



universität
wien

MASTERARBEIT / MASTER'S THESIS

Titel der Masterarbeit / Title of the Master's Thesis

„Sorption of organic compounds by microplastic“

verfasst von / submitted by

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angestrebter akademischer Grad / in partial fulfilment of the requirements for the degree of
Master of Science (MSc)

Wien, 2016 / Vienna 2016

Studienkennzahl lt. Studienblatt / degree programme code as it appears on the student record sheet: A 066 815

Studienrichtung lt. Studienblatt / degree programme as it appears on the student record sheet:

Masterstudium Erdwissenschaften UG 2002

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Declaration of Originality

I hereby declare that this thesis and the work reported herein was composed by and originated entirely from me. Information derived from the published and unpublished work of others has been acknowledged in the text and references are given in the list of references.

Vienna, _____

Date

Signature

Acknowledgements

I want to thank everybody supporting me during my master thesis. Above all I want to thank Univ. Prof. Dr. Thilo Hofmann for giving me the opportunity to work in his department and his supervision.

Furthermore, I would like to thank Dr. Thorsten Hüffer for his co-supervision, suggesting the topic of my thesis, his practical and theoretical support, sharing his expertise, and his time and effort to answer any of my questions. Besides, I want to thank him for the revision of my thesis.

I also want to thank Petra Körner, Wolfgang Obermaier, Anne-Kathrin Weniger and Huichao Sun for their support and helpful advice during my work in the laboratory.

Additionally, thanks to all those people of the department of environmental geosciences (University of Vienna) who supported me with their good advice during my thesis.

Finally, I would like to thank my family for their moral support and providing me every help along the way.

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1. Introduction

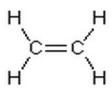
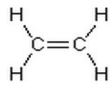
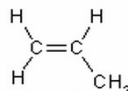
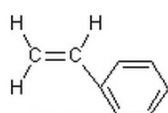
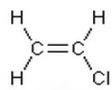
1.1 Microplastic

1.1.1 General information

Plastics are synthetic polymers, which are derived from the polymerisation of monomers extracted from oil or gas [1, 2, 3]. Important classes of plastics are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyamide (PA) (PA 6 and PA 6.6), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) (Table 1) [2]. These are thermoplastics, which can be distinguished into amorphous (PS and PVC) and semicrystalline (PE, PP, PA and PET) types. Amorphous types contain a disordered molecular structure and semicrystalline types have a much more ordered structure in some areas. Due to missing crosslinks between their macromolecular chains, temperature changes have no irreversibly effects on their mechanical and optical properties [4]. Moreover, their amorphous parts pass through a special transition when temperature increases. The glass transition temperature (T_g) indicates the transition between a glassy, hard and brittle polymer, and a rubbery, soft and flexible state [4]. They are a strong, potentially transparent and light-weight material, and their manufacturing is inexpensive. Due to those properties, they are used in almost limitless applications [2]. Their global production increases continuously since the 1950s. In 2013 around 299 million tonnes were produced globally [5]. 10% of plastics enter the marine environment making them important as an environmental concern for a long time [3].

Microplastics (MPs) are small plastic particles and they are also particularly found in the marine environment at numerous global locations. They were first reported in the early 1970s, where they received only minimal attention in the scientific society [1, 2]. MPs are found in the water column and in sediments, and they were first described as 'microplastics' in 2004. Since then, they are in the focus of environmental concern [1].

Table 1: Classes of plastics that are commonly encountered in the marine environment with some of their properties and their monomer structures [2, 4, 6].

Plastic Class		Specific Gravity	Percentage production	Products and typical origin	Glass Transition Temperature [°C]	Temperature of use [°C]	Monomer
Low-density polyethylene	LDPE LLDPE	0.91-0.93	21%	Plastic bags, six-pack rings, bottles, netting, drinking straws	-120		
High-density polyethylene	HDPE	0.94	17%	Milk and juice jugs	-95	-50-90	
Polypropylene	PP	0.85-0.83	24%	Rope, bottle caps, netting	-18	-5-100	
Polystyrene	PS	1.05	6%	Plastic utensils, food containers	97	-20-70	
Polyamide	PA		<3%	Netting and traps	40	-40-100	
Polyethylene terephthalate	PET	1.37	7%	Plastic beverage bottles	70	-40-110	
Polyvinyl chloride	PVC	1.38	19%	Plastic film, bottles, cups	80	-15-60	

1.1.2 Occurrence of MP in the environment

MPs which are found in the natural environment differ strongly in shape and size due to the diversity of sources [1]. Their occurrence may be generated from primary and secondary sources. Primary sources, where they enter the environment directly via runoff, are for example from the use of cleaning products like hand and facial cleaners containing microbeads as exfoliants, production waste from plastic processing plants or accidental spillage from industry [7, 8]. These particles may not be removed from receiving water by simple sewage clarification processes and due to their small size they pass through these facilities mainly unchanged [9]. Secondary sources are caused by processes which lead to fragmentation of larger plastic debris. Such processes are, for example, mechanical degradation which can be associated with thermal or photodegradation, and abrasion due

to wave action [7, 8]. Photodegradation is a light-initiated oxidative degradation and accelerates strongly with higher temperatures and high oxygen availability which can be found rather on beaches than on the surface water [2].

80% of the plastics found in the environment are from land-based sources and around 18% of the plastic debris found in the ocean environment come from the fishing industry which uses plastic gear worldwide [2, 10]. Estimations show that over 23000 tons of plastic packaging materials were thrown away by the global commercial fishing fleet during the 1970s [11]. Factors that are responsible for an increasing future influx into the oceans are among others, due to lack of enforcement and education, fishing, immigration to coastal regions and uses of the oceans in terms of recreation [2].

MP can be transported to different and remote places by winds, rivers and ocean currents and can therefore be found even at the poles or ocean depths [3]. Due to their various properties, like size, shape, composition and specific density, they tend to accumulate in different compartments, including shores, seafloor and oceanic gyres [1]. Their specific density plays an important role in their occurrence. MP of low specific density (e.g., PP and PE) are positively buoyant and hence found predominantly on the sea surface. Consequently, they have the potential to be transported over long distances and are widely distributed across the world's oceans. They have been found in remote places, distant from their sources [1]. In contrast, MP of high specific density (e.g., PVC, PET, PA) are negatively buoyant, tend to accumulate on the seafloor, and hence they are expected to be found in areas near their sources [1]. However, due to a lack of samples from subtidal and deep sea sediments more investigations are needed [1]. There are naturally occurring processes that cause changes in the specific density of MP and some of them are important to mention. Biofouling is the overgrowth by micro- and macroorganisms that causes an increase in specific density and which leads to sinking of MP. Erosion is a process which decreases the specific density and which leads to enhancing buoyancy. Furthermore, there are organisms which are able to transport very small plastic pieces into other compartments due to mix with food items [1].

1.1.3 Environmental impact

There exists a wide variety of MP with multiple shapes, sizes, colours, specific densities and chemical compositions. Furthermore, small plastic particles are hydrophobic and due to very slow degradation processes they are very persistent, and have an extremely long lifetime in the oceans [9].

High concentrations of hydrophobic organic contaminants (HOCs) on plastic debris were recently reported. Mato et al. (2001) collected PP pellets from Japanese waters and identified persistent organic pollutants (POPs), including polychlorinated biphenyl (PCBs) congeners (4 to 117 ng/g), nonylphenol (NP) (0.13 to 16 μ g/g) and dichlorodiphenyldichloroethylene (DDE) (0.16 to 3.1 ng/g) [12]. Furthermore, plastic particles collected from Hawaiian, Mexican and California beaches in 2003 and 2004 contained total concentration of POPs in the particles for polycyclic aromatic hydrocarbons (PAHs), PCBs, and dichlorodiphenyltrichloroethanes (DDTs) ranged from 39 to 1200 ng/g, from 27 to 980 ng/g and from 22 to 7100 ng/g, respectively [13]. As a consequence MPs are able to transport contaminants to remote and pristine locations as they also concentrate in upper layers of the water column [14]. The measured HOCs are persistent, bioaccumulative, and toxic (PBTs), and are therefore of concern for human health and the environment [9]. Furthermore, the physical and chemical sorbent properties of plastic can be modified by the addition of plasticizers, additives, and fillers in plastic products. The partial degradation of plastics can lead to the production of intermediates which may be toxic [2, 15]. Thus, once MPs are in the environment, they can become an environmental hazard [1].

Another important environmental impact of MP is the tendency of marine organisms like animals, including invertebrates, fishes, sea turtles, seabirds, and whales to ingest those small particles. Hence, HOCs may also be ingested due to sorption processes [13]. For instance, DDT concentrations ranging from 64.4 to 87.7 ng/g were reported on MP particles ingested by seabirds in southern Brazil [9]. As a result MP has an influence on transport and bioavailability of PBT, and increases risk throughout the marine food chain [8, 9]. Due to those characteristics, exploration of MP has been an increasing focus in recent years.

1.2 Sorption

1.2.1 Theory of sorption

Sorption is a process which generally describes the association of a chemical with solid phases [16]. It can be divided into adsorption and absorption. Adsorption is the process where chemicals accumulate at the solid-liquid or solid-air interface and absorption where chemicals incorporate within a three-dimensional matrix [17]. The solid phase is then referred to as *sorbent*, the sorbed chemicals as *sorbates* and the dissolved molecules or vapor molecules which could potentially sorb as *sorptives* [17].

The fate and impact of a chemical in the environment depends on its occurrence as a sorbate or a sorptive. There are several mechanisms that induce sorption and the overall distribution is a combination of all of them. It strongly depends on the properties of sorbate and sorbent [16]. Moreover, the equilibrium distribution between the concentration of sorbate (C_s e.g. mol kg⁻¹) and sorptive (C_w e.g. mol L⁻¹) often varies over a range of sorptive concentration. Therefore sorption isotherms are a common method to assess sorption characteristics [16, 17]. If this relationship is linear, sorption can be defined by a single partition coefficient K_d (Equation 1, 2) (Figure 1) [17]:

$$K_d = \frac{C_s}{C_w} \quad (1)$$

$$C_s = K_d \cdot C_w \quad (2)$$

It applies to low sorptive concentrations and/or in systems where the overall sorption is dominated by partitioning into a homogeneous solid phase [17]. The linear model implies that the free energies are constant at all sorbate concentrations and the Freundlich exponent n (Equation 3) equals 1 (Figure 2). In this case, K_d can be derived from experimental data by linear regression performing a least squares fit of C_s versus C_w [16].

At higher concentrations where sorption of further molecules becomes more difficult this relationship shows nonlinearity. In this case the Freundlich isotherm can be applied (Equation 3) (Figure 1). It is the most common empirical expression to describe sorption. The Freundlich model represents the diversity of sorption sites and their sorption free energies [16]. The sorbates show an energetic preference for sorption sites on the surface

of a sorbent, hence, added molecules are bound with weaker free energies [16]:

$$C_s = K_F \cdot C_w^n \quad (3)$$

K_F is the Freundlich coefficient and n the Freundlich exponent (Equation 3).

The exponent is smaller or larger than 1. For the linear fitting of the isotherm model, K_F and n from experimental data can be derived by a least squares fit of $\log C_s$ versus $\log C_w$ (Figure 2) [16].

$$\log C_s = n \log C_w + \log K_F \quad (4)$$

Equation 4 is the logarithmic form of equation 3, and $\log K_F$ and n can be derived by the slope and intercept of the regression line (Figure 2).

The Langmuir model is another approach that can be applied to describe the distribution coefficient (Figure 1). It describes sorption when the sorption sites are energetically constant and only monolayer coverage up to saturation can occur. The number of surface sites per mass of sorbent can achieve a maximum (Equation 5) [16]:

$$C_s = \frac{\Gamma_{max} \cdot K_L \cdot C_w}{1 + K_L \cdot C_w} \quad (5)$$

In this case, K_L represents the Langmuir coefficient and Γ_{max} the total number of surface sites per mass of sorbent (Equation 5). This total number of surface sites per mass of sorbent Γ_{max} usually equals the maximum achievable surface concentration of a given compound $C_{s,max}$ [16]. For the linear fitting of the isotherm model, K_L and $C_{s,max}$ can be derived from experimental data by plotting $1/C_s$ versus $1/C_w$ [16]:

$$\frac{1}{C_s} = \left(\frac{1}{C_{s,max} \cdot K_L} \right) \frac{1}{C_w} + \frac{1}{C_{s,max}} \quad (6)$$

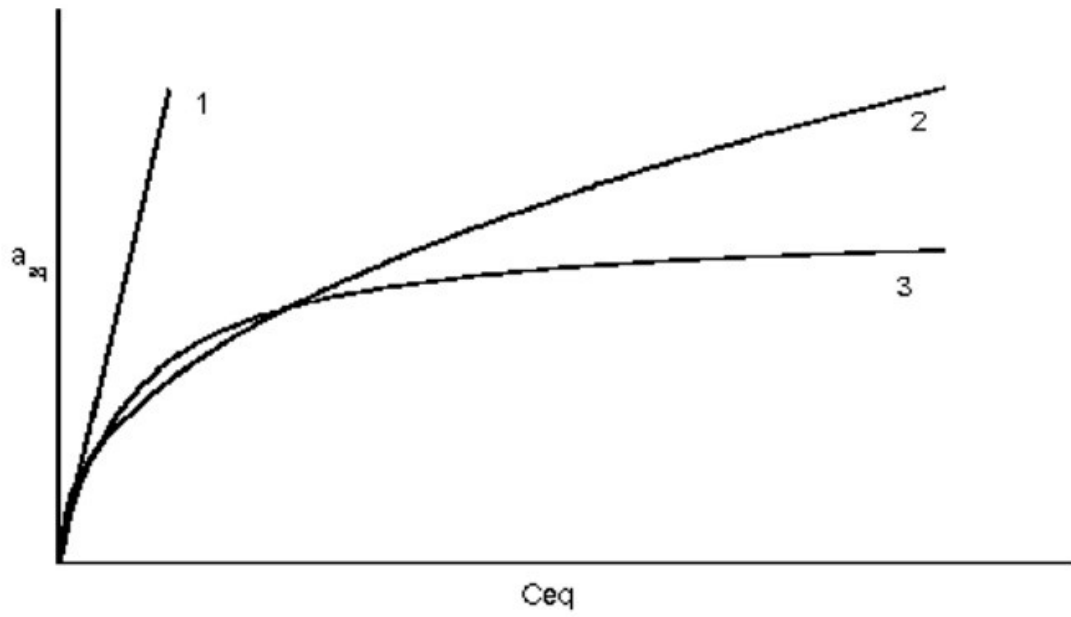


Figure 1: Graphic representation of the linear (1), the Freundlich (2) and the Langmuir (3) isotherm model. a_{aq} represents the sorbed concentration and C_{eq} the sorptive concentration [18].

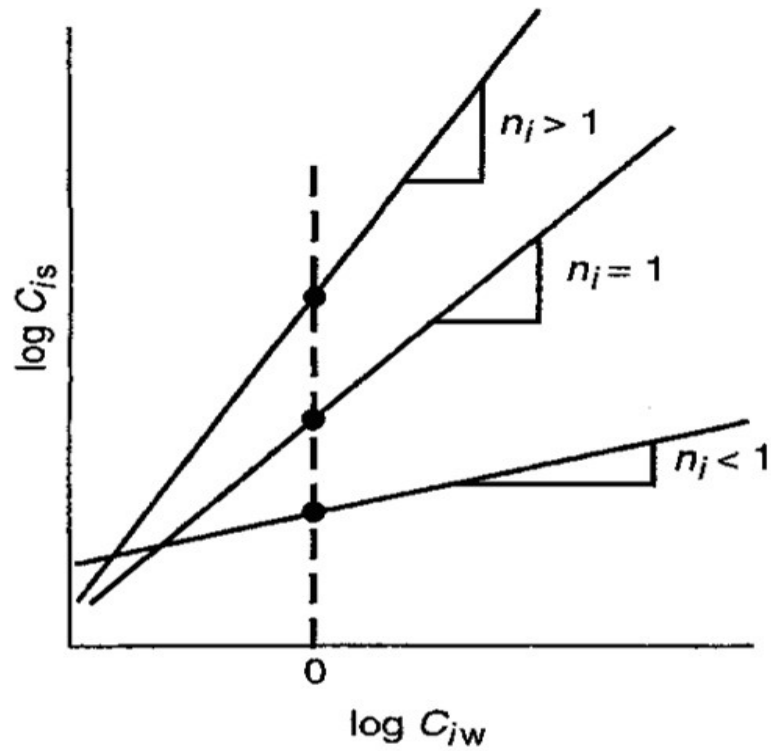


Figure 2: Graphic representation of the Freundlich isotherm. Linear regressions of the logarithmic form of Equation 3 are presented with $n_i < 1$, $n_i = 1$ and $n_i > 1$ [16].

However, there are many cases where a linear, a Freundlich or a Langmuir equation cannot describe sorption processes. Therefore isotherms may have a variety of different shapes and many other model equations (e.g. BET, Dual-Mode, Polanyi-Manes etc.) can be applied [16].

1.2.2 Sorption by microplastic

Investigations have shown that MP sorb persistent, bioaccumulative, and toxic substances (PBTs) and hence, this became an important issue in recent years [9]. There are several studies that demonstrated sorption of HOCs to plastics by laboratory (e.g. Adams et al., 2007 [19]) and field (e.g. Mato et al., 2001 [12]) adsorption experiments. Significant aspects of sorption processes are effects of sorbent and sorbate physicochemical characteristics. Studies which showed different sorption affinity depending on sorbent type are, for instance, a long-term field measurement in San Diego Bay, CA [20]. They quantified relationships between PAHs and PCBs, and HDPE, LDPE, PS, PP, PET and PVC at different locations. Sorption rates and concentrations of the contaminants varied significantly among plastic types and among locations. Estimations showed higher sorption of PAHs and PCBs to HDPE, LDPE, PS and PP than to PET and PVC. Another study revealed the variability between individual particles and differences among beaches [21]. They collected pellets from a beach in Japan and examined concentrations of PCB. The pellets showed higher PCB concentrations on PE than PP. This tendency was also demonstrated by other experiments for PCBs and PAHs [12, 22, 14] and may be explained by the highly hydrophobic nature of PE.

Studies have also demonstrated that sorption of HOCs by plastics is influenced by their crystallinity. Guo et al. (2012), for instance, showed that spatial arrangement of rubbery domains in polymers plays an important role regarding sorption for HOCs [23]. Saquing et al. (2010) showed that toluene, a model HOC, shows higher diffusivity for rubbery than for glassy polymers [15]. They used material characterizations of consumer plastics and model polymers (HDPE, MDPE, LDPE and PVC). The study of Rochmann et al. (2013) also shows greater diffusion of rubbery polymers than glassy polymers and consequently they sorb greater concentrations of contaminants [20]. Lutzow et al. (1999) [24] and Vittoria (1995) [25] have demonstrated that there is a higher chemical diffusion through PE with decreased crystallinity. Karapanagioti et al. (2008) tested the phenanthrene

distribution coefficients for virgin pellets and plastic eroded pellets [22]. Their aim was to show how different degrees of weathering affect the intra polymer diffusion and surface diffusion. A higher surface area of particles leads to an increasing capacity for uptake and transport of hydrophobic compounds and this is largely accompanied by fragmentation of weathered plastics.

Pascall et al. (2005) is one of the few studies which has demonstrated effects of sorbate characteristics [26]. They estimated PCB congeners uptake, partition and diffusion coefficients for PE, PVC and PS films. Properties like chlorination and molar volumes were correlated with the coefficients. It was shown that PCB uptake decreased with increasing chlorination, and partition and diffusion coefficients generally decreased with increasing molar volumes.

In conclusion, the affinity between chemicals and MP differs strongly depending on the chemical and physical properties of the organic compound and the polymer type. The studies showed that sorption affinity depends on sorbent properties like hydrophobicity, crystallinity, surface area and sorbate properties like molar volume. However, most of the studies examined sorption of chemicals only from particular compound classes to MP.

Thus, there is still a lack of information about the influence of the several properties of sorbents and especially of sorbates. Therefore it is very important to expand the knowledge of the relevant sorption mechanisms of MP and chemical pollutants.

2. Aim of study

The main objective of this study was to systematically characterize the sorption behaviour of commonly found MP particles (PE, PS, PA and PVC). Issues concerning the importance of interaction mechanisms like hydrophobicity and polar or hydrogen bonding could be resolved. For this purpose, sorption isotherm batch experiments were conducted with four MP types as sorbents and seven low molecular weight organic compounds as sorbates. The isotherms were fitted with the linear, Freundlich and Langmuir models, and experimentally determined distribution coefficients were correlated with known sorbate (octanol-water partitioning constant, hexadecane-water partitioning constant and aqueous solubilities) and sorbent (Specific surface area and pore volume) properties. Most of the organic compounds are nonpolar and the polymers are highly hydrophobic. Hence, an assumption which could be made is that the dominant sorption interaction mechanism might be hydrophobicity.

3. Materials and methods

3.1. Materials

3.1.1. Sorbates

The low molecular weight organic compounds which were used as probe sorbates are listed in Table 2 with their physicochemical properties.

Table 2: Summary of CAS-Nr., physicochemical properties (MF = molecular formula; MW = molecular weight; Log K_{aw} = logarithmic air-water partition constant; S_w = aqueous solubility; b = boiling point; ρ = density; log K_{ow} = logarithmic octanol-water partition constant, Log K_{hw} = logarithmic hexadecane-water partition constant), supplier (SA = Sigma-Aldrich; Steinheim; Germany; VWR = VWR BDH Prolabo Chemicals) and purity grades [27].

Compound	CAS-Nr.	MF	MW [g mol ⁻¹]	Log K_{aw} [-]	S_w [mg L ⁻¹]	b [°C]	ρ [g cm ⁻³]	Log K_{ow} [-]	Supplier	Log K_{hw} [-]	Grade
nonpolar aromatic compounds											
benzene	71-43-2	C ₆ H ₆	78.1	-0.65	1790	80	0.88	2.18	SA	2.136	ASC 99%
toluene	108-88-3	C ₇ H ₈	92.14	-0.60	526	110	0.87	2.72	SA	2.725	ASC 99%
chlorobenzene	108-90-7	C ₆ H ₅ Cl	112.56	-0.80	498	132	1.11	2.84	SA	2.857	ASC 99%
naphthalene	91-20-3	C ₁₀ H ₈	128.17	-1.74	32	218	1.15	3.36	SA	3.421	99%
nonpolar aliphatic compounds											
n-Hexane	110-54-3	C ₆ H ₁₄	86.2	1.74	10	68.7	0.66	3.90	VWR	4.428	
cyclohexane	110-82-7	C ₆ H ₁₂	84.2	0.89	55	80.7	0.78	3.44		3.854	
monopolar aromatic compounds											
ethylbenzoate	93-89-0	C ₉ H ₁₀ O ₂	150.17	-2.38	720	215	1.05	2.64	SA	2.695	99%

3.1.2. Sorbents

The MP types which were used as sorbents throughout the experiments are medium-density polyethylene (MDPE), polystyrene (PS), polyamide 6 (PA 6) and unplasticised polyvinylchloride (PVC). They are listed in Table 3 with some properties.

Table 3: Summary of BET specific surface area SA (m²/g), pore volume (cm³/g), density (g/cm³), mean particle size (μm), max. particle size (μm) and supplier for the sorbents [28].

Sorbent	SA [m ² g ⁻¹]	Pore Volume (cm ³ /g)	Density [g cm ⁻³]	Mean Particle Size [μm]	Max. Particle Size [μm]	Supplier
MDPE	0.30785	0.0019965	0.935		350	Goodfellow Cambridge Ltd
PS	0.33765	0.002113	1.05	250		Goodfellow Cambridge Ltd
PA 6	0.15585	0.001202	1.13	350		Goodfellow Cambridge Ltd
PVC	0.3167	0.0019555	1.4		250	Goodfellow Cambridge Ltd

3.1.3. Additional chemicals

Additional chemicals used in the experiments are listed in Table 4. Methanol was used for preparation of stock and working solutions, CaCl₂ * 2 H₂O and NaN₂ for the electrolyte background solution and helium as carrier gas for GC measurements.

Table 4: Additional chemicals used in this study for preparation of standard solutions and the electrolyte background solution.

Substance	CAS-Nr.	Purity [%]	Supplier
Methanol	67-56-1	99.8	Acros Organics – Fisher-Scientific, Germany
CaCl ₂ * 2 H ₂ O	10035-04-8	99.0	Merck Millipor, Germany
NaN ₂	-	-	-
Helium	-	-	-

3.1.4. Glassware

In Table 5 all used glass instruments are listed. The glass instruments were cleaned by first rinsing them with tap water and detergent, then by rinsing them several times with ultrapure water and afterwards several times with acetone. Afterwards glassware was dried in a drying oven. Pasteur pipettes were only used once.

Table 5: List of glassware.

Type	Product specification	Supplier
Amber screw vials (20 mL)	20 mL ND18 Headspace Screw vials (amber), 75.5 x 22.5mm, rounded bottom	Markus Bruckner Analysentechnik; Linz, Austria
Microliter syringe (25 µL)	Hamilton 25 µL Microliter™ Syringe	Klaus Trott Chromatographie-Zubehör; Kriftel, Germany
Microliter syringe (100 µL)	Hamilton 100 µL Microliter™ Syringe	Klaus Trott Chromatographie-Zubehör; Kriftel, Germany
Pasteur pipettes	Disposable Glass Pasteur Pipettes 150 mm, ISO 7712	VWR International; Vienna, Germany
Volumetric flasks (25 mL)	Volumetric flasks with glass stopper, Duran; DIN EN ISO 1042; NS 10/19; 25 ± 0.04 mL	Hirschmann Laborgeräte GmbH & Co. KG; Eberstadt, Germany
Graduated pipette (10 mL)	Graduated pipettes *SIMPLEX™; DIN EN ISO 835; 10 ± 0.1 mL	Glasfirn Giessen, Germany
Graduated pipette (1 mL)	Graduated pipettes *SIMPLEX™; DIN EN ISO 835; 1 ± 0.01 mL	Glasfirn Giessen, Germany
Bulb pipette (10 mL)	-	-
Bulb pipette (5 mL)	-	-

3.1.4. Additional materials

Additional materials used in the experiments are listed in Table 6.

Table 6: List of materials.

Type	Product specification	Supplier
Macro Pipette Controller	-	BRAND GMBH + CO KG; Wertheim, Germany
Screw vial caps	ND18 Magnetic Screw Cap with 17 mm Septa butyl red/PTFE grey, 55° shore A, 1.6 mm	Markus Bruckner Analysentechnik; Linz, Austria

3.1.5. Instrumentation

In Table 7 all devices which were used for analyses, including sorption kinetics and isotherms, and sorbent characterization are listed. The kinetic and sorption isotherm experiments were conducted using ITEX2-GC-MS. A Gas Chromatograph coupled to a Mass Spectrometer inert Mass Selective Detector with a quadrupole mass analyzer [29]. A CTC Combi PAL was used as the sampling device including a solventless in-tube microextraction (ITEX-2). Polydimethylsiloxane (PDMS) was used as an adsorbent material which is placed between the heated headspace syringe and the syringe needle.

Sorbent characteristics like surface area and pore volume were determined by using Quantachrome Nova 2000 e-series. Quantachrome Nova 2000 e-series is based on the nitrogen adsorption method, Brunauer-Emmett-Teller (BET). Particle size distributions and shape analyses were obtained by using Eyetech (Ambivalue).

Table 7: List of devices and components.

Type	Product specification	Supplier
Gas Chromatograph	Network GC System 6890N	Agilent Technologies
GC Column	HP-5MS 5% Phenyl Methyl Siloxane, actual length: 30 m; internal diameter: 250 µm; film thickness: 0.25 µm	Agilent Technologies
Mass spectrometer	Inert Mass Selective Detector, MS 5975	Agilent Technologies
Autosampler	CTC Combi PAL	CTC Analytics AG, Switzerland
ITEX-2	PAL ITEX – 2, MSH 05 - 01A, Volume 1.3 ml, Scale 27 mm, ID 25	CTC Analytics AG, Switzerland
ITEX syringe	ITEX syringe 2.5 ml with 1/4"-28 UNF Fitting	CTC Analytics AG, Switzerland
Nova 2000 e-series	-	Quantachrome Corporation
Eyetech	Operating range: 0.6-3600 µm. Magnetic, mechanical and flow through cells	Ambivalue
Balance	METTLER AT200	Mettler Toledo

3.2. Methods

3.2.1. Preparation of stock and working solutions

A stock solution and four to three standard solutions were prepared for each probe sorbate. The stock solutions were prepared by dissolving according amounts of the pure compound in methanol in volumetric flasks (25 mL) using graduated pipettes (1 mL or 10 mL). The standards were prepared by using a ten-fold serial dilution of stock solution, except for first standard of toluene. It was prepared by using a 100 fold dilution of stock solution. The prepared stock and standard solutions were then stored in 20-mL amber headspace vials with rubber-polytetrafluoroethylene (PTFE) septa in a fridge, and were freshly prepared for repeat measurements.

3.2.2. Headspace technique

All analyses, including sorption kinetics and isotherms, were conducted using a Gas Chromatograph (GC 6890N) coupled to a Mass Spectrometer (MS 5975) inert Mass Selective Detector (MSD) with a quadrupole mass analyzer (Agilent Technologies). A CTC Combi PAL was used as the sampling device including a solventless in-tube microextraction (ITEX-2) [29]. This extraction method is based on the headspace technique. It is very useful for volatile or semi-volatile compounds as it taps the partition of these substances between the matrix and the gas phase above the sample [30]. Hence, batch sorption experiments can be conducted in a three-phase system, consisting of sorbent, liquid and air. Only the gas phase is measured after the partition equilibrium is achieved (Figure 3). Components from the matrix are not involved in the measurement procedure. In principle, the extraction is conducted by an adsorbent material within a microtrap. This microtrap is placed between a heated headspace syringe and a syringe needle. As a trap material, polydimethylsiloxane (PDMS) was used for all experiments. The syringe pumped parts of the gaseous phase repeatedly through the microtrap [29]. The number of extraction strokes depended on the sorbate. After extraction, the samples were injected into the GC-MS with a split/splitless injector (SSL). The syringe was flushed with nitrogen for cleaning after each measurement.

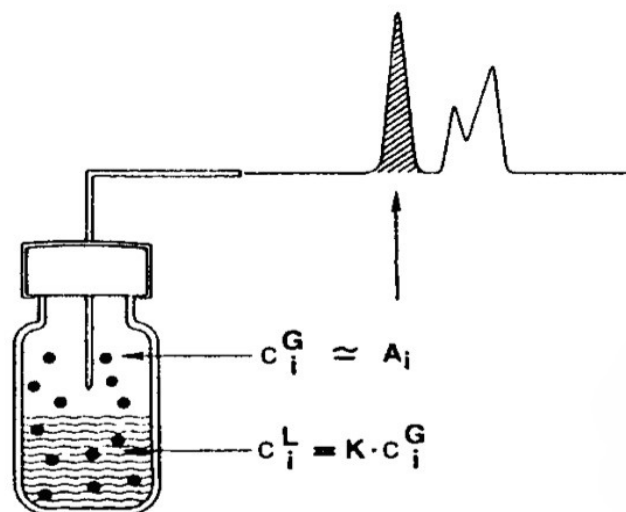


Figure 3: Principle of Headspace Technique. C_{Gi} represents the concentration of the i^{th} component in the gas phase and C_{Li} in the liquid phase. A_i is the area of the GC-MS signal and K the partition coefficient [30].

Preliminary tests were conducted to adjust parameters for the ITEX2, GC and MS (e.g., extraction volume and desorption temperature) for sufficient sensitivity. All parameters, like scanned mass range, ion masses for evaluation and solvent delay for each sorbate, are summarised in the appendix (Table A1 - A3).

For each measurement an external calibration was prepared in order to quantify the gaseous phase concentrations in the sample vials. Weighted calibration curves were used to assess these concentrations in the sample vials. Weighted least squares are an approach to increase the efficiency of estimation. Each data point has an influence over the parameter estimation and the approach helps to give them their proper amount of influence [31]. The calibration standards were filled with 10 mL 0.01 M CaCl_2 plus 25 mg/L NaN_2 background solution in amber screw vials (20 mL) using a bulb pipette (10 mL). The concentration range of the calibration depended on the respective measurement. The closed vials were then intensively mixed by hand and placed on the sample tray of the ITEX2-GC-MS. In order to achieve equilibrium between gas and liquid phase the calibration standards were prepared at least two hours before the measurement. With the quantified gaseous phase concentration C_G , the liquid phase concentration C_w can then be calculated by the partition constant K_{aw} (Equation 7a – 7b) [30]:

$$A \approx C_G = \frac{1}{K_{aw}} \cdot C_w \quad (7a)$$

$$C_G \cdot K_{aw} = C_w \quad (7b)$$

The sorbed concentration of the compound C_s in the sample vials, can be calculated by the mass balance equation:

$$m_s = m_o - m_w - m_G \quad (8)$$

m_s is the amount of sorbed mass from the sample, m_o is the amount of mass from the initial injected sample, m_w is the amount of mass from the sample in the liquid phase and m_G in the gas phase, after equilibrium is achieved. (Equation 8).

3.2.3. Preliminary experiments

Prerequisite for the measurement of sorption isotherms is to reach equilibrium between sorptive and sorbate concentration in the system. For this purpose, kinetic experiments were conducted to ensure equilibration time of the sorption processes. The experiments were conducted by analogy with the batch experiments. The kinetics of toluene and naphthalene were measured in previous studies [15, 23]. Hence, they were used as model sorbates. In principle, a particular amount of sorbent (PE, PS, PA or PVC) was weighted in amber screw vials (20 mL). The vials were then filled with 10 mL 0.01 M CaCl_2 plus 25 mg/L NaN_2 background solution using a bulb pipette (10 mL). Subsequently, 10 μL of the working solution A (1.74 g/L for toluene and 0.45 g/L for naphthalene) were injected with a microliter syringe (25 μL). The closed vials were then intensively mixed by hand and placed on a shaker. For each kinetic experiment, this procedure was conducted eight times where each vial represented a time step. This means that the vials were shaken approximately 1, 2, 3, 4, 5, 6, 8 and 10 days after they were placed on the sample tray of the ITEX2-GC-MS. For each time step duplicate sample vials for each sorbent were prepared to assure reproducibility, except for the second kinetic experiment for toluene due to lack of time. Furthermore, two additional vials were prepared as quality control for

each time step. One was prepared with sorbate but no sorbent to measure loss of sorbate over the experimental period in the vials. The other represented a blank which was only filled with background solution. The gaseous phase concentration was then measured with the ITEX2-GC-MS, and the liquid phase and sorbed concentrations were calculated (Section 3.2.2.). For the determination of the equilibration time the liquid phase concentration (C_w) over the initial injected concentration of the compound (C_o) were plotted against time, as well as the partition coefficient between sorbent and sorptive (K_d). The loss of sorbate was integrated in the calculations.

3.2.4. Sorption isotherms

The concentration of sorptives has a strong influence on sorption and therefore sorption isotherms are a common method to assess sorption characteristics. This involves the measurement of the equilibrium distribution between the concentration of sorbate (C_s) and sorptive (C_w) across a range of sorptive concentration was measured at a constant temperature. To avoid competition for sorption sites individual laboratory sorption isotherm batch experiments were conducted with four MP types as sorbents and seven different low molecular weight organic compounds as sorbates. For the experiments, 20 - 60 mg of sorbent was weighted in amber screw vials (20 mL) depending on sorbate-sorbent combination. The vials were then filled with 10 mL 0.01 M CaCl_2 plus 25 mg/L NaN_2 background solution using a bulb pipette (10 mL). Subsequently, 10, 20 or 50 μL of the stock and working solutions A, B, C or D were injected with a microliter syringe (25, 100 μL). This resulted in concentration ranges covering approximately four orders of magnitude and a maximum concentration of 0.05 of solubility of the respective compound. For quality control, an additional vial was prepared for each isotherm to assess the loss of analytes. The closed vials were then intensively mixed by hand and placed on a shaker. According to the observations of the preliminary experiments, the vials were usually shaken 7 days after they were placed on the sample tray of the ITEX2-GC-MS. The gaseous phase concentration was then measured with the ITEX2-GC-MS, and the sorbed and sorptive concentrations were calculated (Section 3.2.2.). This procedure was repeated for each sorbate-sorbent combination twice or three times to assure reproducibility. For the determination of sorption isotherms the sorbed concentrations (C_s) were plotted against the sorptive concentrations (C_w) for each sorbate-sorbent combination. A log-

converted plotting was used to compare the different sorption isotherms of different sorbate-sorbent combination to better visualize the data. The measured sorption isotherms were then fitted with the most common model equations linear, Freundlich and Langmuir, and their partition coefficients K were calculated. To determine the isotherm model parameters, linear and nonlinear regression analysis was used. The software SigmaPlot was used for the nonlinear fitting of the isotherm models, and the model parameter values and their standard errors were determined. Microsoft Excel was used for the linear fitting of the isotherm models.

To determine the best-fitting to the experimental data the goodness-of-fit parameter R^2 was used. It can range between 0 and 1, and the higher the value the better the respective model fits the data [32]. Another parameter that was used to determine the goodness-of-fit is the residual root mean square error (RMSE). It is a nonlinear error function and can be calculated as follows:

$$RMSE = \frac{1}{N - p} \sum \left(\frac{(C_{s, measured} - C_{s, predicted})^2}{C_{s, measured}^2} \right) \quad (9)$$

N is the number of data points, p is the number of parameters, $C_{s, measured}$ is the sorbed concentration from the batch experiments and $C_{s, predicted}$ is the sorbed concentration predicted from the respective isotherm model. Small values of RMSE indicate better model fitting [33].

For the discussion (Section 4), the isotherm model parameters evaluated by nonlinear fitting of the models by SigmaPlot were used. A nonlinear form is more appropriate because of better error analyses and optimization techniques [33].

3.2.5. Sorbent characterization

Characterization of sorbents can be very useful to improve understanding of interactions mechanisms between sorbates and sorbents. For this purpose, sorbent characteristics like surface area, pore volume and pore size were determined for all four sorbents (PE, PS, PA and PVC) by using Quantachrome Nova 2000 e-series. It is based on the nitrogen adsorption method, Brunauer-Emmett-Teller (BET) [29]. This method allows the characterization of powders and porous materials by using gas adsorption chemistry. The number of gas molecules forming a monolayer of adsorbed molecules can be determined by the adsorption isotherms. The adsorption isotherms are defined by the quantity adsorbed at each pressure. The surface area can then be yield by the cross-sectional area of a molecule. Pore sizes can be estimated by continued addition of gas molecules beyond monolayer formation [34]. The standard multipoint BET procedure is an approach for calculating specific surface areas. In this study, the multi-point N_2 BET specific surface area was calculated based on 6 points in the relative pressure region $P/P_0 = 0.066 - 0.298$. Before measurement, all sorbents were dried in a desiccator for at least 2 weeks, and then outgassed under vacuum at 70 °C over night to free the sample surfaces from contaminants as water [34]. The measurements were conducted twice to assure reproducibility.

Particle size distributions and shape analyses were obtained by using Eyetech (Ambivalue). The Eyetech (Ambivalue) is a particle analyser which is based on the Laser Obscuration Time method. This method uses "Obscuration Time" pulses which are created by the interaction of the rotating laser spot with a particle [29].

4. Results and discussion

4.1 Sorption isotherm fit

The experimental isotherm data were fitted with the model equations: linear, Freundlich and Langmuir (All the fitting parameters are listed in Table A5 in the Appendix). In Table 8 the goodness-of-fit parameter (R^2) and root mean square error (RMSE) for the models are listed to determine the best-fitting to the experimental data. Moreover, the Freundlich exponent (n) is shown to indicate if a sorption isotherm is linear ($n \approx 1$) or nonlinear ($n \neq 1$) [16]. It can be observed that the linear and the Freundlich models provided the best fits for most of the experimental data ($R^2 > 0.90$, $RMSE < 0.3$).

The aromatic compounds show linear sorption for most of the isotherm data. Especially, toluene, ethylbenzoate and naphthalene have n values closer to 1. This linearity implies that affinity for sorption sites seems to be constant over the observed concentration range. Hence, there is no energetic preference for sorption sites on the sorbent surface. These kinds of isotherms are mostly observed when partitioning into a homogeneous sorbent is the dominant sorption mechanism or at low concentration ranges [16]. Deviations of the Freundlich exponents from 1 can be seen for the aliphatic compounds (n-hexane and cyclohexane). They have similar n values ranging from 0.593 to 0.893, except for PE. This nonlinearity implies that sorbates show an energetic preference for sorption sites on the surface of a sorbent, hence, added molecules are bound with weaker free energies. These kinds of isotherms are found primarily in studies of adsorption processes [16]. Only a few isotherm data show slightly better fitting for the Langmuir model than for the Freundlich model. This can be observed, for example, for sorption between toluene and PS, and sorption between ethylbenzoate and PVC. These kinds of isotherms are also found primarily in studies of adsorption processes. Additionally, sorption achieves a maximum with increasing sorbate concentration. This means that additional sorption is not possible [16]. Considering only the sorbents, it can be seen that the sorption isotherms of all compounds by PE show high linearity with n values from 0.957 to almost 1. PE is a nonpolar aliphatic polymer with no functional groups and is only able to interact with all the organic compounds through van der Waals interactions [35]. Koelmans et al. (2014) measured sorption isotherms of PCBs by PE and also determined n values close to 1 [36]. Furthermore, they examined that partitioning into PE plays a dominant role compared to surface adsorption. Pascall et al. (2005) mentioned that the nonpolarity of PE causes high

free volume due to missing attraction forces between the polymeric chains [26]. This increases the possibility for a compound to partition into the polymer. Hence, it can be assumed that the dominant sorption mechanism for the tested compounds by PE is linear partitioning.

Table 8: Freundlich exponent \pm standard errors, and goodness-of-fit parameter R^2 and root mean square error for three non-linear sorption model fits to the experimental isotherm data of all compounds by microplastics.

n-Hexane						Cyclohexane				
Freundlich Model (FM)			Langmuir Model (LM)			Freundlich Model (FM)			Langmuir Model (LM)	
Sorbent	R^2	RMSE	n	R^2	RMSE	R^2	RMSE	n	R^2	RMSE
PE	0.9134	0.2684	0.9613 ± 0.0387	0.7288	0.4751	0.9621	0.2543	0.9574 ± 0.0360	0.7513	0.4316
PS	0.9407	0.2579	0.7622 ± 0.0203	0.8696	0.3376	0.9336	0.1893	0.7423 ± 0.0178	0.9171	0.2434
PA	0.9502	0.1143	0.8793 ± 0.0139	0.9015	0.2072	0.9252	0.2304	0.8929 ± 0.0251	0.8923	0.2905
PVC	0.9497	0.1491	0.5929 ± 0.0172	0.9249	0.1969	0.9278	0.1977	0.6384 ± 0.0160	0.692	0.4083
Benzene						Toluene				
Freundlich Model (FM)			Langmuir Model (LM)			Freundlich Model (FM)			Langmuir Model (LM)	
Sorbent	R^2	RMSE	n	R^2	RMSE	R^2	RMSE	n	R^2	RMSE
PE	0.9583	0.1878	0.9898 ± 0.0181	0.9686	0.1629	0.9306	0.2502	0.9964 ± 0.0252	0.9267	0.2871
PS	0.9814	0.1214	0.8418 ± 0.0106	0.9574	0.1893	0.9201	0.2591	0.9567 ± 0.0206	0.9508	0.2032
PA	0.9675	0.162	0.9145 ± 0.0219	0.9519	0.1969	0.9657	0.1815	0.9951 ± 0.0211	0.9358	0.2189
PVC	0.9677	0.2028	0.8581 ± 0.0147	0.9681	0.2177	0.9515	0.1965	0.9460 ± 0.0191	0.9538	0.1918
Chlorobenzene						Ethylbenzoate				
Freundlich Model (FM)			Langmuir Model (LM)			Freundlich Model (FM)			Langmuir Model (LM)	
Sorbent	R^2	RMSE	n	R^2	RMSE	R^2	RMSE	n	R^2	RMSE
PE	0.9619	0.1895	0.9596 ± 0.0216	0.9467	0.2242	0.9262	0.2984	0.9697 ± 0.0383	0.9094	0.3195
PS	0.9512	0.1677	0.8103 ± 0.0161	0.8853	0.318	0.9585	0.1771	0.9302 ± 0.0208	0.9381	0.2161
PA	0.9479	0.2307	0.9425 ± 0.0320	0.9192	0.2867	0.8726	0.3165	0.9525 ± 0.0515	0.8346	0.3606
PVC	0.9382	0.2377	0.8469 ± 0.0289	0.8859	0.323	0.9361	0.2821	0.9350 ± 0.0468	0.9656	0.2111
Naphthalene										
Freundlich Model (FM)			Langmuir Model (LM)							
Sorbent	R^2	RMSE	n	R^2	RMSE					
PE	0.9632	0.1735	0.9998 ± 0.0272	0.9375	0.2614					
PS	0.9357	0.2415	0.9059 ± 0.0341	0.9367	0.236					
PA	0.9836	0.1212	0.9806 ± 0.0146	0.985	0.1267					
PVC	0.9741	0.1534	0.8542 ± 0.0167	0.9862	0.1171					

The isotherm data for PS and PVC show more nonlinearity, especially for the aliphatic compounds. The nonlinearity describes the heterogeneity of the sorption sites of the sorbents [16]. PS is a nonpolar polymer, hence, the sorption processes are controlled by its general hydrophobic nature. However, it is composed of styrene monomers which consist of benzene rings [37]. Rochman et al. (2013) investigated that PS sorbed greater concentrations of aromatic compounds than nonaromatic polymers like PP, PVC and PE [20]. This means that sorption can be also controlled by the aromaticity of the styrene monomers. Guo et al. (2012) assumed that a pore surface-adsorption mechanism causes the nonlinear sorption behaviour of PS [23]. There are studies which measured sorption of HOCs by carbon based nanoparticles and they showed that hydrophobic and π - π attractions are the main sorption interaction mechanisms [38, 39]. PS is able to form π - π interaction forces to aromatic organic compounds which is caused by the direct attraction between their arene rings [36]. Koelmans et al. (2014) measured sorption isotherms of PCBs by PS and they also determined nonlinearity [36]. Therefore, it can be assumed that sorption of the tested compounds by PS is mainly controlled by its hydrophobicity and π - π -interactions at its aromatic surface. Moreover, PS is a glassy polymer at room temperature and its crystalline regions may not be available for partitioning [23].

All sorption isotherms between PVC and the organic compounds have n values ranging from 0.593 to 0.946. Studies which also showed nonlinearity of sorption isotherms of organic compounds by PVC are, for instance, Teuten et al. (2007) [14] and Xing et al. (1997) [40].

Xing et al. (1997) assumed that the nonlinearity is caused by its nature as a glassy polymer [40]. They observed that an isotherm of 1,3-DCB in PVC changed from nonlinearity at 23 °C (Glassy state) to linearity at 90 °C (Rubbery state) [40]. Hence, this nonlinearity is caused by its heterogeneous character. Furthermore, PVC has polar chlorine atoms as functional groups and its molecular structure is roughly unsymmetrical [37]. The polarity of the chlorine atoms causes a reduction in its free volume due to attraction forces between the individual PVC chains [26]. The reduced free volume decreases the possibility for a compound to partition into the polymer. Therefore, its polarity could also have an influence on its isotherm shape.

All sorption isotherms between PA and the organic compounds have n values ranging from 0.879 to 0.995. These values deviate only slightly from 1, hence, indicate much more linearity. PA is much more amorphous than PS and PVC [23]. Therefore it consists of domains available for partitioning of the compounds.

Figure 4 illustrates log-converted sorption isotherms of the compounds by MP. The slopes of the linear regressions indicate the Freundlich exponent (n) and the y-intercepts indicate the log-converted Freundlich coefficient ($\log K_F$) (Section 1.2.1.). It can be observed that the aliphatic compounds have the highest $\log K_F$ values, and ethylbenzoate, toluene and naphthalene have the lowest $\log K_F$ values for all polymers. This trend correlates with the compounds' hydrophobicity. Cyclohexane and n-Hexane show the highest $\log K_{ow}$ values and ethylbenzoate, toluene and naphthalene show the lowest $\log K_{ow}$ values (Table 2). These observations are further discussed in section 4.2. In Table A5 in the Appendix where the K_F values are listed, it can be seen that they decrease in the order PS > PVC > PE > PA for almost all compounds. This correlates with the surface area and the pore volume of all sorbents (Table 9). These observations are further discussed in section 4.3. Furthermore, It can be seen that the isotherms are roughly parallel for each MP and that their slopes are close to 1, indicating the linearity (Figure 4). The slopes of the n-Hexane and cyclohexane isotherms are smaller compared to the other isotherms for PS, PA and PVC, indicating their nonlinearity.

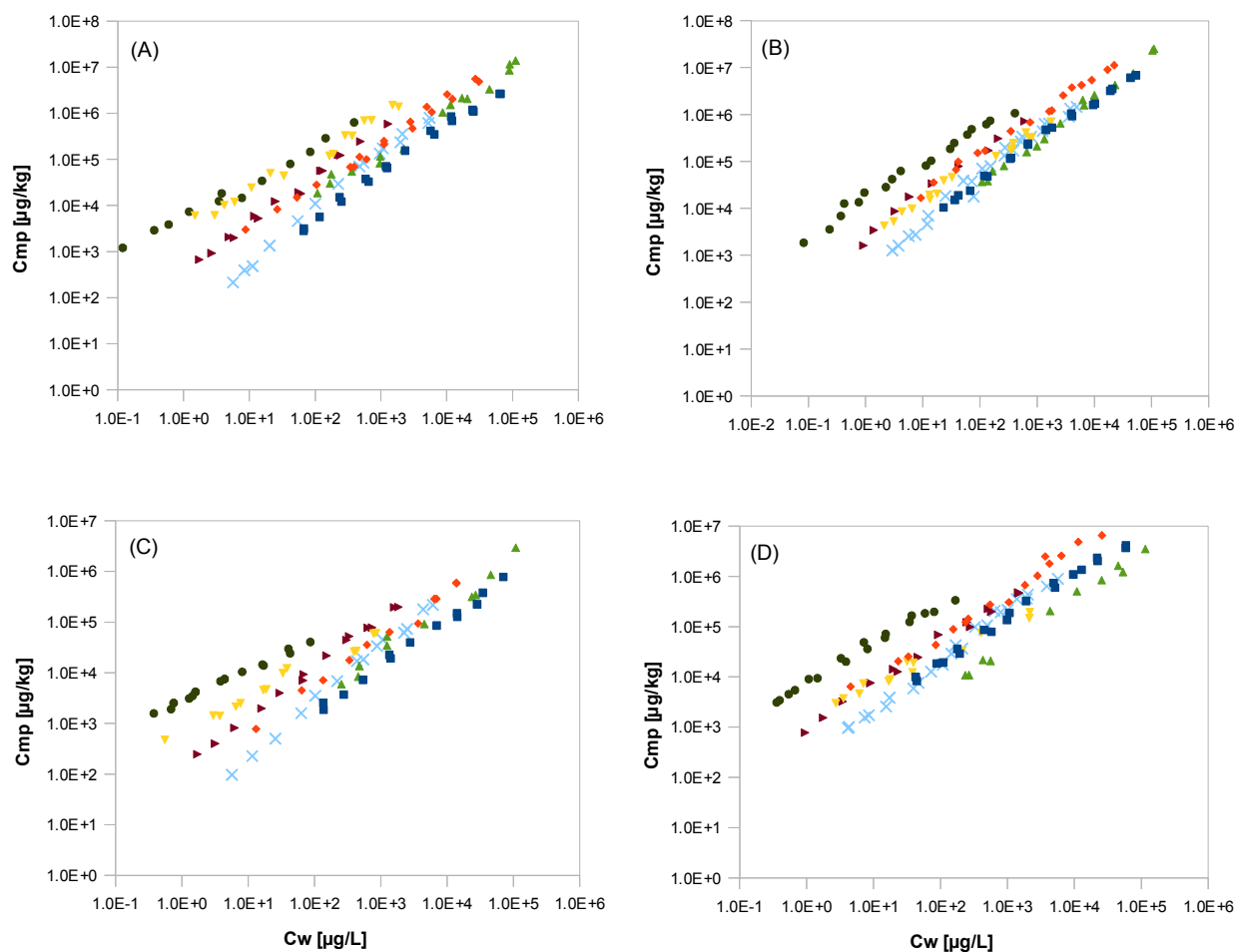


Figure 4: Sorption isotherms of (■) benzene, (◆) chlorobenzene, (▼) cyclohexane, (▲) ethylbenzoate, (▴) naphthalene, (×) toluene, and (●) n-Hexane by PE (A), PS (B), PA (C), and PVC (D), respectively.

4.2 Effect of sorbate properties

Sorption processes are influenced by sorbent and sorbate properties. Correlations of known sorbate properties with experimentally determined distribution coefficients facilitate the understanding of the main interaction mechanisms. In Figure 5 correlations between experimentally determined $\log K_d$ values and two hydrophobicity parameters of sorbates (octanol-water partitioning constant, $\log K_{ow}$, and hexadecane-water partitioning constant, $\log K_{hw}$) are illustrated. The $\log K_d$ values were calculated at concentrations of 10^{-2} of the sorbates aqueous solubility (S_w) from the Freundlich isotherm model. They vary at least two orders of magnitude for each sorbent, and the $\log K_F$ values and the $\log K_d$ values show comparable trends.

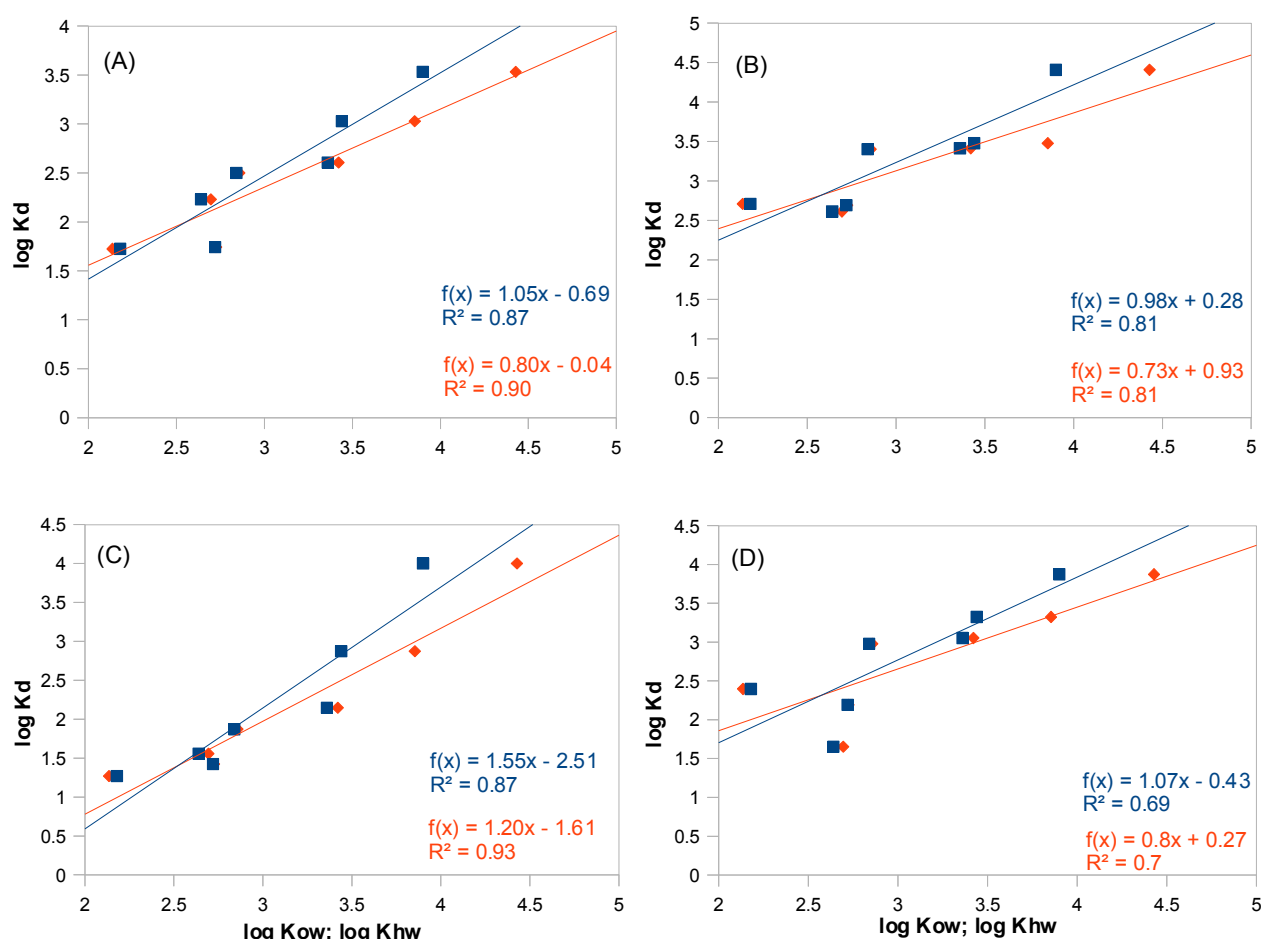


Figure 5: Correlations between experimentally determined $\log K_d$ values to $\log K_{ow}$ (■) and $\log K_{hw}$ (◆) for PE (A), PS (B), PA (C), and PVC (D), respectively. Additionally, regression equations and regression coefficients R^2 are shown.

A positive correlation between log-converted octanol-water partitioning constants, $\log K_{ow}$, and the $\log K_d$ values for all four MPs can be observed. All the sorbents, except from PVC ($R^2 = 0.7$), show relatively high regression coefficients ($R^2 > 0.81$). Correlating the $\log K_{ow}$ values with $\log K_d$ of probe sorbates for PE and PA, it can be observed that with the exception of toluene and naphthalene, the R^2 values are notably higher ranging from 0.95 to almost 1. Correlating the $\log K_{ow}$ values with $\log K_d$ of probe sorbates for PVC, it can be observed that with the exception of toluene and ethylbenzoate, the R^2 value (0.92) is also notably higher. Hence, sorption of almost all compounds by PE, PA and PVC is strongly determined by their hydrophobicity. The correlation of the $\log K_d$ to $\log K_{ow}$ values for PS show a regression coefficient slightly lower than for the other MPs. This supports the assumption that sorption of the tested compounds by PS is not only controlled by its hydrophobicity. The additional π - π interactions between the benzene rings play also an important role (Section 4.1). Müller et al. (2001) analysed sorption of two- through four-ring PAHs by HDPE and LDPE sheets [41]. They determined a positive correlation between the $\log K_d$ and $\log K_{ow}$ values and showed that the two partition coefficients had similar magnitudes. Hence, they assumed that the properties of partitioning were similar for PE and octanol. Adams et al. (2007) investigated sorption between a combined set of HOCs (e.g. PAHs and PCBs) and PE [19]. Good correlations between the $\log K_d$ and $\log K_{ow}$ values ($R^2 = 0.89$) were shown. They also plotted the values for HOCs for the individual compound classes and showed that the regression coefficients were still higher (for PAHs: $R^2 = 0.95$, and for PCBs: $R^2 = 0.97$). This supports the previous assumption and it is possible to predict the $\log K_d$ values for the different HOCs from their $\log K_{ow}$ values.

$\log K_{ow}$ values are a common indicator for the hydrophobicity of an organic compound due to octanol's insolubility in water [16]. However, octanol has the ability to interact with organic compounds via van der Waals, polar and hydrogen-bonding [36]. This means $\log K_d$ values may be overpredicted with $\log K_{ow}$. Lohmann et al. (2012), for instance, investigated that the use of $\log K_{ow}$ as a predictor for $\log K_d$ for PE should be generally avoided, since PE is only able to interact with all the organic compounds through van der Waals interactions [35]. They showed that hexadecane acts as a better predictor, because it is a long-chain alkane that has a similar structure to PE and can also only interact via non-specific interactions [16, 42]. It can be observed that the correlations between $\log K_d$ and the hexadecane-water partitioning constants ($\log K_{hw}$) show higher R^2 values for PE, PA and PVC (Figure 5). The better correlations emphasize the strong hydrophobic

influence on sorption between the probe sorbates and the MPs. PA contains very polar planar amide (-CO-NH-) groups and may act as a hydrogen bonding donor [37]. However, all tested compounds are nonpolar, except from ethylbenzoate. Although, the aromatic compounds have the ability to act as hydrogen bonding acceptors (hydrogen bonding acidity = 0 and basicity > 0 (Table A4 in the Appendix)), their basicity is very low. Hence, the contribution of hydrogen bonding to the overall sorption processes does not play a considerably important role. Lohmann et al. (2012) also pointed out that the use of K_{ow} should be only avoided, if the compound contains functional groups [35]. Since almost all probe sorbates are nonpolar, $\log K_{ow}$ can still act as a good hydrophobicity parameter for this study. Abraham et al. (1994) plotted the $\log K_{hw}$ and $\log K_{ow}$ values for nonpolar, monopolar and bipolar compounds [43]. A good correlation for the nonpolar and weakly polar compounds was found, supporting the assumption that in both systems only van der Waals interactions play a dominating role. Ethylbenzoate is a polar compound, hence, molecular interactions, like hydrogen bonding, could play a role in the octanol-water system. However, the $\log K_d$ values of ethylbenzoate do not deviate from the regression coefficients for all MPs, except from PVC. This means that sorption is also mainly controlled by hydrophobicity.

Various studies assumed that the slopes of the regression equations give also information about sorption interaction mechanisms. Schwarzenbach et al. (2003) [16] pointed out that the slopes of the regression equation of $\log K_{hw}$ and $\log K_{ow}$ for the nonpolar and weakly polar compounds from the study of Abraham et al. (1994) [43] is greater than 1 due to structural differences of the compounds. The deviation from 1 indicates different partitioning behaviours in the hexadecane-water system compared to the octanol-water system. Hüffer et al. (2013) investigated how irradiation and presence of oxygen change surface properties of dispersed fullerenes (nC60) and, therefore, affect sorption of PAHs by nC60 [44]. The slope of $\log K_d - \log K_{ow}$ for aged fullerenes was close to 1 like $\log K_d - \log K_{ow}$ slopes for soils and sediments [16]. Slopes for other carbonaceous materials were much smaller, suggesting that aged fullerenes behave more like the geosorbents than other carbonaceous materials. These observations also show that similar $\log K_d - \log K_{ow}$ slopes indicate similar sorption behaviour. This can be also observed in all the systems of the MPs and the tested compounds. All four MPs have $\log K_d - \log K_{ow}$ slopes close to 1, suggesting that they behave similar concerning the sorption behaviour to the probe sorbates. Lohmann et al. (2012) also showed that the slope of the regression equation ($\log K_d$ vs $\log K_{ow}$) based on selected PAHs did not differ considerably from 1, considering that

the free energy terms are similar in both partitioning systems [35]. Since PAHs do not contain functional groups, they interact with PE and octanol only through van der Waals interactions.

Correlating the experimentally determined $\log K_d$ values with the log-converted aqueous solubilities ($\log S_w$) of the compounds an inverse relationship can be observed. This sorbate parameter can also be used to examine if a sorption is mainly influenced by hydrophobicity. Razzaque and Grathwohl (2002) predicted the organic carbon-water partitioning coefficients, K_{oc} , of HOCs based on the water solubilities [45]. They showed a good inverse correlation between the K_{oc} and S_w values and suggested that there is a maximum solubility of HOCs in organic carbon which has a value of around 0.054 kg/kg. Hence, they showed the efficiency of water solubility as an predictor for organic carbon-water partitioning coefficients. Lohmann et al. (2012) plotted $\log K_d$ values against $\log S_w$ of HOCs for PE and also demonstrated a good inverse correlation with a R^2 value of 0.91 [35]. They showed that solubility acts as a better predictor for PE than K_{ow} , like hexadecane. Since water solubility indicates the inverse property of the compounds compared to K_{hw} and $\log K_{ow}$, these inverse correlations were expected and they support the previous assumptions.

4.3 Effect of sorbent properties

Sorbent properties, like surface area or pore volume, have a strong influence on sorption processes. Figure 6 illustrates log-converted sorption isotherms of the compounds by MP. The slopes of the linear regressions indicate the Freundlich exponent (n) and the y-intercepts indicate the log-converted Freundlich constant ($\log K_F$) (Section 1.2.1.). The $\log K_F$ values and the $\log K_d$ values show comparable trends. It can be observed that the $\log K_F$ values decrease in the order $PS > PVC > PE > PA$ for almost all compounds. This correlates with the surface area and the pore volume of all sorbents (Table 9). PS has the highest surface area and pore volume with values of 0.34 m²/g and 0.002113 cm³/g. PA has the lowest surface area and pore volume with values of 0.16 m²/g and 0.001202 cm³/g. Studies have shown that sorption between HOCs and carbon based nanoparticles highly depends on the sorbent's specific surface area due to hydrophobic and π - π -interactions at the aromatic surface [38, 39]. Koelmans et al. (2014) assumed that the higher sorption of PAHs by PS compared to PE, PVC and PP can be explained by these

interactions at the PS surface area [36]. Rochman et al. (2013) compared sorption of PAHs by PS to other common polymers and they also observed that PS sorbed greater concentrations than PP, PET and PVC [20]. Moreover, they measured that HDPE and LDPE sorbed greater PCB and PAH concentrations than PVC. This was also shown in other studies. Teuten et al. (2007) [14], for instance, examined that phenanthrene sorbed more strongly to PE than PVC, and Pascall et al. (2005) [26] observed this for PCB congeners. All these studies assumed that crystallinity of the MPs has a major influence on the sorption processes. PE is a rubbery polymer at room temperature and has a higher free volume than the glassy polymer PVC (Pascall et al., 2005 [26]). This causes probably higher sorption of the compounds by PE. However, these observations are not consistent with this study. The K_F values of PVC are higher than those of PE for almost all tested compounds. Hence, it can be seen that sorbent properties alone are not sufficient for explaining sorption processes. Wu et al. (2001) observed that two alkylbenzenes had higher K_d values for PVC than PE [46]. Saquing et al. (2010) examined that toluene, an alkylbenzene, sorbed stronger on glassy polymers, like PVC, than on rubbery polymers, like PE [15]. There could be some dipole and H-bonding interactions between toluene and the glassy polymers, but they are probably not of major importance. According to Saquing et al. (2010), the difference of sorption by glassy and rubbery polymers cannot only be explained by specific compound and polymer interactions [15].

Table 9: BET specific surface area SA (m^2/g) and pore volume (cm^3/g) for the sorbents.

Sorbent	SA (m^2/g)	Pore Volume (cm^3/g)
PE	0.30785	0.0019965
PS	0.33765	0.002113
PA	0.15585	0.001202
PVC	0.3167	0.0019555

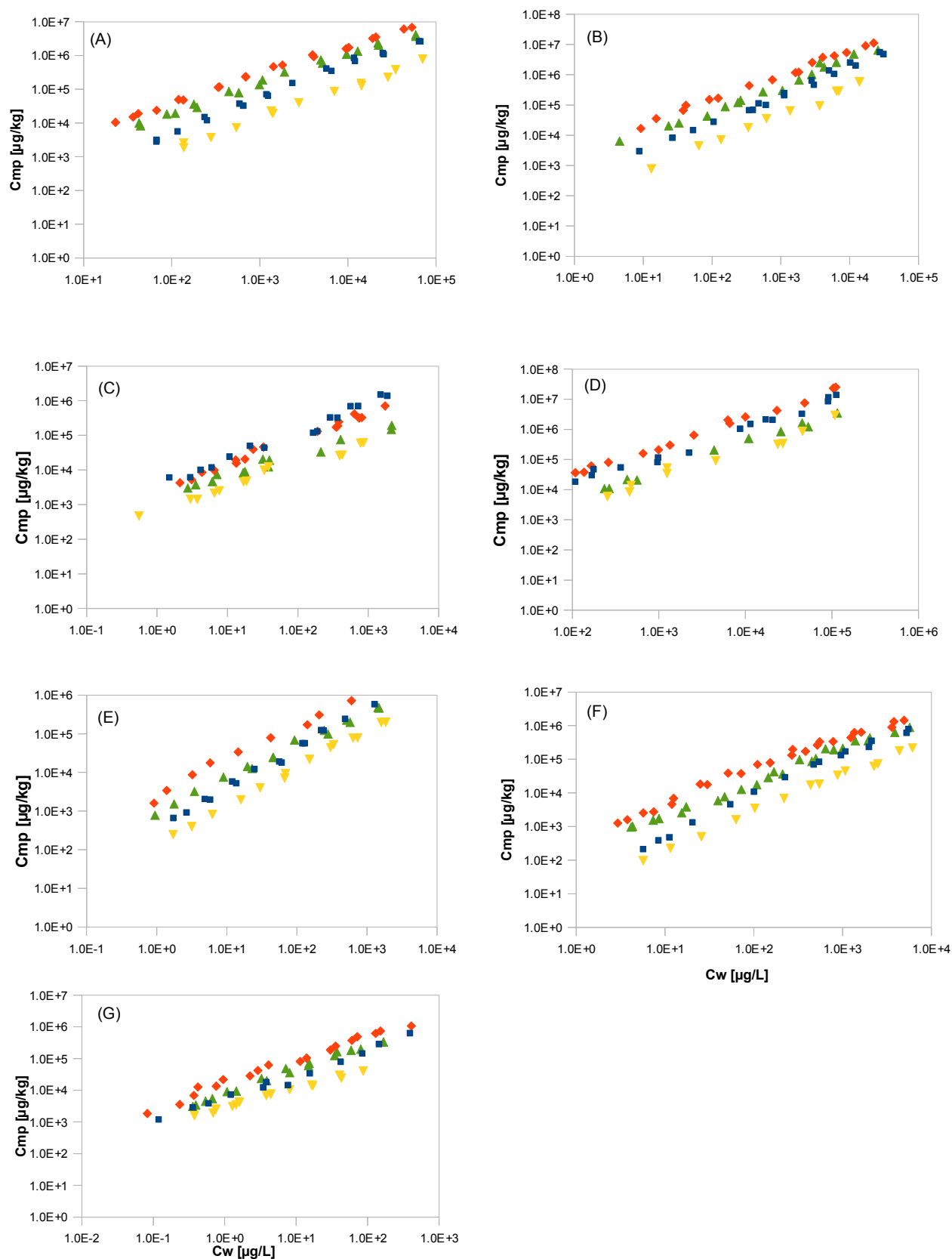


Figure 6: Sorption isotherms of (A) benzene, (B) chlorobenzene, (C) cyclohexane, (D) ethylbenzoate, (E) naphthalene, (F) toluene, and (G) n-Hexane by PE (■), PS (◆), PA (▼), and PVC (▲), respectively.

5. Conclusion and outlook

5.1 Conclusion

The results of this study allowed a systematic characterization of the sorption behaviour of some commonly found MP particles (PE, PS, PA and PVC) and the possibility to identify the contribution of important molecular interactions to overall sorption.

Sorption isotherm batch experiments were conducted with low molecular weight organic compounds as sorbates and then fitted with the linear, Freundlich and Langmuir models. It was shown that the linear and the Freundlich models provided the best fits for most of the experimental data. The aromatic compounds showed sorption linearity and the aliphatic compounds nonlinearity for most of the isotherm data. The linearity implied that there was no energetic preference for sorption sites on the sorbent surface. The nonlinearity implied that sorbates showed an energetic preference for sorption sites on the surface of a sorbent, hence, added molecules were bound with weaker free energies [16]. Considering the sorbents, the isotherm data of PE for all compounds showed linearity. Since this was also shown in other studies [26, 35, 36] and PE is a nonpolar aliphatic polymer with no functional groups, it could be assumed that the dominant sorption mechanism was linear partitioning instead of other interactions. The isotherm data for PS and PVC showed more nonlinearity. PS is a nonpolar polymer which is composed of styrene monomers [37]. Previous studies assumed that the nonlinearity is caused by the ability of PS to form π - π interaction forces to aromatic organic compounds due to the aromaticity of the styrene monomers [20, 23, 36]. Hence, sorption of the tested compounds by PS was mainly controlled by its hydrophobicity and π - π -interactions at its aromatic surface. The nonlinearity of PVC was also shown in other studies [14, 40]. It was assumed that it is caused by its heterogeneous character due to its nature as a glassy polymer. Moreover, the polarity of its chlorine atoms reduces its free volume which decreases the possibility for a compound to partition into the polymer [26]. The isotherm data of PA indicated much more linearity. Due to its amorphous nature, it consists of domains available for partitioning of the compounds [23].

A positive correlation between two hydrophobicity parameters of sorbates ($\log K_{ow}$ and $\log K_{hw}$) and experimentally determined distribution coefficients, $\log K_d$, for all four MPs could be observed. The correlation for PE, PA and PVC showed the highest regression

coefficients, hence, sorption of almost all compounds was strongly determined by their hydrophobicity. There are studies which have shown that hexadecane acts as a better predictor for $\log K_d$ than octanol due to octanol's ability to interact with organic compounds via van der Waals, polar and hydrogen-bonding [35, 42]. However, because of the nonpolarity of the tested compounds the contribution of polar and hydrogen bonding did not play a considerably important role. Hence, octanol could still act as a good hydrophobicity parameter for this study. The regression coefficient of the correlation for PS was slightly lower which could be explained by the additional π - π interactions between the benzene rings. Correlations of the $\log K_d$ values with the log-converted aqueous solubilities ($\log S_w$) showed an inverse relationship which supported the previous assumptions that sorption is mainly influenced by hydrophobicity.

There are studies which assumed that the slopes of the regression equations give also information about sorption interaction mechanisms [16, 35, 44]. Deviation from 1 of the $\log K_d$ - $\log K_{ow}$ slope indicate different sorption behaviours in the two systems. All four MPs had $\log K_d$ - $\log K_{ow}$ slopes close to 1, suggesting that they behaved similar concerning the sorption behaviour to the probe sorbates.

The log-converted Freundlich coefficient, $\log K_F$, and the $\log K_d$ values showed comparable trends. It could be observed that $\log K_F$ also correlated with the compounds' hydrophobicity. Moreover, it could be seen that the $\log K_F$ values decreased in the order PS > PVC > PE > PA for almost all compounds. This correlated with the surface area and with the pore volume of all sorbents. The higher sorption by PS could be explained by the additional interactions at the PS surface area which was also shown in other studies [20, 36]. The higher sorption by PVC compared to PE was not consistent with all previous studies [14, 20, 26]. Some examined stronger sorption by PE than PVC which was probably caused by the higher free volume of PE. However, since there are other studies [15, 46] which have also shown stronger sorption by PVC, it can be said that sorbent properties alone are not sufficient for explaining sorption processes.

All in all, it can be concluded that the results agree with the assumption that hydrophobicity was the most important molecular interaction controlling sorption between the MPs and the compounds.

5.2 Outlook

This study has shown that hydrophobicity was the most important contributor to the overall sorption for almost all MPs. However, although all MPs are hydrophobic, some of them have polar properties. PA contains very polar planar amide (-CO-NH-) groups and may act as a hydrogen bonding donor. PVC has polar chlorine atoms as functional groups and its molecular structure is roughly unsymmetrical [37]. This means, they are able to interact via polar or hydrogen bonding with other compounds. Although, the tested aromatic compounds have the ability to act as hydrogen bonding acceptors (hydrogen bonding acidity = 0 and basicity > 0 (Table A4 in the Appendix)) [43], their basicity is very low. Hence, it might be necessary to extend the set of compounds with varied physical-chemical properties (e.g. polarity) which may be able to interact with the MPs via other molecular interactions in further studies.

Furthermore, there are compound properties which could cause problems concerning the used methodology. Low volatility of compounds or high solubility causing too low sorbed amounts may be reasons for difficulties in measuring the equilibrium aqueous phase concentrations by ITEX2-GC-MS. Additional steps of sample preparation or other measurement techniques may help to resolve these problems. Chen et al. (2007) examined the sorption of organic compounds with varying physical-chemical properties (hydrophobicity, polarity, electron polarizability, and size) to one single-walled carbon nanotube (SWNT) and two multiwalled carbon nanotubes (MWNTs) [47]. They left the prepared vials after reaching equilibrium on a flat surface for more than 24 h. This approach allowed the sorbents to settle completely. Afterwards aliquots of the aqueous solution were removed from the vials and were extracted with a solvent depending on the sorbate. Gas chromatography was then used to analyse the organic extracts. Hence, this methodology could be an opportunity to measure sorption between compounds with varied physical-chemical properties and MPs in further studies.

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9. List of abbreviations and symbols

A	Area of the GC-MS signal
b	Boiling point
BET	Adsorption model Brunauer-Emmett-Teller
CAS-Nr.	Chemical abstracts service – Registry number
C_G	Gaseous phase concentration
C_s	Sorbed sorbate concentration
$C_{s,max}$	Maximum achievable surface concentration of a given compound
C_0	Initial injected concentration of the compound
C_w	Liquid phase concentration
nC60	Aqueous dispersed fullerenes
DCB	Dichlorobenzene
DDE	Dichlorodipenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethanes
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
HDPE	High-density polyethylene
HOCs	Hydrophobic organic contaminants
ITEX-2	In-tube microextraction 2
K_{aw}	Air-water partition constant
K_{hw}	Hexadecane-water partition constant
K_d	Partition coefficient
K_F	Freundlich coefficient
K_L	Langmuir coefficient
K_{ow}	Octanol-water partition constant
LDPE, LLDPE	Low-density polyethylene
MDPE	Medium-density polyethylene
MF	Molecular formula
m_G	Amount of mass from the sample in the gas phase
m_0	Amount of mass from the initial injected sample
m_s	Amount of sorbed mass from the sample
m_w	Amount of mass from the sample in the liquid phase
MP	Microplastic
MS	Mass spectrometry

MW	Molecular weight
MWNT	Multiwalled carbon nanotube
N	Number of data points
n	Freundlich exponent
NP	Nonylphenol
p	Number of parameters
PA	Polyamide 6
PAHs	Polycyclic aromatic hydrocarbons
PBTs	Persistent, bioaccumulative and toxic substances
PCBs	Polychlorinated biphenyls
PDMS	Polydimethylsiloxane
PE	Polyethylene
PET	Polyethylene terephthalate
POPs	Persistent organic pollutants
PP	Polypropylene
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
R ²	Regression coefficients
RMSE	Residual root mean square error
SA	Specific surface area
SSL	Split/splitless injector
S _w	Aqueous solubility
SWNT	One single-walled carbon nanotube
T _G	Glass transition temperature
ρ	Density
Γ _{max}	Total number of surface sites per mass of sorbent

10. Appendix

Table A1: Summary of GC-parameters used during measurement of the different probe compounds.

Compound	Initial oven temp [°C]	Hold time start [min]	Hold time end [min]	Injector temp. [°C]	Split flow [mL min ⁻¹]	Split ratio
nonpolar aromatic compounds						
benzene	60	5.0	5.0	250	20	10
toluene	70	5.0	5.0	250	20	10
chlorobenzene	40	0.01	0.5	250	20	10
naphthalene	80	0.01	0.5	250	20	10
nonpolar aliphatic compounds						
n-Hexane	75	4.0	4.0	250	20	10
cyclohexane	80	4.0	4.0	250	20	10
monopolar aromatic compounds						
ethylbenzoate	50	0.5	0.5	250	20	10

Table A2: Summary of MS-parameters used during measurement of the different probe compounds.

Compound	Start time [min]	Scanned mass range [m/z]	Ion masses for evaluation [m/z]	Solvent delay [min]
nonpolar aromatic compounds				
benzene	1.8	50 - 80	51 + 77 + 78	1.8
toluene	1.8	50 - 150	65 + 91 + 92	1.8
chlorobenzene	1.5	75 - 150	77 + 112 + 114	1.5
naphthalene	1.0	75 - 150	128	1.0
nonpolar aliphatic compounds				
n-Hexane	0.8	50 - 90	57 + 86	0.8
cyclohexane	0.8	50 - 90	56 + 69 + 84	0.8
monopolar aromatic compounds				
ethylbenzoate	1.5	70 - 160	77 + 105 + 122	1.5

Table A3: Summary of ITEX-parameters used during measurement that were not generally the same for the different probe compounds.

Compound	Extraction volume [μL]	Extraction speed [μL/s]	Injection volume [μL]	Desorption temp. [°C]	GC Runtime + Cooling Down [s]	Flush time [s]	Clean temp. [°C]
nonpolar aromatic compounds							
benzene	0	100	500	70	300	180	150
toluene	0	100	500	70	300	180	150
chlorobenzene	0	100	500	70	300	180	150
naphthalene	30000	100	500	250	600	300	250
nonpolar aliphatic compounds							
n-Hexane	0	100	500	70	300	180	150
cyclohexane	0	100	500	70	300	180	150
monopolar aromatic compounds							
ethylbenzoate	30000	100	500	250	600	300	250

Table A4: Summary of substance descriptors (E = excess molar refraction; S = dipolarity/polarizability; A = hydrogen (H)-bond acidity; B = H-bond basicity; V = molar volume; L = logarithmic hexadecane-air partition constant) [48].

Compound	E	S	A	B	V	L
<u>nonpolar aromatic compounds</u>						
benzene	0.61	0.52	0	0.14	0.716	2.786
toluene	0.6	0.52	0	0.14	0.857	3.325
chlorobenzene	0.72	0.65	0	0.07	0.839	3.657
naphthalene	1.34	0.92	0	0.20	1.085	5.161
<u>nonpolar aliphatic compounds</u>						
n-Hexane	0	0	0	0	0.954	2.688
cyclohexane	0.305	0.1	0	0	0.845	2.964
<u>monopolar aromatic compounds</u>						
ethylbenzoate	0.689	0.85	0	0.46	1.214	5.075

Table A5: Fitting parameters \pm standard errors, goodness-of-fit parameter R^2 and root mean square error for three nonlinear sorption model fits to the experimental isotherm data of all compounds by microplastics.

n-Hexane										
Freundlich Model (FM)						Langmuir Model (LM)				
Sorbent	K_F	n	R^2	RMSE	N	Q_{max}	K_L	R^2	RMSE	N
PE	$3.11E+03 \pm 5.53E+02$	0.9613 ± 0.0387	0.9134	0.2684	12	$7.32E+05 \pm 6.37E+05$	$2.57E+02 \pm 2.56E+02$	0.7288	0.4751	12
PS	$1.46E+04 \pm 9.82E+02$	0.7622 ± 0.0203	0.9407	0.2579	18	$7.43E+05 \pm 2.07E+05$	$5.64E+01 \pm 2.04E+01$	0.8696	0.3376	18
PA	$7.54E+03 \pm 8.49E+01$	0.8793 ± 0.0139	0.9502	0.1143	17	$2.50E+04 \pm 3.46E+03$	$8.46E+00 \pm 1.70E+00$	0.9015	0.2072	17
PVC	$2.86E+03 \pm 6.79E+03$	0.5929 ± 0.0172	0.9497	0.1491	17	$3.13E+05 \pm 5.43E+04$	$4.55E+01 \pm 9.83E+00$	0.9249	0.1969	17
Cyclohexane										
Freundlich Model (FM)						Langmuir Model (LM)				
Sorbent	K_F	n	R^2	RMSE	N	Q_{max}	K_L	R^2	RMSE	N
PE	$1.04E+03 \pm 5.05E+02$	0.9574 ± 0.0360	0.9621	0.2543	15	$3.14E+06 \pm 2.96E+06$	$2.62E+03 \pm 2.77E+03$	0.7513	0.4316	15
PS	$2.57E+03 \pm 6.10E+02$	0.7423 ± 0.0178	0.9336	0.1893	17	$3.93E+05 \pm 6.10E+04$	$2.65E+02 \pm 5.58E+01$	0.9171	0.2434	17
PA	$7.00E+02 \pm 7.17E+01$	0.8929 ± 0.0251	0.9252	0.2304	13	$4.07E+04 \pm 7.90E+03$	$1.10E+02 \pm 2.86E+01$	0.8923	0.2905	13
PVC	$1.70E+03 \pm 1.93E+02$	0.6384 ± 0.0160	0.9278	0.1977	13	$7.62E+04 \pm 2.64E+04$	$1.20E+02 \pm 5.68E+01$	0.692	0.4083	13
Benzene										
Freundlich Model (FM)						Langmuir Model (LM)				
Sorbent	K_F	n	R^2	RMSE	N	Q_{max}	K_L	R^2	RMSE	N
PE	$5.46E+01 \pm 7.72E+00$	0.9898 ± 0.0181	0.9583	0.1878	18	$1.16E+07 \pm 5.72E+06$	$2.16E+05 \pm 1.11E+05$	0.9686	0.1629	18
PS	$8.07E+02 \pm 6.40E+01$	0.8418 ± 0.0106	0.9814	0.1214	20	$5.95E+06 \pm 1.01E+06$	$1.72E+04 \pm 3.48E+03$	0.9574	0.1893	20
PA	$2.38E+01 \pm 4.26E+00$	0.9145 ± 0.0219	0.9675	0.162	13	$1.02E+06 \pm 4.03E+05$	$7.44E+04 \pm 3.31E+04$	0.9519	0.1969	13
PVC	$3.75E+02 \pm 4.24E+01$	0.8581 ± 0.0147	0.9677	0.2028	19	$5.34E+06 \pm 8.42E+05$	$3.22E+04 \pm 5.90E+03$	0.9681	0.2177	19
Toluene										
Freundlich Model (FM)						Langmuir Model (LM)				
Sorbent	K_F	n	R^2	RMSE	N	Q_{max}	K_L	R^2	RMSE	N
PE	$5.55E+01 \pm 5.13E+00$	0.9964 ± 0.0252	0.9306	0.2502	15	$8.17E+06 \pm 9.68E+06$	$5.73E+04 \pm 7.22E+04$	0.9267	0.2871	15
PS	$5.28E+02 \pm 6.10E+01$	0.9567 ± 0.0206	0.9201	0.2591	24	$2.94E+06 \pm 8.35E+05$	$5.94E+03 \pm 1.83E+03$	0.9508	0.2032	24
PA	$2.67E+01 \pm 2.08E+00$	0.9951 ± 0.0211	0.9657	0.1815	14	$9.71E+06 \pm 5.73E+05$	$2.80E+04 \pm 1.65E+04$	0.9358	0.2189	14
PVC	$1.70E+02 \pm 2.06E+01$	0.9460 ± 0.0191	0.9515	0.1965	24	$7.11E+06 \pm 7.70E+05$	$3.60E+04 \pm 3.95E+04$	0.9538	0.1918	24

Chlorobenzene

Freundlich Model (FM)						Langmuir Model (LM)				
Sorbent	K _F	n	R ²	RMSE	N	Q _{max}	K _L	R ²	RMSE	N
PE	3.37E+02 ± 5.26E+01	0.9596 ± 0.0216	0.9619	0.1895	18	2.39E+07 ± 1.96E+07	1.13E+05 ± 9.64+04	0.9467	0.2242	18
PS	3.42E+03 ± 3.81E+02	0.8103 ± 0.0161	0.9512	0.1677	16	1.14E+07 ± 4.01E+06	9.51E+03 ± 4.09E+03	0.8853	0.318	16
PA	8.14E+01 ± 1.88E+01	0.9425 ± 0.0320	0.9479	0.2307	11	1.79E+06 ± 1.70E+06	3.76E+04 ± 3.91E+04	0.9192	0.2867	11
PVC	1.22E+03 ± 2.37E+02	0.8469 ± 0.0289	0.9382	0.2377	16	1.39E+07 ± 6.58E+05	2.88E+04 ± 1.97E+04	0.8859	0.323	16

Ethylbenzoate

Freundlich Model (FM)						Langmuir Model (LM)				
Sorbent	K _F	n	R ²	RMSE	N	Q _{max}	K _L	R ²	RMSE	N
PE	1.80E+02 ± 5.99E+01	0.9697 ± 0.0383	0.9262	0.2984	15	1.55E+08 ± 5.73E+08	1.43E+06 ± 5.40E+06	0.9094	0.3195	15
PS	4.71E+02 ± 7.16E+01	0.9302 ± 0.0208	0.9585	0.1771	15	6.36E+07 ± 3.82E+07	2.52E+05 ± 1.61E+05	0.9381	0.2161	15
PA	3.96E+01 ± 1.73E+01	0.9525 ± 0.0515	0.8726	0.3165	10	2.39E+06 ± 2.35E+06	1.12E+05 ± 1.23E+05	0.8346	0.3606	10
PVC	5.10E+01 ± 2.12E+01	0.9350 ± 0.0468	0.9361	0.2821	10	5.29E+06 ± 1.88E+06	1.12E+05 ± 4.99E+04	0.9656	0.2111	10

Naphthalene

Freundlich Model (FM)						Langmuir Model (LM)				
Sorbent	K _F	n	R ²	RMSE	N	Q _{max}	K _L	R ²	RMSE	N
PE	4.03E+02 ± 2.73E+02	0.9998 ± 0.0272	0.9632	0.1735	15	3.16E+06 ± 1.12E+05	6.72E+03 ± 2.68E+04	0.9375	0.2614	15
PS	2.33E+03 ± 3.05E+02	0.9059 ± 0.0341	0.9357	0.2415	9	9.49E+05 ± 4.06E+05	4.43E+02 ± 2.17 E+02	0.9367	0.236	9
PA	1.37E+02 ± 9.95E+00	0.9806 ± 0.0146	0.9836	0.1212	14	1.36E+06 ± 8.49E+05	1.04E+04 ± 6.74E+03	0.985	0.1267	14
PVC	9.58E+02 ± 7.54E+01	0.8542 ± 0.0167	0.9741	0.1534	15	6.07E+05 ± 1.67E+05	9.34E+02 ± 3.04E+02	0.9862	0.1171	15

Abstract

Plastics are synthetic polymers which global production increases continuously since the 1950s due to their specific properties. Microplastics (MPs) are small plastic particles which may be generated from various sources. MPs are hydrophobic, persistent and have an extremely long lifetime in the oceans. Investigations have shown that MPs sorb persistent, bioaccumulative, and toxic substances (PBTs) which became an important issue in recent years. MPs are able to transport contaminants to remote and pristine locations. Previous studies already discussed the interaction of MPs and hydrophobic organic compounds (HOC) but there is still a huge lack in the understanding of relevant sorption mechanisms.

Thus, the aim of this study was to systematically characterize the sorption behaviour of commonly found MP particles (PE, PS, PA and PVC). Sorption isotherm batch experiments were conducted with MPs as sorbents and organic compounds as sorbates. They were then fitted with the linear, Freundlich and Langmuir models. Moreover, experimentally determined distribution coefficients (K_d) were correlated with known sorbate and sorbent properties.

The results of this study showed that the linear and the Freundlich models provided the best fits for most of the experimental data. The linearity of the isotherm data (PE and PA) indicated that there was no energetic preference for sorption sites on the sorbent surface. Some isotherm data showed slightly more nonlinearity (PS and PVC). The nonlinearity for PS was probably caused by the additional π - π interaction forces to the aromatic organic compounds. PVC has a heterogeneous character due to its nature as a glassy polymer. The correlations of the K_d - values with some hydrophobicity parameters of the sorbates showed that sorption of almost all compounds was strongly determined by their hydrophobicity. Moreover, the K_d - values correlated with the surface area of all sorbents. It was shown that PS sorbed the highest concentrations which could be explained by the additional interactions at the PS surface area. It could be concluded that hydrophobicity was the most important molecular interaction controlling sorption between the MPs and the compounds.

Zusammenfassung

Kunststoffe sind synthetische Polymere, deren weltweite Produktion seit den 1950er kontinuierlich steigt. Mikroplastik (MP) sind kleine Kunststoffpartikel, die durch unterschiedliche Quellen erzeugt werden. MP sind hydrophob, beständig und haben eine extrem lange Lebensdauer in den Ozeanen. Untersuchungen haben gezeigt, dass sie persistente, bioakkumulierbare und giftige Stoffe (PBT) sorbieren, was zu einem Problem in den letzten Jahren wurde. Sie sind in der Lage Schadstoffe in entfernte und unberührte Orte zu transportieren. Frühere Studien haben bereits die Wechselwirkung zwischen MP und hydrophoben organischen Verbindungen (HOC) diskutiert, jedoch gibt es immer noch einen großen Mangel am Verständnis der relevanten Sorptionsmechanismen.

Das Ziel dieser Arbeit war daher, eine systematische Charakterisierung des Sorptionsverhaltens von häufig vorkommenden MP Partikeln (PE, PS, PA und PVC). Es wurden Sorptionsisothermen zwischen MP und organischen Verbindungen in Batchversuchen gemessen. Die Sorptionsmodelle: Linear, Freundlich und Langmuir wurden für die Daten angewendet. Außerdem wurden experimentell bestimmte Verteilungs-Koeffizienten (K_d) mit Eigenschaften von Sorbaten und Sorbenten korreliert.

Die Ergebnisse dieser Arbeit zeigten, dass die experimentellen Daten am besten mit dem Linearen und Freundlich Modell beschrieben werden können. Die Linearität der Isothermen (PE und PA) deutet darauf hin, dass es keine energetische Präferenz für die Sorptionsplätze auf der Sorbenten Oberfläche gab. Einige Daten zeigten eine leichte Nichtlinearität (PS und PVC). Bei PS wurde diese wahrscheinlich durch die zusätzlichen π - π Wechselwirkungen zu den aromatischen Verbindungen verursacht. PVC hat einen heterogenen Charakter aufgrund seiner glasartigen Struktur. Die Korrelationen zwischen den K_d - Werten und ein paar Hydrophobizitäts Parametern der Sorbate zeigten, dass die Sorption von fast allen Verbindungen stark von ihrer Hydrophobizität abhing. Außerdem korrelierten die K_d - Werte mit der Oberfläche aller Sorbenten. Es wurde beobachtet, dass PS die höchsten Konzentrationen an organischen Verbindungen sorbierte. Dies konnte durch die zusätzlichen Wechselwirkungen an der PS Oberfläche erklärt werden. Zusammenfassend kann man sagen, dass die Hydrophobizität der wichtigste Wechselwirkungsmechanismus ist, der die Sorption zwischen den MP Partikeln und den Verbindungen steuert.