroughly for use in environmental remediation. These biomaterials possess some advantages over their synthetic counterparts, such as their capability to be environmentally viable and thus recognized by the living microenvironment. Using mostly biomimetic sol-gel method, we also prepared the octadecylammonium (ODA surfactant) coated zeolite, chitosan and alginate composed zeolites as well as lately iron oxihydroxide immobilized zeolite, which showed improved adsorption properties to broaden range of pollutants. Prophylaxis antibiotic (cefazoline) removal using the aqueous solutions and stationary (batch) system at laboratory was applied to compare several adsorbents like native, ODA- and carbonized zeolite (clinoptilolite tuff), montmorillonite, German commercial GEH, active coke and beringite. The best performance in cefazoline uptake proved especially carbon rich adsorbents and ODA-zeolite.

Keywords: biomaterials, zeolite, clinoptilolite tuff, pharmaceuticals, water pollution, cefazoline, biomimetics

Abstrakt: Podľa novej definície sú zeolity klatráty alebo inkluzívne zlúčeniny, schopné vo svojej rozmanitej štruktúre zachytávať rôzne hosťujúce látky. V priemysle najviac využívaným zeolitom je klinoptilolit. Pri environmentálnej remediácii sa spravidla využívajú materiály odvodené resp. získané z biologických zdrojov ako kolagén, chitosan, trojrozmerné polyméme hydrogély ako povrchovo aktívne látky (tenzidy), algináty, rastlinné proteiny a polysacharidy. Oproti ich syntetickým analógom, majú prírodné produkty mnohé prednosti, pretože sú kompatibilné a znášanlivé s biotou. Pomocou biomimetickej sol-gélovej metódy sme aj my v laboratóriu pripravili ODA (oktadecylammónny) – zeolit, chitosan – a alginátový kompozit so zeolitovou matricou ako aj FeO(OH) – zeolit, ktoré sa prejavili k špecifickým polutantom vôd s vyššou účinnosťou. V podmienkách stacionárneho režimu sme overili účinnosť odstraňovania antibiotika cefazolínu z modelových roztokov na niektorých adsorpčných materiáloch ako prírodný, ODA- a karbonizovaný zeolit (klinoptilolitový tuf), montmorillonit, granulovaný oxohydroxid GEH, aktívne uhlie a beringit. Najvyššiu kapacitu k cefazolínu prejavili obzvlášť uhlíkaté adsorbenty a ODA-zeolit.

Kľúčové slová: biomateriály, zeolit, klinoptilolitový tuf, farmaceutiká, znečistenie vôd, cefazolín, biomimetika

INTRODUCTION

Current industrial adsorbents consist of a broad variety of chemical substances and different geometrical structures. In today's society also environmental requirements are becoming of great importance since there is an increased interest in the industrial use of renewable resources. "*Green*" designates in a novel advanced adsorbent fabrication to adopt from a Nature bioinspiring (basically polysaccharide) materials and by the synthesis to mimic the exceptional features of natural species with their impressive behaviour (Biomimetic Materials Chemistry. 1996, Behrens and Bauerlein, 2007).

Actually, biopolymers present fascinating templates for creating bioinorganic materials, e.g. starch that is stored in plants, meets all the required criteria. Combined with the traditional chemical techniques, the biopolymer assisted synthesis may prove promising route how to prepare a „*new generation*"of biomineral adsorbents guiding oriented growth of organic substances on the surface. Some interesting remarks of living cells base on excretion of biogenic surfactants or specific biopolymeric acids like alginic acid and their salts. Alginate is a copolymer of the isomers mannuronic and guluronic acids enabling the dense packing of submicrometer-sized particles in suspensions in order to enhance their colloidal stability (Biomimetic Materials Chemistry. 1996, Chmielewská, Xu, 2015, Behrens and Bauerlein, 2007).

To promote the zeolite performance and to prepare more effective adsorbent for specific post-treatment processes, flexible component, i.e. alginate with a rigid component (powdered) zeolite was crosslinked using Fe(III) and Ca(II) ions. While incorporated Fe(III) cations in new adsorbent were responsible for electrostatic interactions "oxyanionic pollutants vs. biopolymer pelletized zeolite", Ca ions were responsible for exchange of metallic cations. Finally, such as alginate-zeolitic adsorbent showed during examination its adsorption capacity towards metallic pollutants considerably enhanced (Chmielewská, Xu, 2015)

Using the hydrophilic, expandable and permeable hydrogels with low interfacial tension for the novel adsorbent synthesis, substances which resemble to soft living tissues, is another excellent example for advanced surface treatment strategy how to enhance clinoptilolite tuff performance. Various aspects regarding above mentioned surfactant octadecylammonium (ODA) clinoptilolite have been reviewed and highlighted in literature (Chmielewská, Xu, 2015, Altshuller,d 1999, Favret, Fuentes, 2009.)..

Iron oxides are effective, low cost adsorbents for heavy metals and radionuclides removal, respectively. Their sorption process is mainly controlled by complexation. When their particle size is reduced to below 20 nm, the adsorption capacity increases by 10 to 100 times, suggesting a „nanoscale effect". While nanomaterials embedded in a solid matrix like zeolite may expect minimum release into the environment, research is needed to develop simple, low cost technique to immobilize nanomaterials without significantly impacting their adsorption performance. Based upon the encouraging results of Slovakian natural clinoptilolite producer, achieved recently, and simultaneously necessity to immobilize a nanosized iron oxide onto solid surfaces, we study various routes how to prepare environmentally viable as well as economically feasible adsorbent with zeolite matrix (Altshuller,d 1999, Favret, Fuentes, 2009).

EMERGING CONTAMINANTS IN ENVIRONMENT

Pharmaceuticals, as today called emerging contaminants (ECs), can enter the environment by a number of pathways and can be further distributed to various environmental media. One prominent pathway could be the use of wastewater sludge or waste water for field fertilization and irrigation. In water environments, a large variety of these compounds and their metabolites have been detected and also soil could be an important source of water contamination (Petrie et al. 2015, Sabourin et al., 2012, Ort et al. 2010 a, Miao et al. 2005).

The presence and distribution of pharmaceuticals in the soil via land application are far from known because of a lack of appropriate methodologies. Liquid chromatography combined with mass spectrometry (LC-MS) or with tandem mass spectrometry (LC-MS/MS) is popular techniques currently being used in pharmaceutical analyses. The latter allows detection of extremely low concentrations (ng/L or ng/g) of these compounds in various complex liquid or solid matrices.

The presence of ECs in the environment is mainly attributed to the discharge of treated wastewater from water treatment facilities. Conventional secondary processes (activated sludge and trickling filters) represent the most extensively used and studied processes. An increase in drug use may be anticipated during music festivals, public holidays, major sporting events and by students during exam periods (Petrie et al., 2015, Sabourin et al., 2012, Ort et al., 2010, Miao et al., 2005) However, above mentioned bioprocesses are not designed to remove ECs resulting in their discharge to receiving surface waters including rivers, lakes and coastal discharge. E.g. during anaerobic digestion, biosolids (or treated sludge) are generated. These are often applied to agricultural land as a fertiliser in many countries. Despite lengthy digestion (in avarage 4 weeks) and outdoor storage for up to six months following treatment, some ECs have shown to persist.

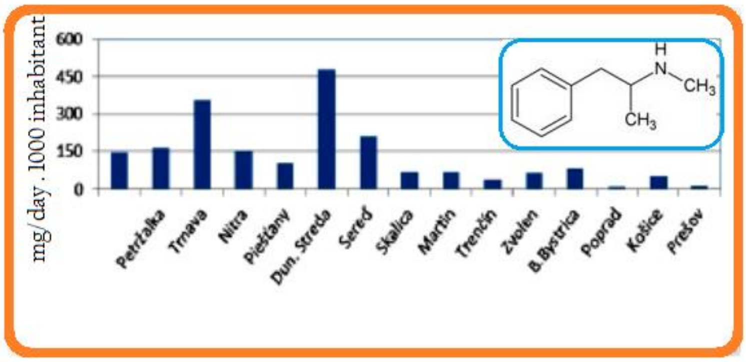


Fig 1 Methamphetamine consumption in Slovakian towns (Mackuľak et al., 2014)

The presence of these chemicals in the environment is more serious considering that they do not appear individually, but as a complex mixture, which could lead to unwanted synergistic effects. Parent chemicals are often excreted from the human body also with a number of associated metabolites. As an example, the ibuprofen is excreted as the unchanged drug. Approximately 70 pharmaceuticals, belonging to a variety of therapeutic classes, have been reported only in UK waters (Petrie et al., 2015). The analgestic tramadol has been observed in river water at the highest concentration up to a maximum of 7731 ng /L (Petrie et al., 2015, Heal et al., 2013). The hallucinogen 3,4-methylenedioxy-N-methylamphetamine (MDMA) and the stimulant cocaine have been observed in river water at concentrations of 25 and 17 ng /L, respectively (Petrie et al., 2015, Gottschalk et al., 2009, European Chemicals Bureau, 2014, European Protection Agency, 2014). To date more than 200 different pharmaceuticals alone have been reported in river waters globally, with concentrations up to a maximum of 6.5 mg /L for the antibiotic ciprofloxacin (Petrie et al., 2015, Heal et al., 2013, Gehrke et al., 2015).

Methamphetamine (locally called pervitin) is an extremely addictive stimulant drug that is chemically similar to amphetamine (Mackuľak, T. et al. 2014). It takes the form of a white, odorless, bitter-tasting crystalline powder. Methamphetamine is taken orally, smoked, snorted, or dissolved in water or alcohol and injected. Smoking or injecting the drug delivers it very quickly to the brain, where it produces an immediate, intense euphoria. According to monitoring provided by the national water authorities and researchers, consumption of this chemical in Czech and Slovak Republics belongs to the highest in the world (Fig 1) (Mackuľak, T. et al. 2014).

AN ATTEMPT TO REMOVE ANTIBIOTICS BY POLISHING OR POSTTREATMENT OF WATER USING THE ADSORPTION

Nevertheless, removal of environmental pollutants released or discharged over a vast area of the world, require preferentially relatively cheap, cost effective or economically viable technology. Current treatment processes for contaminated waste streams used to consist mostly from chemical precipitation, membrane filtration, ion exchange or adsorption. Among those different techniques, adsorption based processes have drawn much interest even in past due to the relatively simple approach for the removal of plenty of environmental pollutants. Activated carbon, clay minerals, biomass, natural zeolites and even some industrial solid waste have been widely used as adsorbents for removal of ions and organics out of contaminated waters. On the base of the excellent selectivity of natural zeolites to different adsorbates as well as worldwide abundance of these precious tuffaceous materials, their utilization in environmental cleanup technologies became since 1960´s popular. Most of the reported applications of natural zeolites in the past decades have focused on the removal of ammonium and heavy metals. Nevertheless, the unique chemical and structural characteristics of natural zeolites made them appropriate for multitude environmental applications, where effectivness and low cost of materials are needed (Chmielewská, 2014). Today, some update or plenty zeolitic applications related to water treatment and purification processes are available by hundreds. However, recent literature reports the state of the art mainly in zeolite surface modification using the hydrophobization (sol-gel technique for coating the zeolitic surface by different surfactants, moreover with zero valent iron ZVI-addition), metal doping or peletization of zeolite matrices with some biopolymeric eco-friendly carbohydrates. Since the last decade by our investigations, several new surface modified or hybridized zeolite adsorbents have been succesfully synthesized whose performance and favourable, much extended adsorption properties towards aqueous pollutants have been achieved.

In general for water and wastewater treatment, a significant majority of recent developments relate to biological processes and treatment technologies using advanced adsorption and filtration media. Adsorption is the capability of all solid substances to attract to their surfaces molecules of gases or solutions with which they are in close contact. Due to their high specific surface area, especially nanoadsorbents show a considerably higher rate of adsorption for organic compounds compared with granular or powdered activated carbon. They have great potential for novel, more efficient, and faster decontamination processes aimed at removal of organic and inorganic pollutants like heavy metals and micropollutants (Gehrke et al., 2015).

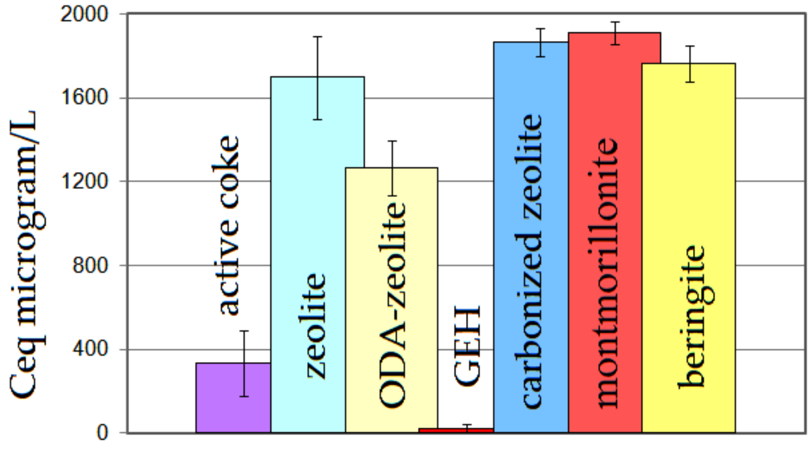


Fig 2 Average equilibrium concentrations of cefazoline removal onto some selected adsorption materials

Nanometals and zeolites benefit from their cost-effectiveness and compatibility with existing water treatment systems since they can be implemented in pellets and beads for fixed absorbers. Evidently, the photocatalytic degradation of organic pollutants incl. ECs by TiO_2 supported solid matrices bolong to the latest progress in field (AOP). Titanium dioxide has been widely used as photocatalytic material in removal of toxic chemicals from waters, but due to its fine sized grains (4-30 nm), it aggregates rapidly by loosing efficiency. TiO_2 is not porous and its surface exhibits polar property, however as immobilized on porous solids (semiconductor graded solids) using mostly the sol-gel route, provides higher specific surface area and facilitates more effective adsorption sites than bare TiO_2 (Bhatnagar, 2013, Ternes et al. 2002).

Prophylaxis antibiotic (cefazoline) removal using the aqueous solutions and stationary (batch) system at laboratory was applied to compare several adsorbents like native, ODA- and carbonized zeolite (clinoptilolite-rich tuff), montmorillonite, German commercial GEH, active coke and beringite (Fig 2). Aqueous model solutions of cefazoline were analysed by means of Diode Array (UV-VIS) Spectrometer Hewlett Packard 8452A at the wavelength 272 nm.

Cefazoline is an antibiotic used for the treatment of a number ofbacterial infections. The drug is usually administered by either injection into a muscle or into a vein. It is on the World Health Organization's List of Essential Medicines - the most important medications needed for a basic health system (Tab 1b).

According to above graphical plot, the highest capacity towards cefazoline showed GEH and active coke, however also ODA-surfactant coated zeolite exhibited acceptable uptake performance. Beringite is basically aluminium silicate rock made up of albite, barkevite and orthoclase. Fig.3 presents some broader range of selected adsorbents for examination of cefazoline uptake. German provenience silcarbon, industrial ashes chezacarb (amorphous carbon) from Chemopetrol Litvínov (Czech Republic), German granulated ferric hydroxide (GEH) with the main components of akaganeite (ß–FeOOH) and goethite [α-FeO(OH)], montmorillonite from the deposit in Slovak Republic, obtained from the rock after sedimentation and purification procedures and commercial Happy End (Great Britain), mostly natural resources derived and mixed products denoted as SK1, SK2, DN2 and CB18 were compared. The SK1 and SK2 contain the mixture of cellulose, calcium carbonate and clays, while DN2 is manufactured mainly from natural silicate resources based on the former commercial Absodan and CB18 means a high quality peat (Tab 1a). Peat contains lignin, cellulose, fulvic and humic acids as major constituents that bear polar functional groups, such as alcohols, aldehydes, ketones, phenolic hydroxides and ethers, using them in chemical bonding (Chmielewská, 2014).

According to Fig 2 and Fig 3 the ODA-zeolite has among the other described mostly commercial and costly products in the removal efficiency for an unpolar heavily substituted carboxylic acid cefazoline competitive position (Tab 1b). As can be seen, carbon based adsorbents (chezacarb and silcarbon) proved the best removal performance beside the GEH and ODA-zeolite while for cefazoline removal the Happy End products under SB18 (peat) was moreover preferred.

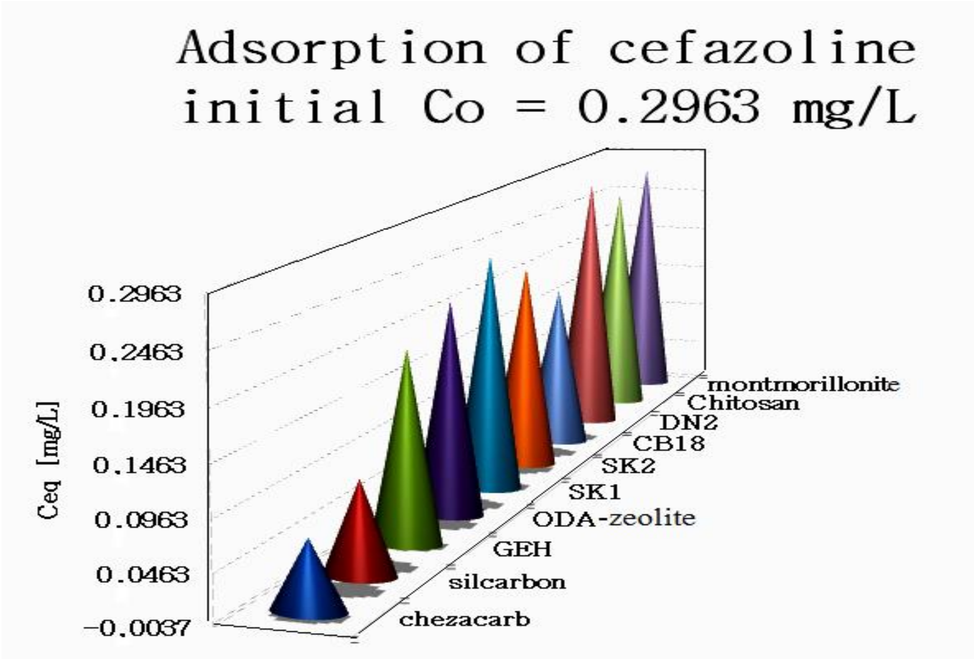
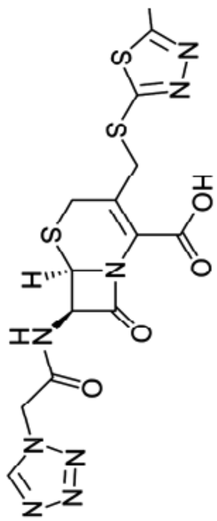


Fig 3 A broader range of selected adsorbents for examination of cefazoline uptake (Chmielewská and Xu, 2015)

Tab 1 Commercial products Absodan and Spilkleen manufactured from natural materials and applied for a) cefazoline removal; b) structure formula of cefazoline (Chmielewská, 2014)

	SK1 denotes a mixture of natural resources, mostly the cellulose, calcium carbonate and clays
	Spilkleen SK2 is a commercial product similar like SK1
	CB18 means a high quality peat
	DN2 is manufactured mainly from natural silicate resources based on the former commercial Absodan



a) **b)**

CONCLUSIONS

The presence of pharmaceuticals (ECs) in the environment has been a topic of concern. Most environmental data focus on the occurrence, fate, and transport of these compounds in wastewater or receiving waters. Their presence in source waters and drinking water is particularly problematic as this pathway represents a vector for human exposure. Several promising options for the pharmaceutical removal from water are available, and many technologies employ an advanced oxidation process (AOP). AOPs have been shown to be better suited for removing recalcitrant pharmaceuticals from water as compared to conventional treatment processes (Muthanna, 2017, Xinbo et al., 2016)

Although numerous adsorbents have been developed and examined in water treatment, their potential needs to be further assessed on pilot scale with real surface/ground water or/and wastewater. Development of some synthetic, hybrid and nano-scale adsorbents show high efficiency towards specific pollutants removal, but more research is needed prior to their use in full-scale application in water and wastewater treatment.

At last but not least has to be mentioned the development of wastewater treatment systems using oyster shells as the biological growth media that prove enhanced affinity to microorganisms or for even trace concentrations of ECs in water, development of biomimetic adsorbents imitating lipids from white whales, arctic wolves, South African fur seals, marketable fish and mussels, based on high accumulation affinity of organism´s lipids towards ECs.

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