Marine Pollution Bulletin xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

Sorption of three synthetic musks by microplastics

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ARTICLE INFO

Keywords:
Microplastics
Musk
Adsorption
Polypropylene
Model

ABSTRACT

Microplastics and synthetic musks (SMs) are two typical organic pollutants in the marine environment. In this study, the sorption of three SMs to microplastics in a simulated seawater environment was examined. Tonalide (AHTN), musk xylene (MX), and musk ketone (MK) were the musks investigated, while polypropylene (PP) was used as the microplastic. It was found that the equilibrium sorption time was about 10 h and the adsorption kinetics model conformed to a Lagergren adsorption model. The adsorption capacity increased with decreasing particle size. Adsorption reached a peak at 25 °C, and the adsorption capacity was not sensitive to the concentration of sodium chloride. There is a need for more research and monitoring of microplastics in the marine environment due to their strong ability to absorb organic pollutants.

In the few decades since the mass production of plastic began in 1950, plastic pollution has spread to terrestrial and oceanic locations, including coastal regions and even the deep sea (Eriksen et al., 2013). Recently, a coastline and ocean survey found that the accumulation of plastic was no longer showing sustained growth, but was in a state of dynamic equilibrium, although the plastic particle size had tended to become smaller (Barnes David et al., 2009). The United States Oceanic and Atmospheric Administration (NOAA) defines microplastics as plastic fragments or particles of less than 5 mm. There are many sources of microplastics, including cosmetic additives, laundry wastewater, and the photolysis of large plastics (Fendall Lisa and Sewell Mary, 2009). Under the action of ocean currents, microplastics have become dispersed around the globe, and have even been found in the ice of the Arctic Ocean (Auta et al., 2017).

Microplastics are potential carriers of heavy metals and organic pollutants due to their recalcitrance and high specific surface area (Dennis et al., 2016). Large concentrations of polyaromatic hydrocarbons (PAHs) have been found in plastics in the North Pacific (Lorena et al., 2015), and studies have shown that copper (Cu), zinc (Zn), polychlorinated biphenyls (PCBs) (Farrington and Takada, 2014), and dichlorodiphenyltrichloroethane (DDTs) (Bakir et al., 2014) can also be adsorbed by microplastics. Moreover, microplastics are easily swallowed by many marine species, including fishes (Jantz et al., 2013), seabirds (Lenzi et al., 2016), and lugworms (Verlis et al., 2013). Although there are many potential hazards associated with microplastics, there have only been a few studies of microplastic particles in the ocean. Synthetic musks (SMs), i.e. organic matter with an odour similar to that of natural musk, have been widely manufactured and used as fragrance additives in chemical commodities for daily use, such as perfumes, cosmetics, soaps, shampoo, household cleaners, and other household products (Reiner and Kannan, 2006).

In this study, the sorption of SMs by polypropylene (PP) was investigated. The purpose of the study was to: (1) establish an adsorption equilibrium curve model for the adsorption by PP of the three musks under study; (2) determine the effects of different conditions on the adsorption capacity; and (3) determine the reasons for any difference in adsorption among the three musks.

Tonalide (AHTN), musk xylene (MX), and musk ketone (MK) were all purchased from Dr. Ehrenstorfer (Augsburg, Germany). Sodium chloride (NaCl) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). PP, obtained from the Saudi Basic Industry Corporation (SABIC; Riyahd, Saudi Arabia), was cut into pieces smaller than 5 mm, ground to achieve a smaller particle size, and finally screened with mesh, with pore sizes of 5, 2, 0.85, 0.425, and 0.125 mm, to obtain microplastics with particle sizes of 2–5, 0.85–2, 0.425–0.85, or 0.125–0.45 mm. Solvents, including methanol, n-hexane (HEX), dichloromethane (DCM) isooctane, and acetone, were all of high performance liquid chromatography (HPLC) grade. Simulated seawater was prepared with a 3.5% NaCl solution.

To ensure the accuracy of the experiment, PP particles were washed with acetone and deionised water, and then dried at 40 °C. A mixed standard solution of the musks was prepared from stock solution diluted with isooctane. The calibration curves for the different SM standards are shown in Table 1.

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http://dx.doi.org/10.1016/j.marpolbul.2017.09.025
Received 18 May 2017; Received in revised form 9 September 2017; Accepted 11 September 2017

Table 1
Regression equations, correlation coefficients, limits of detection (LOD), and limits of quantitation (LOQ) of three synthetic musks.

Compounds	Linear equations	Correlation coefficients (R^2)	LOD (ng/g)	LOQ (ng/g)
AHTN	y = 101.57X + 772.89	0.999	0.12	0.36
MK	y = 39.176X + 172.89	0.998	0.09	0.28
MX	y = 16.476X + 440.48	0.998	0.11	0.3

The sorption experiments were performed at room temperature. A 20-mg mass of microplastics, with a particle size of 0.45–0.85 mm, was accurately weighed and packed in nine 15 ml colorimetric tubes filled with 10 ml simulated seawater. Then, 50 µl of 1 mg/l mixed standard solution was added. The concentration of working solution was 5 ng/g. The solutions were shaken for 30 min at 220 rpm; plastic debris was collected after 0, 2, 4, 6, 8, 10, 12, 15, and 24 h, and then washed with HEX and DCM, concentrated to 0.5 ml, and finally transferred to a bottle (Agilent, Santa Clara, CA, USA). The concentrations of the musks were determined by gas chromatography (GC) (7890 A; Agilent) equipped with a mass spectroscopy (MS) detector (5975C; Agilent) and an HP-5 chromatographic column (30 m × 0.32 mm × 0.25 µm). The temperature program for the GC oven was set as follows: initial temperature of 90 °C (held for 2 min), increased to 170 °C at 10 °C/min, then increased to 180 °C at 1 °C/min, and finally increased to 270 °C at 30 °C/min (where it was held for 7 min) (Lou et al., 2016).

The sorption kinetics of AHTN, MX, and MK to PP in the simulated seawater are shown in Fig. 1.

Fig. 1 shows that the adsorption equilibrium time of the three musks to the PP was about 10 h in the simulated seawater. Zhiwei et al. (2016) found the equilibrium sorption time of PCB77 to PP to be about 8 h; however, the adsorption equilibrium time of PCBs in natural water is of the order of a few months (Rochman et al., 2013). It was therefore concluded that the equilibrium time of the three musks exceeded 10 h in natural water. These differences might be due to natural water being a complicated system, with many components and mediums, and complex adsorption conditions (Li et al., 2016). The maximum amount of adsorption was about 1300, 1800, and 1200 ng/g for AHTN, MX, and MK, respectively, at a concentration of 5 µg/l. The concentrations of musks in the simulated water were similar to the concentrations in waste water from sewage treatment plants, while the maximum adsorption capacity was close to the absorptive capacity of sludge. Microplastics cannot be treated by sewage disposal plants (Kai, 2004), and more attention should therefore be given to the concentration of microplastics in sewage treatment plants.

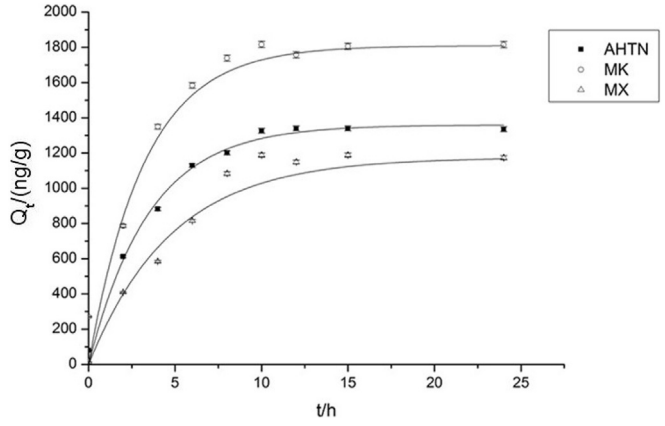

Fig. 1. Sorption kinetics of three musks to polypropylene (PP) in simulated seawater at room temperature.

Table 2
Kinetic constants for the adsorption of three musks to polypropylene (PP).

Compounds	Linear equations	Correlation coefficients (R2)
AHTN	$y = 1365 \times (1 - e - 0.2829)$	0.9917
MK	$y = 1842 \times (1 - e - 0.3163)$	0.9738
MX	$y = 1258 \times (1 - e - 0.1956)$	0.9640

The adsorption kinetics conformed to a Lagergren adsorption model (Skrip et al., 2013):

$Q_t = Q_e \times (1 - e^{-kt})$where Q_t (ng/g) is the adsorption amount at time t, Q_e (ng/g) is the equilibrium absorption capacity, and k is the rate constant. The kinetic constants for the adsorption of the three musks to PP are shown in Table 2.

All of the correlation coefficients were greater than 0.95, which indicated that the adsorption of the three musks to PP could be described with a first-order model. The first-order adsorption kinetic model was based on a single adsorption process, in which the reaction rate was limited only by the adsorption site (Vrind Bea et al., 2006). Therefore, MK may have more adsorption sites than AHTN and MX, but it was difficult to determine whether the adsorption was physical or chemical. Further research is needed to determine the mechanism of adsorption under different sorption conditions.

The results under different conditions, including the particle size, temperature, and concentration of NaCl are shown in Figs. 2, 3, and 4, respectively.

Fig. 2 shows the effect of particle size on the adsorption of AHTN, MX, and MK to PP, at initial musk concentrations of 5 µg/l, after 10 h. MK could be detected in all samples, but it was adsorbed less effectively than the other musks. AHTN and MX were not detected in plastics with a particle size of 2–5 mm; however, in the other samples, AHTN had the highest adsorption capacity of the three musks tested. This may be due to the surface of the microplastics forming a functional group that could form a coordination bond with MK, producing coordination adsorption. The adsorption capacity increased significantly with a reduction in plastic particle size. It is possible that the smaller-sized particles had larger specific surface areas (Heister, 2016). Due to the chemical inertness of microplastics, the specific surface area could be a key factor affecting the adsorption capacity of plastics. Some studies have reported that plastic particle sizes have tended to become smaller (Terepocki et al., 2016). The decreasing size of plastic particles poses a potential risk to the marine environment.

Fig. 3 shows that at temperatures of 25 °C, the highest adsorption capacities of AHTN, MX, and MK were 1696, 2109, and 1846 ng/g, respectively, and the lowest adsorption capacities were 943, 736, and 937 ng/g. This indicates that 25 °C is probably the optimum

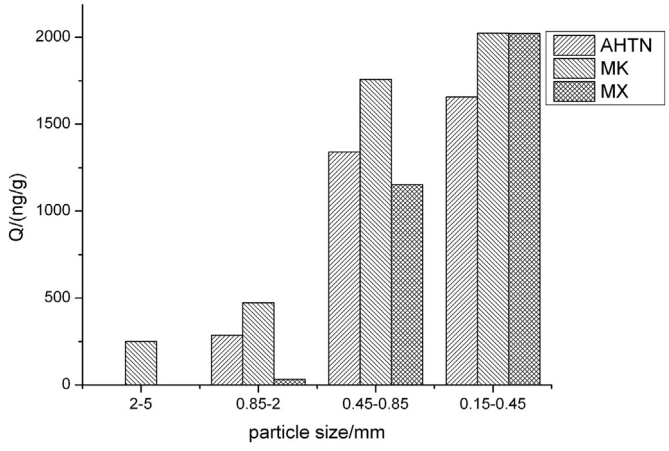

Fig. 2. Relationship between particle size and the sorption of tonalide (AHTN), musk xylene (MX), and musk ketone (MK).