

## Research Article

### Polishing of Water Contaminated with Diclofenac or Antimony using the Clinoptilolite Tuff

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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. The main objective of this contribution was to provide some literature review of state-of-the-art and the future prospects of green synthesis, with special emphasis on membrane based processing as one part and on another with pharmaceuticals as emerging contaminants in environment. Both parts are completed briefly with laboratory results dealing with antimony removal onto various Fe-oxihydroxides and FeO(OH) covered clinoptilolite tuff and diclofenac uptake onto carbon-rich adsorption materials incl. zeolites. Clinoptilolite tuff occurs in Slovakia in huge deposits and as natural resource is considered for economic accessible adsorption material, potentially useful also for water polishing. Based on the preliminary results, diclofenac adsorption proceeds with the highest efficiency especially onto various carbon-rich materials, incl. onto zeolite (commercial product KlineCarb), however antimony removal onto FeO(OH)-zeolite could be considered for competitive especially in treatment of large volumes of highly acidic mine waters.

**Keywords:** Adsorbent processing; Antimony removal; Biomimetics; Clinoptilolite tuff; Diclofenac; Pharmaceuticals; Progressive membrane; Water polishing; Zeolite

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### Membrane Based Technologies under Progressive Development

Membranes can occur at any level within the hierarchy of the organism. Plants contain much simpler membranes than animals, whilst multicellular plant membranes are relatively rigid and stationary, most animal membranes are mobile. In both, plant and animal, the skin is specialized not only as a covering but also as a selective barrier to passage in both directions of mechanical, physical and chemical stimuli, such as force, heat, water and volatiles. Any conflict with these phenomena occurred during the evolution of biological life. Current bio-inspired design (biomimetic engineering) try to benefit from such concepts by integrating them into novel practical solutions and technological processes. There is another difference regarding biology and current material engineering. Energy persists still as the main controlling parameter in the processing of human goods, while biology uses initially the information from DNA [1-6].

Also, surface or immobilized membranes of industrial adsorbents are considered to be relevant for fulfilling all above functions by pollutants removal. Here, a membrane could be defined as a thin sheet of natural or synthetic material that is permeable to substances in solution or any thin, flexible layer or material designed to separate, filter, purify, treat, etc., Thin-film composite membranes are semipermeable membranes manufactured principally for use in water purification or water desalination systems. This membrane can be considered as a molecular sieve constructed in the form of a film from two or more layered materials. Other materials, usually zeolites, are also used in the manufacture of such thin-film membranes. Zeolites are basically crystalline solids and their structure is made from silicon, aluminium and oxygen atoms, that form a characteristic framework with cavities and channels inside, where cations, water and/or small molecules may reside. 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 (here indicated as clinoptilolite tuff) [3,7].

Metal oxides such as iron oxide, titanium dioxide and alumina are effective, low cost materials for heavy metals and radionuclides removal as well as pathogen detection. Their cleanup process of pollutants removal 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, like in presented paper with zeolite (clinoptilolite tuff), to avoid technological disadvantages of their nano-scale form. Current immobilization techniques usually result in significant loss of treatment efficiency. Therefore, research is needed to develop simple, low-cost methods to immobilize nanomaterial without significantly impacting its performance. Nevertheless, to overcome a potential human risk from environmental spreading, nanomaterials need to be embedded in a solid matrix, respectively, to have minimum release until they are disposed of [8-11].

Electrospinning is another simple, efficient and inexpensive way to make ultra fine fibers using various materials like polymers, ceramics

or even metals, that may be incorporated as above nano-oxides onto porous support or membrane. However, mainly nano-zeolites have been the most frequently used dopants in 250 nm-thin film nanocomposite membranes since several years and have shown potential in enhancing membrane permeability. Moreover, nano Ag usually incorporated into zeolite matrix is currently the most widely used antimicrobial nanomaterial damaging proteins and suppressing DNA replication, which possess low human toxicity and a broad antimicrobial spectrum [1-3]. Certain emerging membrane based technologies, such as nanocomposite membranes, show substantial promise for energy reduction and have been recently commercialized. When zeolite nanoparticles were embedded within the polyamide active layer, the water permeability across such as membrane was enhanced. Also, mimic aquaporin membranes constructed onto porous support were considered to be 100 times more permeable than commercial reverse osmosis membrane [2-5].

Membranes incorporating carbon nanotubes have been found to be promising candidates for water desalination, as the size and uniformity of the tubes can achieve the desired salt rejection. They have shown higher efficiency than activated carbon on removal of various organic chemicals due to diversified contaminant interactions, larger surface area and porous system. While nanomaterials embedded in a solid matrix may expect minimum release into the environment, research is also needed to develop simple, low cost methods to ensure their integrity with the existing infrastructure either as slurry reactor or in form of pellets/beads fixed adsorber [1-4].

Also, 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 emerging contaminants in water, development of biomimetic materials imitating lipids from white whales, arctic wolves, South African fur seals, marketable fish and mussels, based on high accumulation affinity of organism's lipids especially towards polyaromatic substances [10-13].

One of the most fascinating examples of microbial synthesis of nanostructures is the biomineralization of magnetosomes (magnetic nanoparticles) by magnetotactic bacteria. Magnetosomes consist of a magnetic mineral crystal magnetite  $\text{Fe}_3\text{O}_4$  or greigite  $\text{Fe}_3\text{S}_4$  and were identified in fossilized sediments or rocks. To date about 60 biomineral deposits were identified on the Earth, developed by such a biomineralization process (e.g., silica, calcium carbonates, sulfates, calcium phosphates, etc.). When iron is stored as a nanoparticle of iron oxide (ferrihydrite) inside the protein cage ferritin, it is completely sequestered and rendered inert. Thus the encapsulation and sequestration of the iron oxide nanoparticle in biological systems highlights its tremendous potential for use as a synthesis platform for material design. From understanding direct biomineralization in ferritin, scientists developed a model for surface-induced metal oxide formation and have used this as a guiding principle for the synthesis of metal oxide nanoparticles in other natural or engineered architectures [5,7,14-25].

Materials designed using components derived from biological sources such as collagen, chitosan, three-dimensional polymeric hydrogels like surfactants, alginate, plant proteins and polysaccharides have also 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. Since the beginning of 21<sup>st</sup> century, several types of hydrogels with excellent mechano-chemical properties have been developed through applying different synthesis routes, while especially biomimetic sol-gel strategy presents the most frequently one [14-16]. Using mostly biomimetic sol-gel method, we also prepared the octadecylammonium (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 [20].

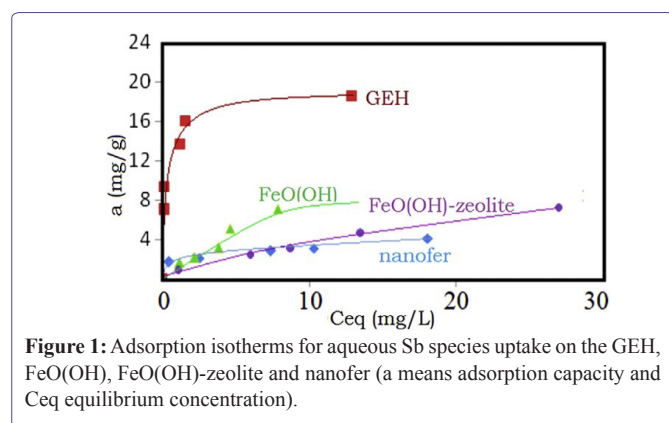
Another progress in the new synthesis development presents simultaneously cavitation and microwave processing. Cavitation reactors based on the use of sound energy or the energy associated with the fluid flow, offer immense potential for process intensification. The driving mechanism in the case of cavitation reactors is the generation of cavities based on alterations of pressure followed by growth and collapse of the cavities, while releasing a significant amount of the accumulated energy during the growth phase [26]. Due to significant energy release over a very small active area, it is expected that conditions of very high pressures and temperatures (a few thousand atmospheres and a few thousand degrees) are generated locally by producing free hydroxyl radicals with a strong oxidizing power, while simultaneously avoiding agglomeration. Also, microwave processing for various chemical transformations is more efficient than conventional heating. Solvents like water, methanol or acetone with high dielectric constants are easily heated with microwaves by providing the necessary driving force for mass transfer. Above described systems employ lower capital and operating costs and higher throughput as well [22,23,26].

### **Antimony removal onto ferrihydrite coated zeolite (experimental results)**

Due to the very high price of commercial granulated Fe-oxihydroxide (GEH) on the inland market, which is quite frequently used for As and Sb removal from some underground water reservoirs in Slovakia, we tried to prepare a new  $\text{FeO}(\text{OH})$ -zeolite (clinoptilolite tuff) from the domestic zeolite resources, which we compared with the above imported GEH product [18,20,24]. Following procedure was used: a 20 g of (0.2-0.8 mm) grain-sized zeolite was mixed with 0.5 L of 10% aqueous solution of iron (III) nitrate nonahydrate  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ , Alfa Aesar, crystalline, Germany] and aged at 60°C in water bath shaker. Aforementioned treatment was simultaneously intensified with ultrasound cavitation for 3 days. The ultrasound treatment was used in order to enhance Fe content in zeolite matrix and also in order to stabilize and disperse  $\text{FeO}(\text{OH})$  species in the structure of clinoptilolite more effectively [20]. After then, the 200 mL of 2.5 M KOH solution was added dropwise to prepare the final suspension of pH=12, keeping that aged for another 6 days at room temperature. After this reaction the suspension was filtered and washed with deionized water followed by drying at 105°C for 2 h. Figure 1 records antimony removal by using several Fe-rich adsorption materials incl. new synthesized  $\text{FeO}(\text{OH})$ -zeolite.

Czech commercial product nanofer 25 S (Nano iron, s.r.o, Rajhrad) was used for comparing the product adsorption capacity with all other examined samples due to some similarities with its iron oxides composition especially after air-oxidation and drying.  $\text{FeO}(\text{OH})$  separately synthesized without zeolite carrier was identified, based on XRD and SEM micrographs, as ferrihydrite. Metastable ferrihydrite is

known to be a precursor of more crystalline hematite and goethite and generally exists as a fine grained and highly defective nanomaterial with flake-like morphology. SEM micrographs of FeO(OH) zeolite revealed small inclusions filled with iron oxides, while some crystal habits of iron oxide were seen round or disc-shaped hematite coordinating rod-shaped goethite beside the main flake-like ferrihydrite, respectively [20].



**Figure 1:** Adsorption isotherms for aqueous Sb species uptake on the GEH, FeO(OH), FeO(OH)-zeolite and nanofer (a means adsorption capacity and Ceq equilibrium concentration).

Sb concentration in all water solutions was analysed on AAS instrument ZEE nit 700 in cooperation with Zeocem Company, Bystré (Slovakia). In highly acidified solutions ( $\text{pH} < 2.7$ ) antimony was predominantly dissolved in Sb(III) valency as  $\text{Sb}(\text{OH})_3$ ,  $\text{SbO}^+$ ,  $\text{Sb}(\text{OH})_2^+$  and  $\text{H}_3\text{SbO}_3$ . A broad variety of physically and chemisorbed Fe species in zeolite rock may serve then in enhanced  $\text{Sb}(\text{OH})_3$ ,  $\text{SbO}^+$ ,  $\text{Sb}(\text{OH})_2^+$ ,  $\text{H}_3\text{SbO}_4$  and  $\text{H}_3\text{SbO}_3$  uptake via intercalation, electrostatic interaction and other sorption processes. It was supposed that considerably part of Fe neutral species as well ionic clusters were probably deposited outside zeolite framework because clinoptilolite structure contains channels with the size of  $0.33 \times 0.46$  nm;  $0.3 \times 0.76$  nm and  $0.26 \times 0.47$  nm not sufficient large for their entrance. The plotting of adsorption isotherms in the system studied clearly confirmed the increasing uptake capacity of the adsorbents with the increased S(BET) data. As aforementioned, the highest surface area possess GEH, then ferrihydrite, followed by FeO(OH) zeolite, whereas the lowest surface area belongs to nanofer [14-16,20].

## Pharmaceuticals-Emerging Contaminants in Environment

The presence of pharmaceuticals in the environment has been a topic of concern in the last several decades. 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 [7-11].

Pharmaceuticals, as today called emerging contaminants, 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 [12,13,27,28].

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 emerging contaminants 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 of drugs in surface waters may be anticipated during music festivals, public holidays, major sporting events and by students during exam periods [12,13,27,28]. Unfortunately, above mentioned bioprocesses are not designed to remove emerging contaminants thoroughly resulting in their discharge to receiving surface waters including rivers, lakes and coastal discharge. Moreover, during the anaerobic digestion, biosolids (or treated sludge) is generated that is often applied to agricultural land as a fertiliser in many countries. Despite lengthy digestion (in average 4 weeks) and outdoor storage for up to six months following treatment, some emerging contaminants have shown to persist. 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. Therefore a tertiary adsorption process mostly onto active coke used to be proposed for water polishing [12,13,27,28].

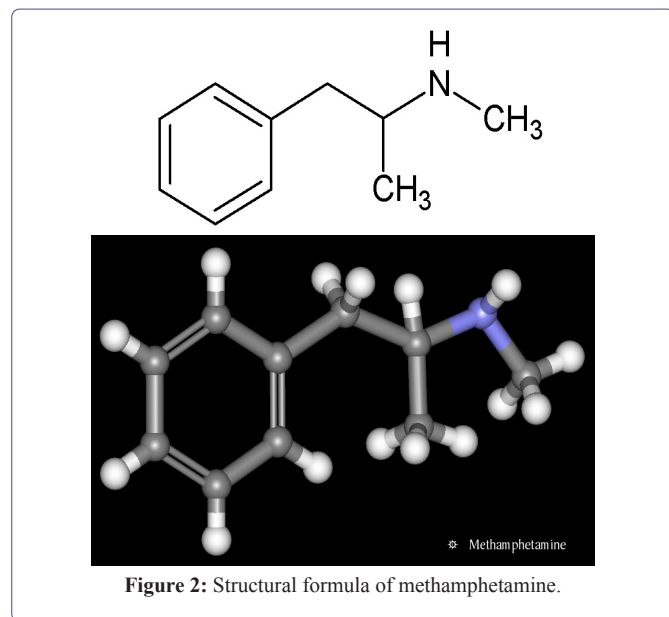
Parent chemicals are often excreted from the human body also with a number of associated metabolites. As an example, the ibuprofen is excreted as the unchanged drug. Approximately 70 pharmaceuticals, belonging to a variety of therapeutic classes, have been reported only in UK waters [12]. The analgesic tramadol has been observed in river water at the highest concentration up to a maximum of 7731 ng/L [12,29]. The hallucinogen 3,4-Methylenedioxy-N-Methyl-Amphetamine (MDMA) and the stimulant cocaine have been observed in river water at concentrations of 25 and 17 ng/L, respectively [12,30-32]. 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 [12,29,33].

Methamphetamine (Figure 2, locally called pervitin) is an extremely addictive stimulant drug that is chemically similar to amphetamine [34]. 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 Europe [34-36].

## Diclofenac adsorption onto some natural and commercial materials (experimental results)

Nonsteroidal Anti-Inflammatory Drugs (NSAID) are a class of

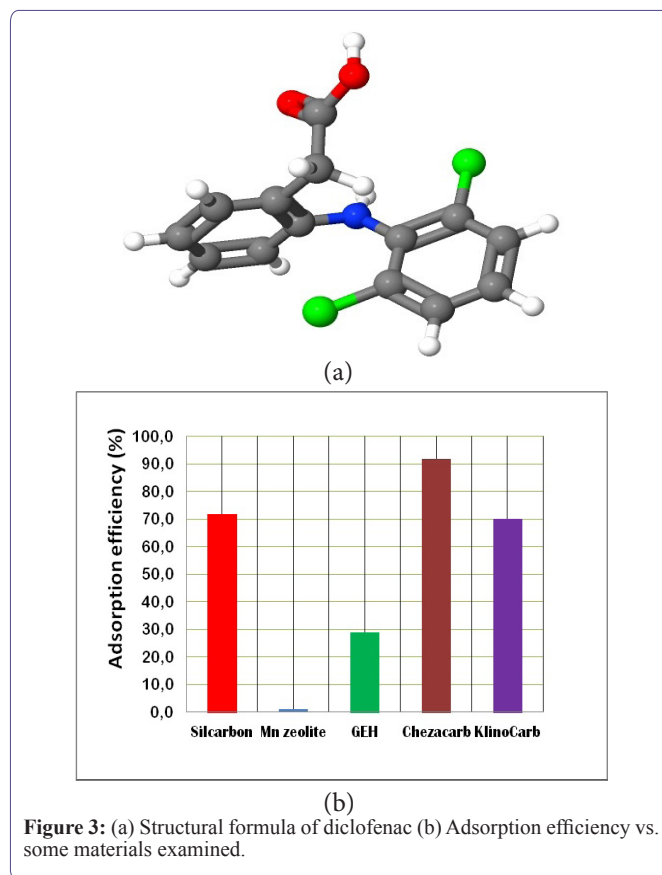
drugs that provides analgesic, antipyretic, and, at higher doses, anti-inflammatory effects without addictive reactions. From this group, diclofenac [sodium 2-(2, 6-dichlorophenylamino) phenyl acetate with summary formula of  $C_{14}H_{11}Cl_2NO_2Na$ ] was found in concentrations of about 2000 ng/L, but its concentration often varied in the range of 3000-4000 ng/L in Slovakian wastewaters (Figure 3a) [34,35].



Based upon these facts, we compared the adsorption performance of some commercial and natural adsorption materials towards diclofenac using its aqueous solutions. Following adsorbents were selected for examination: The domestic natural clinoptilolite (repository Nižný Hrabovec at the eastern Slovakia) was chosen on the base of its low-price availability in the local market (15-35 Euro per ton for size-granulation of 0, 3-1 mm), cost effectiveness and due to its sufficiently large surface area ( $\sim 60 \text{ m}^2/\text{g}$ ), the highest one among the other natural materials, rigidity and surface functionality. Moreover, this zeolite was upgraded by its surface covering with MnOx membrane (Mn-zeolite, Figure 3b) as well as by mixing with powdered activated carbon and offered on the market by Zeocem Company under commercial name KlinoCarb. Granulated ferric hydroxide (GEH) was developed at the Department of Water Quality Control in Technical University Berlin in the beginning of the nineties for removal of arsenic from natural waters and is an approved commercial adsorbent manufactured by GEH Wasserchemie GmbH & Co. KG Osnabrück (Germany). The main components of GEH are akaganeite ( $\beta\text{-FeOOH}$ ) and goethite [ $\alpha\text{-FeO(OH)}$ ]. Furthermore, activated carbon of German provenience Silcarbon and industrial ashes Chezacarb (amorphous carbon) from Chemopetrol Litvinov (Czech Republic) were compared with above adsorption materials, respectively.

Measurements of diclofenac in aqueous solutions were performed on an Agilent Technologies 1200 Series Liquid Chromatography, in conjunction with an automatic dispenser and a DAD detector. The ZorbaxSB-C18 Chromatographic Column  $3.5 \mu\text{m}$ ,  $150 \times 2.1 \text{ mm}$  was used for the analysis. Diclofenac was detected at 278 nm and quantified by the calibration curve method at a concentration range of 0.45-450 mg/L.

As the figure 3b displays, the highest adsorption efficiency towards diclofenac exhibits Chezacarb, Silcarbon and KlinoCarb, ordered according to their adsorption capacity data. So called magnetic adsorbents like GEH and Mn-zeolite show considerably lower performance.



We observed approximately 10% difference between Silcarbon and KlinoCarb capacities in diclofenac uptake and found out that 80% of natural powdered zeolite (clinoptilolite tuff) was added into activated carbon (20%) and mixed to get KlinoCarb product currently selling by Zeocem Company.

Since the natural zeolite possess any affinity to hydrophobic and anionic species due to its net negative charge and presence of exchangeable cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) at the hydrophilic surface, it was confirmed that neither natural zeolite nor MnOx coated zeolite (Mn-zeolite) were effective in diclofenac adsorption (data for natural zeolite are not shown). Nevertheless, pure zeolite (clinoptilolite tuff) was the most effective in diclofenac adsorption among the examined modifications like ODA-, carbonized,  $\text{FeO(OH)}$ - or Mn-zeolite (also not recorded). We may conclude following: Based on our preliminary results, diclofenac adsorption proceeds with the highest efficiency especially onto various carbon-rich materials and commercial activated carbon (Silcarbon). In the literature, there are published many procedures how to produce low cost carbon-rich adsorbents, using even plenty waste products from agriculture, chemical industry or communal branche [37-40]. In our case, industrial ashes Chezacarb as waste

product from Chemopetrol Litvínov (Czech Republic) was considered for the most effective in diclofenac removal. Above discussed research and diclofenac removal onto various adsorption materials is currently under further investigation.

## Conclusion

Metal oxides such as iron oxide are natural, low cost adsorbents for aqueous pollutants removal, however their nanoscale counterparts with higher specific surface area must be usually compressed into porous pellets or to be impregnated onto some carriers (like zeolite) to achieve better filtration performance. Therefore, we prepared and at laboratory examined antimony removal onto iron oxide nano-particles embedded on the Slovakian clinoptilolite tuff which based on its nano-porous structure worked as a nanoreactor.

Main advantages of such a synthesized FeO(OH)-zeolite might be the relatively low capital cost and therefore applicability to a large volume of waters, especially to highly acidic mine waters. Domestic zeolite is available in the local market for the price which is approximately 100 times lower than the price of commercial iron oxihydroxide (GEH product).

Based on our preliminary results, diclofenac adsorption proceeds with the highest efficiency especially onto various carbon-rich materials and commercial activated carbon (Silcarbon). Natural zeolite or some zeolite modified samples did not prove more or less any affinity towards diclofenac except commercial product of Zeocem Company KlineCarb.

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