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Biodegradation of the Personal Care Products †

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Abstract: Excessive consumption of cleaning and disinfecting agents, which constitute a distinct group of emergent pollutants known as PPCPs ("Pharmaceutical and Personal Care Products"), results in their accumulation in aquatic environments. Conventional wastewater treatment plants are unable to effectively remove the emergent pollutants that are present, including personal care product residues. This article focuses on the determination of surfactant substances in model samples prepared from selected personal care products and their biodegradability under laboratory-created aquatic ecosystem conditions. The conducted biodegradation processes, based on the monitored indicator (surfactants) in the model samples, confirm that the utilization of aquatic vegetation and gravel substrates can efficiently eliminate the present contaminants. Insights gained from researching the biodegradability of PPCP group products are applicable, including experiences with plant compositions used in aquatic environments, particularly in the construction of root-zone wastewater treatment systems.

Keywords: pharmaceutical and personal care products (PPCPs); surfactants; biodegradation; aquatic ecosystem

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1. Introduction

Wastewater constitutes a high-risk mixture of pollutants which contaminates the environment and threatens human health. In most cases, wastewater treatment plants (WWTP) only partially reduce the content of the specific pollutants present in the treated water. Treated wastewater can still contain a complex mixture of toxic pollutants, which include, e.g., detergents, various disinfectants and cleaning agents, drug and pharmaceutical residues, or pesticides [1,2]. The wastewater treatment process is aimed at achieving the quality of discharged purified water in terms of selected physico-chemical indicators resulting from valid legislation, but not at monitoring the content of specific substances. The content of specific substances has been constantly increasing in recent years.

Specific pollutants can mix in wastewater causing a "cocktail effect" to occur. This effect represents a significant risk caused by the uncertain and unclear response of toxicants and their difficult to predict impact on the recipient and the aquatic environment [3]. The presence of specific pollutants in waters can result in a change in their sensory, organoleptic, and physical properties and affect chemical and biological processes [4,5]. Unstudied substances present in the aquatic environment can be called "contaminants of emerging concern" (CECs)—emerging pollutants. They can potentially or have even been confirmed to threaten human health and the environment [6]. These are substances that reach recipients for a long time, but their importance and impact on the quality of the aquatic environment has not been investigated.

Emerging pollutants have attracted worldwide attention due to their highly toxic effects, very low degradation, long-term action, and extensive distribution in the environment [7]. Determining the presence of emergent pollutants currently brings new challenges in the field of pollution control in all areas of the environment. The presence of emergent pollutants is beginning to be determined primarily in sewage wastewater, but also in surface and drinking water worldwide [6], with the aim of improving the level and quality of environmental analysis.

A special group of emergent pollutants consists of "Pharmaceutical and Personal Care Products" (PPCP's). These are new, modern polluting substances that have been entering the environment over the last several decades. These include, e.g., medicines, nutritional supplements, cleaning and disinfecting agents, cosmetics, and other products commonly used by society [8,9].

Their continuous use and release into the environment causes serious biological damage (persistence in the form of bioaccumulation in the environment, damage to fauna and flora, etc.) [10–12]. In addition to the abovementioned products, the consumption of washing powders, tablets, gels, capsules, etc. has also increased [13,14].

In article [15], we present the results of monitoring surfactants contained in PPCPs. The results of monitoring their content in surface waters prove the need to pay increased attention to them within the treatment process. This article deals with the biodegradation of surfactants contained in PPCPs in the aqueous environment in model samples.

2. Methods and Material

2.1. Model Samples

The model samples used in the research present the real use of the products in households, hotels, schools, etc. The model samples were prepared using products from the group of PPCPs (Tables 1 and 2). The selected products were dissolved in drinking water based on the dosage and method of use which is indicated on the labels of these products (the products in Table 1 have an MSDS—Material Safety Data Sheet, the products in Table 2 are health tested and harmless).

Table 1. Cleaning and disinfecting agents used for the preparation of model samples.

Standard Products	Ecological Products
Washing gels	
Savo chlorine free Persil Sensitive Ariel Touch of Lenor	Delizia Lavatrice Actilife Universe gel
Washing powders/tablets	
Persil Lovela Sensitive	Universe tablets
Products for the toilet	
Domestos Extended power	Toilet Supergel Frosch Eko WC
Means for cleaning and disinfecting surfaces, removing dirt—floors	
Alex Extra Protection	Lamino & Lino
Kitchen products	
Jar	Ecobalsam aquatix

Table 2. Cosmetic preparations used on model samples.

Ziaja—shower gel with goat's milk Ziaja—shampoo with goat´s milk Balea—Creamy shower gel Dove—body and face gel for men	Dove—hard soap for hands Sanytol—nourishing liquid soap Sensodyne—toothpaste Elmex—toothpaste

2.2. Biodegradation

The model samples were poured into glass containers. In laboratory conditions, in the presence of selected aquatic plants, surfactant degradation processes took place. Their content was continuously checked. The surfactant indicator represents non-active substances that primarily ensure the cleaning effect in the tested products and are water soluble.

Detailed approach and optimization of conditions:

1. Description of the container (aquarium):
    - created to ensure a natural aquatic ecosystem;
    - container volume of 32 L, model sample volume of 25 L;
    - substrate: aquarium gravel substrate;
    - plant communities were formed by plants of the species: *Egeria*, *Limnophila*, *Cabomba*, *Anubias*, *Echinodorus*, *Ceratophyllum*, and *Lemna minor*;
    - aeration: aerating motors with pebbles;
    - addition of CO_2: the Neo CO_2 system based on the production of this oxide by the yeast Saccharomyces cerevisiae.
2. Evaluation of the dismantling process:
    - Determination of surfactants at the beginning, after 24 h, and after 48 h.
3. Optimization of surfactant degradation conditions in model samples:
    - the concentration of surfactants in the samples;
    - effect of aeration (addition of O_2) or addition of CO_2;
    - dismantling time.

The biodegradation process took place under laboratory conditions at a constant air-conditioned room temperature.

2.3. Determination of the Surfactant Content

The determination of surfactant content was based on the reaction of a water sample with methylene blue. Anionic surfactants in alkaline media form coloured ionic associates with methylene blue, which are extracted with chloroform. The absorbance of the samples at 650 nm is evaluated. The WTW CINTRA 20 spectrophotometer (GBS Scientific Equipment Pty. Ltd., Melbourne, Australia) was used (STN EN: 903; Water Quality) [16].

3. Results and Discussion

3.1. Process Optimization

The process of the biological degradation of surfactants, which was carried out in the model samples, required the optimization of the conditions.

We found that high surfactant contents in model samples are not suitable for degradation. The reason is the excessive load on aquatic plants and their related damage (destruction of phytomass), which caused the process of their regeneration to be long-term and in many cases their reuse was not possible. A special case were products that contained higher amounts of aggressive ingredients, such as hydrogen peroxides, hydroxides, and other biocidal components that caused an immediate lethal effect on aquatic plants.

Based on previous experience [17], we diluted the model samples so that the total surfactant content was in the range of 15–20 mg/L. We also based on the information that the total content of surfactants in sewage wastewater is lower than the determined content of individual personal care products (wastewater containing various cleaning and disinfecting agents is mixed and diluted in the sewage system).

During the biodegradation process, we used aeration motors to provide O_2. Based on the monitored concentrations of surfactants in the samples obtained during the degradation process, we found that the addition of oxygen significantly slowed down the process. A negative impact was also caused by the intensive formation of foam, which prevented the access of atmospheric oxygen to the aquatic ecosystem that was created.

CO_2 occurs naturally in aquariums (flora respiration and gas exchange above the water's surface). By using the Neo CO_2 system, we ensured the gradual release of natural CO_2 into the water. CO_2 is the basis for photosynthesis and its supply stimulates the growth of flora and maintains good health. The use of this system significantly slowed down the degradation of the surfactants that were present. The plants were in good condition. We conclude that as a source of nutrition, the plants used more easily available CO_2 (for the needs of photosynthesis) and therefore the content of the surfactants did not change significantly during the degradation process. Based on these findings, we continued the biodegradation process without the addition of O_2 and CO_2.

For the efficiency of the use of biodegradation processes on a larger scale in practice, it is necessary that the retention time and the time of the degradation of surfactants be as short as possible. If the concentration of surfactants in the model samples is kept to 20 mg/L, the degradation time is in the range of 24–48 h. The maximum permissible concentration of anionic surface substances in surface waters (1 mg/L) was also observed in accordance with the Regulation of the Government of the Slovak Republic, No. 269/2010 Coll., which specifies the requirements for achieving good water status.

3.2. Evaluation of the Biodegradation Process

The biodegradation process is described in Table 3. Ecological washing gels had a higher % degradation after only 24 h compared to "standard" washing gels. The average % degradation of "standard" washing gels after 48 h is 91.77%, i.e., 6.34% less than the average value for ecological gels (98.11%). In the Persil washing powder, the content of surfactants after 24 h was reduced by 51.21% and after 48 h, the surfactant concentration was only 0.98 mg/L. The Lovela Sensitive washing powder and Universe tablets had no significant differences during degradation and after 48 h > 98% was degraded. The biodegradation of Domestos WC gel ended after 0.5 h from the addition of the model sample to the aquatic ecosystem. This product contains biocidal ingredients that caused permanent damage and death to the aquatic plants. From the point of view of the protection of water ecosystems it is more appropriate to use ecological WC gels whose % degradation after 48 h was > 96%. Alex Extra Protection floor cleaner is 49.97% less biodegradable after 24 h and 9.34% less biodegradable after 48 h compared to the ecological product Lamino & Lino. The ecological product Ecobalsam is more biodegradable by 8.03% after 48 h compared to Jar.

Table 3. The biodegradation process.

Cleaning/Disinfectant Product	Concentration of the Surfactants				
	At the Beginning mg/L	After Biodegradation 24 h		48 h	
		mg/L	%	mg/L	%
Washing gels					
Savo chlorine free	10.32	4.22	59.11	0.83	91.96
Persil Sensitive	9.82	3.88	60.49	0.91	90.73
Ariel Touch of Lenor	10.57	4.15	60.74	0.78	92.62
Delizia Lavatrice Actilife	11.01	2.94	73.30	0.27	97.55
Universe gel	10.47	2.11	79.85	0.14	98.66
Washing powders/tablets					
Persil	12.85	6.27	51.21	0.98	92.37
Lovela Sensitive	10.38	4.15	60.02	0.13	98.75
Universe tablets	12.01	4.28	64.36	0.21	98.25

Table 3. *Cont.*

Cleaning/Disinfectant Product	Concentration of the Surfactants				
	At the Beginning mg/L	After Biodegradation 24 h		48 h	
		mg/L	%	mg/L	%
Products for the toilet					
Domestos Extended power	9.86	the process ended after 0.5 h. (biocide)			
Toilet Supergel	9.97	4.36	56.27	0.37	96.29
Frosch Eko WC	9.91	3.11	68.62	0.31	96.87
Means for cleaning and disinfecting surfaces. removing dirt—floor					
Alex Extra Protection	8.44	5.15	38.98	0.94	88.87
Lamino & Lino	9.15	2.02	77.925	0.18	98.03
Kitchen products					
Jar	11.39	5.3	53.47	0.96	91.57
Ecobalsam aquatix	12.87	1.47	88.54	0.06	99.57

Organic products biodegrade faster than "standard" products. Some of them (e.g., Lamino & Lino floor cleaner, Universe tablets and Universe washing gel) have a higher surfactant content than "standard" products from their categories but they still biodegrade faster.

4. Conclusions

Emergent pollutants, including PPCPs require attention due to their highly toxic effects, low degradation, long-term effects, and extensive distribution in the environment. Determining their presence in the environment brings new challenges in the field of pollution control and in finding ways to quickly remove them.

One of the methods of their removal is biological degradability using aquatic flora. By optimizing the conditions of the surfactant biodegradation process in model samples a suitable concentration of up to 20 mg/L was found. This is the concentration that plants can effectively break down. Excessive loading (at a higher concentration) of vegetation can result in permanent damage or the limitation of its functionality and thereby slows down the degradation process. We found that the artificial addition of O_2 to the biodegradation process is not suitable. It significantly slows down decomposition and increases foam production. The addition of CO_2 also slowed surfactant degradation as the plants began to use the more readily available CO_2 from the Neo system for their growth. For the effective use of biodegradation processes on a larger scale in practice, the retention time and the time of degradation must be as short as possible. At a concentration of up to 20 mg/L the degradation time is up to 48 h and the content of surfactants in the water meets the criterion from the Regulation of the Government of the Slovak Republic, No. 269/2010 Coll., which specifies the requirements for achieving good water status (<1 mg/L).

We found that products labelled as organic biodegrade faster than "standard" products. Through the implemented biodegradation processes under laboratory conditions, we managed to break down the surfactants in all samples made from cleaning and disinfecting agents with a break down time of up to 48 h without the addition of O_2 and CO_2.

PPCP products are widespread, and their assortment is very large, therefore, it is important to pay increased attention to the indicator of surfactants in wastewater as well as in surface water. Based on the principle of biodegradation which we implemented under laboratory conditions, root wastewater treatment plants work. The results of this research can be used precisely in the construction of root wastewater treatment plants (experience with plant compositions used in the aquatic environment). Another option for the use of root wastewater treatment plants is the addition of conventional municipal wastewater treatment plants where they would perform the function of purifying wastewater before discharging it to the recipient [18].

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