

Article

Exploring Sustainable Solutions: Dynamic Adsorption, Isotherm Models, and Kinetics of Organic Contaminants on Polystyrene Microplastics

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Abstract: As the world transitions towards a more sustainable future, it is imperative to develop innovative solutions that address the pressing issue of plastic pollution. Microplastics, in particular, have become a significant concern due to their widespread presence in the environment and potential to interact with toxic pollutants. Organic compounds, which include a variety of harmful chemicals, such as pesticides and other industrial chemicals, are often released into the environment and can readily bind to microplastics. In this context, understanding the adsorption of organic compounds on microplastics is crucial for designing effective strategies to mitigate their environmental impacts. This study investigates the adsorption dynamics of organochlorine pesticides (OCPs) on polystyrene microplastics, exploring the influence of pH and contact time, as well as utilizing kinetic models and isothermal equations to elucidate the adsorption mechanism. The results suggest that the pH level has a negligible impact on the adsorption capacity of PS for OCPs. In contrast, the contact time plays a significant role in the amount of OCPs adsorbed onto the PS surface. Interestingly, a relatively short time of up to 6 h was sufficient to reach equilibrium. The adsorption of OCPs on PS follows a uniform pattern consistent with the Freundlich isotherm model, indicating a multilayer adsorption process. The use of kinetic models to describe the adsorption process was also found to be useful in understanding its mechanism. Specifically, the pseudo-second-order kinetic model proved to be a suitable descriptor for the adsorption process of organochlorine pesticides on PS. This study highlights the importance of understanding the interactions between microplastics and organic pollutants, which is crucial for developing sustainable solutions to mitigate the environmental impacts of plastic pollution, ultimately contributing to a more environmentally conscious future.

Keywords: microplastics; organochlorine pesticides; adsorption; kinetic models; GC-ECD



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1. Introduction

As the world grapples with an escalating environmental crisis, the interplay between microplastics and persistent organic pollutants (POPs), like organochlorine pesticides (OCPs) has emerged as a critical area of study [1,2]. OCPs are a class of chemical compounds characterized by the presence of at least one carbon ring and several chlorine atoms [3]. They were widely used around the globe until the 1970s when harmful effects began to be observed and they began to be investigated in more detail. Over time, more and more pesticides have been identified as persistent organic pollutants, and their use was banned in several countries. In 2001 the Stockholm Convention was established, an agreement between the signatory states to ban them completely [4]. Following European Union (EU) regulations outlined in Directive 2020/2184, the maximum permissible limits for pesticides in drinking water are set at 0.1 µg/L for individual pesticide compounds,

0.3 µg/L for specific pesticides, such as aldrin, dieldrin, heptachlor, and heptachlor epoxide, and 0.5 µg/L for the total concentration of all pesticides [5].

The main characteristic of organochlorine pesticides is their high stability, which allows them to persist in nature for long periods. As most of them are lipophilic molecules, they can also accumulate in the fatty tissue of living organisms and are therefore capable of bioaccumulating, which increases their risk to the environment. The most common toxic effects observed both in humans and animals following prolonged exposure to OCPs are neuronal disorders, liver diseases, kidney damage, reproductive system disorders, impairment of the immune system, and potential carcinogenic effects [6]. Also worth noting are the negative effects that OCPs can manifest on developing fetuses and infants, where growth can be severely impaired and malformations can occur [7].

On the other hand, microplastics (MPs) are a class of pollutants that have relatively recently come to public attention and consist of plastic particles of very small size, usually less than 5 mm in diameter [8]. They can either come from the decomposition of larger plastics or can be manufactured directly at smaller sizes. Microplastics can take various forms: fragments, granules, fibers, or finer particles. They can have a negative impact on the environment and human health, as their very small size means they can enter all environmental compartments (water, soil, and air) where they can be ingested by organisms. They can also affect food chains, and the long-term impact of exposure to these particles is still a subject of intense research [8,9].

A broad classification of MPs can be made according to their origin. Primary microplastics are purposely made of small particles, usually produced as beads to be included in cosmetics or cleaning products, as granules for some agricultural applications, or as fibers resulting from the textile industry. The other class of MPs, called secondary microplastics, are particles resulting from the degradation of larger pieces or objects under the influence of natural factors, such as exposure to sunlight, temperature variation, or mechanical breakdown [7]. Plastic waste thrown into nature is the source of this category of MPs. The global production of plastics in massive quantities and the wide and varied range of uses have led to the spread of microplastics across the globe and it is a matter of concern that they can be detected in all environments, from streams to seas and oceans, soils, sediments, and even in the Antarctic ice caps and ocean depths [8–13].

Recent studies have shown that microplastics can retain chemicals on their surface, especially persistent organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs), etc. [14], producing a significant preconcentration and altering the interactions and toxicity of these contaminants in living organisms [15,16]. Thus, there has been extensive investigation of the adsorption mechanisms of various materials onto microplastics, including heavy metals and other hazardous substances. Research has shown that factors, such as particle size, surface chemistry, and environmental conditions, significantly influence the adsorption dynamics [17,18]. However, while these studies have established a foundation for understanding adsorption processes, there is a notable gap regarding the specific interactions between organic contaminants, particularly organochlorine pesticides (OCPs), and microplastics.

This study represents a pioneering investigation into the adsorption mechanism of 16 organochlorine compounds on polystyrene (PS) microparticles. It aims to determine the adsorption capacity of PS for these organochlorine pesticides, evaluate the influence of pH and contact time on the adsorption process, study adsorption isotherms to understand the nature of the interactions between adsorbates and the adsorbent, and compare experimental results with those predicted by kinetic models. As the first research paper to examine this specific interaction, it contributes valuable insights into the environmental behavior of microplastics and their potential role in the transport of harmful pesticides.

These two pollutants not only coexist but also interact chemically and physically, with microplastics exhibiting an alarming capacity to adsorb and transport OCPs through various environmental compartments. By investigating the adsorption processes, isotherm

models, and kinetics of OCPs on polystyrene microplastics, this study aims to provide crucial insights into these interactions. Understanding the mechanisms governing the adsorption of OCPs onto microplastics is vital for developing sustainable remediation strategies, thereby reducing the environmental risks associated with both microplastics and organic pollutants. The knowledge gained from this study will inform policy-makers and researchers as they seek solutions to mitigate the impacts of these dual hazards, emphasizing the need for sustainable practices in plastic production and waste management to protect our ecosystems for future generations.

The importance of this study lies in its relevance to international research efforts aimed at understanding the complex relationships between persistent organic pollutants, like organochlorine pesticides and microplastics. As international collaborations continue to grow in response to global environmental concerns, this study's findings will contribute significantly to our understanding of how microplastics interact with OCPs in aquatic environments. The results will also inform strategies for mitigating pollution risks associated with OCPs and microplastics in waterways worldwide. Furthermore, this study's findings will contribute to a broader understanding of how microplastics can serve as vectors for transporting pollutants into ecosystems, emphasizing the need for sustainable practices in plastic production and waste management.

2. Materials and Methods

2.1. Materials

A mixture of 16 organochlorine pesticides in acetone was used in this study, including α -Hexachlorocyclohexane; β -Hexachlorocyclohexane; γ -Hexachlorocyclohexane (Lindane); δ -Hexachlorocyclohexane; Aldrin; Dieldrin; Endrin; Endrin Aldehyde; Heptachlor, Heptachlor Epoxide; 4,4'-DDT; 4,4'-DDE; 4,4'-DDD; Endosulfan I; Endosulfan II and Endosulfan Sulfate (Table 1). Pentachloronitrobenzene (PCNB) was used as internal reference standard. The mixture was purchased from LGC, and the analytical standard from CPA Chem. Aqueous solutions were prepared using Milli-Q ultra-purified water from a Millipore system. Liquid-liquid extractions were performed using hexane from Merk.

Table 1. Studied organochlorine compounds.

No.	Compound	Molecular Formula	Molecular Mass	CAS
1	α -Hexachlorocyclohexane	C ₆ H ₆ Cl ₆	290.8	319-84-6
2	β -Hexachlorocyclohexane	C ₆ H ₆ Cl ₆	290.8	319-85-7
3	γ -Hexachlorocyclohexane	C ₆ H ₆ Cl ₆	290.8	58-89-9
4	δ -Hexachlorocyclohexane	C ₆ H ₆ Cl ₆	290.8	319-86-8
5	Aldrin	C ₁₂ H ₈ Cl ₆	364.9	309-00-2
6	Dieldrin	C ₁₂ H ₈ Cl ₆ O	380.9	60-57-1
7	Endrin	C ₁₂ H ₈ Cl ₆ O	380.9	72-20-8
8	Endrin Aldehyde	C ₁₂ H ₈ Cl ₆ O	380.9	7421-93-4
9	Heptachlor	C ₁₀ H ₅ Cl ₇	373.3	76-44-8
10	Heptachlor Epoxide	C ₁₀ H ₅ Cl ₇ O	389.3	1024-57-3
11	4,4'-DDT	C ₁₄ H ₉ Cl ₅	354.5	50-29-3
12	4,4'-DDE	C ₁₄ H ₈ Cl ₄	318.0	72-55-9
13	4,4'-DDD	C ₁₄ H ₁₀ Cl ₄	320.0	72-54-8
14	Endosulfan I	C ₉ H ₆ Cl ₆ O ₃ S	406.9	959-98-8
15	Endosulfan II	C ₉ H ₆ Cl ₆ O ₃ S	406.9	33213-65-9
16	Endosulfan Sulfate	C ₉ H ₆ Cl ₆ O ₄ S	422.9	1031-07-8

The plastic material used was polystyrene (PS), manufacturer Sigma-Aldrich (Darmstadt, Germany).

2.2. Batch Experiments

pH and contact time are critical variables in the study of organochlorine pesticide adsorption onto microplastics due to their influence on the physicochemical properties of

both the adsorbent and the adsorbate. pH affects the charge and solubility of pesticides, which in turn can alter the interaction strength between the pollutants and the microplastic surfaces. For instance, many organochlorine pesticides can become more ionized at different pH levels, impacting their adsorption capacity. Additionally, contact time is essential as it determines the duration for which the pesticides have the opportunity to interact with the microplastics. Longer contact times generally facilitate greater adsorption as the system approaches equilibrium, allowing for the maximum interaction between the contaminants and the sorbent. Given the complex dynamics of these variables, understanding their roles is vital for accurately assessing the environmental fate of pesticides associated with microplastics.

For determination of the influence of pH and contact time for the microplastic, 200 mL of OCP mix solution, 50 µg/L concentration, were prepared from the stock solution using ultrapure water as solvent. For the experiments to determine the adsorption kinetics, aqueous solutions at concentrations of 1, 10, 25, 50, and 75 µg/L OCPs were prepared in ultrapure water. Equal volumes of all aqueous solutions were transferred in Erlenmeyer flasks with 0.5 g of PS granules. Microplastic granules with a diameter of less than 100 µm were obtained by milling and separated using a sieve.

To achieve adsorption of the pesticides on the added microplastics, the above-mentioned solutions were stirred at about 150 rpm. The stirring time was 24 h, apart from the experiment, to determine the influence of contact time, and samples were collected at 2, 4, 6, 8, and 24 h from the start. The experiments were carried out at a room temperature of 23–24 °C [19].

2.3. OCP Extraction

After finalizing the stirring, the samples were filtered on filter paper to remove the microplastics. The aqueous microplastic-free samples thus obtained were collected in 50 mL centrifuge tubes and subjected to liquid–liquid extraction with hexane. Each sample was extracted three times. The extracts were collected in concentrator tubes and concentrated under nitrogen flow to a volume of 1 mL and then collected using a Pasteur pipette and placed in GC vials, where 50 µL of PCNB 2 mg/L internal standard solution was added.

2.4. OCP Chromatographic Determination

The analysis was conducted using an Agilent GC-ECD 7890B gas chromatograph equipped with an autoinjector, split/splitless injection port, 14% cyanopropyl phenyl/86% polysiloxane capillary column type 1701 (30 m long, 0.25 mm inner diameter and 0.25 µm stationary phase film thickness) and an electron capture detector. The chromatographic parameters are as follows: the injector was set at 260 °C, injection volume was 1 µL, 5:1 split ratio, Helium 6.0 purity carrier gas with a flow of 1 mL/min, oven temperature program starting at 50 °C, hold for 3 min, ramp-up with 10 °C/min up to 260 °C, where it is held for 15 min. Detector temperature was set at 350 °C

2.5. Quality Assurance and Quality Control

A stock solution of 10 mg/L was made from the OCP mixture standard solution, which has a concentration of 2000 mg/L of each compound, using hexane as solvent. An internal reference standard solution containing 2 mg/L PCNB was prepared in iso-octane. From the stock, six more solutions were made containing 2, 5, 10, 50, 100, 200 µg/L pesticides. To each solution, internal reference standard was added. All calibration solutions were made in hexane and 1 mL of each was analyzed by gas chromatography. The experiments were performed in duplicate. Each batch of samples contained blank samples and a control standard solution analysis.

2.6. PS Characterization

The surface morphology of the PS material was analyzed using the Quanta 250 FEG scanning electron microscope (Thermo Fisher Scientific, Waltham, MA, USA).

2.7. Adsorption Study

To determine the amount of pesticide retained per gram of microplastic, the following formula was applied [20,21]:

$$Q_t = ((C_0 - C_t) \times V)/m \quad (1)$$

where Q_t represents the retention capacity (adsorption) at time t , expressed as the amount of pesticide retained per unit of adsorbent/microplastic (mg/g); C_0 defines the initial concentration of pesticide in solution (mg/L); C_t represents the concentration of pesticide at time t (mg/L); V is the volume of the solution (L); and m defines the amount of adsorbent material used (g).

2.8. Adsorption Isotherms

To express the balance of pollutant removal from wastewater and synthetic aqueous solutions, adsorption isotherms are used, which are expressed mathematically. Whether it is the removal of metal ions or organic compounds, two widely used isotherms are the Freundlich isotherm and the Langmuir isotherm [22].

The Freundlich isotherm is used to describe non-ideal adsorption processes, in which it is assumed that adsorption does not occur exclusively on a single mono-molecular layer on the surface of the adsorbent material. The Freundlich isotherm equation (an equation of the type $y = mx + c$) is given by:

$$\ln(Q) = (1/n) \times \ln(C_e) + \ln(K_f) \quad (2)$$

where Q is the amount of pollutant adsorbed at equilibrium (mg/g); C_e is the concentration of pollutant in solution at equilibrium ($\mu\text{g/L}$); K_f is the Freundlich constant representing the capacity of the adsorbent material to retain the pollutant (mg/g) at a given concentration; and (n) is the exponent indicating the intensity of adsorption: $\ln(K_f) = c \rightarrow K_f = \exp(c)$

The Langmuir isotherm is used to describe ideal adsorption processes, in which adsorption takes place on a single mono-molecular layer on the adsorbent surface. The Langmuir isotherm equation (it is an equation of the type $y = mx + c$) is given by:

$$Q = Q_{\max} \times (K_L \times C_e)/(1 + K_L \times C_e) \quad (3)$$

where $Q_{\max} = 1/m$; $K_L = 1/(c \times Q_{\max})$; Q_{\max} is the maximum adsorption capacity (mg/g); and K_L is the Langmuir equilibrium constant indicating the ratio of adsorption to desorption rate.

2.9. Kinetic Study

The interactions that occur between the active centers of the adsorbent material (microplastic) and the retained pollutant (pesticide) are determined by kinetic study. In the retention process of organochlorine pesticides, experimental results are correlated with kinetic models widely used to characterize the adsorption process [19,23].

The pseudo-first-order kinetic model is used to characterize physical adsorption processes, in which interactions are predominant between the pollutant and the surface of the adsorbent material (microplastic). This model assumes that the adsorption rate is directly proportional to the concentration of the pollutant in the solution.

The pseudo-order II kinetic model is used to describe adsorption processes involving chemical reactions between the active centers of the adsorbent material (microplastic) and the retained pollutant (pesticide). This model assumes that the adsorption rate is influenced by the chemical reactions taking place between the pollutant and the adsorbent surface.

Analysis of experimental results using these kinetic models helps to determine the mechanisms involved in the adsorption process and to determine the type of interactions that take place between the adsorbent material and the retained pollutant [20,21].

The mathematical equations used to express the two mentioned kinetic models, the pseudo-order I kinetic model (Equation (4)) and the pseudo-order II kinetic model (Equation (5)) are:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (4)$$

where k_1 = first order rate constant (min^{-1}); t = time (min).

$$t/Q_t = 1/(k_2 \times Q_e^2) + 1/Q_e \quad (5)$$

where k_2 = second-order rate constant (g/mg/min).

3. Results

3.1. Polystyrene Characterization

PS surface morphology plays an important role in determining its adsorption capacity for OCP compounds. SEM analysis was performed to evaluate the changes in PS surface before and after the adsorption of different OCPs, as shown in Figure 1. The SEM images showed that the original PS shows a smooth and regular surface, indicating a homogeneous surface without significant features. However, after the adsorption of the POC compounds, significant changes in surface morphology were observed. Deposits related to the adsorption of the pesticides were observed on the PS surface. These surface changes provide visual evidence of the adsorption capacity of microplastics for POC compounds [24].

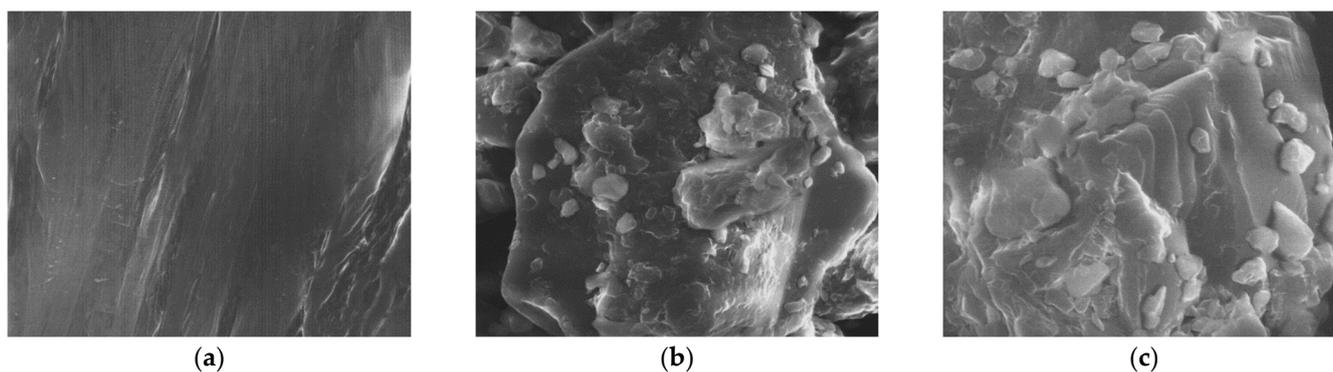


Figure 1. SEM images recorded for PS (a) and PS after pesticide adsorption (b,c).

3.2. Adsorption Parameters Optimization

3.2.1. pH Influence

pH can influence the adsorption process by altering the charge and structure of the adsorbent material, as well as changes in the charge and structure of the pollutant molecules. pH can also affect the solubility properties of the pollutants, which can influence the adsorption capacity of the adsorbent material. Previous studies have shown that changing pH can have significant effects on the adsorption processes of organic compounds, such as dyes, pesticides, heavy metals, etc. In the case of organochlorine pesticide pollution, whose physicochemical properties differ significantly, it is important to investigate the influence of pH on the adsorption capacity for each individual compound.

The study of the influence of the pH of the organochlorine pesticide solution showed that the pH value does not significantly influence the adsorption capacity of polystyrene (Figure 2). This value remains almost constant over the whole pH range studied, for most of the pesticides. A slight increase in the adsorption capacity of PS was observed for α -HCH, γ -HCH, and δ -HCH at pH higher than 9. This may be caused by the formation of ionized species of these compounds at higher pHs, which could interact more efficiently with the adsorbent material. These results indicate that pH is not a determining factor for the adsorption capacity of the adsorbent material, at least in the case of polystyrene for most of the OCPs studied. It can be an advantage for applications to remove pollutants from water or aqueous solutions, as pH can fluctuate significantly over time and affect other

adsorption processes. This observation may also be useful for the design of adsorption technologies, where regeneration processes may require adjustment of solution pH.

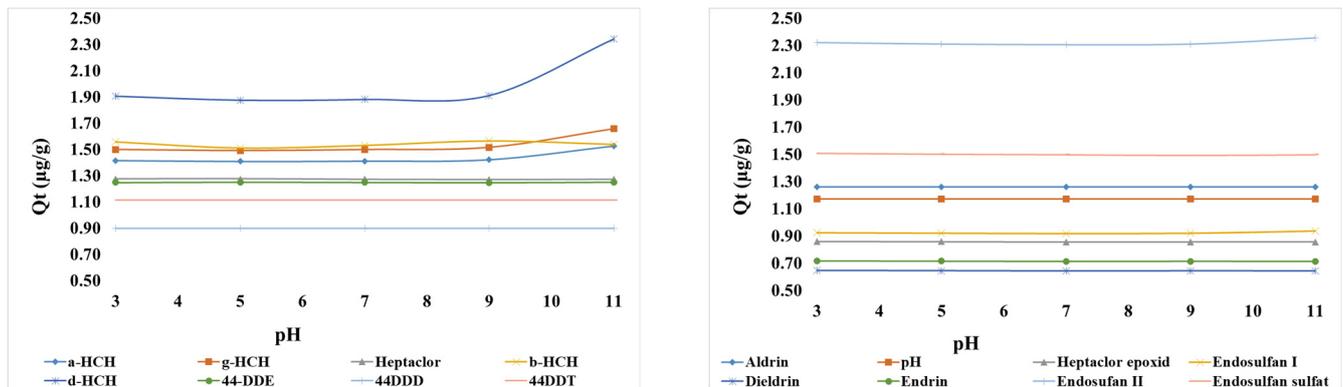


Figure 2. The pH Influence on pesticide adsorption capacity of PS.

To ease the experimental procedure, it was chosen to run the experiments at the initial pH of the samples, i.e., at approximately 5.5 pH units.

3.2.2. Effect of Contact Time

Contact time refers to the period of time that the pollutant solution and the adsorbent material are in contact to allow the adsorption of the pollutant. Different factors, such as particle size, surface structure configuration of the adsorbent material, concentration gradient, temperature, and pH, can influence the effectiveness of the adsorption process depending on the contact time. For this reason, it is important to study the influence of contact time on the adsorption capacity of the material.

The data show that the adsorption of the pesticides Aldrin, Endosulfan I, DDE and DDT increased rapidly during the first two hours of contact, after which the adsorption rate slowly decreased, reaching equilibrium after only four hours of contact (Figure 3). These data suggest that these pesticides can be removed efficiently using PS as adsorbent material with a relatively short contact time. These findings could be used to develop effective solutions for removing pesticides from aqueous solutions.

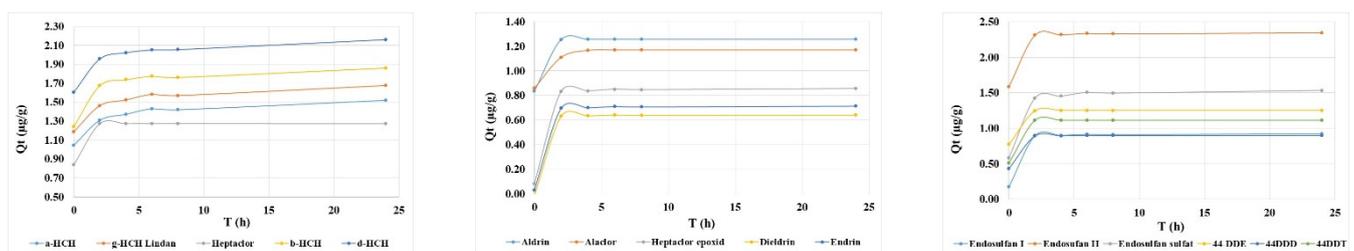


Figure 3. Influence of contact time on the adsorption capacity of PS.

In the case of the organochlorine compounds Alachlor and Dieldrin, adsorption increased rapidly in the first four hours, reaching a plateau after only six hours of contact. These findings are in agreement with previous results in the literature and indicate that the removal of these compounds requires longer periods of time in order to be affected by the adsorption process [25–28].

3.3. Adsorption Isotherms

Adsorption isotherms are an essential component in the study of adsorption phenomena and provide important information about the behavior of the adsorbent material in contact with the adsorbed substances. These curves reflect how the amount of adsorbed substance varies with its concentration in the liquid medium. By analyzing the

adsorption isotherm, important data can be obtained about the adsorption capacity of the material, the interactions between the adsorbent surface and the adsorbed substance, and the mechanisms involved in the adsorption process.

The adsorption process of organochlorine pesticides on polystyrene particles is a complex phenomenon involving interactions between pesticide molecules and the surface of polystyrene particles. It is important to understand the mechanism of this process in order to develop effective technologies for treating pesticide-contaminated water. In order to study and understand the adsorption mechanism of organochlorinated pesticides on polystyrene particles, Langmuir (Figure 4) and Freundlich (Figure 5) adsorption isotherms were plotted.

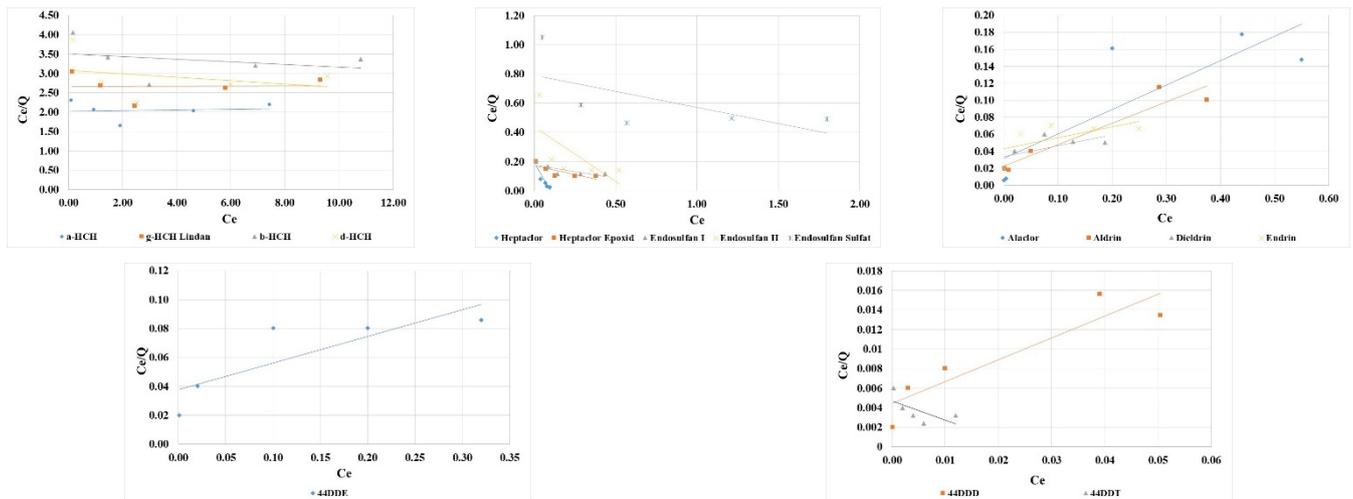


Figure 4. Langmuir adsorption isotherms.

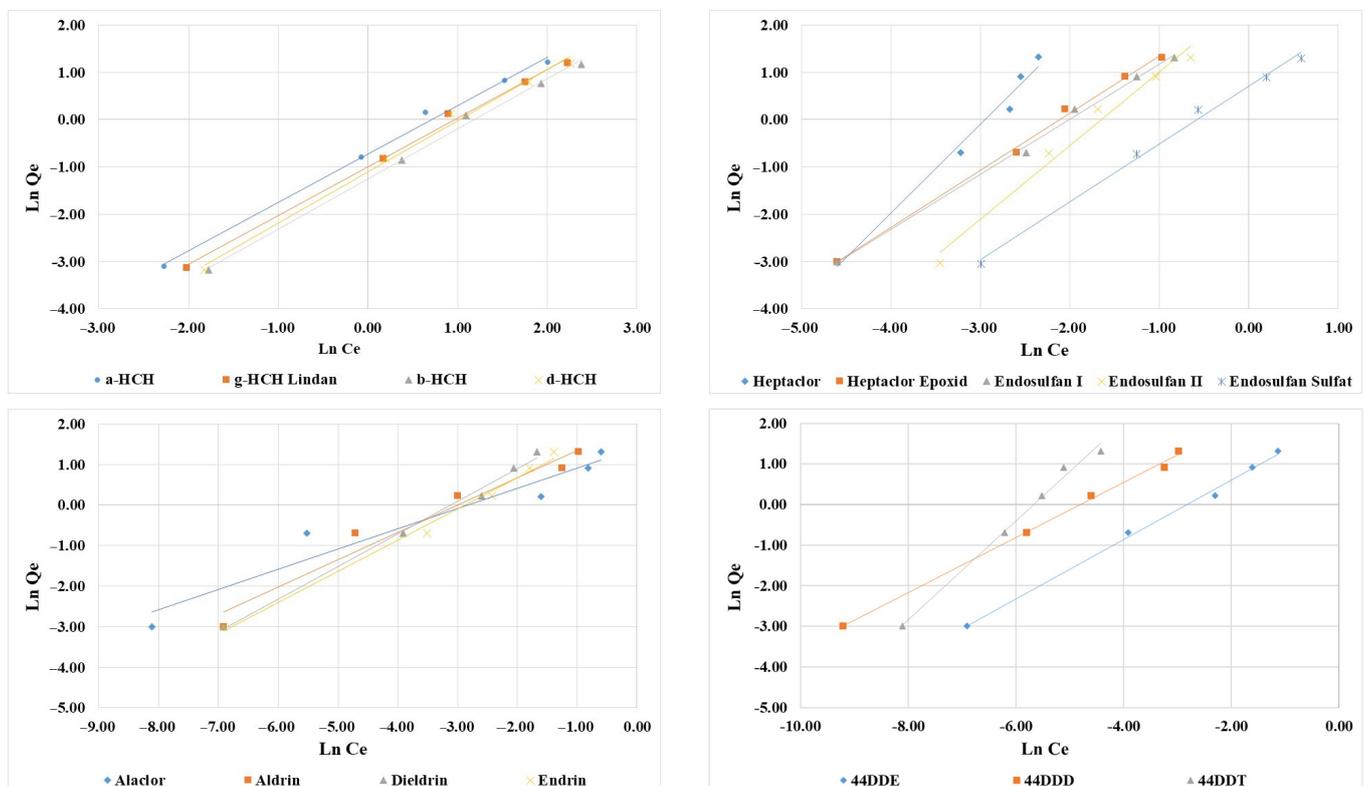


Figure 5. Freundlich adsorption isotherms.

The Langmuir adsorption isotherm is based on the assumption that the adsorption surface is uniform and that each adsorption site is independent. This is a simplification of reality because polystyrene particles have a porous structure and different adsorption sites with different binding energies. The Langmuir isotherm may underestimate adsorption if there are non-specific interactions between the pesticide and polystyrene.

On the other hand, the Freundlich adsorption isotherm is more flexible and can better describe non-ideal adsorption and heterogeneous interactions between pesticide molecules and polystyrene particles. Correlation coefficients higher than 0.9 indicate that the Freundlich model fits the experimental data very well and that the adsorption process is more complex, which is expected in this case.

An analysis of the values of the Langmuir equation parameters for the adsorption of organochlorine pesticides on polystyrene particles shows a significant variation in the maximum adsorption capacity (Q_{\max}), the Langmuir equilibrium constant (K_L) and the correlation coefficient (R^2) (Table 2). Values for Q_{\max} ranging from 1.02 to 29.7 $\mu\text{g/g}$ indicate a variable adsorption capacity of polystyrene particles for different types of organochlorine pesticides. Higher values of Q_{\max} suggest that polystyrene particles have a high adsorption capacity for these pesticides, which may be useful in contaminated water treatment processes. The Langmuir equilibrium constant (K_L) is important to determine how tightly pesticide molecules bind to the surface of polystyrene particles. Values between 0.0003 and 12.4 L/mg indicate a significant variation in the adsorption efficiency of polystyrene particles. Higher K_L values indicate more efficient adsorption of organochlorine pesticides on polystyrene. The correlation coefficient (R^2) is a measure of how well the Langmuir model fits the experimental data. Values between 0.0009 and 0.8389 indicate a large dispersion in the fit of the Langmuir model to the experimental data. Lower R^2 values indicate that this model does not fit the experimental data perfectly and more complex models or additional adjustments may be needed to correctly describe the adsorption process.

Table 2. Langmuir and Freundlich equation parameters for OCP adsorption on PS.

Compound	Langmuir Parameters			Freundlich Parameters			
	Q_{\max} ($\mu\text{g/g}$)	K_L (L/mg)	R^2	K_F ($\mu\text{g/g}$)	n	$1/n$	R^2
a-HCH	1.02	0.004	0.0101	2.05628	0.9767	1.0238	0.9951
b-HCH	29.7	0.009	0.092	0.84783	0.9461	1.0569	0.9959
d-HCH	22.6	0.014	0.0818	0.97658	0.9257	1.0802	0.9926
g-HCH	1.25	0.0003	0.0009	2.70689	0.9709	1.03	0.9954
Alachlor	3.47	9.127	0.7062	0.35354	2.01	0.4975	0.9356
Aldrin	4.69	12.38	0.3839	0.2271	0.8444	1.1843	0.9718
Dieldrin	7.78	3.813	0.4167	0.3203	1.2396	0.8067	0.9936
Endrin	7.67	3.033	0.3987	0.3468	1.2989	0.7699	0.9909
44'-DDT	5.13	4.145	0.4118	0.1762	0.8235	1.2143	0.9915
44'-DDE	5.41	4.917	0.6949	0.35273	1.3644	0.7329	0.9963
44'-DDD	4.48	5.678	0.8389	0.2079	1.4741	0.6784	0.9969
Heptachlor	3.7	9.681	0.0588	0.21757	0.8655	1.1553	0.9834
Heptachlor epoxide	8.28	0.869	0.4558	0.47402	0.8211	1.2179	0.996
Endosulfan I	7.15	1.835	0.1537	0.50086	0.8399	1.1906	0.9963
Endosulfan II	1.33	1.705	0.4421	0.60637	0.6421	15574	0.9805
Endosulfan sulfate	6.23	0.564	0.2514	1.55008	0.927	1.0787	0.994

Analysis of the Freundlich equation parameters shows a significant variation in Freundlich adsorption constant (K_F), n and $1/n$ constants, and correlation coefficients. Values

of Freundlich adsorption constant K_F ranging from 0.176 to 2.707 $\mu\text{g/g}$ show a variable adsorption capacity of polystyrene particles for different types of organochlorine pesticides. Higher K_F values suggest stronger and more efficient adsorption of organochlorine pesticides on polystyrene particles. The constant n in the Freundlich equation can be interpreted as a measure of adsorbent heterogeneity. Values ranging from 0.8211 to 1.36 suggest significant variation in polystyrene particle structure and adsorption sites for different types of organochlorine pesticides. Another metric of heterogeneity is $1/N$, which can be interpreted as a measure of adsorbability. Values between 0.678 and 1.55 show that the adsorption process on polystyrene particles can be characterized by a significant variation in the adsorbent's ability to attract organochlorine pesticide molecules. Correlation coefficients (R^2) greater than 0.9 indicate that the Freundlich model fits the experimental data well. Values between 0.9356 and 0.9963 indicate a good fit between the Freundlich model and the experimental data.

This suggests that the sorption process is characterized by a heterogeneous distribution of sorption sites on the adsorbent surface, implying that the energy of adsorption varies across different sites [26,29]. Consequently, the adsorption of OCPs onto PS is not confined to a single layer, which is consistent with the multifaceted interactions that can occur in complex environmental matrices. The Freundlich model is particularly suitable for systems where the surface properties are uneven, allowing for variations in the energy of adsorption. As such, the findings highlight the complexity of the sorption dynamics in contaminated environments, emphasizing that multiple factors influence the extent and nature of the adsorption processes for MPs on various pollutant substrates. This information can be critical for understanding the behavior of MPs in the environment and their potential to absorb and transport hazardous contaminants.

3.4. Adsorption Process Kinetics

The kinetics of adsorption processes is an important topic in chemical engineering and the treatment of contaminated water. Among the best-known kinetic models are the pseudo-order I (Figure 6) and pseudo-order II models (Figure 7).

Comparing the experimental and calculated values for adsorption capacity (Table 3) it was observed that, when the pseudo-order II kinetic model was applied, the experimental values were extremely close to the directly calculated values. These ranged from 0.64 to 2.18 $\mu\text{g/g}$ and are considered to be very accurate.

In contrast, the adsorption capacity values determined by the pseudo-order I model were between 0.28 and 2.04 $\mu\text{g/g}$ and showed some discrepancies from the directly calculated values (Table 2). These discrepancies between the calculated values and those obtained by kinetic models can be attributed to the fact that the pseudo-order I model is less suitable for the study of adsorption of organochlorine pesticide-contaminated water on polystyrene particles. This kinetics model assumes a dependence on the initial concentration and may underestimate the adsorption capacity for lower concentrations.

In contrast, the adsorption capacity values obtained by the pseudo-order II model are very close to the directly calculated values. This suggests that the pseudo-order II model is more appropriate in describing the adsorption process. This kinetics model takes into account both the amount of adsorbed substance and the adsorbent capacity, leading to a more accurate description of the adsorption process.

The pseudo-order II kinetic model describes the adsorption process as dependent on the concentration of adsorbate and the capacity of the adsorbent. An important parameter in this model is the rate constant k_2 , which represents the adsorption rate of the substance. The fast adsorption rates indicated by the k_2 values—ranging from 0.5908 to 1.6349—align with the theory that higher rate constants reflect increased interaction between the adsorbate and adsorbent at the molecular level. Specifically, the hydrophobic nature of organochlorine pesticides promotes stronger van der Waals forces and enhances the affinity for polystyrene surfaces, which contributes to rapid adsorption [16,24]. Furthermore, prior studies corroborate that the physical characteristics of microplastics, such as surface area

and functional groups, play critical roles in adsorption dynamics. Therefore, our findings are consistent with established literature, providing a more solid theoretical framework for the observed adsorption behaviors.

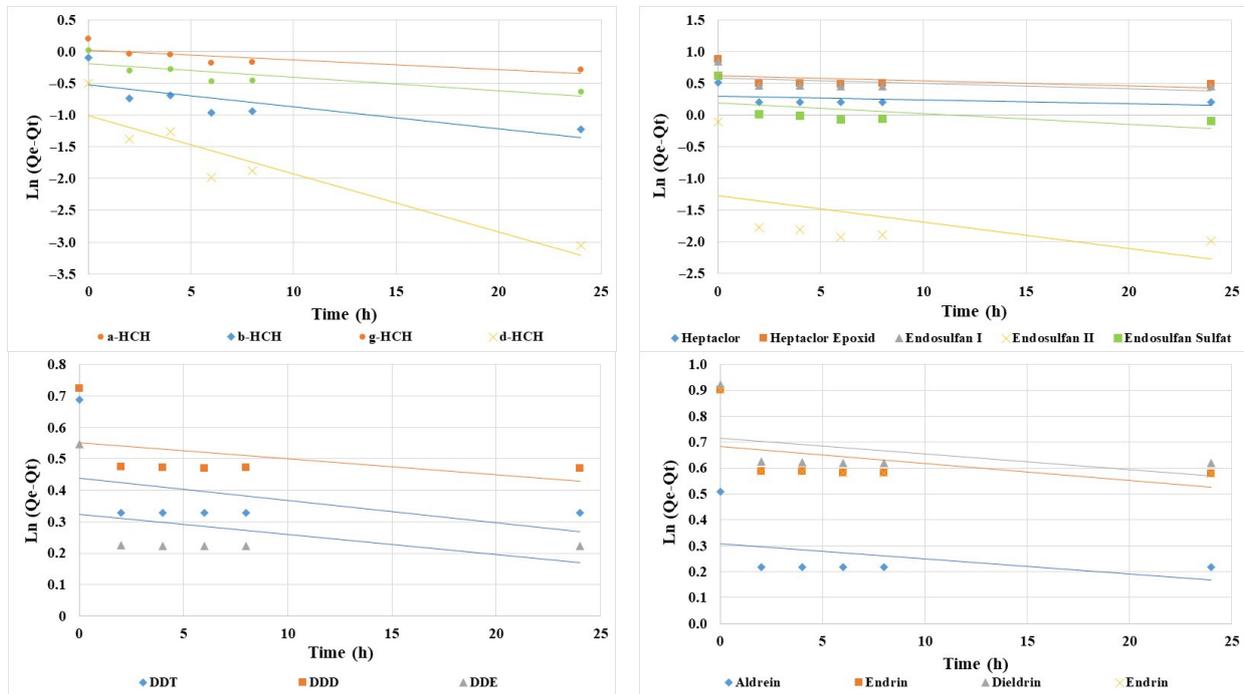


Figure 6. Correlation of experimental results with the pseudo-order I kinetic model for the adsorption process of OCPs on PS.

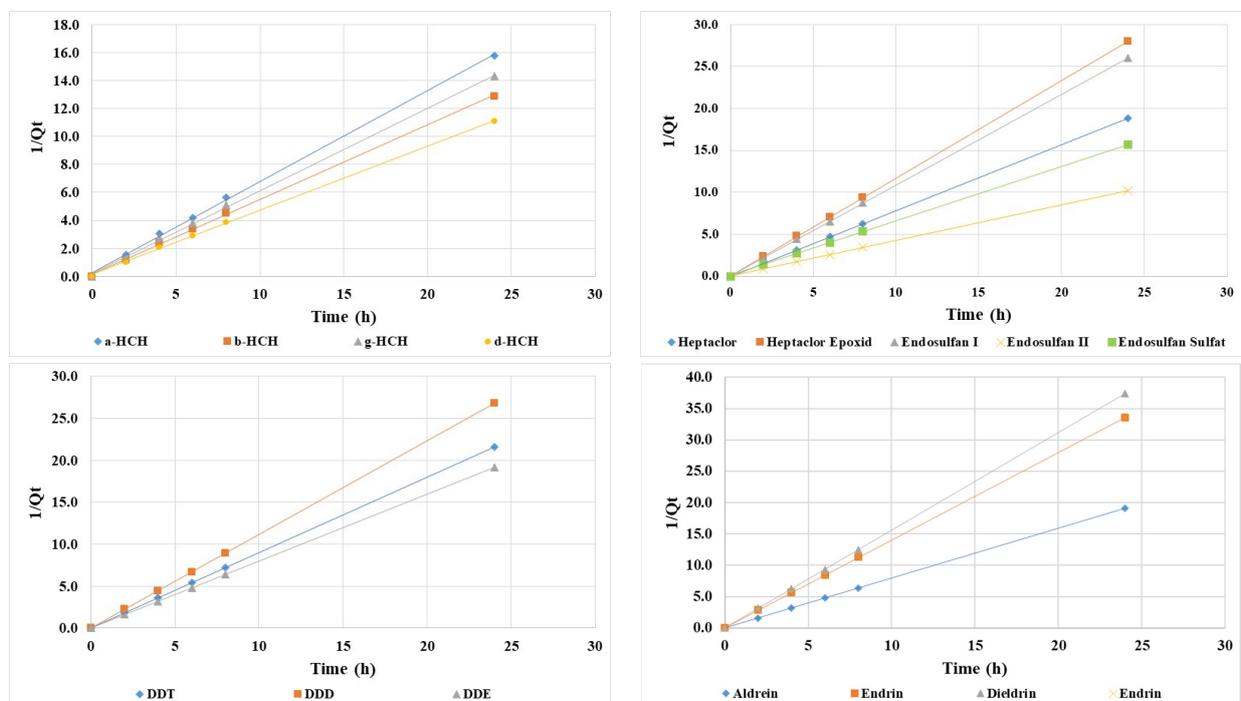


Figure 7. Correlation of experimental results with the pseudo-order II kinetic model for the adsorption process of OCPs on PS.

Table 3. Values of the kinetic parameters and correlation coefficients (R^2) for the retention process of organochlorine pesticides on PS.

Compounds	Calculated Q_e ($\mu\text{g/g}$)	Pseudo-Order I			Pseudo-Order II		
		$Q_{e, \text{exp}}$ ($\mu\text{g/g}$)	k_1 (min^{-1})	R^2	$Q_{e, \text{exp}}$ ($\mu\text{g/g}$)	k_2 ($\text{g/mg}\cdot\text{min}$)	R^2
a-HCH	1.43	1.03	0.0007	0.6341	1.54	1.6349	0.999
b-HCH	1.86	0.59	0.0014	0.6005	1.52	0.533	0.999
g-HCH	1.58	0.82	0.0009	0.6635	1.69	0.5908	0.999
d-HCH	2.16	0.37	0.0038	0.8548	2.18	0.459	1.003
Aldrin	1.26	1.36	0.0002	0.1749	1.26	0.7953	1.001
Dieldrin	0.64	2.04	0.0003	0.1816	0.64	1.5555	1.012
Endrin	0.71	1.98	0.0003	0.1889	0.72	1.3976	1.006
44DDT	1.11	1.55	0.0003	0.1729	1.11	0.8987	1.002
44-DDE	1.25	1.38	0.0003	0.1762	1.25	0.7995	1.007
44DDD	0.9	1.73	0.0002	0.1768	0.89	1.1157	1.001
Heptachlor	1.27	1.34	0.0003	0.172	1.27	0.7856	1.008
Heptachlor epoxide	0.85	1.85	0.0003	0.194	0.86	1.165	1.015
Endosulfan I	0.9	1.78	0.0003	0.1986	0.92	1.082	1.023
Endosulfan II	2.34	0.28	0.0017	0.244	2.35	0.4262	1.006
Endosulfan sulfate	1.51	1.27	0.0003	0.172	1.44	0.7856	1.003

The adsorption mechanism of OCPs on PS can be explained as follows. The beginning of the adsorption process is dominated by the diffusion of the adsorbed substance from the solution into the PS phase. This is due to the fact that, in the beginning, the active surfaces of the PS are available for the adsorbed substances in solution and the adsorbate loading process is relatively fast, with a higher adsorption rate. As the active surfaces of the PS become more loaded, the adsorption process enters a phase where the binding process becomes more important. This is the process that causes the formation of the stable adsorbed layer and leads to a decrease in the adsorption rate on the PS surface [24,30]. The adsorption mechanism of POC on PS is thus explained by means of adsorption kinetic models, such as the pseudo-order II kinetic model, which allow the analysis of the steps and mechanisms involved in this process and the determination of optimal adsorption conditions.

4. Conclusions

The main objectives of the study included determining the adsorption capacity of PS for organochlorine pesticides, assessing the influence of pH and contact time on the adsorption process, studying the adsorption isotherm to understand the nature of the interaction between adsorbates and adsorbent, and comparing experimental results with those obtained using kinetic models. It was observed that pH does not influence the adsorption efficiency in a significant way. The contact time study showed that OCPs are adsorbed on the PS surface in a relatively short time of up to 6 h, reaching equilibrium after this time. The adsorption isotherm study provided valuable information on the nature of the interaction of pesticide molecules with the PS surface. The results show that the adsorption of organochlorine pesticides on PSs follows unanimously the Freundlich adsorption isotherm model, suggesting a multilayer adsorption process. The use of kinetic models to describe the kinetics of the adsorption process was also useful in understanding the mechanism of this process. The pseudo-order II kinetic model was found to be more suitable for describing the adsorption process of organochlorine pesticides on PS compared

to the pseudo-order I model, due to the higher accuracy of the results obtained. This study demonstrated that PS can be effective in adsorbing organochlorine pesticides from water and that variations in pH, contact time, and kinetic patterns can significantly influence the efficiency of this adsorption process. The results obtained may be useful in developing optimal strategies for treating organochlorine pesticide-contaminated water using PS as adsorbent material.

The findings of this study are of significant international importance, particularly in the context of environmental sustainability and the global challenge of water pollution caused by organochlorine pesticides (OCPs). As the first research paper to investigate the adsorption mechanism of 16 organochlorine compounds on polystyrene (PS) microplastics, this work not only expands the scientific understanding of how microplastics can interact with harmful contaminants but also offers practical implications for water treatment strategies. Given the widespread prevalence of microplastics in aquatic environments and their potential to adsorb hazardous substances, the results underscore the need for effective remediation techniques aimed at mitigating the ecological and health impacts of pesticide contamination. By demonstrating the capacity of PS to adsorb OCPs efficiently, this study paves the way for the development of sustainable solutions to purify contaminated waterways, thereby contributing to global efforts in achieving cleaner and safer water resources. Ultimately, the insights gained from this research could inform policy decisions and promote practices that enhance environmental protection and public health on an international scale.

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