Adsorption of silver on virgin and aged microplastics

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Abstract
When microplastics enter aquatic ecosystems they are submitted to environmental aging which change their properties. Especially colonization by microorganisms alter their properties in term of density and adsorption properties. Hence the aim of the study was to evaluate the adsorption and leaching properties of virgin and aged microplastics. Silver (in form of silver nitrate) was selected as a model metal used for adsorption study. Results showed that silver is quickly adsorbed on both types of microplastics while aged microplastics adsorbed significantly more silver than virgin ones. However, also leaching of silver from aged particles proceeds much faster - after 48 hours in Steinberg medium (pH = 5.8), only 23.7% of silver was leached out from virgin microplastics in comparison to 45.6% leached out from aged microplastics. In OECD medium (pH = 7.3) leaching was minimal. Our results showed that aging of microplastics and development of biofilm can significantly alter their properties and thus it is necessary to enhance our knowledge about microplastics' aging in the aquatic environment, which is still far from well-understood.
Keywords: aging, adsorption, biofilm, microplastics, silver

1. Introduction

Enormous global production of plastics has been, for the last decades, strongly reflected in global plastic pollution. Recently the most discussed topic regarding plastic pollution is generation, occurrence, and impact of microplastics (MPs) on the environment (Sagawa et al. 20108). MPs represent small plastic fragments that exhibit a size from a few µm to 5000 µm. They can be subdivided into primary MPs, which are manufactured at a specific size range, and secondary MPs, which are fragmentation products of larger plastic materials (Andrady, 2011) entering inland waters when plastic is illegally disposed, accidentally lost or carelessly handled (Morritt et al., 2014). Primary MPs entering inland waters are mainly represented by polyethylene microbeads used in personal care products. According to the market analysis and consumer survey, about 15.2 mg of MPs per person can be daily released from cosmetic peelings in Ljubljana (Kalčikova et al., 2017). Although the removal efficiency of wastewater treatment plants is high (up to 98%, Murphy et al., 20106) MPs can be retained in wastewater treatment plants, a substantial amount is released into freshwater ecosystems. In freshwaters, MPs are rapidly colonized by microorganisms and algae altering their properties (Reisser et al., 2014). Furthermore, MPs can interact with anthropogenic pollutants - in freshwaters most probably with pesticides and metals. They can be adsorbed on MPs surface and therefore, MPs can be a potential vector for long-distance transport of pollutants. In this context the aim of the study was to evaluate adsorption of model metal ion - silver in the form of silver nitrate - and consequent leaching under different conditions.

2. Materials and Methods

MPs used in this study were polyethylene particles extracted from a common body scrub. MPs were submitted to environmental aging by exposing to simulated natural conditions for three weeks by incubation in stream water. The stream water contained naturally active microorganisms that can develop biofilm on the MPs surface (Figure 1). Furthermore, virgin and aged MPs were placed (1 g/L) into Ag solution (10 mg Ag/L, prepared from $AgNO_3$ in OECD medium (Test No. 202), 160 rpm) for seven days. During the experiment, the concentration of Ag in solution was monitored daily. Afterward, virgin and aged MPs were removed from the solution by filtration and analyzed for Ag content. MPs (100 mg/L) with adsorbed Ag were again placed into OECD medium (pH = 7.3) and Steinberg medium (ISO 20079, 2005) (pH = 5.8) and concentration of Ag released into the medium after 48h was monitored. Ag adsorbed on MPs and in solutions was determined by ICP-MS (Agilent 7900ce, Agilent Technologies, Palo Alto, CA, USA).

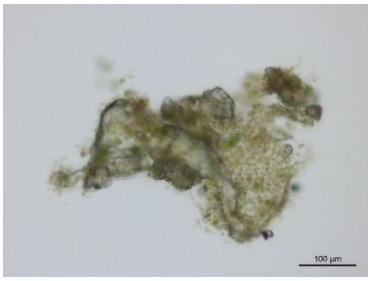

Figure 1. MPs with developed biofilm – aged MPs

3. Results and Discussions

MPs extracted from a body scrub were in the form of a white powder and made of polyethylene. They had a low density and floated on a water surface. During the aging study, biofilm was developed very quickly. Already after 24 h of the experiment green and brown spots were noticed, indicating presence of algae and microorganisms. It also led to the increase of density and sinking of MPs.

Adsorption of Ag on virgin and aged MPs proceeded very quickly, as most of the available Ag was adsorbed during the first day in both cases (Figure 2). However, the decrease of Ag in solution was probably not only due to adsorption of Ag on MPs but also due to the reduction of Ag^{+} into Ag^{0}. In flask with virgin MPs, grey pieces of reduced silver metal were noticeable already after one day of the experiment, while in flasks with aged MPs no such precipitate was observed. At the end of the experiment, the amount of adsorbed silver on aged MPs was significantly higher than on virgin MPs being 3.51 ± 0.50 mg/g and 2.44 ± 0.22 mg/g, respectively.

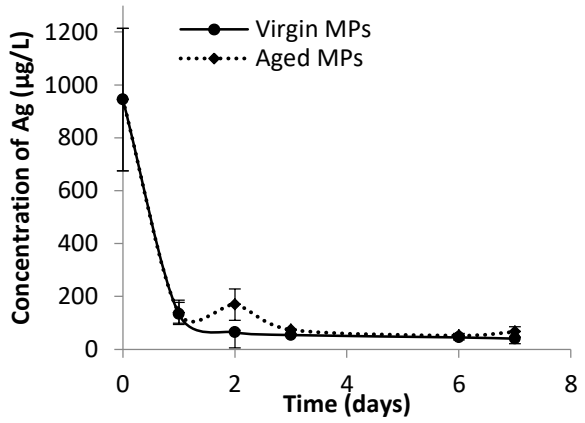

Figure 2. Decease of Ag concentration during adsorption of Ag on Virgin and Aged MPs

The leaching experiment showed that silver is quickly leached out from both types of MPs when they are introduced into the Steinberg medium while in OECD medium the leaching was minimal (Table 1). In all experiments more Ag was always leached from aged MPs which is probably caused by weak adsorption of Ag on algal and bacterial biomass of formed biofilm.

Table 1. Leaching of Ag from virgin and aged MPs in Steinberg and OECD medium after 48h

Microplastics	Leaching from medium (%)	
	Steinberg	OECD
Virgin	23.7	1.2
Aged	45.6	1.9

Both media are used for the growth of plant species, but they strongly differentiate by contents of various ions and also by pH. In the OECD medium, the leaching was minimal which is caused probably by the higher pH value (pH = 7.3), that could lead to precipitation of silver(I) oxide on the surface of MPs and thus preventing release of soluble silver, which is in accordance with lower solubility of Ag_2O reported for higher pH (Molleman and Hiemstra, 2017). Whilst in Steinberg solution almost two orders of magnitude lower pH value (pH = 5.8) enabled significally more Ag to be released into solution, presumably as hydrated Ag^{+} ions and/or in the form of soluble complexes.

4. Conclusions

Our experiments showed that the aging of MPs significantly alters their properties. Development of biofilm increase MPs density and it also alter their adsorption potential. Aged MPs with developed biofilm adsorb more Ag and when they appear in freshwaters they can also release more Ag due to the weak adsorption of Ag on biomass in comparison to virgin MPs surface. Obtained results showed that MPs have a potential to adsorb and carry a substantial amount of Ag and when natural conditions are changed (e.g. in acidified freshwaters) Ag can be further released into the environment

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