



Antibiotic sorption onto microplastics in water: A critical review of the factors, mechanisms and implications

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ABSTRACT

Microplastics as vectors for contaminants in the environment is becoming a topic of public interest. Microplastics have been found to actively adsorb heavy metals, per-fluorinated alkyl substances (PFAS), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), pharmaceuticals and personal care products (PPCPs) and polybrominated diethers (PBDs) onto their surface. Particular interest in microplastics capacity to adsorb antibiotics needs further attention due to the potential role this interaction plays on antibiotic resistance. Antibiotic sorption experiments have been documented in the literature, but the data has not yet been critically reviewed. This review aims to comprehensively assess the factors that affect antibiotic sorption onto microplastics. It is recognised that the physico-chemical properties of the polymers, the antibiotic chemical properties, and the properties of the solution all play a crucial role in the antibiotic sorption capacity of microplastics. Weathering of microplastics was found to increase the antibiotic sorption capacity by up to 171%. An increase in solution salinity was found to decrease the sorption of antibiotics onto microplastics, in some instances by 100%. pH also has a substantial effect on sorption capacity, illustrating the significance of electrostatic interactions on the sorption of antibiotics onto microplastics. The need for a uniform experimental design when testing antibiotic sorption is highlighted to remove inconsistencies in the data currently presented. Current literature examines the link between antibiotic sorption and antibiotic resistance, however, further studies are still required to fully understand this emerging global crisis.

1. Introduction

Plastic was first developed in the early 1900's and due to an exponential increase in production from the 1950's, approximately 359 Mt of virgin plastic was produced in 2018 (Wayman and Niemann, 2021). Microplastics are small plastic pieces, less than five millimetres long, which occur in the environment as a consequence of plastic pollution. Due to the widespread plastic pollution, microplastics have been found heavily throughout aquatic environments (Alimi et al., 2018) and soils (Zhang et al., 2021), but also in atmospheric fallouts (Truong et al., 2021). Microplastics have been found to accumulate in the aquatic food chain in both freshwater and saltwater environments (Tang et al., 2021). This contamination throughout the natural environment has inevitably led to the exposure of microplastics within the human body (Zarus et al., 2021). Due to the substantial extent of the spread of microplastics, it is important to understand what underlying problems occur within the natural environment due to microplastics.

The characterisation of microplastic pollution is dependent upon polymer type, size and source. Demand for different requirements for plastic has led to the creation of various polymer types, each with their own varying chemical structure. Despite the large variety of polymers available, only eight polymers, seen in Supplementary Table S1, make up 95% of the plastics ever made (Geyer, 2020). Of the eight main plastics, polypropylene (PP) and polyethylene (PE) make up 45% of global production (Lear et al., 2021). The size criteria for microplastics previously differed substantially between the academic literature, e.g., <10 mm (Graham and Thompson, 2009), 0.06 mm – 0.5 mm (Andrady, 2011), and <1 mm (Costa et al., 2010), which prompted the need for a uniform size criteria to be adopted for the group of plastics. Since 2014, a clear adoption of the size criteria for microplastics of <5 mm is seen in the literature (Alimi et al., 2018; Eriksen et al., 2014; Hale et al., 2020; Zarus et al., 2021; Zhang et al., 2021). Microplastic pollution in the environment is classed as either primary or secondary particles (Duis and Coors, 2016). Manufactured microplastics such as beads, pellets and

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fibres are considered to be primary microplastics, whereas the degradation of macro plastics into microplastics are considered secondary microplastics. Secondary microplastics are estimated to be the key source for microplastics in the marine environment (Atugoda et al., 2021).

One of the biggest issues associated with microplastics is their potential to become vectors for contaminants when in aquatic environments. Microplastics have been found to accumulate heavy metals, perfluorinated alkyl substances (PFAS), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), pharmaceuticals and personal care products (PPCPs) and polybrominated diethers (PBDs) on their surface (Ateia et al., 2020; Atugoda et al., 2021; Llorca et al., 2018; Pyl et al., 2021; Singla et al., 2020; Sørensen et al., 2020). Although, hydrophobic organic contaminants are found to already sorb onto suspended organic material and sediments in aquatic environments, the anthropogenic surface of the plastic particles tends to have higher concentrations of sorbed organic contaminants (Carbery et al., 2018). With the rate of plastic pollution increasing and microplastic surfaces accumulating contaminants at higher concentrations than in the surrounding water (Mato et al., 2001), it is important to understand the sorption behaviours of microplastic and contaminants to reduce the potential toxicological effects on the environment.

Sorption of antibiotics onto microplastics needs particular attention due to the role antibiotics presence in the environment plays in spreading antibiotic resistance (Caruso, 2019). A growing body of evidence highlights the occurrence and problems associated with over-prescription of antibiotics (Australian Commission on Safety and Quality in Health Care, 2016). Worldwide, a study on 76 countries between 2000 and 2015 found daily antibiotic consumption rates to increase by 39% (Klein et al., 2018). Indiscriminate use and disposal of antibiotics and their inefficient removal by the existing wastewater treatment plants lead to their spread within the natural environment. Research has begun into the interrelationship of microplastics and antibiotics in aquatic environments, but due to the widespread pollution and complex interactions involved, a clear understanding of the fate and toxicity and microplastics as vectors of antibiotics is yet to be developed.

Recent reviews on microplastics as vectors for various inorganic and

organic chemicals (Koelmans et al., 2016; Torres et al., 2021; Wang et al., 2020c), particularly pharmaceuticals and personal care products (Atugoda et al., 2021) provide useful information on the topic. However, critical reviews on the specific interactions and behaviours between microplastics and antibiotics have not yet been reported. It is important to comprehensively review this topic to improve our understanding of the potential factors increasing the risk of antibiotic pollution. The objective of this review is thus to provide an in-depth evaluation of the physicochemical properties of plastic polymers and antibiotics, including the mechanisms governing antibiotic sorption onto microplastics. A particular focus has been given on the properties of reaction mixture and the environmental conditions that significantly affect the extent of microplastic sorption. Finally, the implications of antibiotic sorption on microplastics in terms of the fate of antibiotics, environmental toxicity and antibiotic resistance have been critically explored to understand the implications of these interactions.

2. Understanding the interactions between microplastics and antibiotics

Due to the potential environmental risk, research on the sorption behaviours of antibiotics onto microplastics has continued to grow in the recent years (Fig. 1). The choice of microplastic to be studied has been based upon the most used plastic in society, with PE, polystyrene (PS), polyvinyl chloride (PVC) and PP being the most prominent in the literature. Plastics, such as polylactic acid (PLA), which are less commonly used but are associated to being 'biodegradable' have also been studied to see if the ease of degradation affect the sorption capacity (Sun et al., 2021b). Ciprofloxacin and tetracycline are the most studied antibiotics in terms of antibiotic sorption onto microplastic. Ciprofloxacin is stated to be the most widely used antibiotic (Igwegbe et al., 2021) and tetracycline is ranked the second most produced and consumed antibiotic in the world and ranked first in China (Daghrir and Drogui, 2013). The current approach to understanding the interactions between microplastics and antibiotics has been through sorption kinetic and sorption isotherms experiments (Table 1).

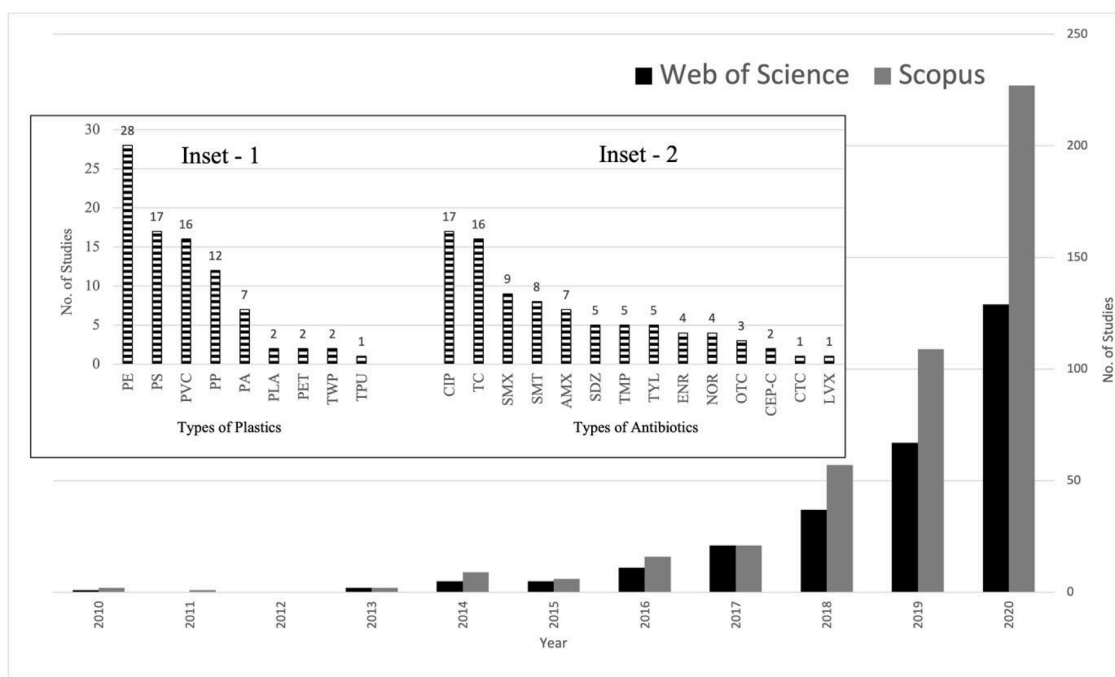
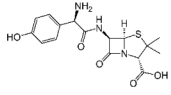
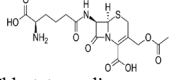
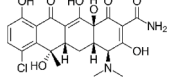
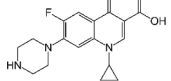
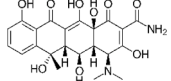


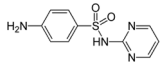
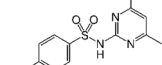
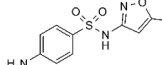
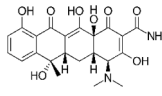
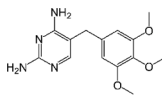
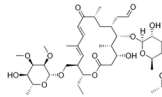
Fig. 1. Number of publications published per year based on the search: (microplastic OR micro-plastic) AND (sorption OR absorption OR adsorption OR sorbed); Number of times different microplastics (inset 1) and antibiotics (inset 2) have been studied in antibiotic/microplastic sorption experiments.

Table 1
Experimental Kinetics and isotherm studies on antibiotic sorption onto microplastics.

Antibiotic	Microplastics Type	Equilibrium time (h)	Kinetics Models Initial Antibiotic Concentration (mg/L)	Microplastic Concentration (g/L)	First-order Pseudo ($\mu\text{g/g}$)	Second-Order Pseudo ($\mu\text{g/g}$)	Isotherm models Antibiotic Concentration range (mg/L)	Langmuir Q_{max} (mg/g)	Linear K_d (L/kg)	Freundlich K_f ($\text{mg}^{1-N} \text{L}^N / \text{kg}$)	Ref.	
 Amoxicillin	PE	48	–	0.4	550	1650	0.5 – 8	0.752	–	0.132	(Fan et al., 2021a)	
	Aged PE				660	2720		1.110		0.142		
	TWP				430	2250		2.150		0.193		
	Aged TWP	96	–	–	–	–	0.5 – 15	13.10		0.219	(Li et al., 2018)	
	PP				490	2910		0.294	17.5	60		
	PVC							0.523	24.7	20		
 Cephalosporin C	PE	16	–	–	–	–	0 – 10	–	23.6	5.03	(Guo and Wang, 2019)	
	PS								37.0	99.9		
	PE											
	PA							22.7	756	700		
 Chlortetracycline	PE	30	10	10	61	66	0 – 50	0.3555	–	0.0240	(Chen et al., 2021)	
	Aged PE	48	–	0.4	260	720	0.5 – 8	0.317	–	0.0387	(Fan et al., 2021a)	
 Ciprofloxacin	TWP				380	1570		1.540		0.551	(Fan et al., 2021b)	
	Aged TWP				220	900		0.240		0.047		
	PLA	48	5	0.4	390	910	0 – 10	3.19	–	0.2106		
	Aged PLA				690	1190		3.77		0.2518	(Li et al., 2018)	
	PVC				340	610		0.67		0.4572		
	Aged PVC				440	770		0.85		0.5441		
	PP	96	–	–	–	–	0.5 – 15	0.615	57.1	252	(Liu et al., 2019c)	
	PS							0.416	51.5	205		
	PVC							0.453	41.5	184		
	PE							0.200	55.1	222		
PA							2.20	96.5	170			
PS	24	10	0.4	0.4	2580	3170	–	–	–	–	(Liu et al., 2019c)	
Aged PS					4860	5480						
PVC					2790	3410						
Aged PVC					3070	3280						
PS	24	0.2	1	1	540	860	0.2 – 1.2	5.19	–	5.41	(Yilimulati et al., 2021)	
		0.4			1180	2040						
		0.8			2430	3820						
Levofloxacin	PVC	144	10	0.5	290	1740	2 – 16 @ 288 K	2.317	–	1.194	(Yu et al., 2020a)	
							2 – 16 @ 298 K	2.472		1.783		
							2 – 16 @ 318 K	2.402		5.605		
 Oxytetracycline	PE	30	10	10	51	66	0 – 50	0.3526	–	0.0226	(Chen et al., 2021)	
	PLA	48	–	–	–	–	0 – 12	0.581	48.94	119.675	(Sun et al., 2021b)	
	Biofilm PLA							0.728	60.03	104.322		
	Aged PLA							1.193	82.08	197.158		
	TPU	48	10	3.3	3.3	280	318	2.5 – 50	0.582	–	0.141	(Xue et al., 2021)
	Aged TPU					372	398		1.113		0.137	
PS	54	–	–	–	–	–	2 – 50	1.520	0.0417	425	(Zhang et al., 2018)	

(continued on next page)

Table 1 (continued)

Antibiotic	Microplastics Type	Equilibrium time (h)	Kinetics Models Initial Antibiotic Concentration (mg/L)	Microplastic Concentration (g/L)	First-order Pseudo ($\mu\text{g/g}$)	Second-Order Pseudo ($\mu\text{g/g}$)	Isotherm models Antibiotic Concentration range (mg/L)	Langmuir Q_{max} (mg/g)	Linear K_d (L/kg)	Freundlich K_f ($\text{mg}^{1-N} \text{L}^N/\text{kg}$)	Ref.								
Sulfadiazine 	PP	96	–	–	–	–	0.5 – 15	–	7.85	8.00	(Li et al., 2018)								
	PS								7.39	4.10									
	PVC								6.61	3.20									
	PE								6.19	2.20									
	PA								7.36	1.10									
Sulfamethazine 	PA	16	2	2	82.1	90	0 – 12	–	38.7	28.6	(Guo et al., 2019b)								
	PE				54.6	60			23.5	20.9									
	PS				61.2	63.7			21.0	27.0									
	PET				40	53			22.6	12.0									
	PVC				65.7	68			18.6	46.6									
	PP				74	77.2			15.1	35.3									
	PS				–	–			–	–		0 – 10	–	29.3	5.73	(Guo and Wang, 2019)			
PE	–	–	–	–	–	38.3	110												
PA	–	–	–	–	–	96.4	284	205	(Guo et al., 2019a)										
PE	–	–	–	–	–	0.660	30.0	61.3											
PS	–	–	–	–	–	0.712	29.7	51.5											
PET	–	–	–	–	–	114	22.2	24.7											
PVC	–	–	–	–	–	2.80	28.2	14.2											
Sulfamethoxazole 	PP	16	–	–	–	–	0 – 10	–	30.9	5.84	(Guo and Wang, 2019)								
	PS								232.8	14.4									
	PE								–	–		–	–	–	591.7	665	(Xu et al., 2018b)		
	PE								–	–		–	–	–	0.2539	–		0.0192	
	Tetracycline 								PLA	48		5	0.4	460	900	0 – 10	2.51	–	0.1820
Aged PLA		1280	1970	5.49	0.2855														
PVC		430	750	0.96	0.6003														
Aged PVC		870	1360	1.57	0.8665														
PA		96	–	–	–	–	–	0.5 – 15	3.84	356	588	(Li et al., 2018)							
PE									24	–	–		–	–	0.2 – 5	0.109	–	0.0859	(Xu et al., 2018a)
PP									–	–	–		–	–	0.113	–	0.1010		
PS									–	–	–		–	–	0.167	–	0.1380		
Trimethoprim 	PE	80	5	0.5	12	116	1 – 35	–	0.067	0.231	(Yu et al., 2020b)								
	PS							–	0.058	0.055									
	PVC							–	0.055	0.016									
	PP							96	–	–		–	–	0.102	9.71	32.3	(Li et al., 2018)		
	PS							–	–	–		–	–	0.174	9.51	32.1			
	PVC							–	–	–		–	–	0.481	8.41	13.4			
PE	–	–	–	–	–	0.154	8.38	22.0											
Tylosin 	PA	24	–	–	–	–	0.5 – 15	0.468	17.1	36.0	(Guo et al., 2018)								
	PE							–	–	–		–	–	1.66	–	131.71			
	PP							–	–	–		–	–	3.33	–	183.46			
	PS							–	–	–		–	–	3.33	–	284.43			
	PVC							–	–	–		–	–	3.33	–	362.06			

2.1. Sorption kinetics

Sorption kinetics reveal the rate at which antibiotics are sorbed onto microplastics and gives the equilibrium times and concentrations of the reaction. Sorption experiments can be used to determine how microplastics and antibiotics may behave in nature. As depicted in Table 1, equilibrium times and concentrations varied depending on what antibiotic/microplastic combination was studied, e.g., PVC was reported to have greater sorption capacity of tylosin compared to PP, PE or PS (Guo et al., 2018). Using sorption kinetics experiments, the antibiotic/microplastic interaction that presents a higher sorption capacity may be assumed to pose a greater risk as it has the ability to transport larger concentrations of antibiotic through various environments.

Antibiotic equilibrium concentration was established in the studies listed in Table 1 between three hours (Atugoda et al., 2020) and six days (Yu et al., 2020b), with around 80% of the studies reaching equilibrium at 48 h or less. The initial concentrations of the antibiotic in solution ranged from 0.2 mg/L to 25 mg/L and the microplastic concentrations ranged from 0.4 – 10 g/L. Yilimulati et al. (2021) found that the initial antibiotic (ciprofloxacin) concentration (i.e. 0.2 – 0.8 mg/L) does not affect the equilibrium time, however, this study only evaluated low initial antibiotic concentrations. Other studies have examined the effect of higher initial antibiotic concentrations (Atugoda et al., 2020; Liu et al., 2019c; Zhang et al., 2018) but did not compare them to low antibiotic concentrations to understand if a greater difference in initial concentration alters the equilibrium time.

2.2. Sorption isotherms

To understand the antibiotic sorption process and mechanisms, sorption isotherm models are utilised to give insight into parameters such as maximum sorption concentration. While environmental concentrations of antibiotics are found to be in the range of ng/L to µg/L (Atugoda et al., 2021), the studies listed in Table 1 use initial antibiotic concentrations of 0.2 – 50 mg/L. High antibiotic concentrations are applied in the experimental studies for ease of analysis and to evaluate the maximum sorption capacity of microplastics. Having this information allows future research to understand which microplastic or antibiotic needs greater focus. For example, Chen et al. (2021) examined the difference in sorption capacity of PE for three different antibiotics; chlortetracycline, oxytetracycline and tetracycline. Through the Langmuir model, chlortetracycline gave a higher Q_{max} value of 0.3555 mg/L compared to oxytetracycline and tetracycline, 0.3526 and 0.2539 mg/L, respectively. This study provides an insight into how various tetracyclines and PE behave in an environment. Although the initial antibiotic concentration in majority of the available studies does not reflect those seen in the natural environment, studies such as those by Fan et al. (2021a) and Sun et al. (2021b) have attempted to mimic environmental settings by evaluating the antibiotic sorption capacity of weathered microplastics. Both Fan et al. (2021a) and Sun et al. (2021b) found that aged microplastics had a higher sorption capacity than the virgin counterpart. This was attributed to the physiochemical and morphological changes that occurred to the surfaces of aged microplastics. Studies such as these provide awareness of the behaviours that microplastics and antibiotics exhibit in natural scenarios. Preliminary studies on how microplastics and antibiotics behave in laboratory conditions, i.e. virgin microplastics and high antibiotic concentrations, are necessary to develop a baseline understanding, but crossing the boundary between laboratory and natural environmental settings is vital in recognising the potential difficulties that arise through antibiotic sorption onto microplastics. To achieve this, future research can be designed around incorporating the complexities of natural matrices into experimental methodologies, e.g., using a mixture of antibiotics/microplastics as it would occur in natural waterways, instead of focussing on one particular combination. By doing this, the current research can expand from single variable methodologies to systems that more closely represent natural

environments and achieve a greater understanding of how a mixture of antibiotics interact with microplastics.

3. Mechanisms of microplastic-antibiotic compound interactions

3.1. Electrostatic interactions

The chemical structures of antibiotics and the surface charge of the microplastics both play a critical role on the sorption process through electrostatic interactions. Electrostatic interactions occur when molecules are attracted by oppositely charged molecules or repulsed by molecules of the same charge (Bolan et al., 1999; Tourinho et al., 2019). Electrostatic interactions are highly influenced by the pH of the solution, the pH value at the point of zero charge (pH_{PZC}) of the microplastic and the charge of the contaminant. A study by Razanajatovo et al. (2018) demonstrated this by looking at the sorption of one negatively charged antibiotic, sulfamethoxazole, and two positively charged pharmaceuticals, propranolol and sertraline, on PE in freshwater. They found that the pH_{PZC} of PE was 4.30, which was less than the pH of the test solution, making the surface of PE negatively charged. The negatively charged PE, therefore, favoured the sorption of the two positively charged pharmaceuticals and had higher sorption rates compared to the negatively charged antibiotic. This can be attributed to the electrostatic forces of repulsion between the PE and sulfamethoxazole and shows the influence that electrostatic forces can have on the sorption rates of microplastics. A study by Guo et al. (2019b) further confirmed the significance of electrostatic interactions when the sorption of sulfamethazine onto polyamide (PA), PE, PS, PP, PVC and polyethylene terephthalate (PET) was examined. It was found that an increase in solution pH led to a repulsion between the six microplastics and sulfamethazine due to the increasing electro negativity of the microplastics surfaces.

3.2. Hydrophobic interactions

Hydrophobic interactions are non-covalent forces that occur in a polar medium (such as water) which causes two non-polar substances to aggregate. Most microplastics found in the environment are hydrophobic (PS, PE, PP, and PET) making hydrophobic interactions for sorption one of the most dominant (Torres et al., 2021). The surface structure of microplastics and the chemical nature of the contaminants significantly determines the strength of the hydrophobic interactions (Atugoda et al., 2021). Studies on antibiotics have showed high levels of partitioning to PE due to hydrophobic interactions (Guo and Wang, 2019; Li et al., 2018; Razanajatovo et al., 2018; Xu et al., 2018b). Guo and Wang (2019) reported that the sorption of sulfamethazine, sulfamethoxazole and cephalosporin C onto PE was affected by the differences in their hydrophobicity. It was found that the hydrophobicity of the antibiotics decreased in the following order: sulfamethoxazole > sulfamethazine > cephalosporin C. Because PE is hydrophobic, the sorption of the antibiotics onto PE mirrored the order of hydrophobicity, with sulfamethoxazole having the highest and cephalosporin C having the lowest sorption rates. Huang et al. (2021) further confirmed the significance of hydrophobic interactions while investigating the sorption of tylosin onto PS. High sorption rates was seen due to the chemical structure of tylosin containing hydrophobic groups which directly interact with the hydrophobic surface of PS.

3.3. Van der Waals and π - π interactions

Van der Waals interactions and π - π interactions are non-covalent bonds that take place around aliphatic polymers, such as PVC and PE (Van der Waals interactions) and aromatic polymers, such as PS (π - π interactions) (Guo et al., 2012; Hüffer and Hofmann, 2016; Hüffer et al., 2018). It has been reported that the antibiotics, sulfadiazine, trimethoprim and ciprofloxacin had higher adsorption rates on PS rather than PE

due to the higher π - π interactions between the antibiotics and the aromatic polymer (Li et al., 2018). Although, π - π and Van der Waals interactions have not been studied in depth for determining their effect on antibiotics sorption capacities of microplastics, through the studies that have been done it is evident that they do play a role in the overall interaction.

3.4. Pore-filling interactions

As a result of pore-filling interactions, contaminants fill the nano and micro pores of glassy and rubbery polymers at their solubility limits (Liu et al., 2019d; Uber et al., 2019). Commonly, pore-filling interactions display non-linear sorption isotherms on glassy polymers, signifying selective sorption on the glassy polymer heterogenous surface (Liu et al., 2019d). The rate in which molecules can diffuse onto a plastics surface is controlled by the pore diameter and the size of the diffusing molecule. The rate of sorption gradually decreases through pore-filling interactions as larger diameter pores are occupied quicker and at a greater rate compared to the smaller pores of the plastic which cannot adsorb as many molecules (Atugoda et al., 2021). One study found that pore-filling was the primary mechanism for sorption of ciprofloxacin onto PVC and PS (Liu et al., 2019b). Pore-filling plays an important role in the interactions between microplastic and contaminants, especially in cases where weathering has occurred, allowing the plastic to generate more pores on its surface (Zhang et al., 2018).

4. Polymer properties affecting sorption capacity

4.1. Polymer type

The wide variety of polymers produced plays a vital role in determining whether microplastics can behave as a vector for antibiotics. Because microplastics are generated from a diverse range of polymer resins, they exhibit different physical and chemical characteristics, including the molecular arrangement, functional groups, surface charge and polarity (Atugoda et al., 2021). The main characteristic that needs to be evaluated in relation to microplastics becoming a vector for antibiotics is the polarity of the polymer. Non-polar polymers contain C—C and C—H covalent bonds which create high chemical resistance and structural strength, but when different functional groups are incorporated to the C, H, or sidechains of a polymer it can impart polarity (Liu et al., 2019a). Microplastic polarity therefore plays an important part in determining the potential for microplastics becoming vectors for antibiotics.

Many studies have been performed to determine how the characteristics of different polymers affect the adsorption of antibiotics. Guo et al. (2018) studied the adsorption capacity of tylosin onto four different microplastics. The results from the kinetic experiments found tylosin sorption to decrease in the following order: PVC > PP > PS > PE. On the other hand, Guo et al. (2019b) reported the sorption capacity of sulfamethazine onto a variety of polymers decreased in the following order; PA > PP > PVC > PS > PE > PET. Comparing the two studies by looking only at the common polymers tested it is evident that the sorption capacity of tylosin is higher on PVC than PP whereas sulfamethazine sorption capacity is higher on PP than PVC. The variance in sorption could be attributed to the difference in the antibiotics hydrophobicity, $\text{Log}(k_{ow})$ of tylosin and sulfamethazine is 1.63 (Loke et al., 2002) and 0.1944 (Chen et al., 2020b), respectively, and how the physical properties of the polymer react with the antibiotic. This shows that the sorption capacity of polymers is not uniform with different antibiotics and it is due to the differences in physical and chemical properties of both the polymer and the sorbed antibiotic.

4.2. Crystallinity

The degree of crystallinity determines the main physical properties

(i.e., density, hardness, thermal, diffusion and mechanical) of a polymer (Yang et al., 2018). High amounts of energy is required to disrupt the hydrocarbon chains in a dense crystalline region of a polymer compared to its amorphous region which consists of randomly orientated polymer chains (Karapanagioti and Werner, 2019). A study by Li et al. (2018) stated that the degree of crystallinity of five polymers (PE, PP, PS, PA, and PVC) was unrelated to the sorption of five antibiotics (sulfadiazine, amoxicillin, tetracycline, ciprofloxacin and trimethoprim). The degree of crystallinity of the five polymers decreased in the following order PE > PP > PA = PS > PVC, however the sorption of all five antibiotics was reported to be highest in PA, intermediate in PE and lowest in PVC. It has been stated that the degree of crystallinity of a polymer may affect antibiotic sorption by microplastics but it is not the defining factor (Atugoda et al., 2021).

4.3. Particle size, shape and surface area

Even though particle size plays a minor role compared to other physical parameters (Atugoda et al., 2021), it can still affect the adsorption capacity, adsorption/desorption rate and the rate of equilibrium (Tourinho et al., 2019). This is evident in studies whereby the sorption capacities of different microplastics increased as the particle size decreased i.e., surface area increased (Ma et al., 2019). However, although sorption rates tend to increase as the particle size decreases, Wang et al. (2019) found that for particles below 235 nm in size, the sorption rate decreases due to particle aggregation.

Microplastics can occur in different shapes i.e., fibers, fragments, beads, films, and foam. In the available literature, the effect of microplastics shape has not been specifically discussed. However, it is noted that particle shape can alter the surface area, and the impact of surface area on adsorption can be significant as discussed below.

Surface area has been observed to have a significant influence on the interactions between antibiotics and microplastics (González-Pleiter et al., 2021; Guo et al., 2012; Zhang et al., 2018). Surface area can vary depending on the particle shape Pores and cracks that are induced by weathering or biodegradation can increase the surface area of microplastics and are seen to also increase the accumulation of antibiotics to the microplastics surface. Zhang et al. (2018) investigated the sorption capacity of PS foam (collected from beaches of north China) and found it to have significantly higher sorption rates of oxytetracycline compared to virgin PS foam. It was stated that the increase in pores and cracks from weathering contributed to the enhanced sorption of the antibiotic.

4.4. Degree of weathering

Weathering of microplastics in the environment can dramatically change the physical shape and size of the polymer, which has the potential to increase the microplastics ability to become a vector for antibiotics (Fan et al., 2021a, 2021b; Liu et al., 2019c; Xue et al., 2021). Weathering of microplastics can occur through UV degradation, exposure to wind and changes in temperatures. Results of experimental studies aiming to understand the effect that microplastic weathering plays on sorption capacity are summarised in Fig. 2 and Supplementary Data Table S2. From the data, it is evident that the change in the physical surface properties (fractures, deep cracks and increased porosity) of microplastics, caused by weathering, can increase the sorption capacity by up to 171% (Fan et al., 2021b). In all studies, the weathered microplastic had higher sorption capacities than the virgin microplastics.

The increase in sorption capacity after microplastic weathering is dependent not only on the microplastics type but also the antibiotic. Fan et al. (2021b) studied the effect of UV weathering on the sorption capacity of microplastics. PLA and PVC were degraded using UVA lamps and the sorption of ciprofloxacin and tetracycline was tested. It was found that after UVA treatment, ciprofloxacin sorption onto PLA and PVC increased by 34% and 20.6%, respectively. In contrast, when tetracycline was tested after UVA treatment, the sorption capacity of

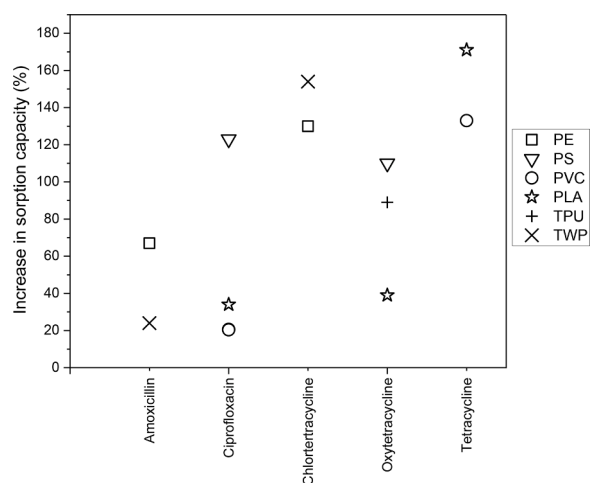


Fig. 2. Impact of plastic weathering on its antibiotic adsorption capacity (data from Supplementary Data Table S2).

PLA and PVC increased by 171% and 133%, respectively.

The current research suggests that the increase in antibiotic sorption capacity of weathered microplastics is due to the increase in pores and cracks generated on the surface of the microplastics (Fan et al., 2021a, 2021b). However, studies performed on contaminants other than antibiotics have observed the opposite effect. The sorption of BPA and BDE-47 was found to decrease on certain aged microplastics compared to their virgin counterparts (Liu et al., 2021a; Sun et al., 2021a; Wu et al., 2020). Wu et al. (2020) reported that sorption of BDE-47 onto aged PS decreased as a result of UV irradiation producing large amounts of oxygen rich functional groups on the surface of the polymer, ultimately affecting sorption of the compound. Understanding that sorption of different contaminants onto aged microplastics is not uniform further reinforces the need for future research into this field.

5. Properties of the solution affecting antibiotic sorption onto microplastics

5.1. Impact of pH

The pH of a natural water source typically ranges from 5 to 9, but due to various types of contamination, the pH can vary erratically (Boyd, 2020). For pharmaceutical contaminants, including antibiotics, it is stated that 85% - 95% of their active ingredients are ionizable compounds when found in weak acid or base solutions (Karlsson et al., 2017). This can greatly change their ability to be adsorbed onto microplastics. For example, as pH levels increased, the adsorption rate for tetracycline onto PE, PP and PS decreased (Xu et al., 2018b). Similar adsorption behaviour of sulfamethoxazole onto PA, PE, PS, PET, PVC and PP (Guo et al., 2019a) and of tylosin onto PE, PP, PS, and PVC (Guo et al., 2018) was confirmed.

It is evident that the pH of the solution can affect the sorption of antibiotics by microplastics, but it is also dependent upon the particular antibiotic/microplastic combination. The study by Puckowski et al. (2021) exhibits this idea clearly with the sorption of norfloxacin onto LDPE, HDPE, PP and PVC. LDPE and HDPE have peak sorption of norfloxacin at pH 4 and 2, respectively, whereas PP and PVC's peak sorption is at pH 12. Results differing due to the change in pH implies that the polymer surface charge plays a vital role in the sorption of antibiotics. Puckowski et al. (2021) states that this result is due to the electrostatic interactions influence on the sorption process, which has also been confirmed in other studies (Chen et al., 2021; Guo et al., 2019a, 2019b; Liu et al., 2019c).

The range of pH values that promote maximum antibiotic sorption depend on the microplastics- antibiotic combination (Fig. 3 and

Supplementary Data Table S3). The sorption of ciprofloxacin onto PVC was studied by both Liu et al. (2019c) and Puckowski et al. (2021), however the results produced for the peak sorption pH value differed drastically (pH 9 and pH 2, respectively). A closer look into the experimental conditions reveals that the concentration of ciprofloxacin that Liu et al. (2019c) used in the solution was 10 mg/L whereas Puckowski et al. (2021) only had 0.5 mg/L. The difference in the reported results could be due to the effect of the initial antibiotic concentration within the solution. The same conflict in information is seen in the sorption of sulfamethoxazole on PE. Guo et al. (2019a) states that sulfamethoxazole sorption onto PE peaks at pH of 3, whereas Xu et al. (2018b) states that it peaks at a pH of 12. The initial concentration of sulfamethoxazole (1 vs. 2.4 mg/L) and other experimental conditions (e.g., test duration, shaking speed and particle size) were not significantly different between the two studies. It is clear from Fig. 3 that the pH of a solution affects the sorption capacity of antibiotics onto microplastics through electrostatic interactions, however, with the lack of comprehensive studies performed, firm conclusions are still difficult to be drawn.

5.2. Salinity

Marine plastic pollution is a major concern (Wang et al., 2021). It is therefore important to understand how microplastic sorption behaviour is affected in saline environment. Previous research has simulated ocean environments by adding sodium chloride (NaCl), calcium chloride (CaCl₂), potassium nitrate (KNO₃) or sodium nitrate (NaNO₃) to the solution (Atugoda et al., 2020; Guo et al., 2019b, 2018; Liu et al., 2019c; Puckowski et al., 2021). A study by Li et al. (2018) used real seawater, but was filtered by 0.45µm membranes and treated with UV to ensure that there were no dissolved organic matter (DOM) present that could affect the results.

It has been indicated that the varying combination of electrolytes, adsorbents, adsorbates and solution chemistry strongly contribute to the sorption capacity of a microplastic (Tang et al., 2021). When NaCl concentration was increased from 8.8% to 35%, PVC sorption capacity of ciprofloxacin decreased steadily (Liu et al., 2019b). Similarly, this trend has been found to occur for the sorption of sulfamethoxazole and sulfamethazine on PE, PS, PA, PVC, PP, and PET at NaCl concentrations of 10%, 20% and 35% (Guo et al., 2019a, 2019b).

The studies presented in Fig. 4 and Supplementary Data Table S4 show that salinity can inhibit antibiotic adsorption onto microplastics surfaces. It is noteworthy that although antibiotic sorption did decrease as the concentration of salt increased, there were certain salinity concentrations that promoted antibiotic adsorption. Guo et al. (2018) reported that the antibiotic adsorption onto the four microplastics (PP, PS, PE and PVC) slightly increased at 0.01 M before beginning to decrease again. Yu et al. (2020b) showed that tetracycline sorption onto PE decreases from 0.0 - 0.05 M NaCl, then sharply increases from 0.05 - 0.1 M of NaCl to a level of sorption greater than at 0 M of NaCl, and then reduces to almost negligible sorption at 0.4 M of NaCl. Further examination of Fig. 4 reinforces the results reported by Yu et al. (2020b). Looking at the effect of salinity concentrations on ciprofloxacin, it can be concluded that lower salt concentrations (0 - 0.1 M) has a greater ability of inhibiting the sorption of ciprofloxacin compared to higher salt concentration (0 - 0.6 M). Guo et al. (2019a), Guo et al. (2019b) and Liu et al. (2019c) simulated salinity levels that were higher than other studies but were still within realistic levels that would be found in nature. Through simulating higher levels of salinity, the information reported may provide ideas for potential ex-situ remediation methods to reduce the ability for microplastics to be vectors for antibiotics and ultimately reduce the risk of being hotspots for antibiotic resistance genes (ARGs) and antibiotic resistant bacteria (ARBs).

An obvious reason for the discrepancies between results from different studies may be the differences in experimental methods. The adsorption of tetracycline onto PE has been studied in three different papers (Chen et al., 2021; Shen et al., 2018; Yu et al., 2020b), all of

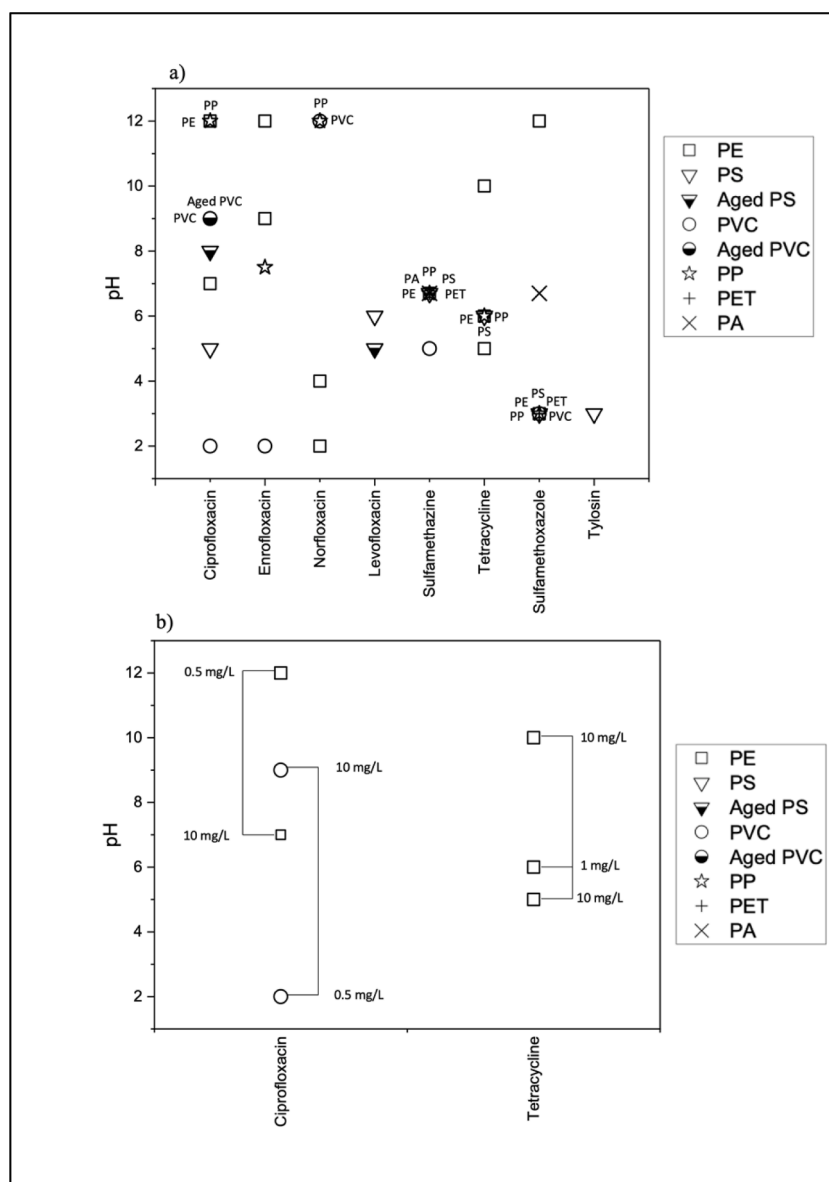


Fig. 3. a) Impact of pH on antibiotic sorption by microplastics. pH values represented in figure are where peak sorption occurred b) effect of initial antibiotic concentration on peak pH value (data from Supplementary Data Table S3).

which state that with increasing salinity comes the decrease in sorption capacity, however the amount by which the sorption capacity decreases is vastly different, 35%, 5% and 90.9%, respectively. Shen et al. (2018) and Yu et al. (2020b) both used NaCl to change the salinity of the solution, however the concentration ranges were varied from 0 – 1 M and 0 - 0.4 M, respectively. Thus the results between these studies show large discrepancies. It is apparent that further systematic studies are required to develop a systematic understanding on the effect of salinity of antibiotic sorption.

5.3. Dissolved organic matter

Dissolved organic matter (DOM), such as fulvic acid (FA) and humic acid (HA), have the ability to either inhibit or enhance the sorption capabilities of organic materials onto microplastic surfaces (Bolan et al., 2011). A study looking at the sorption capacities when concentrations of FA was 1 - 20 mg/L, observed the sorption of tetracycline on PE, PP, and PS to decrease by 96%, 95% and 92%, respectively (Xu et al., 2018a). However, Zhang et al. (2018) showed an increase in oxytetracycline

sorption on aged PS when FA and HA concentrations increased in the solution from 10 to 100 mg/L, by 25% and 62%, respectively. The variance in PS results reported by Xu et al. (2018a) and Zhang et al. (2018) can be attributed directly to the weathering of the polymer. Zhang et al. (2018) only experimented with the effect of DOM on aged PS which shows the increasing effect that FA has on antibiotic sorption onto aged polymers. When inspecting the effect of the presence of DOM in the solution on the antibiotic sorption capacity of microplastics, it appears that it depends on the antibiotic type, the type of microplastics, the type of DOM and the concentration. As seen in Fig. 5(a) and Supplementary Data Table S5, two references showed a decrease in sorption (Atugoda et al., 2020; Xu et al., 2018a), one showed an increase (Zhang et al., 2018) and one showed no effect (Xu et al., 2018b). The variance in the results can be correlated to the difference in DOM concentrations, the type of antibiotic and the type and condition of the polymer. Furthermore, Fig. 5(a) lacks sufficient data points to completely understand the effect of DOM on the antibiotic sorption capacity of microplastics.

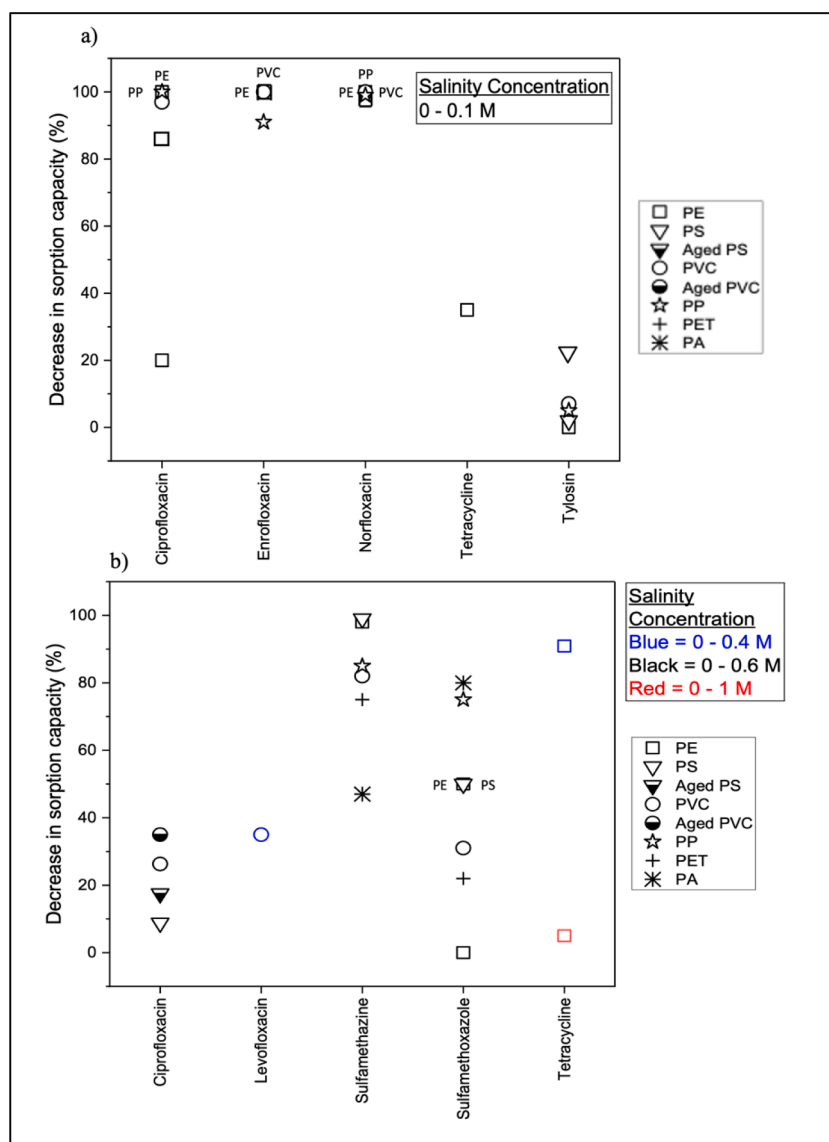


Fig. 4. a) Impact of salinity on antibiotic sorption by microplastics, b) Impact of salinity on sorption per molarity of salt used (data from Supplementary Data Table S4).

5.4. Competing contaminants

Competing sorbents such as heavy metals have the ability to reduce or promote the sorption of antibiotics onto microplastics (Fig. 5(a) and Supplementary Data Table S5). Huang et al. (2021) and Yu et al. (2020a) investigated the effect of heavy metals on sorption capacity and reported that the sorption capacity would either increase or decrease based on the competing heavy metal. Cu^{2+} , Cr^{3+} and Zn^{2+} were all seen to increase the sorption of levofloxacin onto PVC and Cd^{2+} and Pb^{2+} decreased the sorption (Yu et al., 2020a). It was reported that due to the larger ionic radius of Cd^{2+} and Pb^{2+} (fifth period in periodic table compared to Cu^{2+} , Cr^{3+} and Zn^{2+} being in the fourth) they had the ability to occupy more sites on PVC, therefore inhibiting the sorption of levofloxacin. Huang et al. (2021) also looked at the effect of Cd^{2+} on the antibiotic sorption capacity of microplastics and found similar results to Yu et al. (2020a) i. e., Cd^{2+} decreased the sorption capacity of tylosin onto PS. Both authors state that this reduction in sorption capacity potentially is due to the electrostatic interactions. Huang et al. (2021) explain that Cd^{2+} is adsorbed onto the surface first and neutralises the surface charge which ultimately reduces the sorption of tylosin.

5.5. Summary of the impact of the solution properties on antibiotic sorption

Solution properties have been found to significantly affect the sorption of antibiotics onto microplastics. The influence of pH on sorption was heavily dependent upon the microplastic and antibiotic combination. For example, enrofloxacin showed a peak sorption on LDPE at pH 12, whereas norfloxacin showed a peak on LDPE at pH 4 (Puckowski et al., 2021). Similarly, competing contaminants effect on sorption capacity varied upon the microplastic/antibiotic combination as well as the competing contaminant that was studied. In all papers reviewed it was observed that salinity decreases the ability for antibiotics to be sorbed onto microplastics irrespective of the microplastics/antibiotic combination that was examined. To continue crossing the investigation boundary from laboratory to natural environments, the interactions between solution properties on antibiotic sorption deserves further coverage in future research.

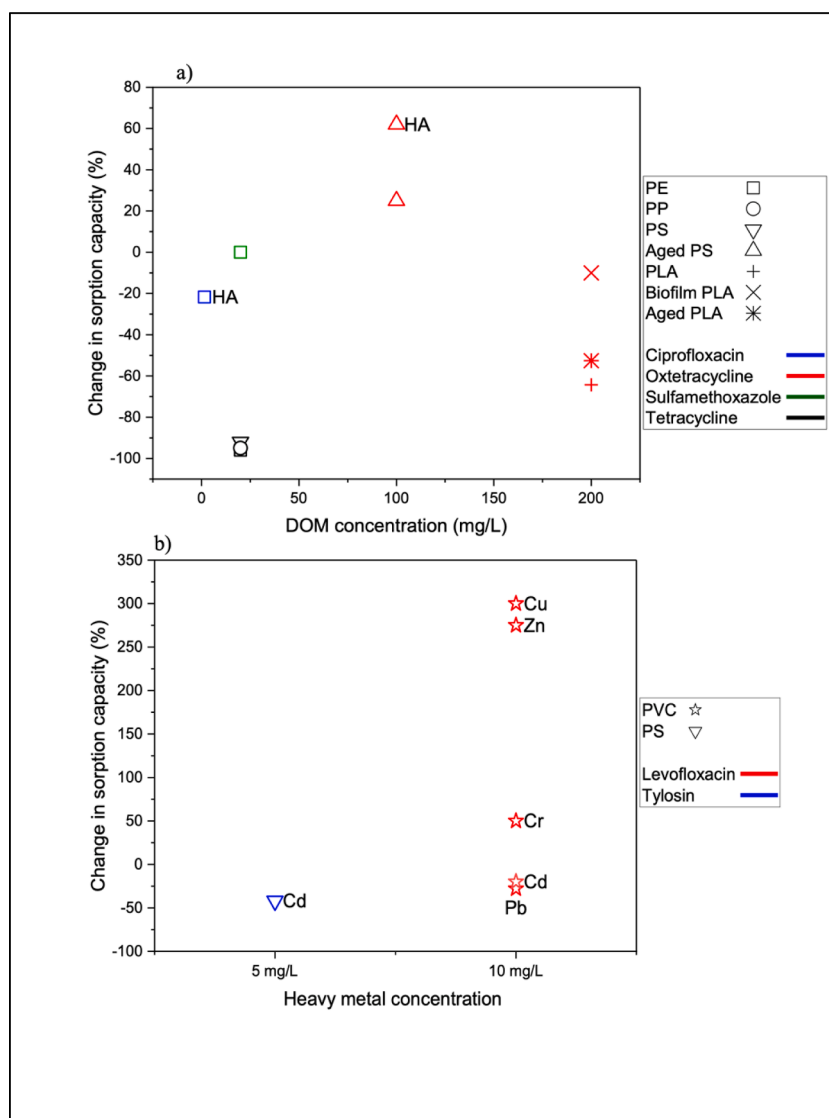


Fig. 5. a) Impact of DOM and b) heavy metals on microplastics antibiotic sorption capacity (data from Supplementary Data Table S5).

6. Properties and structure of antibiotics affecting sorption onto microplastics

The functional groups and ionic properties displayed by antibiotics contribute to their overall hydrophobicity (Torres et al., 2021). The polarity of an antibiotic is commonly described by its aqueous solubility or its K_{ow} value. A contaminant with a high positive K_{ow} value is classed as being highly hydrophobic, whereas a contaminant with a low K_{ow} or negative K_{ow} value is classed as being weakly hydrophobic or polar (Moldoveanu and David, 2015). Based on K_{ow} value, contaminants can be categorised into three subcategories: strongly hydrophobic ($\text{Log}(K_{ow}) > 5$), moderately hydrophobic ($4 \leq \text{Log}(K_{ow}) \leq 5$) and hydrophilic ($\text{Log}(K_{ow}) < 4$) (Gao et al., 2019). Antibiotics are found to mostly have $\text{Log}(K_{ow})$ values less than or around 1, making them hydrophilic/polar contaminants (Wang and Wang, 2016). Li et al. (2018) illustrated the effect antibiotic hydrophobicity has on their sorption onto microplastics. When studying the antibiotics ciprofloxacin, amoxicillin, sulfadiazine, tetracycline, and trimethoprim, it was found that the varying $\text{Log}(K_{ow})$ exhibited by the antibiotics correlated to the sorption amounts onto the microplastics PE, PS, PP and PVC. However, the same correlation was not seen between the five antibiotics and PA, leading to the conclusion that it was possibly electrostatic interactions that predominately governed the sorption onto PA not hydrophobic interactions.

The structure and functional groups of antibiotics have been found to be a significant factor affecting the antibiotic sorption onto microplastics. Shen et al. (2018) illustrates this through comparing the antibiotic tetracycline to the anticonvulsant drug carbamazepine. Tetracycline is rich in hydroxyl functional groups compared to carbamazepine which correlates to their differences in $\text{Log}(K_{ow})$ values; tetracycline: $\text{Log}(K_{ow}) = -1.19$, carbamazepine: $\text{Log}(K_{ow}) = 2.45$. Tetracycline is therefore more hydrophilic than carbamazepine allowing for greater sorption onto microplastics. The influence of tetracycline functional groups on sorption was also seen in a study by Fan et al. (2021b) who compared it to the antibiotic ciprofloxacin. Ciprofloxacin has a $\text{Log}(K_{ow})$ of 0.28 (Takács-Novák et al., 1992). The chemical structure of ciprofloxacin does not contain as many hydroxyl groups as tetracycline, which Fan et al. (2021b) reported was a key component to high sorption capacity of the antibiotics onto the microplastics due to the formation of hydrogen bonds.

7. Implications of antibiotic sorption on microplastics

7.1. Environmental toxicity

Consumption of microplastics by aquatic species has been heavily documented in the literature. This is attributed to the abundance of

microplastics in nature and their resemblance to plankton and food particles by non-selective filter feeders, crustaceans and fish (Horton et al., 2017). A study on six species of fish from the Texas Gulf Coast found that 42.4% of the analysed fish ($n = 1381$) had ingested microplastics (Peters et al., 2017). Difference in the amount of ingested microplastics was seen amongst the six species of fish due to their respective foraging habits. It was found that selective invertebrate foragers were less likely to ingest microplastics compared to the fish species exhibiting non-selective foraging methods. Throughout the literature possible implications of ingested microplastics on aquatic organisms include obstructions in the digestive tract, complications in reproduction, reduced growth and nutritional deficiency due to false satiation (Sun et al., 2022). False satiation was seen in a study by Cole et al. (2013) who investigated the effects of microplastic ingestion on zooplankton, and the complications in reproduction was illustrated in a study by Luan et al. (2019) on clams. Trophic transport of microplastics through the aquatic food chain is also thought to be a potential source for microplastics detection in human beings (Fig. 6) (Zarus et al., 2021). Though numerous studies have focussed on the fate of microplastics in aquatic environments, it is also important to understand their behaviour in soils as it accounts for the largest storage place for particulate plastics (Wu et al., 2021). Studies investigating the effect of particulate plastics found decreased root lengths (Qi et al., 2018), decreased number of fruits (Qi et al., 2018), inhibited seed germination (Boots et al., 2019) and a noticeable decrease of chlorophyll content (Wang et al., 2020a).

Antibiotics may be transported through the uptake and ingestion of microplastics by plants and aquatic organisms. Limited research on the toxicity of the antibiotics released from microplastic on aquatic organisms currently exists, but Tang et al. (2021) suggest, if antibiotic-sorbed microplastic are ingested by aquatic organisms, the combined pollution would have greater toxicity and side effects. To understand the potential effect that antibiotic-sorbed microplastics have on organisms, studies conducted on other contaminants can be examined. For example, Stollberg et al. (2021) examined microplastics spiked with the polycyclic aromatic hydrocarbon, fluoranthene on the digestive gland tissues of blue mussels. It was found that the blue mussels which had been exposed to the spiked microplastic exhibited higher levels of fluoranthene in their tissues than the control, thus concluding contaminant transfer from the microplastic to the blue mussel. The combined effects of heavy metals and microplastics on aquatic organisms have been studied

thoroughly, providing a greater understanding of the potential risk antibiotic-sorbed microplastics have on the environment. PS sorbed with copper, magnesium and zinc was found to inhibit the growth of microalgae (Tunali et al., 2020), and embryo development of zebrafish was found to be affected after being exposed to PS sorbed with cadmium (Zhang et al., 2020a). It is evident that microplastics have the ability to undergo trophic transfer (Atugoda et al., 2021) and to sorb antibiotics (Guo et al., 2019a, 2019b; Guo and Wang, 2019; Xu et al., 2018b). While the experimental evidence of the ecotoxicological effects of antibiotic-sorbed microplastics is still limited, by consulting the above references regarding other contaminants, the potential risk can be perceived.

7.2. Antibiotic resistance

Antibiotics have been used for the treatment of bacterial infections since the early 1900's (Magalhães et al., 2021; Valent et al., 2016), but their overuse and indiscriminate disposal have seen the emergence of the global health problem of antibiotic resistance (Region et al., 2015). Antibiotic resistance is the generalised term when referring to antibiotic resistance genes (ARGs) and antibiotic resistant bacteria (ARB). ARB is recognised as bacteria that can resist antibiotics, generally caused by long exposure to sub-therapeutic level of antibiotics. ARG is a genetic material which can be acquired by bacteria to generate resistance against antibiotics. Four main mechanisms are commonly adopted to explain antibiotic resistance within an organism: drug inactivation, permeability barriers, target modification and modification of efflux pumps (Syafiuddin and Boopathy, 2021). Antibiotic resistance is now seen as one of the biggest emerging threats to public health, food safety and the natural environment (Lin et al., 2021).

Understanding potential sources of antibiotic resistance is key to tackling the global crisis. Antibiotic sorption on microplastics has been thoroughly studied and confirmed in laboratory conditions (Table 1), alluding to the possible outcome of microplastics behaving as hotspots for antibiotic resistance. As well as antibiotic sorption, microplastics have the ability to host bacterial communities on their surface, providing an environment which promotes the occurrence of ARB and ARGs (Liu et al., 2021b). Studies on the occurrence of ARG's on microplastics have begun with results showing that microplastics have the capacity to be vectors for ARGs in sewage (Zhao et al., 2021), landfill

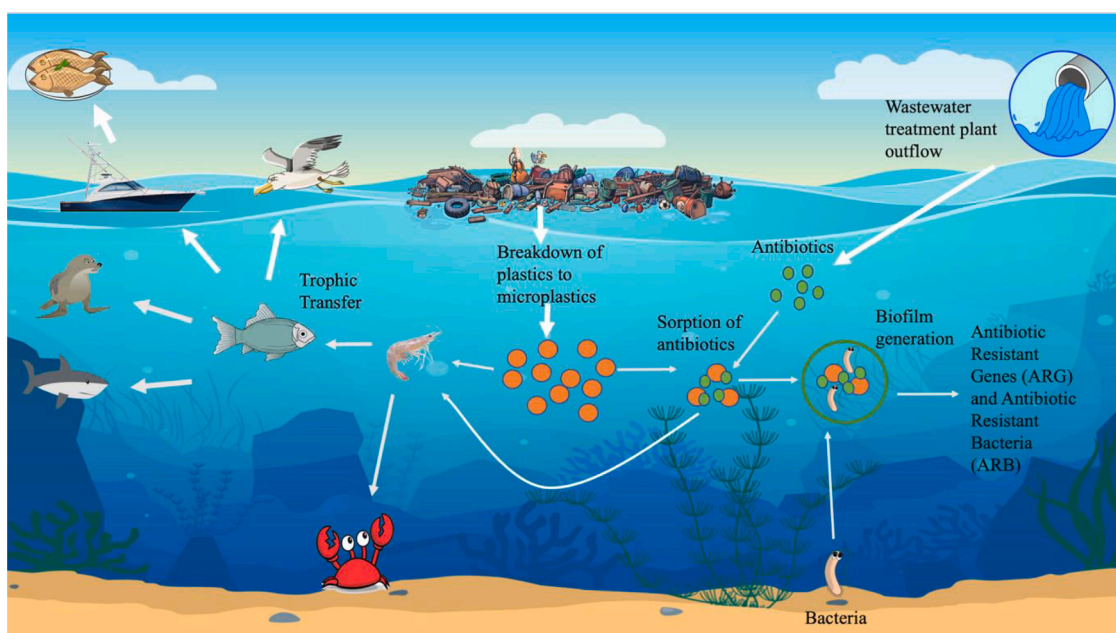


Fig. 6. Fate of microplastics and antibiotics in the environment.

leachate (Su et al., 2021), and a variety of aquatic (Guo et al., 2020; Zhang et al., 2020b) and terrestrial environments (Lu et al., 2020). With antibiotics sharing many of the same pathways into the environment as microplastics and recognising the ability of microplastics to be carriers of ARGs, ARB and chemical contaminants, it is important to continue research into this field of study to develop a full understanding of this emerging global crisis.

7.3. Antibiotic degradation

Antibiotics chemical structure can be degraded in nature through a range of processes including solar degradation and biodegradation (Liao et al., 2016; Michael et al., 2012; Mitchell et al., 2015; Zuurro et al., 2014). It is evident that there are gaps in the research surrounding the implications of antibiotic degradation while adsorbed to microplastics. However examining similar scenarios involving antibiotic degradation, potential correlations can be discovered. Two main ideas are discussed surrounding antibiotic degradation: factors affecting the photodegradation process of antibiotics and the toxicity of the transformed products. Chen et al. (2020a) investigating the impacts of microplastics on the photodegradation of organotin compounds found that photodegradation can either be enhanced or inhibited depending upon the microplastic the compound was attached too. The results showed that PS promoted the antibiotic photodegradation process due to producing radicals under UV irradiation, but PE inhibited photodegradation due to light scattering properties of the plastic. Furthermore, it is reported that factors affecting degradation of trace organic contaminants through advanced oxidation processes include the water chemistry, molecular structure, and ions co-occurring in the water source (Tufail et al., 2020, 2021). Although no studies have directly looked at the effect of microplastic sorption on antibiotic photodegradation, previous studies can be used as a comparative tool to develop methods for antibiotic removal and compare results of future findings (Chen et al., 2020a; Tufail et al., 2020); Tufail et al. (2021). The implication of the antibiotic degradation products is still limited due to the complexity of the issue. Studies have shown that the toxicity of the metabolites generated from antibiotic degradation is widely variable. Guo and Chen (2012) reported that the metabolites from UV photolysis of chlortetracycline have adverse effects on freshwater phytoplankton. Tegze et al. (2018) showed the newly transformed products of fluoroquinolones through gamma-irradiation degradation to be more toxic on *Vibrio fischeri* bacteria compared to the antibiotic. Zhu et al. (2021) illustrated that the toxic effects of sulfonamides on bioluminescent bacteria greatly decreased with degradation. Further research is still required to understand the complete environmental toxicity of newly transformed products of antibiotics and the implications of antibiotic degradation while adsorbed to microplastics.

8. Future perspectives

This critical review provided a summary of the factors, mechanisms, and implications of antibiotic sorption onto microplastic that has been reported in the literature. Analysis of the data that is available enables us to identify further research areas that need to be explored:

- 1 To simulate a realistic environment, mixtures of multiple antibiotics and microplastics need to be studied. Will competing environments promote the sorption of certain antibiotics over the others? Can certain microplastics be disregarded for future experiments if they do not sorb as much antibiotics as others when in a mixed environment?
- 2 Continuing to understand how the sorption interaction occurs in nature is vital by using real water samples from oceans, rivers, lakes, ponds and wastewater effluent as the solution for antibiotic sorption experiments. Understanding their behaviour in nature will gauge the true associated risk that this interaction plays on ecological health.

- 3 Throughout the literature the methodology for testing microplastic sorption of antibiotics differs. The initial antibiotic concentration, the size of the microplastics (powder or pellets) and the shake speed are all different, providing discrepancies between results. Developing a uniform standardised methodology for future antibiotic sorption experiments will provide results that will be comparable between studies.
- 4 The literature regarding antibiotic sorption on microplastics what was reviewed for this paper all conducted their batch experiments at room temperature (20 – 25 °C). Therefore, the effect of temperature on antibiotic sorption could not be critically reviewed. However, temperature has been shown to affect the sorption capacity of metal ions onto microplastics (Wang et al., 2020b). Research into temperature as an influencing environmental factor needs to be examined for the sorption of antibiotics onto microplastics.
- 5 Sorption of antibiotics onto microplastics is a complex process that encompasses both sorption and de-sorption occurring simultaneously. Many of the studies currently have focussed on sorption equilibrium times and sorption capacity. Further research should focus its attention on the de-sorption process to assess the risks that microplastics may have in acting as vectors for antibiotics in the natural environment.

Uniformity in methodologies and reliability to natural environments are the greatest gaps in the current literature. By continuing research down these pathways, a greater understanding of the potential risk associated with microplastics acting as vectors for antibiotics can be discovered. The research in this area is critically important due to the emerging nature of the issue and the considerable number of unknowns that still exist.

9. Conclusions

This review discusses the factors and mechanisms that affect sorption of antibiotics onto microplastics. Hydrophobic and electrostatic interactions were reported to be the main interactions influencing the sorption process of antibiotics onto microplastics, however, pore-filling, π - π , and Van der Waals interactions did play a minor role in the process. pH, salinity, and competing contaminants of the solution significantly affected sorption of antibiotics, by either suppressing or promoting the interaction. Studies using weathered polymers to synthesis natural scenarios, found aged polymers to have a significant increase in sorption capacity compared to their virgin counter parts due to a change in the surface chemistry and structure of the polymer. It is known that microplastics have a detrimental effect on the environment by entering food chains, stunting growth and reproduction of fauna and flora, however the ecotoxicity effect of sorbed antibiotics onto microplastics is still relatively unknown. With the potential for microplastics to increase antibiotic concentrations in natural waterways comes the associated risks of ARGs and ARBs. Consequently, it is important to continue research into antibiotic sorption onto microplastics to comprehensively understand the implications associated with the interaction.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2023.119790.

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