doi.org/10.52568/000685/JCSP/42.05.2020

Hydrophobic Pesticide Endosulfan (α + β) and Endrin Sorption on Different Types of Microplastics

[1]Meral Yurtsever, [1]Nurtac Oz*, [2]Abdullah Aksu, [2]Nuray Balkis, [3]Gulsen Altug and [2]Ömer Suat Taşkın
[1]*Department of Environmental Engineering, Engineering Faculty, Sakarya University, 54187 Sakarya, Turkey.*
[2]*Department of Chemical Oceanography, Institute of Marine Science and Management, Istanbul University, 34134, Istanbul, Turkey.*
[3]*Department of Marine Biology, Faculty of Aquatic Science, Istanbul University, Istanbul, Turkey.*
mevci@sakarya.edu.tr, nuroz@sakarya.edu.tr*

(Received on 8th August 2019, accepted in revised form 2th June 2020)

Summary: Ease of plastics production has caused high usage in many areas from water bottles, furniture and packaging to cosmetics during the last decade. Plastic products cause environmental pollution due to the high demand in the industry. It is known that pesticides are used to prevent various pests in order to increase production efficiency. With the use of such substances, there is considerable growth in the amount of product. However, pesticides remain on the water, soil, fruits, and vegetables for a long time, causing environmental pollution and thus leading to various damages that can reach people through the food chain. Since some of the mostly found pesticides in the environment are endosulfan and endrin, the sorbing capacities of endosulfan and endrin on microplastics have been investigated. The kinetic parameters at 23 °C in ultrapure water, hexane and saline water have been tested to show the effect of solvents on sorption behaviors.

Keywords: Microplastics; Endosulfan; Endrin; Sorption; Pesticide, Pollution.

Introduction

Plastics are materials produced for multipurpose uses highly resistant to degradation. Large plastic materials are degraded as a result of physical, chemical and biological processes and microplastics (MPs) are formed with sizes smaller than 5 mm [1-5]. MPs are among the greatest threats to aquatic organisms [6-8]. MPs can also be transferred as food from trophic level 1 to organisms at higher trophic levels, inducing biomagnification and bioaccumulation through food chains [9-12].

Intake of MPs at elevated levels can be toxic, especially when they may contain hazardous additives (BPA, phthalates, Pb), and as they have a high sorption capacity for some metals [13] and organic pollutants, they can act as carriers of pollutants. [14-17]. Since many hydrophobic organic compounds (HOCs) are long-lived, they may spread widely via soil, water [18] and air. MPs can adsorb HOCs, polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs), perfluoroalkyl acids (PFAA), pharmaceuticals and personal care products (PPCP) and metals found in water. Hydrophobic organic compounds (HOCs) particularly have a higher affinity for microplastics than water. Therefore, adsorption is affected by the nature of chemical material, the size of the plastic particle, and physical or chemical environment. Hydrophobic Organic Compounds (HOCs) may be transferred to tissues and cells of aquatic organisms due to accumulation mechanism through food chain [19- 28].

In this study, the adsorbing capacity of some plastic derivatives (LDPE, PP, PVC, PS, PA, and PET) against six hydrophobic pesticides such as endosulfan and endrin insecticides was investigated to determine the adsorption rates of pollutants by various types of plastics in three types of media chosen as hexane, saline water, and pure water.

Materials and Methods

Materials

The commercially available pellets, obtaining from SIGMA, are low-density polyethylene (LDPE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS), polyamide (PA, N6), and polyethylene terephthalate (PET). The PS, PA and PET pellets were bigger than the LDPE (100 µm-800 µm), PP (25 µm-250 µm) and PVC (50 µm-350 µm) pellets.

The average dimensions of plastic pellets are 500 µm for LDPE, 200 µm for PVC, 140 µm for PP, 3 mm for PS, 3 mm for PA and 5mm for PET. High purity endosulfan (α+β) (99.0%) and endrin (99.5%) were obtained from Dr. Ehrenstorfer GmbH. The stock endosulfan ($C_9H_6C_{l6}O_3S$) and endrin ($C_{12}H_8C_{l6}O$) solutions were prepared in acetone and

*To whom all correspondence should be addressed.

used for all the experiments after the necessary dilutions with distilled water. All the solution mixtures were prepared with 18.2 MΩ deionized water from a Direct-Q 5 Ultrapure Water System (Millipore Co.). In the pesticide adsorption test, raw ((LDPE)r, (PA)r, (PS)r, (PP)r, (PVC)r and (PET)r) and aged ((LDPE)a, (PVC)a, (PS)a and (PA)a) pellets were used. Plastics identified as aged plastic pellets were treated with concentrated H_2SO_4, NaOH, n-hexane, NaCl, anionic surfactants, bleacher, acetone and ethanol solutions in a UV cabinet for two hours each. All the procedures were performed under a UV lamp by continuous mixing. At the end of each step, the pellets were washed with pure water and filtered. Following these treatment procedures, the plastics were finally kept in an oven at 50 °C for one night [29].

Procedure for adsorption measurement

Batch experiments were performed using pellets of 1 g L^{-1} with endosulfan and endrin solutions prepared with initial concentrations of 0.5, 1 and 2 mg L^{-1}. No adjustment was performed for pH, and the procedures were performed with the initial pH values of the solutions. The pH values were around 7.5 for endosulfan and 6 for endrin. All the experiments were carried out at 23 ^oC. The experiments were performed in three replicates. The procedures were carried out in three different liquid phase using ultrapure water, hexane, saline water (35% NaCl). The samples were taken from batch experiments carried out for 72 hours [20] in a shaker (Biosan PSU-20i) onto glass vials at 10, 24, 48 and 72 hours were analyzed with the HPLC device (Agilent 1100 UV-DAD FL). Therefore, the endosulfan and endrin adsorption on raw and aged pellets were examined and compared in different types of media. Using the differences between the initial and final pesticide concentrations, the adsorbed concentrations were obtained in water solution. The amount of pesticide adsorption onto plastics is calculated by,

$$q_e = \frac{C_i - C_e}{m}.V$$

where q_e is the pesticide adsorbed onto the plastics (mg g^{-1}), Ci is the initial pesticide concentration (mg L^{-1}), C_e is the final pesticide concentration in the solution (mg L^{-1}), V is the volume of the solution (L) and m is the amount of plastics (g) used.

Analysis of Endosulfan and Endrin

Sample water of 20 ml was taken and 200 mL of 1:2 (v/v) acetone: n-hexane mixture was added. Then the samples were shaken for 5 min and organic phase was transferred to a clean flask. Organic phase was removed with rotary evaporator. The extract was concentrated to 1-2 mL n-hexane. Approximately 20 µl of the extract was injected into HPLC-DAD. The mobile phase system was 85% methanol and 15% water/acetonitrile 1/2 (v/v). The flow rate was 0.5 mL min^{-1}, and the wavelength was 190-360 nm. The analysis was completed in 16 min. The column was Octyl C_8 (250 x 4 mm i.d., 5 µm thickness) [30].

The limit of detection and recovery values of the designated endosulfan and endrin in this study are given in Table 1.

Table-1: Limit of detection and recovery values of the method.

Compound Name	LOD (µg/l)	LOQ (µg/l)	Recovery (%)	R^2
Endosulfan	**0,1**	**0,3**	**92**	**0,9917**
Endrin	**0,3**	**0,9**	**88**	**0,9993**

The adsorption balance was demonstrated using the Langmuir and Freundlich adsorption isotherm models.

According to the Langmuir isotherm model (Eq. 1), the adsorbed molecules form a single saturated layer on the surface of the adsorbent. This isotherm model is a theoretical model assuming that the surface reaches saturation at a certain pollutant concentration.

$$q_e = bq_mCe/(1+bCe) \quad (1)$$

where q_e is the amount of adsorbed material on MPs (mg.g^{-1}) at equilibrium, Ce the equilibrium concentration of the adsorbed material (mg.L^{-1}), q_m and b are Langmuir constants which are adsorption capacity (mg/g) and adsorption constant (L.mg^{-1}), respectively.

The Freundlich isotherm model is a model that expresses adsorption on heterogeneous surfaces. In this model, the amounts absorbed at equilibrium increase as the pollutant concentration rises.

The Freundlich isotherm model is expressed with Eq. 2.

$$q_e = K_f \times Ce^{(1/n)} \quad (2)$$

where q_e is the amount of adsorbed material on MPs (mg.g^{-1}) at equilibrium, C_e the equilibrium

concentration of the adsorbed materials ($mg.L^{-1}$), 1/n and K_f are the Freundlich isotherm parameters of adsorption intensity and adsorption capacity ($mg.g^{-1}$), respectively [31-32].

Results and Discussions

The results of the adsorption experiments carried out with endosulfan and endrin on various plastics pellets like LDPE, PA, PS, PP, PVC, PET and PA in aqua solutions are presented in charts in Fig. 1.

As can be understood from the charts, in adsorption experiments carried out using 1 ppm of active substances such as endosulfan and endrin, the highest adsorption efficiency was obtained in experiments performed in saline water environment with all the plastics, either raw or processed. The second highest adsorption level occurred in the ultrapure water environment, and the least adsorption was observed in the existence of hexane. The adsorption rates of the aged pellets were higher than the rates of the raw pellets. The results showed that even the raw forms of the pellets could adsorb these pesticides by over 50%.

The SEM images of the (LDPE)r and (PVC)r plastic pellets and the pellets that were chemically treated were taken under the UV lamp. The samples of these images are shown in Fig. 2.

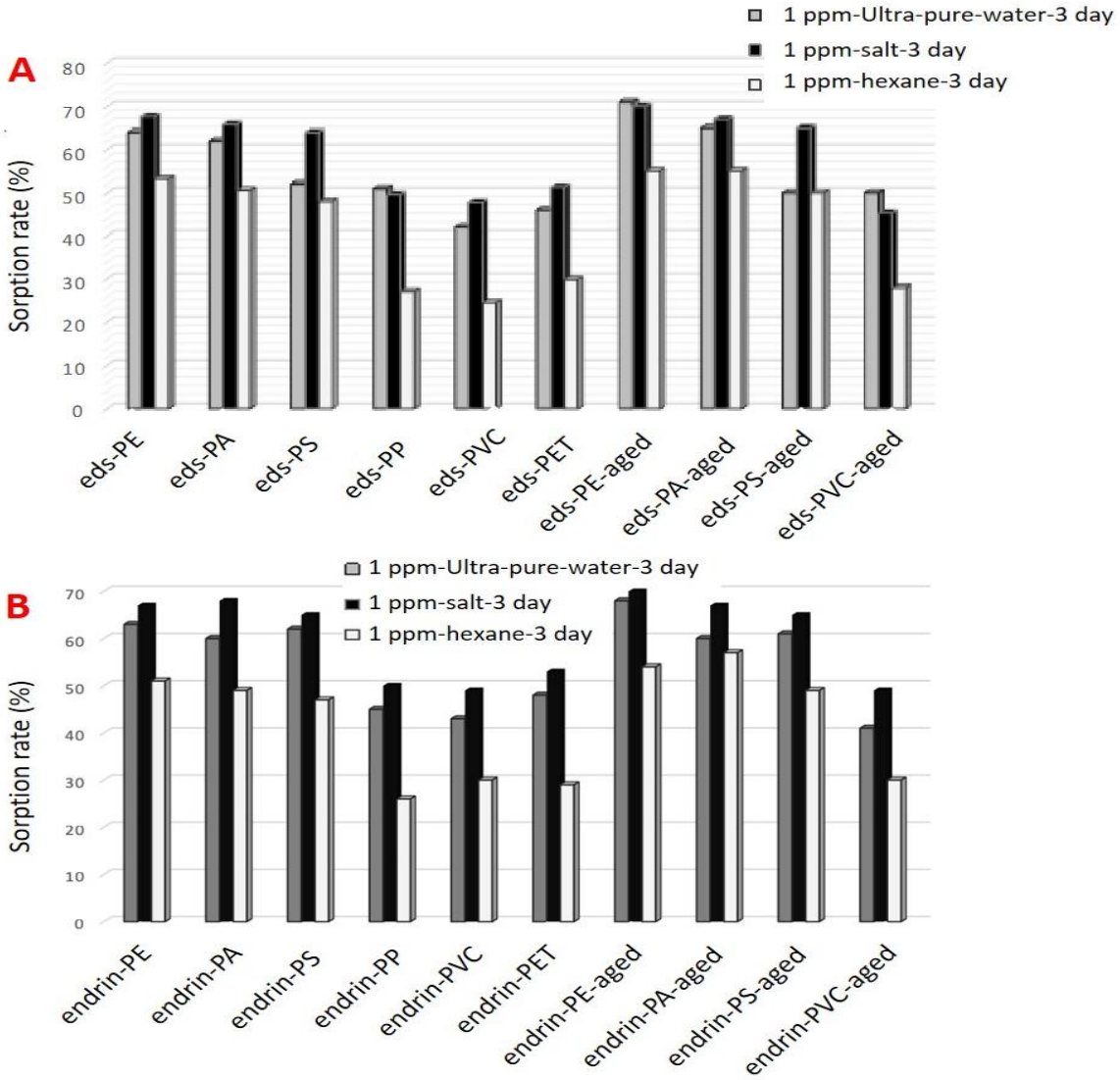

Fig. 1: Graphical illustration of endosulfan (A), and endrin adsorption rates (B).

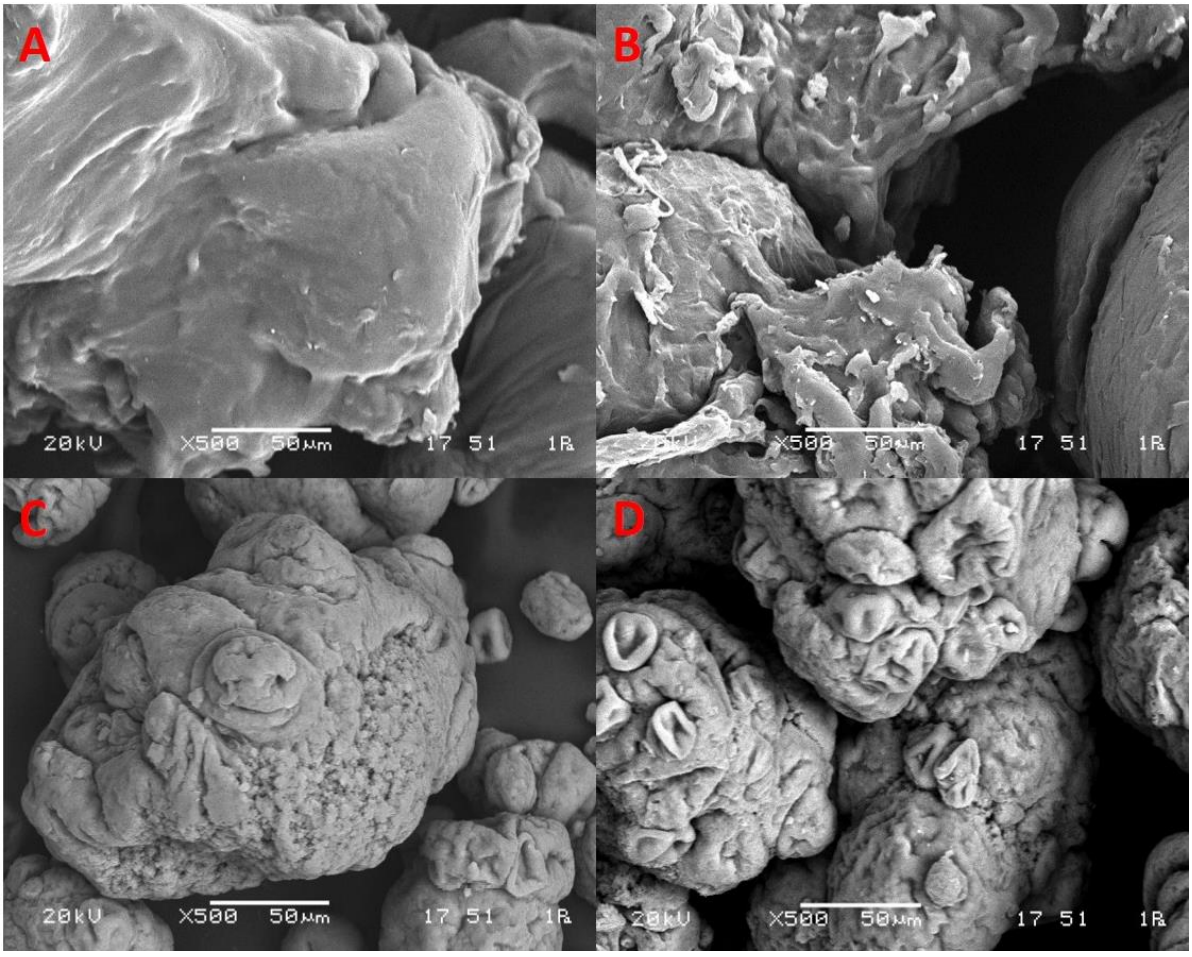

Fig. 2: SEM images of (LDPE)r (A), (LDPE)a (B) (PVC)r (C), (PVC)a (D) pellets.

Adsorption and kinetic models

The isotherm and kinetic data obtained from the charts drawn according to the results of the experiments carried out in ultrapure water environment with a pH value of around 7.5 for endosulfan and 6 for endrin were summarized in Table 2-5, respectively.

Sorption of Endosulfan to MPs in Ultrapure Water

The Langmuir and Freundlich isotherms gave highly balanced values R^2 =0.9996 and 0.9988, respectively, for endosulfan onto PA**.** The adsorption process was measured by using the Langmuir and Freundlich isotherm models at the maximum adsorption capacity of 33.3 mg g^{-1} for endosulfan onto PA (Table 2). When different studies are examined, it is seen that the adsorption of pollutants on microplastics fits well with the Freundlich model [33-36].

Table-2: The Langmuir and Freundlich isotherms for the adsorption of endosulfan.

Endosulfan	Langmuir Isotherm			Freundlich Isotherm		
	Qmax (mg g^{-1})	b (L mg^{-1})	R^2	n	K_f	R^2
LDPE	11.49	3.1	0.9824	1.04	6.45	0.9876
PP	12.5	1.96	0.9576	1.25	6.46	0.9466
PVC	3.84	1.8	0.9972	5.26	330	0.8655
PS	8.3	1.75	0.9095	0.8	1.28	0.9856
PA	33.3	4.34	0.9996	1.06	6.02	0.9988
PET	7.14	2.2	0.9740	1.36	9.23	0.9433

R^2 and k coefficients obtained from kinetic models are shown in Table 3. The experimental data fitted well to the pseudo-first-order kinetic model with a high R^2 value.

Table-3: Kinetic parameters for the sorption of endosulfan on different microplastics.

Endosulfan	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model	
	k_1	R^2	k_2	R^2
LDPE	0.0342	0.98939	0.34	0.88909
PP	0.0227	0.99157	0.2	0.80568
PVC	0.0332	0.98962	0.25	0.839
PS	0.0293	0.99036	0.36	0.90542
PA	0.02	0.99204	0.39	0.48449
PET	0.0291	0.99039	0.28	0.9311

Sorption of Endrin to MPs in Ultrapure Water

The adsorption process was measured by using the Langmuir and Freundlich isotherm models at the maximum adsorption capacity of 400 mg g^{-1} for endrin onto PP (Table 4).

Table-4: The Langmuir and Freundlich isotherms for the adsorption of endrin.

Endrin	Langmuir Isotherm			Freundlich Isotherm		
	Qmax (mg/g)	b (L/mg)	R^2	n	K_f	R^2
LDPE	100	4.54	0.9975	0.92	3.98	0.9968
PP	400	2	0.9996	2.94	2.18	0.9994
PVC	25	1.5	0.9984	0.87	125	0.8397
PS	50	4.04	0.9937	50	1.05	0.9971
PA	33.3	4.34	0.9944	1.2	3.98	0.9927
PET	10	2.38	0.9875	1.28	6.3	0.9730

The Langmuir and Freundlich isotherms gave highly balanced values R^2 =0.9996 and 0.9994, respectively, for endrin onto PP**.** R^2 and k coefficients obtained from kinetic models are shown in Table 5. The experimental data fitted well to the pseudo-first-order kinetic model with a high R^2 value.

Table-5: Kinetic parameters for the sorption of endrin on different microplastics.

Endrin	Pseudo-first-order kinetic model		Pseudo-second-order kinetic model	
	k_1	R^2	k_2	R^2
LDPE	0.0491	0.98622	0.045	0.73682
PP	0.0351	0.98921	0.008	0.6451
PVC	0.046	0.98692	0.025	0.54175
PS	0.045	0.98712	0.054	0.78286
PA	0.0268	0.98036	0.013	0.68526
PET	0.0357	0.98909	0.05	0.92033

Endosulfan and endrin are used as organochlorine insecticides in the control of agricultural pests. Although the use of endrin has been banned or restricted due to its effects of toxicity and persistence in the environment [37], it is still used for agricultural pest control. The solubility of endosulfan in water is low, and its persistence in soil and water is between 3 and 6 months or longer. Endosulfan is considered to be a highly toxic pollutant [38-39].

The adsorption rates of various pollutants to plastics depending on medium conditions studied previously are summarized in Table 6 and Table 7.

Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models were used in order to identify the adsorption of endosulfan (α+β) onto bentonite clay. Kinetic models like first-order equations, second-order equations, intra-particle diffusion model and its thermodynamics were studied. It was observed that bentonite clay was effective in the adsorption of endosulfan from solution (pH 5). It was also seen that the adsorption depended on the endosulfan concentration, adsorbent dosage, and temperature. The isotherm data showed that the Freundlich and Temkin were the most suitable isotherm models for endosulfan (α+β), respectively. According to the data, the pseudo-second-order chemical reaction kinetics provided the best correlation (R^2 >0.99) [40].

Kumar and Philips (2006) reported that the adsorption of endosulfan was determined using clay soil [38]. It was seen that the adsorption kinetics of the α+β endosulfan demonstrated differences according to the soil type used (28±2°C). The adsorption capacities of different soil types were calculated through the Langmuir and the Freundlich isotherm models. It was concluded that the adsorption of endosulfan in all the soils obeyed the Langmuir isotherm model and that the adsorption was single layer. These values ranged from 0.1 to 0.45 mg g^{-1} for alpha endosulfan and from 0.0942 to 0.2722 mg g^{-1} for beta endosulfan.

Atasoy et al. (2009) reported that for the adsorption rate of alpha and beta endosulfan with vertisol, the Freundlich isotherm model was suitable (R^2 > 0.98) [41]. The adsorption coefficients (k_f) were found to be between 21.63 and 16.33 for alpha endosulfan and between 14.01 and 17.98 for the beta endosulfan adsorption coefficient

The adsorption of endrin to montmorillonite and kaolinite clays was examined. It was seen that pH values affected sorption rates. Endrin adsorption to both montmorillonite and kaolinite adsorbents occurred clearly at the pH level of 7.2 and 5.4, respectively. The correlation coefficients were found to be 0.97 and 0.98, and the sorption coefficients 0.18 g L^{-1} and 0.21 g L^{-1}, respectively. It was observed that the sorption isotherm of endrin to montmorillonite and kaolinite was linear [37].

In this study, the high adsorption rates of aged pellets recorded for endosulfan and endrin in saline water showed that particularly benthic fauna is under a greater risk than the other organisms. This study contributed to the increasing data related to the roles of microplastics in transporting Hydrophobic Organic Compounds (HOCs) like endosulfan and endrin.

Table-6: The conditions and results of adsorption kinetic experiments under laboratory conditions.

Plastic Type	Adsorbed Pollutant Type	Experiment time (hour)	Adsorption Rate (μg g^{-1})	pH	^{0}C	Isotherms R^2	Isotherms R^2	References
Virgin pellets PE (~4 mm)	Cu,	168 h	0.100	3-10	19 ± 2	0.944 (Langmuir)	0.988 (Freundlich)	[13]
	Hg,		0.170			0.735	0.978	
	Pb,		0.191			0.841	0.977	
Beached pellets (~2 - 6 mm)	Ag,		1.068			0.365	0.882	
	Hg,		2.78			0.132	0.994	
	Pb		2.74			0.783	0.967	
PVC, (200–250 μm)	Phe,	360 h (from 24 to over 360 h)		seawater pH	18	0.95 (Linear)	0.95 (Freundlich)	[20]
	DDT,					0.98	0.99	
	PFOA,					0.92	0.87	
	DEHP,					0.97	0.97	
PE, (200–250 μm)	Phe,					0.95	0.96	
	DDT,					0.98	0.99	
	PFOA,					0.91	0.88	
	DEHP					0.98	0.89	
PE, (150 μm)	PFOS	7 d agitation time	0.6-1.8	3-7	25	0.943 (Linear)		[23]
	FOSA					0.974		
PS (250 μm)	PFOS					n.a.		
	FOSA					0.994		
PVC (230 μm)	PFOS		0-0.3			0.998		
	FOSA					0.966		

Table-7: The conditions and results of adsorption kinetic experiments under natural environment conditions.

Plastic Type	Adsorbed Pollutant Type	Experiment time (hour)	Adsorption Rate (μg g^{-1})	pH	^{0}C	Kinetic R^2	Reference
HDPE, LDPE, PP (D = 3 mm)	PCBs	1, 3, 6, 9, and 12 months	Shelter Island Total: HDPE, 25 LDPE, 34 PP, 27 PET, 1 PVC, 2 Harbor Excursion Total: HDPE, 797 ng/g LDPE, 722 ng/g PP, 122 ng/g PET, 14 ng/g PVC, 27 ng/g			Shelter Island PCB 153 HDPE, 0.97 LDPE, 0.91 PP 27, 0.98 PET, 0.72 PVC, 0.76 Harbor Excursion Benzo(ghi)pery HDPE, 0.89 LDPE, 0.87 PET, 0.46 Total PAHs PP, 0.83 Fluoranthene PVC, 0.009	[42]
	PAH						
PS (Ø2 mm×3 mm)	Indeno(123-cd)pyrene	1, 3, 6, 9, and 12 months	Shelter Island 27.6-30.7 5.67-7.98 Harbor Excursion 27.7-39.6 6.26-8.33			0.99	[43]
	2,6-dimethylnaphthalene					0.95	
	Indeno(123-cd)pyrene					0.97	
	2,6-dimethylnaphthalene					0.73	
PVC (200–250 μm)	Phe,	360 h	2-4	Seawater pH		0.975	[19]
	DDT					0.99	
PE (200–250 μm)	Phe,					0.979	
	DDT					0.993	

Certain management systems have been established in some of the European countries within the scope of ″Plastic Pesticide Packaging Wastes Management″. Nevertheless, in many other countries, there are still no plans for the management of such wastes, which cause adverse consequences for the environment and public health. Pesticides that remain on the packaging pouches of agricultural chemicals after the application or containers contaminated with pesticides lead to the pollution of soil, air and water sources. This is a serious environmental issue in numerous countries all over the world [44]. Furthermore, the fact that plastic pesticide packages adsorb the pesticides they contain stands out as a secondary environmental problem. In situations in which plastic containers are transformed into another product through recycling, however, the size of this risk gets even greater [45-46]. Plastic wastes discharged into the environment can act like a “polluting accumulator” which transfers hydrophobic pollutants to the biota. Pesticide packages are mostly made of plastic materials. Since these plastic packages adsorb pesticides, empty pesticide packages that are uncontrollably discharged into the

environment and their inappropriate disposal can lead to huge problems for the environment. Packing wastes that have adsorbed pesticides can cause the transfer of pesticides to living organisms in water and on land by means of environmental phenomena like rain or snow and lead to bioaccumulation in those organisms.

Conclusion

The results of kinetic studies for the sorption on different microplastics demonstrated that endrin and endosulfan adsorption was slow. Evidently, both isotherms gave highly balanced values for all the microplastic compounds. However, the Langmuir isotherm is more suitable than the Freundlich isotherm. In other words, it can be said that pesticides are adsorbed onto microplastics in a single layer in accordance with the Langmuir isotherm and that adsorption from liquid to solid surfaces occurs in the form of hydrophobic interaction in accordance with the Freundlich isotherm. The sorption of endosulfan and endrin to LDPE, PP, PVC, PS, PA, and PET pellets was investigated, and the influence of ultrapure water, hexane, and saline water on the sorption capacities was evaluated accordingly. It was observed that raw forms of pellets have a capacity to absorb endosulfan and endrin by over 50%. Lastly, the highest adsorption rates for endosulfan and endrin were recorded in the media of saline water using aged pellets. In terms of the obtained experimental data, it fitted well to the pseudo-first-order kinetic model and the Langmuir equation.

Acknowledgments

The authors would like to thank TUBITAK (The Scientific and Technological Research Council of Turkey) for their financial support (Project No: 115Y303).

References

1. A. Bakir, S. J. Rowland, R. C. Thompson, Competitive sorption of persistent organic pollutants onto microplastics in the marine environment, *Mar. Pollut. Bull.*, **64**, 2782 (2012).
2. C. Wu, K. Zhang, X. Huang, J. Liu, Sorption of pharmaceuticals and personal care products to polyethylene debris, *Environ. Sci. Pollut. Res.*, **23**, 8819 (2016).
3. A. L. Andrady, The plastic in microplastics: A review, *Mar. Pollut. Bull.*, 119: 12 (2017).
4. G. Peng, B. Zhu, D. Yang, L. Su, H. Shi, D. Li, Microplastics in sediments of the Changjiang Estuary, China, *Environ. Pollut.*, **225**, 283 (2017).
5. W. Zhang, S. Zhang, J. Wang, Y. Wang, J. Mu, P. Wang, X. Lin, D. Ma, Microplastic pollution in the surface waters of the Bohai Sea, China, *Environ. Pollut.*, **231**, 541 (2017).
6. R. C. Thompson, Y. Olsen, R. P. Mitchell, A. Davis, S. J. Rowland, A. W. G. John, D. McGonigle, A. E. Russell, Lost at sea: Where is all the plastic? *Sci.*, **304**, 838 (2004).
7. Z. M. Wang, J. Wagner, S. Ghosal, G. Bedi, S. Wall, SEM/EDS and opticalmicroscopy analyses ofmicroplastics in ocean trawl and fish guts, *Sci. Total Environ.*, **603**, 616 (2017a).
8. H. A. Nel, T. Dalu, R. J. Wasserman, Sinks and sources: Assessing microplastic abundance in river sediment and deposit feeders in an Austral temperate urban river system, *Sci. Total Environ.*, **612**, 950 (2018).
9. S. L. Wright, R. C. Thompson, T. S. Galloway, The physical impacts of microplastics on marine organisms: A review, *Environ. Pollut.*, **178**, 483 (2013).
10. J. A. I. Sul and M. F. Costa, The present and future of microplastic pollution in the marine environment, *Environ. Pollut.*, **185**, 352 (2014).
11. L. I. Devriese, B. D. Witte, A. D. Vethaak, K. Hostens, H. A. Leslie, Bioaccumulation of PCBs from microplastics in Norway lobster (Nephrops norvegicus): An experimental study, *Chemosphere*, **186**, 10 (2017).
12. C. G. Avio, S. Gorbi, F. Regoli, Plastics and microplastics in the oceans: From emerging pollutants to emerged threat, *Mar. Environ. Res.*, **128**, 2 (2017).
13. [13] A. Turner and L. A. Holmes, Adsorption of trace metals by microplastic pellets in freshwater, *Environ. Chem.*, **12**, 600 (2015).
14. E. Fries and C. Zarfl, "Sorption of polycyclic aromatic hydrocarbons (PAHs) to low and high density polyethylene (PE), *Environ. Sci. Pollut. Res.*, **19**, 1296 (2012).
15. L. Liu, R. Fokkink, A. A. Koelmans, Sorption of Polycyclic Aromatic Hydrocarbons to Polystyrene Nanoplastic, *Environ. Toxicol. Chem.*, **35**, 1650 (2016).
16. J. Wang, J. Peng, Z. Tan, Y. Gao, Z. Zhan, Q. Chen, L. Cai, Microplastics in the surface sediments from the Beijiang River littoral zone: Composition, abundance, surface textures and interaction with heavy metals, *Chemosphere*, **171**, 248 (2017b).
17. N. B. Hartmann, S. Rist, J. Bodin, H. S. Louise, L. H. Jensen, S. N. Schmidt, P. Mayer, A. Meibom, A. Baun, Microplastics as Vectors for Environmental Contaminants: Exploring

Sorption, Desorption, and Transfer to Biota, *Integr. Environ. Assess. Manage.*, **13**, 488 (2017).
18. J. Anderson, A. Gitter, R. Lacey, R. Karthikeyan, Transport, fate, and toxicity of selected public health insecticides in waterways, *Toxicol. Environ. Chem.*, **100**, 32 (2018).
19. A. Bakir, S. J. Rowland, R. C. Thompson, Transport of persistent organic pollutants by microplastics in estuarine conditions, *Estuar. Coast. Shelf Sci.*, **140**, 14 (2014a).
20. A. Bakir, S. J. Rowland, R. C. Thompson, Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions, *Environ. Pollut.*, **185**, 16 (2014b).
21. H. Lee, W. J. Shim, J. H. Kwon, Sorption capacity of plastic debris for hydrophobic organic chemicals, *Sci. Total Environ.*, **470**, 1545 (2014).
22. J. Gauquie, L. Devriese, J. Robbens, B. D. Witte, A qualitative screening and quantitative measurement of organic contaminants on different types of marine plastic debris, *Chemosphere*, **138**, 348 (2015).
23. F. Wang, K. M. Shih, X. Y. Li, (2015). The partition behavior of perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonamide (FOSA) on microplastics, *Chemosphere*, **119**, 841 (2015).
24. W. Zhang, X. Ma, Z. Zhang, Y. Wang, J. Wang, J. Wang, D. Ma, Persistent organic pollutants carried on plastic resin pellets from two beaches in China, *Mar. Pollut. Bull.*, **99**, 28 (2015).
25. A. Pariatamby and Y. L. Kee, Persistent organic pollutants management and remediation, *Procedia Environ. Sci.*, **31**, 842 (2016).
26. A. Bakir, I. A. O'Connor, S. J. Rowland, A. J. Hendriks, R. C. Thompson, Relative importance of microplastics as a pathway for the transfer of hydrophobic organic chemicals to marine life, *Environ. Pollut.*, **219**, 56 (2016).
27. M. C. Fossi, M. Baini, C. Panti, M. Galli, B. Jiménez, J. M. Arnanz, L. Marsili, M. G. Finoia, D. R. Macías, Are whale sharks exposed to persistent organic pollutants and plastic pollution in the Gulf of California (Mexico)? First ecotoxicological investigation using skin biopsies, *Comp. Biochem. Physiol. Part C.*, **199**, 48 (2017).
28. C. Goedecke, U. M. Stollin, S. Hering, J. Richter, C. Piechotta, A. Paul, U. Braun, A First Pilot Study on the Sorption of Environmental Pollutants on Various Microplastic Materials, *J. Environ. Anal. Chem.*, **4**, 191 (2017).
29. G. Liu, Z. Zhu, Z., Y. Yang, Y. Sun, F. Yu, J. Ma, Sorption behavior and mechanism of hydrophilic organic chemicals to virgin and aged microplastics in freshwater and seawater, *Environ. Pollut.*, **246**, 26 (2019).
30. EPA, *3620B EPA (Environment Protection Agency)*, Standard methods.
31. M. Yurtsever and I. A. Şengil, Biosorption of Pb (II) ions by modified quebracho tannin resin, *J. Hazard. Mater.*, **163**, 58 (2009).
32. Z. Zhan, J. Wang, J. Peng, Q. Xie, Y. Huang, Y. Gao, Sorption of 3,3′,4,4′-tetrachlorobiphenyl by microplastics: A case study of polypropylene, *Mar. Pollut. Bull.*, **110,** 559 (2016).
33. H. Zhang, J. Wang, B. Zhou, Y. Zhou, Z. Dai, Q. Zhou, P. Chriestie, Y. Luo, Enhanced adsorption of oxytetracycline to weathered microplastic polystyrene: Kinetics, isotherms and influencing factors, *Environ. Pollut.*, **243**, 1550 (2018).
34. M. Llorca, G. Schirinzi, M. Martínez, D. Barcelo, M. Farre, Adsorption of perfluoroalkyl substances on microplastics under environmental conditions, *Environ. Pollut.*, **235**, 680 (2018).
35. P. Wu, Z. Cai, H. Jin, Y. Tang, Adsorption mechanisms of five bisphenol analogues on PVC microplastics, *Sci. Total Environ.*, **650**, 671 (2019).
36. N. Oz, G. Kadizade, M. Yurtsever, Investigation of heavy metal adsorption on microplastics, *Appl. Ecol. Environ. Res.*, 17, 7301 (2019).
37. X. Peng, J. Wang, B. Fan, Z. Luan, Sorption of endrin to montmorillonite and kaolinite clays, *J. Hazard. Mater.*, **168**, 210 (2009).
38. M. Kumar and L. Philip, Adsorption and desorption characteristics of hydrophobic pesticide endosulfan in four Indian soils. *Chemosphere*, **62**, 1064 (2006).
39. L. J. Banasiak, B. V. Bruggen, A. I. Schäfer, Sorption of pesticide endosulfan by electrodialysis membranes, *Chem. Eng. J.*, **166**, 233 (2011).
40. N. Rauf, S. S. Tahir, J. H. Kang, Y. S. Chang, Equilibrium, thermodynamics and kinetics studies for the removal of alpha and beta endosulfan by adsorption onto bentonite clay, *Chem. Eng. J.*, **192**, 369 (2012).
41. A. D. Atasoy, A. R. Mermut, H. Kumbur, F. Ince, H. Arslan, E. D. Avcı, Sorption of alpha and beta hydrophobic endosulfan in a Vertisol from southeast region of Turkey, *Chemosphere*, **74**, 1450 (2009).
42. C. M. Rochman, E. Hoh, B. T. Hentschel, S. Kaye, Long-term field measurement ofsorption of organic contaminants to five types of plastic pellets: implications for plastic marine debris, *Environ. Sci. Technol.*, **47**, 1646 (2013a).
43. C. M. Rochman, C. Manzano, B. T. Hentschel, S. L. M. Simonich, E. Hoh, Polystyreneplastic: a

source and sink for polycyclic aromatic hydrocarbons in the marine environment, *Environ. Sci. Technol.*, **47**, 13976 (2013b).

44. D. Briassoulis, M. Hiskakis, H. Karasali, C. Briassoulis, Design of a European agrochemical plastic packaging waste management scheme–Pilot implementation in Greece. *Resour. Conserv. Recycl.*, **87**, 72 (2014).
45. V. Patarasiriwong, P. Wongpan, R. Korpraditskul, C. B. Iwai, Pesticide distribution in pesticide packaging waste chain of Thailand, *Internationa Conference on Chemical, Environmental Science and Engineering (ICEEBS'2012)*, Pattaya, Thailand, 26 (2012).
46. A. V. Hinson, F. Dossou, P. E. Yehouenou, H. Hountikpo, H. Lawin, B. Aguèmon, A. Koudafoke, P. Houngbégnon, F. Gounongbé, B. Fayomi, Risk Factors of Pesticide Poisoning and Pesticide Users' Cholinesterase Levels in Cotton Production Areas: Glazoué and Savè Townships, in Central Republic of Benin, *Environ. Health Insights*, **11**, 1 (2017).