Natural Resources and Waste Products in Aquatic Media Remediation and Diclofenac Uptake

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Abstract: Environmental requirements are becoming of great importance in today’s society since there is an increased interest in the industrial use of renewable resources. For this reason, the objective of the work presented was to examine and compare several natural, commercial or even waste products in diclofenac uptake, using synthetic water solutions in laboratory measurements. Diclofenac belongs to a class of drugs that provides analgesic, antipyretic and anti-inflammatory effects. To date, more than 200 different pharmaceuticals alone have been reported in river waters globally. According to the monitoring provided by the national water authorities and researchers, consumption of pharmaceuticals in the Czech and Slovak Republics are among the highest in Europe. According to our research, the results of the most effective adsorbents in diclofenac uptake from aqueous solutions were products in the following order: Chezacarb, with a capacity nearly 300 mg/g, Peatsorb CB18, with a capacity close to 250 mg/g, the German Silcarbon and the commercial product KlinoCarb, from the company Zeocem, with a capacity of ca. 200 mg/g. The domestic product KlinoCarb, which proved to have sufficiently high adsorption towards diclofenac, including a favourable price, was characterized by 1H-13C CP MAS NMR, Raman spectroscopy, XRD, and moreover, as with the other materials studied, by the SEM and S(BET) methods.

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1. INTRODUCTION

Recent literature dealing with natural zeolite valorization reports state of the art, mainly in their external surface modification using the sol-gel technique, surfactants coating, deposition of Zero Valent Iron (ZVI), silver clusters, iron oxihydroxide nanoparticles and semiconductor like titanium dioxide or their pelletizing with some biopolymeric eco-friendly carbohydrates [1-7]. Some interesting remarks of living cells based on excretion of biogenic surfactants or specific biopolymeric acids like alginic acid and its salt alginate. Alginate is a copolymer of the isomers of mannuronic and guluronic acids which enable the dense packing of submicrometer-sized particles in suspensions in order to enhance their colloidal stability. To promote the zeolite adsorption performance and prepare a more effective amphoteric product for specific water purification, a flexible component, i.e. alginate biopolymer with a rigid component zeolite powder, was crosslinked using Fe(III) and Ca(II) salts, according to the several cited literature reports [1]. Using the hydrophilic, expandable and permeable hydrogels with low interfacial tension for the novel hybridized adsorbent synthesis, substances that resemble soft living tissues, is another excellent example for advanced surface treatment strategy to broaden the zeolite’s adsorption abilities. Various aspects regarding octadecylammonium (ODA) - zeolite adsorbents have been examined as well [1, 7]. The Bowman school in the USA has mainly initiated synthesis and investigation of hydrophobized grain-sized zeolites so far in a pilot measurement, due to its superior hydrodynamic properties. Nano Ag, which is usually incorporated into zeolite matrix, is currently the most widely used antimicrobial agent, damaging proteins and suppressing
DNA replication. Clinoptilolite tuff enriched with nano Ag, followed by UV disinfection, is able to remove microorganisms such as Giardia and Cryptosporidium, which have a spore stage and become resistant to common disinfectants [8]. All of the imported adsorption products on the market such as GEH, Reo Amos, Absodan, Nanofer, Bayoxide and plenty others, are extremely expensive in regard to domestic zeolite (clinoptilolite tuff), despite that some of them are fabricated from natural or waste materials.

Environmental requirements are becoming of great importance in today’s society since there is an increased interest in the industrial use of renewable resources. At the same time, it is believed that nature’s pattern may indicate in the near future the synthesis development of such adsorbents, which may remove pharmaceuticals, drugs, endocrine disrupting compounds and other recalcitrants in a more extensive way, e.g. inspired by the lotus effect or skin of some mammalia (dolphins, sharks). At present, a lot of techniques for the preparation of bionic superhydrophobic and self-cleaning surfaces have already been designed [4, 5, 9].

Pharmaceuticals, which are known today as 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 aquatic environments, a large variety of these compounds and their metabolites have been detected [10-13]. Due to a lack of appropriate methodologies, the presence and distribution of pharmaceuticals in the soil via land applications are far from known. Liquid Chromatography combined with Mass Spectrometry (LC-MS) or with tandem Mass Spectrometry (LC-MS/MS) are popular techniques currently being used in pharmaceutical analyses. The latter allows for the detection of extremely low concentrations (ng/L or ng/g) of these compounds in various complex liquids or solid matrices. 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 along with a number of associated metabolites. 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 [10, 11, 13]. Methamphetamine (locally known as pervitin) is an extremely addictive stimulant drug that is chemically similar to amphetamine. According to the monitoring provided by the national water authorities and researchers, consumption of this chemical in the Czech and Slovak Republics is among the highest in Europe [12].

For this reason, the objective of the work presented was to examine several natural, commercial or even waste products in diclofenac uptake, by using synthetic water solutions in laboratory measurements. Diclofenac belongs to a class of Non-steroidal Anti-inflammatory Drugs (NSAID) that occurs often and persists for a long time in Slovak wastewater because of its difficult removal in conventional wastewater treatment plants which use the activated sludge process.

2. EXPERIMENTAL METHODS

Conventional batch equilibrium experiments were performed at laboratory to compare removal efficiency of the materials studied in diclofenac uptake. Unified initial concentration of diclofenac in D.I. water Co = 300 mg/L for all samples examined was prepared from diclofenac sodium salt (obtained by Sigma-Aldrich, Belgium).

Following samples for diclofenac removal were examined: The domestic natural clinoptilolite (repository Nižný Hrabovec at the eastern Slovakia) was chosen on the base of its cost effectiveness and due to its sufficiently large surface area (~ 60 m²/g), the highest one among the other natural materials, rigidity and surface functionality. Moreover, this zeolite was upgraded by its surface covering with MnO₂ (Mn-zeolite) as well as by mixing with powdered activated carbon Norit GL 50 and brought in the market by Zeocem Company under commercial name Klinocarb. Another adsorption or waste products like Absodan DN2, Reo Amos EcoDry Plus, German activated carbon Silcarbon, Czech industrial waste Chezacarb, Reo Amos Peatsorb CB18, cationic surfactant octadecylammonium coated ODA-zeolite, carbonized zeolite, Fe(OH)-zeolite, German granulated ferric hydroxide GEH, Chitosan, Spilkleen SK1(ReoAmos) and domestic geocomposite Slovakite were also used for diclofenac uptake and efficiency evaluation.

Measurements of diclofenac in aqueous solutions were performed on an Agilent Technologies 1200 Series Liquid Chromatograph, in conjunction with an automatic dispenser and a DAD detector. The Zorbax SB-C18 Chromatographic Column 3.5 µm, 150 x 2.1 mm was used for the analysis. Diclofenac was detected at 278 nm and quantified by the peak area or signal intensity.

DXR Raman Microscope (Thermo Fisher Scientific, USA) was used to identify all the samples studied. Measurements were performed at room temperature. Raman spectra were excited using the 532 nm line of a Nd:YAG laser, with power emission conditions of 10 mW (except diclofenac - 0.4 mW). Peak position was calibrated with a neon glow lamp and a polystyrene standard. Each spectrum was collected in two accumulations of 5 s. The obtained spectra were adjusted and corrected for fluorescence.

The X-ray powder diffraction (XRPD) patterns were accomplished at room temperature on a BRUKER D8 Advance Apparatus with Cu antikathode, Ni Kα filters and LynxEye detector at 40 kV and 40 mA. The resulted patterns were compared with the JCPDS Catalogue (Joint Committee on Powder Diffraction Standards No. 22-1236, 13-0304 for clinoptilolite verification).

Solid-state NMR experiments were performed on a Varian 400 MHz solid-state NMR spectrometer (Palo Alto, CA, USA) at Department of Physics FEI TU in Košice (Slovakia). The high-resolution ¹³C NMR spectra were recorded at a resonance frequency of approximately 100 MHz with the use of 4 mm ZrO₂ rotors and magic angle spinning (MAS) frequency of 10 kHz at room temperature. The spectra were recorded using cross-polarization (CP) technique with ¹H 90° pulse of 2.6 µs, with contact time of 2 ms, acquisition time

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of 20 ms, high power proton decoupling of 88 kHz, recycle delay of 6 s and averaging over 14, 000 scans.

Scanning Electron Micrographs SEM of samples studied were performed on JEOL JSM 6390LV Electron Microscope after their sticking onto carbon band and metallized with gold using the coating apparatus JEOL JFC-1200.

For material characterization the external surface area and porosity of samples were determined at liquid nitrogen temperature (76 K) on a Micromeritics ASAP 2400 Apparatus, using the static volumetric technique and t-plot methods.

3. RESULTS AND DISCUSSION

Diclofenac [sodium 2-(2,6-dichlorofenylamino) fenyl acetate] belongs to a class of drugs that provides analgesic, antipyretic and anti-inflammatory effects without addictive reactions [14]. In Slovak wastewaters, pharmaceuticals are commonly found in concentrations varying in the range of 2000-4000 ng/L. Therefore, a tertiary adsorption process mostly onto activated carbon was already proposed for water post treatment in some countries. Other methods as well, such as ozonation, UV - irradiation and flocculation including their combinations, have been applied for removal of these Emerging Contaminants (ECs) from waters, however, some of them were too expensive and others were ineffective. Due to the extremely high price of imported water purification products to the Slovak market, we tried to examine and evaluate several domestic adsorption materials, including self-synthesized ones in the laboratory, with the commercial or waste products for diclofenac removal.

Metal oxide-based adsorbents are effective, low cost adsorption materials for heavy metals and other pollutants removal. Their sorption process is mainly controlled by complexation. When their particle size is reduced to below 20 nm, the specific surface area of normalized adsorption capacity increased 10 - 100 times, suggesting a “nanoscale effect”. They may be combined with other carriers or pelletized so to say, enriched for a broader range of functional groups and thus, separated magnetically. Nevertheless, to overcome the potential human risk from environmental spreading, nanomaterials need to be embedded in a solid matrix, that is to say, to have minimum release until they are disposed of [15]. Therefore, we used zeolite (clinoptilolite tuff) from an inland deposit as a template or nanoreactor in a more effective biomimetic sol-gel synthesis and thus, prepared new, upgraded and economically feasible adsorbents FeO(OH)-zeolite as well as Mn-zeolite.

As (Fig. 1) presents, natural zeolite (clinoptilolite tuff), including its surface modified forms, in grain-size 0.2-0.5 mm did not reach the adsorption capacity towards diclofenac higher than 40 mg/g, whereas the most effective was the zeolite in its native form and a grain-size fraction under 100 µm, reaching a capacity somewhat higher than 40 mg/g. The lowest adsorption performance towards diclofenac proved to be Mn-zeolite from Hungary. The commercial products Chitosan and Spilkleen SK1 (ReoAmos) seemed to be approximately 3-times more effective to diclofenac. Chitosan (a chelating scavenger of heavy metals) is produced from chitin, which is the second most abundant natural biopolymer (after cellulose) on the planet. It is made by alkaline N-deacetylation of chitin, widely found in the exoskeleton of shellfish and crustaceans, such as crab, lobster, but also in insects, mushrooms and bacteria. High adsorption performance of chitosan onto various pollutants is attributed to a large number of hydroxyl- and aminogroups, including the chitosan flexible polymer chain structure.

The product ReoAmos, decoded as Spilkleen SK1, was manufactured from recycled cellulose, calcium carbonate and clay. Approximately twice as effective, regarding that products in diclofenac uptake, appeared to be commercial Slovakite. Slovakite decodes a commercial geocomposite manufactured by IPRES engineering, Ltd. Bratislava from domestic dolomite, bentonite, diatomic clays, alginate and zeolite, justified only with clinker and final pressurizing. Slovakite is purchased for about 700 Euro per ton in the size granulation of 0.2 - 0.5 mm.

Almost the same level, however a little less than the capacity of 40 mg/g, was reached by the products Spilkleen SK2 a DN2 (Absodan). Adsorbent Spilkleen SK2 is similar to the SK1 mixture of kaolin, calcium carbonate and cellulose. The commercial product Absodan DN2 was manufactured mainly from natural silicates. For the most effective adsorbent considered from this series was the product ReoAmos EcoDry (composed basically from silicon), which proved towards diclofenac to have a little lower capacity than the expensive GEH product. Granulated ferric hydroxide (GEH) was developed at the Department of Water Quality Control at the Technical University of Berlin in the beginning of the nineties for removal of arsenic from natural waters and is an approved commercial adsorbent manufactured by GEH Wasserrchemie GmbH & Co. KG Osnabrück (Germany). The main components of GEH are akaganeite (β-FeO(OH)) and goethite [α-Fe(OH)]. The product costs 3750 Euro per ton.

Grained peat offered on the market as Peatsorb ReoAmos CB18 was very effective in diclofenac uptake, according to capacity values comparable even with the best adsorbents studied. 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, and uses them in chemical bonding.

German provenience activated carbon Silcarbon produced by the company Silcarbon Aktivkohle GmbH (Kirchhundem) and industrial ashes Chezacarb (amorphous carbon as a waste product from Unipetrol RPA Litivinov, the Czech Republic) were also used for diclofenac removal. The granulated activated carbon with the specification Silcarbon SC-40 is offered on the market for 10,31 Euro/kg and produced from coconut shells, charcoal (wood) or coal as alternative at the temperatures of 700-900°C.

In conclusion, from all of the experimental results discussed above and graphically recorded in (Fig. 1), the following statements can be drawn. The most effective adsorbents in diclofenac uptake from aqueous solutions were these products in the following order: Chezacarb with a capacity of nearly 300 mg/g, Peatsorb CB18 with a capacity close to 250 mg/g, the German Silcarbon and the commercial product KlinoCarb from the company Zeocem with a capacity around 200 mg/g.
Even though peat does not possess acceptable hydraulic properties and only KlinoCarb appears on the inland market as economically accessible and an effective product on diclofenac, we thoroughly searched its composition and properties. Accordingly, KlinoCarb was examined using several identification and analytical procedures to find out which components form this material. Raman spectra in Fig. 2 (middle left) expressively indicated the presence of activated carbon. Also in Fig. 2 (right), XRD diffractogram of KlinoCarb confirmed that this product, in regard to pure clinoptilolite (lower diffractogram), consists of a poorly crystalline substance similar to amorphous carbon. Based on the personal communication, the composition of KlinoCarb with 80% of pure powdered clinoptilolite tuff and 20% of powdered activated carbon Norit GL50 (a fraction under 100 µm) was confirmed [16, 17]. This product is sold in the market for 0.7 Euro/kg.

The ¹H - ¹³C CP MAS NMR spectra of diclofenac, diclofenac adsorbed onto KlinoCarb and onto commercial activated carbon in Fig. 3 (left), refer clearly to the highest density of interactions between KlinoCarb and diclofenac, based on hydrocarbons comprised in pharmaceutical molecules vs. an activated carbon (zeolite) surface. At the same time, the largest broadness of NMR resonance line appeared by diclofenac onto the KlinoCarb spectrum, reflecting the highest binding intensity between both substances. The NMR spectrum of diclofenac (Fig. 3a, right) displays signals at chemical shifts of 182.5 ppm (carbon 8), 141.2 - 115.7 ppm (carbons 1-6 and 1'-6'), and 44.5 and 43.2 ppm (carbon 7), characteristic for carbons in the diclofenac structure [18]. The NMR spectrum of the clinoptilolite tuff sample (Fig. 3b, right) confirmed the presence of ionized diclofenac salt. In general, the signals are broadened, and reflecting in less resolved spinning sidebands in the spectrum. The signals from carbons 7 (CH₃) are shifted to lower values, the signal from carbons 8 is split into two lines, which may indicate some changes of this carbon environment, probably due to the interaction of diclofenac with the zeolite surface or other ions, since they are too large to enter zeolite pores. The NMR spectrum of the peat sample (Fig. 3c, right) displays signals characteristic for peat soils according to literature [19]. In this case, the presence of diclofenac cannot be identified clearly since the signals are overlapped, as indicated by the arrows.

Fig. (4) illustrates Scanning Electron Micrographs (SEM) of all the used adsorption materials. SEM micrographs of the studied samples, as complementary investigations, visualize typical morphologies of individual adsorbents. FeO(OH) - zeolite outlines the boundary of a pore filled with more or less tabular, euhedral crystals of zeolite (clinoptilolite), which are small, and in some cases coated with a thin sheet of authigenic clay. Through this SEM, various phases of iron oxides (FeO(OH), GEH) reveal small inclusions filled with iron oxides. Some crystal habits of iron oxide are seen round or disc-shaped hematite, coordinating rod-shaped goethite. Dark areas are dominantly goethite, whereas light areas are hematite. The SEM micrographs correspond well with several other published results dealing with iron oxides immobilization and visualization. Examination of the SEM micrographs of activated carbon, peat, carbonized zeolite and Chezacarb indicates the presence of many pores, cracks and oval shaped objects on the surface. Zeolite shows typical sheets and Absodan DN2 presents typical needle morphology. Mn - zeolite is characteristic with highly visible prismatic MnO₂ (pyrolusite) crystals.

Finally, (Table 1) summarizes all the measured surface areas of the adsorbents studied using the S(BET) method. As
Fig. (2). Raman spectra of materials studied (left) and XRD diffractograms of KlinoCarb and clinoptilolite tuff (right).

Fig. (3). $^1$H-$^{13}$C CP MAS NMR spectra of diclofenac, diclofenac adsorbed onto KlinoCarb and commercial activated carbon (left) and $^1$H-$^{13}$C CP MAS NMR spectra of a) diclofenac, b) zeolite, c) peat adsorbed with diclofenac (right, spinning sidebands are denoted by asterisks).
**Fig. (4).** SEM (downwards from the left to the right): clinoptilolite tuff, Absodan DN2, Reo Amos EcoDry Plus, activated carbon, Chezacarb, Reo Amos Peatsorb CB18, ODA-zeolite, carbonized zeolite, FeO(OH)-zeolite, GEH, Mn-zeolite, Chitosan, Spilkleen SK1(ReoAmos), Slovakite.
Table 1. Specific surface areas and porosity values of some materials studied (fr.0.2-0.5 mm).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) (m²/g)</th>
<th>(S_t) (m²/g)</th>
<th>(V_{\text{micro}}) (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slovakian clinoptilolite tuff (Nižný Hrabovec)</td>
<td>31.7</td>
<td>21.4</td>
<td>0.0045</td>
</tr>
<tr>
<td>Carbonized Slovakian clinoptilolite tuff</td>
<td>23.7</td>
<td>17.6</td>
<td>0.0026</td>
</tr>
<tr>
<td>ODA-modified Slovakian clinoptilolite tuff</td>
<td>10.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Slovakian clinoptilolite tuff (fr. under 20 µm)</td>
<td>59.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Alginate (Pinciná, Slovakia)</td>
<td>27</td>
<td>27</td>
<td>0</td>
</tr>
<tr>
<td>Shungite rock silicate (St. Petersburg, Russia)</td>
<td>18.3</td>
<td>17.8</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Fe – Mn – clinoptilolite tuff; fr. under 100 µm</td>
<td>31.4</td>
<td>28.8</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe-alginate-clinoptilolite tuff pellet (1:2)</td>
<td>21.2</td>
<td>19.3</td>
<td>0.001</td>
</tr>
<tr>
<td>Mn–zeolite (clinoptilolite tuff) fr. under 100 µm</td>
<td>27.5</td>
<td>22.9</td>
<td>0.002</td>
</tr>
<tr>
<td>FeO(OH)–clinoptilolite tuff; fr. under 100 µm</td>
<td>52.2</td>
<td>38.2</td>
<td>0.007</td>
</tr>
<tr>
<td>GEH (German granulated ferric hydroxide)</td>
<td>298</td>
<td>299</td>
<td>0</td>
</tr>
<tr>
<td>German Activated carbon Silcarbon</td>
<td>942</td>
<td>55.6</td>
<td>0.459</td>
</tr>
<tr>
<td>Commercial product Slovakite</td>
<td>61.5</td>
<td>47.7</td>
<td>0.007</td>
</tr>
<tr>
<td>Chezacarb (Czech industrial ashes)</td>
<td>1078</td>
<td>1041</td>
<td>0.010</td>
</tr>
<tr>
<td>Klinocarb (Zeocem commercial product)</td>
<td>715</td>
<td>385</td>
<td>0.174</td>
</tr>
</tbody>
</table>

\(S_{\text{BET}}\) - active surface area determined by nitrogen adsorption and BET isotherm
\(S_t\) - surface area of mesopores plus external surface area determined by t-plot method
\(V_{\text{micro}}\) - volume of micropores determined by t-plot method

can be seen, mainly carbon-rich adsorption materials distinguish high \(S_{\text{BET}}\) values, whereas according to our capacity measurements, those values correspond excellently with their efficiency towards diclofenac uptake. More or less, except for the carbonized and ODA-modified zeolites which \(S_{\text{BET}}\) values were measured in grain-sized fraction 0.2-0.5 mm, all the other samples (natural, FeO(OH)-, Fe-Mn- and Mn- zeolite) were powdered into fraction under 100 µm, and therefore, those \(S_{\text{BET}}\) values correspond also very well with their capacity data to diclofenac (in order natural zeolite > FeO(OH)-zeolite > Fe-Mn-zeolite > Mn-zeolite) Table 1.

CONCLUSION

Attention was focused on various natural, commercial or even waste products, accessible in Slovak market, which were able to remove diclofenac from synthetic water. Moreover, the scope of the presented work was to characterize the inland most effective and economic favourable zeolite based adsorbent Klinocarb and to define the interaction of the used zeolite (clinoptilolite tuff) vs. activated carbon as well as adsorbed diclofenac, using the \(^1\text{H}-^{13}\text{C}\) CP MAS NMR, Raman spectroscopy, SEM, \(S_{\text{BET}}\) and XRD methods.

Following conclusion was stated:

(i) The ability of several, mainly C-rich materials, for diclofenac uptake, was validated. The most effective adsorbents in diclofenac uptake from aqueous solutions were products in the following order: Chezacarb, with a capacity nearly 300 mg/g, Peatsorb CB18, with a capacity close to 250 mg/g, the German Silcarbon and the commercial product Klinocarb, from the company Zeocem, with a capacity of ca. 200 mg/g.

(ii) Klinocarb with 80% of pure powdered clinoptilolite tuff and 20% of powdered activated carbon Norit GL50 was verified satisfactorily by XRD, Raman spectroscopy and \(^1\text{H}-^{13}\text{C}\) CP MAS NMR. However a predominant content of activated carbon in this commercial product was supposed.

(iii) Scanning Electron Micrographs (SEM) at Fig. (4) visualize explanatory all the surface morphologies of the materials studied.

(iv) According to \(S_{\text{BET}}\) values (Table 1), especially carbon-rich adsorption materials distinguish a high \(S_{\text{BET}}\) values, whereas according to the capacity measurements those values correspond excellently with their efficiency towards diclofenac uptake.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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