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Possibilities of New Types of Nanoparticles in the Field of Monitoring and Removal of Micropollutants from Waters

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In recent years, nanomaterials and nanotechnologies have received a lot of attention from various scientific branches and have considerable potential for use in various fields of industry, medicine, biology, electrical engineering, and environmental fields. There are many different types of nanomaterials, from which various composites are gradually created to improve their properties or reduce the cost of their production. Drinking and harmless water is inevitable for mankind. Therefore, proper attention is paid to its preparation and cleaning.

1. Introduction

Nowadays, the environment and all forms of life on Earth are seriously threatened due to the uncontrolled release of harmful substances into the water, air or soil. During the last century, a huge amount of toxic chemicals entered the environment, which was caused by rapid industrialization and significant population growth. The vast majority of these substances were detected in surface, underground and, in some cases, in drinking water sources. In recent decades, therefore, research has focused on the possibilities of removing these pollutants in different types of water (Pal et al.,2014), (Chen et al.,2020).

Several technologies based mainly on separation methods were gradually developed for water purification. Over time, another important technology for water purification has become biological purification, which is mainly based on the removal of nutrients and organic pollution with the help of microorganisms. However, these processes are often not effective enough in removing the so-called micropollutants such as medicines, drugs, hormones, pesticides or steroids. This results in these substances entering the environment, where their accumulation subsequently occurs. Research shows that promising technologies for removing micropollutants are advanced oxidation processes (AOPs), which use e.g. strongly oxidizing species of radicals such as hydroxyl radicals (HO.), which start chain reactions for the decomposition of complex organic compounds (Fernández-Castro et al.,2015), (Amenta and Rakshit Amenta,2018).

The applications of nanoparticles as photocatalysts have attracted the increasing interest of the scientific community in recent years. This is due to their unique physical and chemical properties, which increase their reactivity, mechanical, optical, electrical and magnetic properties. The advantages of using nanophotocatalysts are also associated with their highly specific surface area, chemical stability and high degradation efficiency. This fact means their lower dose and faster reaction kinetics compared to conventional catalysts. Several studies have also demonstrated that the use of nanoparticles as photocatalysts improved the oxidation potential of the reaction compared to microscale photocatalysts (Chong et al.,2010), (Lee et al.,2013), (wang and Zhuan,2020).

Nanoadsorbents are nanoparticles, made of organic or inorganic materials, exhibiting a high adsorption capacity for the removal of various groups of substances. Due to their high porosity, small size and active surface, nanoadsorbents are able to adsorb contaminants with different molecular sizes, hydrophobicity, or specific behavior with high efficiency (Pacheco et al.,2006), (Andrade et al.,2018).

Adsorbents based on nanomaterials, however, have a certain adsorption capacity, after exceeding which they are no longer able to bind any other molecules to their surface. However, their chemical regeneration is possible. For these reasons, interest in the use of nanotechnologies in water treatment has grown rapidly worldwide in

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recent years. Nanoscale materials exhibit various unique properties, and despite their small size, they exhibit a large active surface area and a large ratio of surface area to their total volume. These properties significantly improve their adsorption capacity (Andrade et al.,2018), (Hristovski et al.,2007). Precisely because of their large active surface, nanoparticles are able to interact with various chemical compounds (Kumar et al.,2020). The presented contribution discusses the properties of different types of nanomaterials, while on a theoretical level it processes the scientific knowledge published in this field so far, but it mainly focuses on the possible applications of nanomaterials in the field of monitoring, cleaning and water treatment.

2. Material and methods

2.1 Municipal waste water sampling procedure

Wastewater samples from the municipal wastewater treatment plant (WTP) used for the experimental purposes of this work were collected in the period 2016-2019 as point samples from the inflow and outflow. The selected WWTP has a capacity of approximately 650,000 population equivalents (EO) and consists of a mechanical and biological stage (with nitrification and denitrification). The average daily rain-free inflow to the WWTP is around 110,000 m3/day. The produced sludge is anaerobically stabilized (mesophilic fermentation) and the produced biogas is subsequently converted into heat and electricity in the cogeneration unit.

2.2 Adsorption of micropollutants from municipal wastewater samples using biochar

The biochar of batch 4073, which was used in the tests, was prepared by fast pyrolysis at 470°C from a digestate containing 60% wood pulp and 40% corn separate. Adsorption tests were performed on waste water samples from the municipal wastewater treatment plant. The selected concentration of tested nanoparticles with assumed good sorption properties was weighed into 100 ml of the sample. The experimental conditions were as follows – mixing speed (200 rpm), temperature 20±1°C, pH ≈ 7. The experiment lasted 120 minutes, while samples were taken after 10, 30 and 120 minutes of the duration of the experiment. The samples were subsequently filtered through a cellulose membrane filter (Pragopor, Pragochema s.r.o., Slovakia, pore size 0.4 µm), frozen (-20°C) and transported to the analytical laboratory at the Faculty of Fisheries and Water Conservation, University of South Bohemia in České Budějovice.

2.3 Monitoring and removal of selected micropollutants from wastewater samples using ZnO nanoparticles

Zinc oxide nanoparticles were prepared by a precipitation reaction of 0.5 M ZnSO4 solution and 1 M NaOH solution, while the resulting milky white precipitate of zinc hydroxide Zn(OH)2 after titration, subsequent mixing and settling was filtered through filter paper and dried in the next step in an oven at 70°C for 2 hours. The dye methylene blue (MM) was used to modify the prepared ZnO nanoparticles (the purpose was to shift the photoactivity of the nanoparticles to the visible region of the sunlight spectrum). Degradation tests were performed on wastewater samples from the inflow and outflow of the municipal WWTP. The selected concentration of tested nanoparticles was weighed into 100 ml of the sample. The experiment took place for 1 hour in different conditions (in the dark, under VIS - 40 W source, under UV radiation with a wavelength of 365 nm, in the presence of oxygen) at a temperature of approximately 20±1°C and a pH of approximately 7. The samples were homogenized throughout the experiment on a magnetic stirrer (200 rpm). After the degradation tests, the samples were filtered through a folded paper filter and part of their volume was transported to the microbiological laboratory at the Department of Nutrition and Food Evaluation at the Faculty of Chemical and Food Technology, Slovak Technical University in Bratislava, and the other part of the sample volume was frozen (-20°C). and transported to the analytical laboratory at the Faculty of Fisheries and Water Conservation, University of South Bohemia in České Budějovice.

2.4 Analysis of samples by the LC-MS/MS method

Water samples were allowed to thaw at room temperature prior to analysis. Subsequently, 10 ml was filtered from each sample (regenerated cellulose filter, pore size 0.2 µm – Labicom, Czech Republic) and isotopically labeled internal standards were added to each sample. Extraction and analysis were performed in one step using solid phase extraction (SPE) liquid chromatography combined with a triple quadrupole mass spectrometer (TSQ Quantiva, Thermo Fisher Scientific, USA). 1 mL of sample was injected and captured on a Hypersil Gold aQ column (20 mm length, 2.1 mm ID, and 12 µm packing particle size). The analytes were subsequently eluted with a mobile phase consisting of acetonitrile (acidified with 0.1% formic acid) and water from the SPE column into a Hypersil Gold aQ analytical column (50 mm length, 2.1 mm ID and 5 µm packing particle size). Dilution methods of isotopes and internal standards along with matrix-matched standards were used to eliminate matrix

3. Results and discussion

3.1 Structure of biochar and ZnO nanoparticles

The structure of the tested biochar and ZnO nanoparticles was analyzed using a scanning electron microscope (SEM JEOL 7500F, SEM ZUOVA QUANTA FEG 450) and is shown in the following figures.

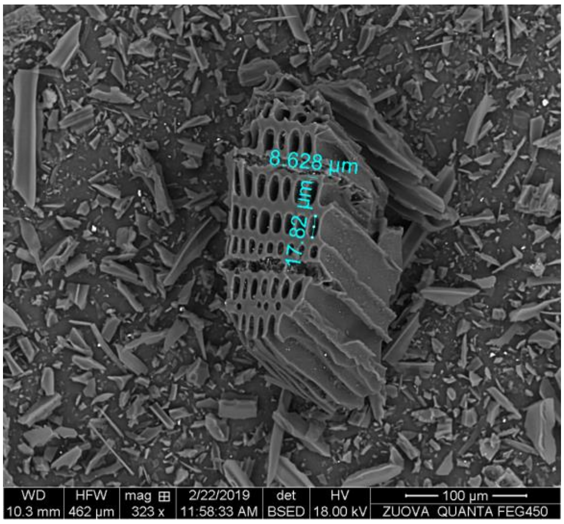

Figure 1 Structure of the tested batch of biochar 4073 under SEM

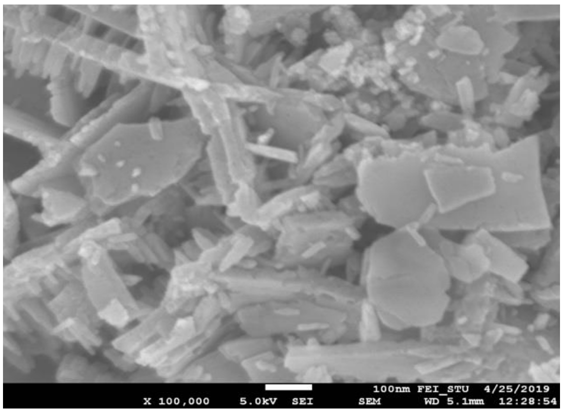

Figure 2 SEM image of the surface of ZnO nanoparticles

3.2 Degradative efficiency of removing drugs, pharmaceuticals and their metabolites from wastewater using ZnO nanoparticles

Degradation tests were carried out in waste water samples from the inflow (diluted inflow) and from the municipal WWTP outflow. Unmodified and modified ZnO nanoparticles were tested in three concentrations (32.2 mg/l; 72.2 mg/l and 122.2 mg/l), while the tests took place in the dark (in the case of modified nanoparticles), under VIS and under UV and degradation in the case of modified nanoparticles also took place in the presence of oxygen. The results show that none of the tested types of ZnO nanoparticles achieve high degradation efficiency for the selected drugs and their metabolites. Since the efficiency of degradation was similar under all conditions, only the results of degradation under UV radiation (365 nm, 60 min) are presented, which are shown in Figure 3. However, the use of ZnO nanoparticles in the case of removing micropollutants such as drugs or pharmaceuticals from water appears to be effective when these nanoparticles are incorporated, for example, into the ceramic surface of membranes intended for ultrafiltration. In a study by Bhattacharya et al. investigated the effectiveness of drug removal from a synthetic water sample using a membrane modified in this way. In the case of the drugs atenolol and ibuprofen, 96% and 99% removal efficiency were achieved (Bhattacharya et al.,2020).

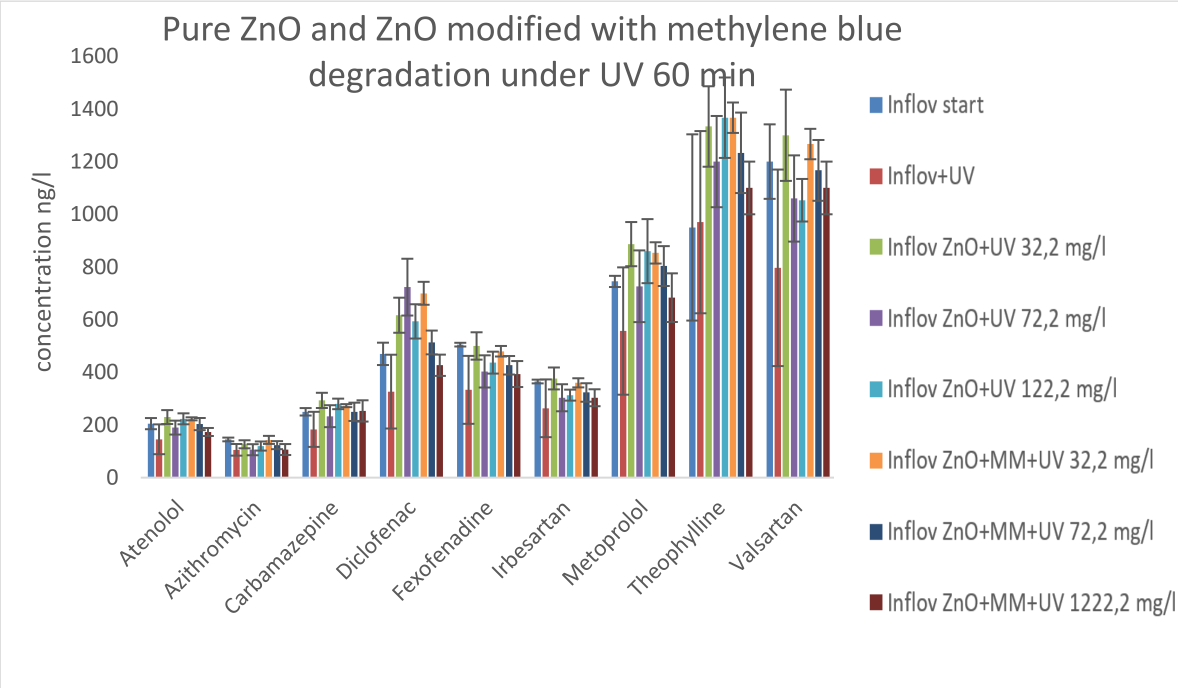

Figure. 3 Results of degradation tests of ZnO and ZnO+MB under UV radiation (365 nm, 60 min) for selected drugs.

3.3 Adsorption capacity of biochar in removing selected micropollutants from water

The tested biochar of batch 4073 (mixed from raw materials in the ratio of 60% wood separate and 40% corn separate) demonstrated the ability to remove several types of pharmaceuticals and their metabolites from wastewater originating from the municipal sewage treatment plant. The highest removal efficiency was achieved for the drugs carbamazepine, cetirizine, telmisartan, irbesartan, metoprolol and venlafaxine (more than 80% removal efficiency even at the lowest amount of added biochar). All these drugs belong to micropollutants, which are regularly found in waste water samples in the order of hundreds to thousands of ng/l (Mackuľak et al.,2016). The graphs in the following figures (Figs. 4 and 5) show the influence of the amount of biochar used on the efficiency of the removal of individual drugs and their metabolites.

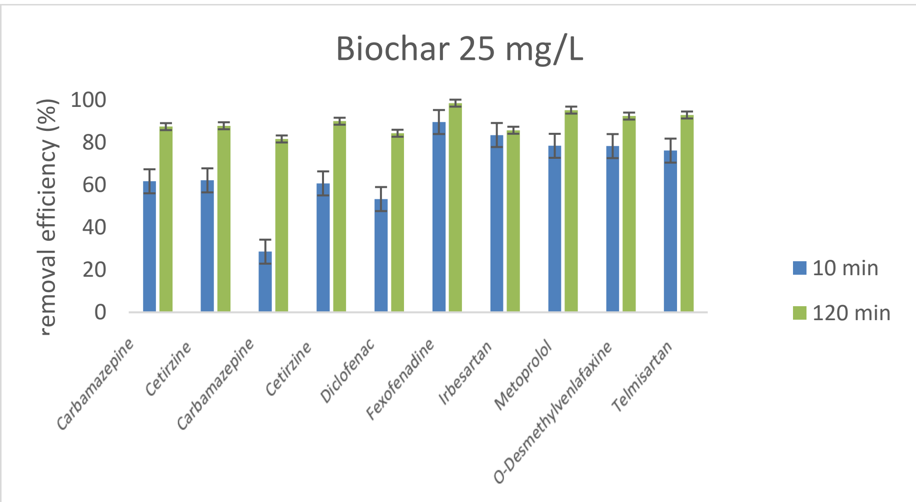

Figure 4 Effectiveness of the removal of selected pharmaceuticals from a waste water sample from the municipal WWTP effluent at a biochar concentration of 25 mg/l at different times

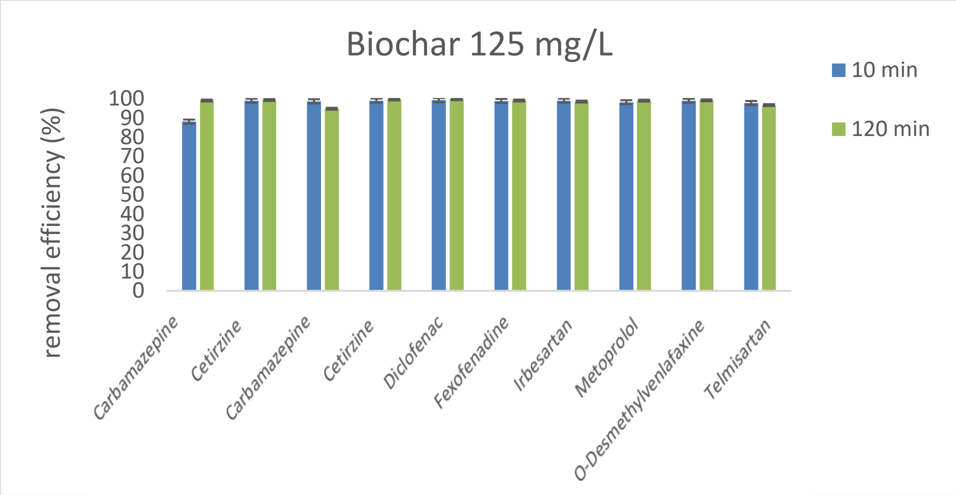

Figure. 5 Effectiveness of the removal of selected pharmaceuticals from a waste water sample from the effluent of a municipal WWTP at a biochar concentration of 125 mg/l at different times

It is clear from the results that the use of 125 mg/l biochar achieved more than 90% efficiency in the removal of selected drugs. Similar results were also recorded in the case of the drugs sulfamethoxazole and ibuprofen using biochar made from wood chips (Lin et al.,2017). Another study used biochar made from plant substrates and sewage sludge as an adsorbent for antibiotics (sulfamethazine, ciprofloxacin, oxytetracycline, florfenicol) present in pig manure. In this case, biochar prepared from plant substrates proved to be a more effective adsorbent (Ngigi et al.,2019).
Conclusion

4. Conclusions

In recent years, nanomaterials and nanotechnologies have received a lot of attention from various scientific branches and have considerable potential for use in various fields of industry, medicine, biology, electrical engineering, and environmental fields. There are many different types of nanomaterials, from which various composites are gradually created to improve their properties or reduce the cost of their production. Drinking and harmless water is inevitable for mankind. Therefore, proper attention is paid to its preparation and cleaning. Since nowadays a large number of different micropollutants, such as residues of drugs, pharmaceuticals, hormones or microplastics, enter the waters, it is necessary to deal with new technologies for removing these substances from waste, surface or drinking water. One of these newly researched technologies is the use of nanomaterials and their composites to remove various contaminants from water. The research carried out in this work was mainly focused on nanomaterials showing good adsorption properties, such as biochar, but also on nanomaterials showing photocatalytic properties, for example zinc oxide. In the case of biochar, it has been found to be capable of significantly removing a wide range of contaminants from different types of water. Its good adsorption properties depend mainly on the structure of its surface, which is porous, which was also confirmed by surface analyses. However, compared to biochar, ZnO nanoparticles did not show high degradation efficiency. However, this does not mean that these particles are not effective for removing micropollutants, but it is necessary to consider the possibility of incorporating them into various surfaces, such as ceramic tiles, which can increase their degradation efficiency.

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