

Adsorptive interaction of antibiotic ciprofloxacin on polyethylene microplastics: Implications for vector transport in water

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ABSTRACT

This study investigates the adsorption behavior of Ciprofloxacin (CPX) antibiotic on polyethylene (PE) microplastics through batch adsorption experiments under various environmental conditions, i.e., ionic strengths, pH and in the presence of dissolved organic matter (DOM). The adsorption of CPX showed a gradual increase with increasing pH reaching the maximum adsorption at pH 6.5–7.5 and then decreased, which is likely due to the redistribution of CPX species with pH. The overall CPX adsorption capacity of PE microplastics decreased with an increase in the ionic strength revealing the hydrophobic and electrostatic interactions. Fourier-transform infrared spectra (FTIR) bands ascribable to $-\text{CH}_2$ and $-\text{CH}_3$ functional groups exhibited non-polar hydrophobic properties of PE microplastics. CPX adsorption kinetics data were compatible with the parabolic diffusion model and the Elovich model in the presence of humic acid, suggesting that the adsorption was assisted through diffusion-controlled processes. The isotherm equilibrium data fitted well for Hill and Dubinin–Radushkevich models implying multilayer adsorption through physical adsorption processes on the heterogeneous PE microplastics surface. Hence, PE microplastics could be a potential vector to transport CPX in a natural aquatic environment where the adsorption mechanism is being influenced primarily by the pH, ionic strength, DOM of the water system, and the properties of the plastic.

1. Introduction

Microplastics are small plastic particles, including plastic fragments, fibers, or beads. Although microplastics are defined in numerous size ranges, generally, the term of microplastics is attributed to plastic particles in size range of 100 nm to <5 mm diameter (Alimi et al., 2018; Guo and Wang, 2019). Discarding and overuse of plastics have led to its accumulation in the environment, enabling them to persist for years due to its durability and resistance for biodegradation

(Wright et al., 2013). In the environment, microplastics can create deleterious effects on the aquatic ecosystem by releasing phthalates and bisphenol which may disrupt the endocrine system of mammals and has high potential to be ingested by freshwater/marine invertebrates and vertebrates due to the small size (Morét-Ferguson et al., 2010; Li et al., 2018b).

Recent studies have found microplastic in the freshwater environments ranging from 0.003–2.6 gL⁻¹ including rivers, lakes, lagoons, estuaries and wastewater plant effluents (Li et al., 2020).

Furthermore, microplastics act as a vector to transport various contaminants through the water to soil. Hydrophobicity and high surface area to volume ratio of microplastics facilitate adhesion of various pollutants especially hydrophobic organic contaminants (HOC) including Polycyclic aromatic hydrocarbons (PAH), Polychlorinated biphenyls (PCB), Polyfluorinated alkyls (PFAS), Polybrominated diethers (PBDs), pharmaceuticals and personal care products (PPCPs) (Guo and Wang, 2019). As organisms consume contaminant sorbed microplastics, feeding process may lead to biomagnification of these contaminants, whereas the impacts of microplastics on aquatic biota remain mostly unstudied (Teuten et al., 2009; Tourinho et al., 2019).

The accumulation of organic contaminants on the plastic surface could be several orders of magnitude higher than the surrounding waters. Hydrophobic organic contaminants tend to sorb to sediments and organic matter. However, the affinity towards non-polar plastic surfaces is high (Hüffer and Hofmann, 2016). Plastic fragments in environmental samples have shown high adsorption of persistent organic pollutants (POP's) in the range of 1.1–8600 µg g⁻¹ (Rios et al., 2007). Mato et al. (2001) reported that plastic particles accumulate PCBs, 10⁵–10⁶ times higher than surrounding seawater. The extent of adsorption of contaminants by microplastics depends on the compound-specific factors, polymeric properties of microplastics (crystallinity, surface area, and charge) and matrix effects (salinity, pH, and dissolved organic matter).

The focus with regard to adsorption to microplastics was mostly towards non-polar organics (Lee et al., 2014; Zhan et al., 2016; Liu et al., 2019a; Xu et al., 2019) and most recently, studies have focused on the adsorption behavior of polar ionizable compounds such as antibiotics by microplastics. Li et al. (2018a) revealed that polyamide microplastics had high affinity to sorb and transport antibiotics over other studied plastic types. The effect of salinity, pH, and organic matter was found to have an essential role in the adsorption of sulfamethoxazole and tetracycline by different types of microplastic (Xu et al., 2018a; Guo et al., 2019). However, studies on polyethylene microplastics are inadequate, although the use of polyethylene is widespread over other plastics. Recently scientists focused their attention on microplastics as drivers for transmitting antibiotic resistance bacteria as antibiotics are being released into the aquatic environment at dangerous levels, and exposure of antibiotics to microbial communities may likely develop genetic resistance and cause a significant threat to non-target species (Laganà et al., 2019; Kumar et al., 2020; Ram and Kumar, 2020). Multiple interactions may take place as microplastics and antibiotics co-exist in the environment, which in terms makes the possibility of microplastics being potential over antibiotics to transport in the water. Further, the influence of environmental factors such as pH, ionic strength, and the presence of DOM is again yet insufficient to foresee the fate of microplastics in the water.

Ciprofloxacin (CPX) has been frequently detected in wastewater effluent and has become an emerging contaminant of concern recently. Although surface water contains low concentrations of CPX (typically < 1 µg L⁻¹), relatively high concentrations of CPX have been observed in general wastewater (120 µg L⁻¹) and hospital wastewaters (150 µg L⁻¹) (Mato et al., 2001). Even though many ionizable antibiotics have shown its potential to be adsorbed onto various plastics (Xu et al., 2018b; Guo et al., 2019), studies are limited on the role of CPX-microplastics interaction and the influence of pH, DOM, and electrolytes on its adsorption capacities. Furthermore, the effects of environmental conditions played on the behavior of adsorption isotherm, kinetic mechanisms of antibiotics and microplastics have not yet been investigated. Notably, the pH-dependent ionization of CPX may play an essential role in its interactions with microplastics, which has not been studied in detail. Further, information regarding the mechanistic interactions of CPX at the presence of DOM and ionic strength is lacking. Hence, this study was aimed at examining the binding ability of CPX to PE microplastics at varying pH due to speciation of CPX and the effect of various ionic strengths and DOM concentrations, thereby assess its capacity in facilitating vector transport of CPX in the aquatic environment.

2. Materials and methods

2.1. Materials and chemicals

Pure polyethylene microplastics (size ~100 µm Microscrub®), were purchased from MicroPowders, Inc. Tarrytown, New York, USA. Ciprofloxacin hydrochloride monohydrate was obtained from HIMEDIA Laboratories, India. For pH adjustments, 0.1 M nitric acid and 0.1 M sodium hydroxide were used. All chemicals (analytical grade), including sodium nitrate and humic acid were obtained from Sigma-Aldrich, USA. A stock solution of CPX (1000 mg L⁻¹) was made by initially dissolving the solid in a minimum amount of methanol followed by de-ionized water (Maya et al., 2001). The sodium salt of HA was used to prepare a 100 mg L⁻¹ of stock solution in de-ionized water.

2.2. Characterization

The surface physical characterization of PE microplastics was done by the Field Emission Scanning Electron Microscopy (FE-SEM) at 15 kV. The surface chemical characterization of PE microplastics and CPX adsorbed microplastics (dried sample) was done by Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) spectroscopy analysis (Thermo scientific NICOLET iS10 FTIR Spectrometer, USA) in the range of 550–4000 cm⁻¹ with 64 repetitive scans and resolution of 4 cm⁻¹.

2.3. Batch adsorption experiments

2.3.1. Effect of pH, ionic strength and DOM on CPX adsorption to polyethylene

Polyethylene microplastics suspension of 2 g L^{-1} was prepared with water and kept in the shaking water bath (GEMMYCO VCW-012S, Taiwan) overnight for dispersion with vigorous stirring (Guo et al., 2019; Xu et al., 2018b). After spiking with an initial concentration of 10 mg L^{-1} of CPX, the pH was adjusted to a range of 4–9 using 0.1 M HCl or NaOH (Liu et al., 2019b). At each pH, 10 ml of the suspension was dispensed into 30 ml glass vials and kept in a shaker for 12 h at a speed of 400 rpm in the horizontal shaker at room temperature. The final pH was recorded, and the samples were filtered through 0.45 filters to remove microplastics. The filtrate was analyzed for CPX by the Thermo Scientific 10S UV-Vis spectrophotometer at the wavelength of 276 nm. The control experiment was carried out without microplastics.

The pH edge experiment was repeated for the same range to examine the effect of ionic strength and the effect of DOM on CPX adsorption. Ionic strength experiment was performed with 0.001, and 0.1 M NaNO_3 and Humic acid (HA) at concentrations of 0.5, 1.5, and 2.5 mg L^{-1} were used to study the effect of DOM.

2.3.2. Kinetic experiment

The adsorption kinetics were performed with an initial CPX concentration of 25 mg L^{-1} at the optimum pH derived from the pH edge experiment (Li et al., 2018a). The dosage of microplastics suspension was maintained at 2 g L^{-1} shaking at the speed of 150 rpm. Samples were withdrawn at the time intervals of 10, 20, 45, 30 min, 1, 1.5, 3, 5 h, and filtered through $0.45 \mu\text{m}$ PTFE filters. The kinetics experiment was repeated with HA 2.5 mg L^{-1} to analyze the influence of DOM.

2.3.3. Isotherm experiment

Adsorption isotherms experiments were carried out with CPX concentrations ranging from 30 to 500 mg L^{-1} in glass vials. The dosage of PE microplastics was kept as 2 g L^{-1} and the optimum pH was maintained at 6.5–7.5. All the vials were kept in a horizontal shaker for 5 h of equilibrium time determined by the kinetics experiment. The isotherm experiment was repeated with HA 2.5 mg L^{-1} to analyze the influence of DOM.

All the experiments were conducted in duplicate to minimize errors. The kinetic and isotherm data were modeled, and the parameters were determined using Origin 8.0 statistical computer software.

3. Results and discussion

3.1. Characterization of polyethylene microplastics

3.1.1. Morphology of polyethylene microplastic

Surface area, morphology, and degree of crystallinity of microplastics play an essential role in the adsorption of HOC (Wang et al., 2015). The PE microplastics particles could be observed as particles in different sizes and shapes, displayed at the lowest magnification (Fig. 1). The surface seems to be coarse because of multiple irregular folds on the particle surface, creating more voids and pore spaces. Both folds and pore spaces collectively provide extended surface area for adsorption to take place successfully. In previous studies by Xu et al. (2018a) and Hüffer and Hofmann (2016) revealed that the BET surface area of PE microplastics was found to be 0.2341 and $0.308 \text{ m}^2 \text{ g}^{-1}$, respectively, which is comparatively higher than PS and PVC. The polymer surface property is affected by the degree of crystallinity of the polymer chain. Organic contaminants can easily mobilize into the loosely arranged polymer chains of amorphous polymers but restricted in crystalline glassy polymers due to highly dense molecular structures (Teuten et al., 2009). Polyethylene exhibits a low degree of crystallinity and has a high proportion of amorphous region than PS and PVC, enabling molecules to sorb into the loosely arranged polymer structure with Vander Waals forces (Guo et al., 2012). However, other than the degree of crystallinity, there are other inherent factors of microplastics that can correlate with the adsorption intensity, which may need to be looked upon (Li et al., 2018a; Wang et al., 2015)

3.1.2. FT-IR ATR Analysis

The ATR FTIR bands obtained showed distinctive characteristic peaks for PE microplastics and CPX (Fig. 2). The spectrum of pristine PE microplastics was well defined with peaks at 2915 cm^{-1} attributed to $-\text{CH}_2$ asymmetric stretching and 2848 cm^{-1} $-\text{CH}_2$ asymmetric stretching. Peaks at 1472 and 1463 cm^{-1} showed for $-\text{CH}_2$ bending deformation and 1368 cm^{-1} for $-\text{CH}_3$ symmetric deformation. The peak at 1349 cm^{-1} was attributed to wagging deformation and 730 and 719 cm^{-1} for rocking deformation (Otdak et al., 2005). The spectrum of CPX displayed the fingerprint region from 700 to 1700 cm^{-1} (Ashiq et al., 2019). The peaks at 1706 and 1620 were attributed to the $\text{C}=\text{O}$ stretching vibration of the carboxylic group and ketone group of CPX (Dias Murbach et al., 2014). The C-F stretching peak was showed up at 1045 cm^{-1} , and the two intense peaks at the 804 cm^{-1} and 1267 cm^{-1} were identified as C-N stretching and C-O stretching vibration of carboxylic acid, respectively (Jiang et al., 2013). The influence of CPX on microplastics was well identified through characteristic peaks of CPX located in the 750 – 1650 cm^{-1} region, of CPX, bound PE microplastics. Sharp bands in the 1550 – 1650 cm^{-1} region were evident for $\text{C}=\text{O}$ stretching of keto group while the regions for 1000 – 1050 and 1250 – 1300 cm^{-1} for C-F and C-O-C stretching vibrations respectively (Dias Murbach et al., 2014). The deficiency of functional groups and low surface energy of PE makes it chemically inert, which is confirmed by the stability of the ATR FTIR peaks ($-\text{CH}_2$ and $-\text{CH}_3$) the contact of CPX (Shen et al., 2018).

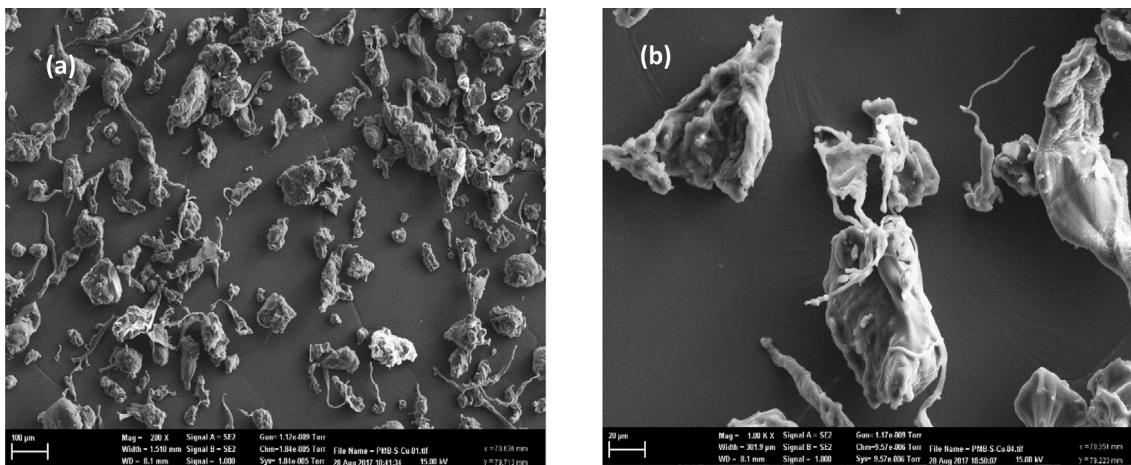


Fig. 1. SEM images of the pristine PE microplastics, (a) magnification of 200x, and (b) magnification of 1000x.

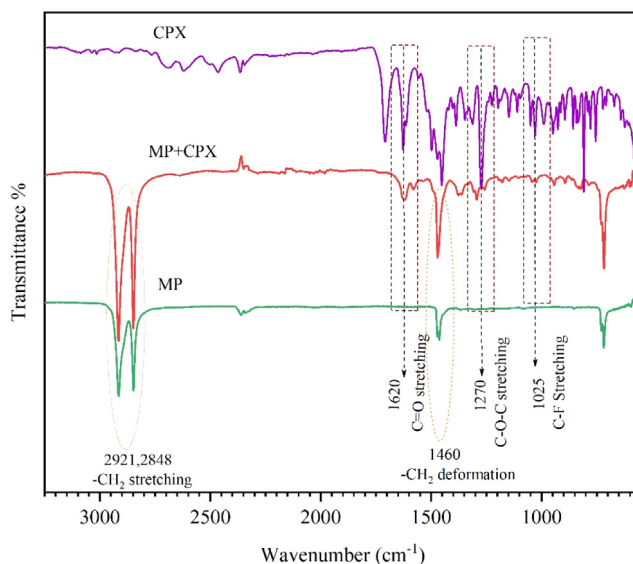


Fig. 2. ATR-FTIR spectra of the pristine PE microplastics, CPX adsorbed microplastics and CPX from 400 to 3500 cm^{-1} wavelength.

3.2. Influence of pH on CPX adsorption

The adsorption of CPX onto microplastics exhibited a prominent dependency on pH (Fig. 3a), acquiring a maximum adsorption capacity around the pH range of 6.5 to 7.5. Such adsorption behavior can be explicated by the CPX speciation and the surface potential of at different pH levels. The pH zero-point charge (pH_{pzc}) of microplastics is 4.3, exhibiting a net negative surface charge throughout the experimental conditions (pH 4–9). In low pH values (< 6.1), protonation of the negative PE surface and cationic form of CPX ($\text{pK}_{\text{a}1}=6.1$) lead to electrostatic repulsion between CPX and microplastics. As pH reached up to 6.5, the microplastic surface became more negative, giving rise to electrostatic forces and hydrophobic interactions displaying a gradual increase of CPX adsorption by microplastics. Between pH 6.1 ($\text{pK}_{\text{a}1}$) and 8.7 ($\text{pK}_{\text{a}2}$), CPX dominates the zwitterionic form ($\text{CPX}^{-/+}$) (Ashiq et al., 2019) implying that electrostatic and hydrophobic interactions both have played a significant role in the CPX adsorption mechanism around the neutral condition (Xu et al., 2018a). The adsorption capacity decreased significantly above pH 7.5 because of electrostatic repulsive forces as both CPX and microplastics are in their negatively charged forms. Similar adsorption trends were observed for CPX with polystyrene and polyvinyl chloride due to speciation and surface charge (Liu et al., 2019b). Hence, the sorption mechanism between CPX and microplastics is suggested to be governed by electrostatic interactions and hydrophobic interactions (Xu et al., 2018b; Liu et al., 2019b). Nonetheless, microplastics have a great potential to transfer CPX through sorption as natural fresh surface waters provide a circumneutral environment (Li et al., 2018a).

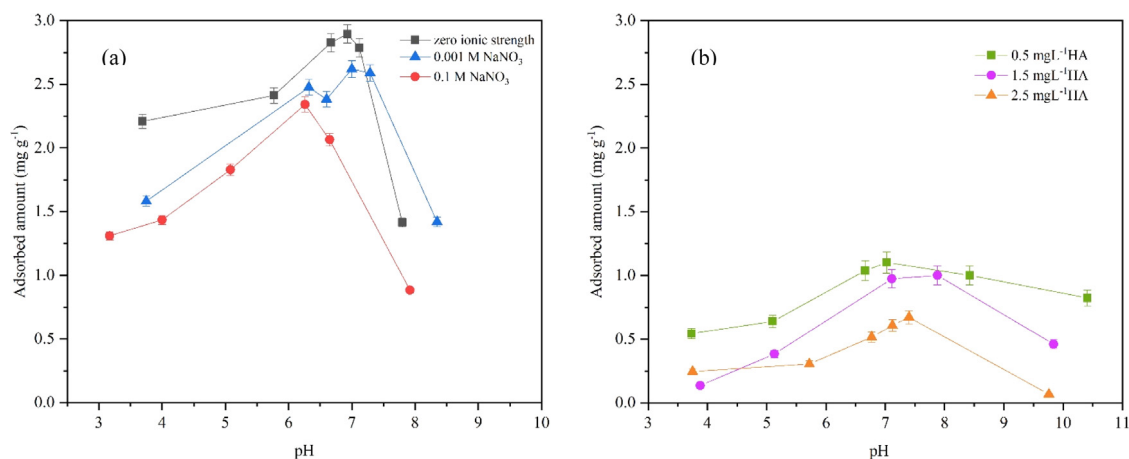


Fig. 3. Adsorption variation of CPX (a) in the presence of 0.001 and 0.1 M NaNO₃ (b) in the presence of 0.5, 1.5 and 2.5 mg L⁻¹ of HA.

3.3. Influence of ionic strength

In the natural waters, the interaction of CPX and microplastics is generally influenced by dissolved salt ions in the natural waters. As shown in Fig. 3a, the adsorption capacity of CPX was reduced to some extent, with the increase of ionic strength from 0.001 to 0.1 M NaNO₃. In a previous study, the adsorption capacities of all five antibiotics declined in seawater compared to their adsorption capacities in freshwater (Li et al., 2018a). When salinity increases, Na⁺ ions bind electrostatically to the negatively charged PE disturbing the charge equilibrium of the surface, thereby reducing binding sites for CPX. The competitions between the sorbent and electrolytes for the electrostatic sites confirm that electrostatic interactions have played a notable role in the adsorption process (Guo et al., 2018). The adsorption decrease of cations with the increase of ionic strength suggests that the electrostatic potential of the adsorption plane of the microplastics is negative. The decline of CPX adsorption with increasing ionic strength implies that the negative potential of the PE surface decreased above the p*H*_{pzc} (Naidu et al., 1994).

Studies have shown that ionic strength could influence the aggregation possibility of plastic particles, especially in nanoplastics. The increase of NaCl concentration promotes the aggregation of polystyrene nanoplastics by compressing or even eliminating the electrical double layer (EDL), thus decreasing the repulsive forces between the particles (Wu et al., 2019). Similar behavior was observed by Li et al. (2018b) for polystyrene microplastics, where the presence of divalent electrolytes accelerated the aggregation compared to monovalent electrolytes. As a result, the particles become more compact and might reduce the adsorption sites on the PE microplastics surface, which in turn depresses the overall CPX adsorption (Liu et al., 2019a,b).

The salting-out effect is another factor that influences the adsorption of organic compounds in the presence of ions. Inorganic salts can decrease the solubility of especially nonpolar and weakly polar organic compounds, thus shifting the adsorption equilibrium of HOC towards the organic phase (Alimi et al., 2018). Hence the salting-out would enhance hydrophobic interactions of organic contaminants between microplastics (Liu et al., 2019a). However, the experimental results exhibited adsorption enhancement of CPX due to the salting-out of CPX was compensated by the fewer adsorption sites on microplastics due to lowering of surface potential and particle aggregation. Therefore, based on current and previous work, the influence of ionic strength for the adsorption behavior may vary depending on the type of sorbent, sorbate, and the electrolyte.

3.4. Influence of dissolved organic matter

The effect of DOM in the aquatic environment was simulated with HA in this experiment. In this study, overall CPX adsorption was significantly reduced in the presence of HA. Adsorption capacities were declined from 3.0 mg g⁻¹ to 1.0, 0.75, and 0.25 mg g⁻¹, respectively, with the concentrations of HA increasing from 0.5, 1.5 and 2.5 mgL⁻¹ of HA (Fig. 3b). A drastic shift in adsorption was observed even at a low concentration of HA in comparison to the adsorption levels in the absence of DOM, indicating that competitive adsorption interactions exist in-between organic pollutants, DOM and microplastics.

Dissolved organic matter had either inhibited or enhanced adsorption capacities depending on the physicochemical properties of the sorbent, sorbate, and the adsorption mechanism (Bolan et al., 2011). Zuo et al. (2019) discovered that DOM lowered adsorption for phenanthrene on four types of microplastics. In accordance, adsorption capacities on PE microplastics declined for non-polar compounds; 17 α -ethinyl estradiol, 4-methylbenzylidene camphor, and TCS with an increase of HA (Wu et al., 2016).

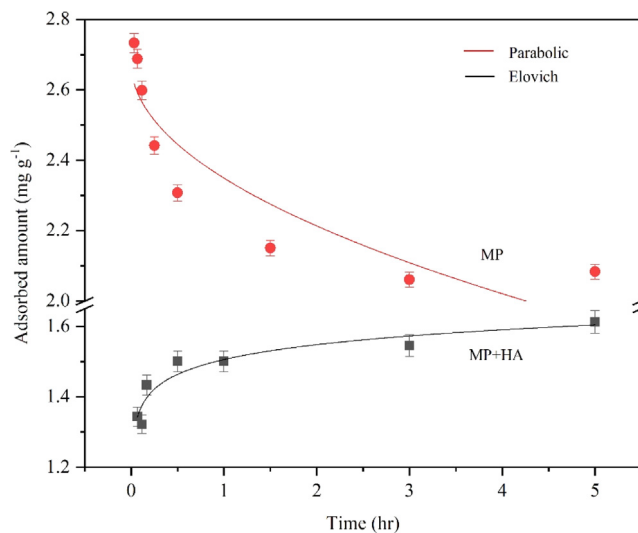


Fig. 4. Elovich and parabolic kinetic models for CPX adsorption at an initial concentration of 25 mg L^{-1} at pH range 6.5–7.5 and the solid lines represent the calculated results using non-linear curve fitting.

The presence of DOM is likely to decline bioavailability of hydrophobic chemicals through attaining partitioning equilibrium with HA altering the partitioning of CPX between microplastics and water (Seidensticker et al., 2017). Both hydrophobic and hydrophilic domains of HA may result in increasing complex interactions contributing to the adsorption of antibiotics on organic matter surface. Intramolecular hydrogen bonding interactions provide the key to the complexation of HA and CPX (Aristilde and Sposito, 2010). A study conducted by Liu et al. (2017) on the adsorption behavior of antibiotics by HA found that CPX exhibited higher adsorption levels compared to sulfamethoxazole. Thus, CPX inherits a higher affinity towards HA complexation thereby suppressing the adsorption ability of microplastics.

The adsorption process preferentially occurs in the amorphous phase confined to some regions of the polymer, consequently creating a competition between HA and organic pollutants for limited adsorption sites on the microplastics surface (Teuten et al., 2009). Humic acid may adsorb on the microplastics surface and either increase the hydrophobic surface to enhance adsorption or occupy the limited adsorption sites available to adsorb organic pollutant molecules. Furthermore, long term coexistence of microplastics and DOM in the environment could also induce structural changes in microplastics altering the surface morphology affecting the transport of hydrophobic contaminants (Chen et al., 2018).

3.5. Adsorption kinetics

Kinetics experiment was carried out to investigate the adsorption variation with the change of contact time. Adsorption of CPX onto microplastics showed an intense adsorption capacity at the initial time of incubation and subsequently decreased, achieving an equilibrium after 3 h (Fig. 4). The equilibrium is maintained at 2.1 mg g^{-1} adsorption capacity throughout the experimental period. Adsorption behavior of CPX with HA was entirely different, with an increasing trend at the beginning approaching an equilibrium of less than 1 h. However, the equilibrium adsorption capacity declined from 2.1 to 1.5 mg g^{-1} in the presence of HA.

The partitioning of a sorbent is governed by all forms of rate-controlling mechanisms such as adsorption on the surface, mass transfer chemical reaction, external or internal diffusion, and/or pore diffusion mechanism, which can be elaborated with the use of kinetic models (Ashiq et al., 2019). The kinetic results of CPX adsorption could be described by the parabolic diffusion model. The parabolic diffusion model is representative of diffusion-controlled processes. Therefore the conformity of CPX adsorption data to this model suggests that diffusion is the rate-limiting process resulted either by intra-particle diffusion or surface diffusion (Jalali et al., 2019).

The kinetic results for the adsorption of CPX in the presence of HA were well-fitted with the Elovich model with an R^2 of 0.90 (Table 1). The model explicates how the overall adsorption process is controlled by the rate of chemisorption and external mass transfer on a heterogeneous substrate surface (Wang et al., 2019). Elovich model assumes that the adsorption energy on the surface is heterogeneously distributed, and the adsorption process is a heterogeneous diffusion process. The adsorption efficiency decreases with time as the number of vacant active sites of the MP surface becomes less to be utilized by CPX, subsequently attaining an equilibrium state when all active sites are occupied. The adsorption process is driven by physical adsorption and diffusive mass transfer between the solution and the amorphous matrix of the PE (Wagner and Lambert, 2018).

Table 1Comparison of different kinetic models and correlation coefficients (R^2) for CPX adsorption.

Nonlinear kinetic model	Parabolic		Elovich		
	$Q_t = a + Rt^{1/2}$		$\frac{dq_t}{dt} = a \exp^{-bQ_t}$		
	a (mg g^{-1})	R^2	a ($\text{mg g}^{-1} \text{min}^{-1}$)	b (g mg^{-1})	R^2
MP	2.6779	0.8358	–	–	–
MP with HA	–	–	3.3825	0.978	0.9039

Note: a is the initial adsorption rate constant, and b is the Elovich constant related to the extent of surface coverage.

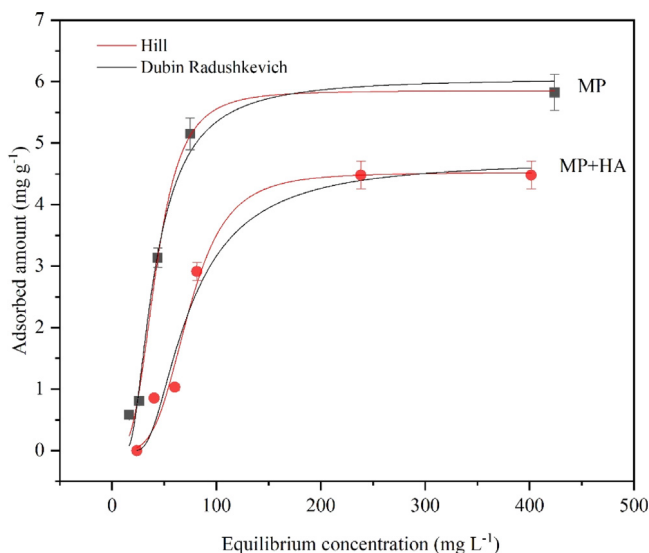


Fig. 5. Hill isotherm models for CPX adsorption in the absence and presence of 1.5 mg L⁻¹ HA, at pH 6.5–7.5 and the solid lines represent the calculated results using non-linear curve fitting.

3.6. Adsorption isotherms

The non-linear CPX adsorption isotherm data by PE microplastics were fitted to commonly used non-linear isotherm models, i.e., Freundlich, Langmuir, Hill, and Dubin Radushkevich models. The adsorption isotherms of CPX on PE microplastics are shown in Fig. 5. The maximum adsorption capacity was reduced with the introduction of DOM. Adsorption behavior was non-linear and agreed on the Hill model according to R^2 value. Fitting parameters derived from the Hill model are summarized in Table 2.

Previous studies exhibited highly linear adsorption isotherms for perfluoroalkyl acids (PFAAs), polychlorinated biphenyls (PCBs), and PPCPs on various other plastic particles (Wu et al., 2016; Xu et al., 2019). However, the linearity or the non-linearity of the adsorption isotherm varies depending on the properties of the organic chemicals and plastic types (Hüffer and Hofmann, 2016). According to the Hill model, CPX binding onto microplastics surface could be explained as a cooperative adsorption process, where the binding capacity of CPX at a particular site of microplastics tends to influence the binding capacity of other sites of the homogeneous microplastics surface (Ashiq et al., 2019). When the Hill cooperativity coefficient, $n > 1$, it indicates a positive cooperativity binding, $n = 1$ non-cooperative binding, and $n < 1$ negative cooperativity binding (Stasinakis, 2012). Both adsorption isotherms exhibit positive values for n , depicting that the binding interaction between CPX and microplastics was in the form of positive cooperativity. On the other hand, it is evident that each adsorption site was occupied by more than one sorbent molecule; hence the adsorption process was multi-molecule adsorption (Lin et al., 2019). Also, positive K_H value displays that intermolecular attractions such as hydrophobic and electrostatic interactions have played a prominent role in the adsorption process of CPX on microplastics (Sarici Özdemir, 2018).

The Dubinin–Radushkevich isotherm is generally applied to express Gaussian energy distribution on a heterogeneous surface where adsorption is followed by a pore-filling mechanism, which is a fundamental model to differentiate between chemisorption and physisorption. A study done by Wang and Wang (2018) revealed that adsorption efficiencies of pyrene by PE decreased as the initial concentration was increased. This phenomenon could take place as the PE surface is assumed to be heterogeneous with selective adsorption sites. In low concentration, CPX may first occupy the high energy sites and later with increasing concentrations occupy on lower energy sites, subsequently resulting in a drop in the adsorption efficiency and achieving saturation (Wang and Wang, 2018).

Table 2

Adsorption isotherm parameters calculated from the isotherm models.

Hill isotherm $Q_e = \frac{Q_m(K_h C_e)^n}{1+(K_h C_e)^n}$	$Q_m(\text{mg g}^{-1})$	$K_h (\text{L mg}^{-1})$	n	R^2
MP	5.852	0.02376	3.373	0.9939
MP with HA	4.521	0.01361	3.994	0.9780
Dubinin-Radushkevich isotherm $Q_e = Q_m \exp(-\beta E^2)$	$Q_m(\text{mg g}^{-1})$	β		R^2
MP	6.0503	2E-04		0.9820
MP with HA	4.7134	6.5E-04		0.9674

Note: Q_m is the maximum adsorbed capacity, K_h is the Hills constant, n is the Hill cooperativity coefficient, and β is the Dubinin-Radushkevich constant.

3.7. Adsorption mechanism

The interaction between microplastics and pollutants is of high importance in order to predict the fate of microplastics. Thus, the adsorption mechanism provides supportive evidence to determine the behavior of microplastics and CPX and the possible interactions that exist between them (Fig. 6).

The chemical nature of CPX and the surface morphological and chemical properties of the microplastics simultaneously contribute to the adsorption process. Generally, the chemical and physical properties of the sorbent and the sorbate are affected by the solution environment and chemistry. Distribution of CPX species (CPX^+ , CPX^-) at different pH, greatly influenced the adsorption behavior displaying declining trends under acidic and alkaline conditions due to the electrostatic repulsive forces (Guo et al., 2019). Around the circumneutral pH range, repulsive forces were dominated by hydrophobic interaction and electrostatic attractions between the zwitterionic CPX and PE surface. Usually, the adsorption process of ionizable organic contaminants is governed predominantly by both hydrophobic and electrostatic interactions (Tourinho et al., 2019). Once Na^+ is introduced to the medium cationic CPX was replaced by Na^+ ions electrostatically on the microplastic surface in the lower pH. However, the reduction of CPX adsorption was observed throughout the experimental pH range as Na^+ forms the electrical double layer and disturb the charge equilibrium on the PE surface. The competition between CPX and Na^+ was intensified with the increase of NaNO_3 concentration in the medium resulting in further adsorption suppression (Fig. 3a). In the presence of HA the interaction of CPX formed a complex between CPX-HA because CPX inherits a higher affinity towards HA instead of MP. Complexation of CPX with HA has been reported in numerous studies suggesting that strong hydrophobic interactions and hydrogen bonds between CPX and HA are feasible (Aristilde and Sposito, 2010) (Fig. 3b).

The adsorption isotherms models determined the adsorption mechanism was governed primarily by physisorption accompanied by partitioning into the heterogeneous surface. Ciprofloxacin molecules diffused into the porous polymer bulk of the PE, adsorb on the polymer surface through weak Van Der Waal's forces and electrostatic interactions. The kinetics results in the presence of HA fitted to the Elovich model, possibly could exhibit the adsorption of CPX happened, preferably on HA rather the plastic surface though chemical interactions existed between CPX and HA. Physisorption is considered to be a weak and reversible process governed by competitive adsorption and desorption occurring at different rates that depends on the conditions of the matrix (Heinrich et al., 2020). For instance, when the water represents low and high pH or high salinity and HA levels the adsorbed CPX is inclined to desorb from the surface into the water, that might even contaminate an unpolluted site.

Except for C=O at 1620 cm^{-1} , C-O-C at 1270 cm^{-1} and C-F at 1025 cm^{-1} , the absence of new peaks in the adsorbed microplastics can conclude that no alteration occurred in the PE polymer structure when the adsorption process took place. The FTIR spectra of microplastics before and after adsorption of CPX further supports the fact that the adsorption mechanism was primarily based on physical adsorption.

In the environment ultimately microplastics are prone to chemical and physical weathering that leads to fragmentation of the polymer matrix, formation pores and cracks on the surface. As weathering proceeds the oxidation of the surface chemicals groups impart hydrophilic properties on the plastic surface. The increased surface area and polarity of the polymer will consequently enhance the adsorption tendency of CPX on the PE surface than the pristine plastics (Zhang et al., 2018; Liu et al., 2020). In natural waters, contaminants are often present as a mixture, the influence of other contaminants may alter the adsorption behavior of CPX in the water. The competitive interactions between multiple contaminants and microplastics might also govern the fate of microplastics in the actual environment. Along with the organic contaminants, inorganic nutrients such as NO_3^- and PO_4^{3-} , heavy metals in the water has the potential to influence the adsorption (Lin et al., 2020). Microbial colonization and biofilm formation on the particle surface can also alter the surface properties which in turn could affect the adsorption tendency (Wang et al., 2020).

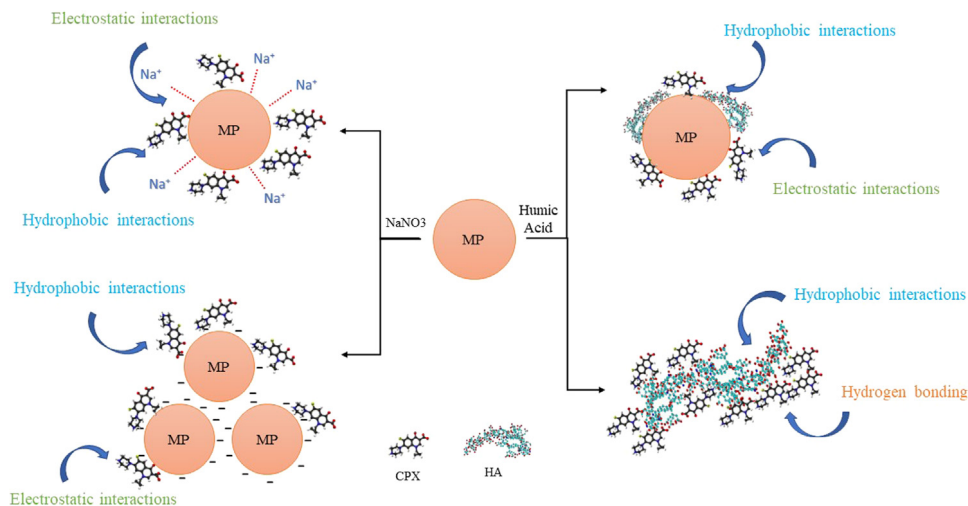


Fig. 6. Adsorption mechanism of PE microplastic and CPX in the presence of NaNO₃ and HA.

4. Conclusions

In this study, CPX adsorption onto PE microplastics was studied, and the influence of pH, ionic strength, and DOM was evaluated. Adsorption behavior onto microplastics varied with pH, depending on the surface charge of PE and the speciation of CPX. The maximum adsorption of CPX to PE microplastics was observed around pH 6.5–7.5. The presence of ionic strength exhibited a decrease in CPX adsorption by 17% at 0.1 M NaNO₃. The introduction of HA declined CPX adsorption by 89% depicting a higher affinity of CPX towards complexation with HA. Postulated possible interactions of CPX on microplastics in the simulated environmental conditions are suggested as electrostatic and hydrophobic interactions dominated by physisorption. Physisorbed CPX to microplastics may easily be released into the environment with a slight change in the environmental conditions such as pH. These results support the understanding of the environmental behavior of PE microplastics concerning its adsorption and transportation of CPX and the potential of PE microplastics to act as a vector.

CRedit authorship contribution statement

Thilakshani Atugoda: Formal analysis, Investigation, Writing - original draft. **Hasintha Wijesekara:** Resources, Writing - review & editing. **D.R.I.B. Werellagama:** Supervision, Writing - review & editing. **K.B.S.N. Jinadasa:** Supervision, Writing - review & editing. **Nanthi S. Bolan:** Resources, Writing - review & editing. **Meththika Vithanage:** Conceptualization, Supervision, Funding acquisition, Writing - review & editing.

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.

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References

- Alimi, O.S., Farner Budarz, J., Hernandez, L.M., Tufenkji, N., 2018. Microplastics and nanoplastics in aquatic environments: Aggregation, deposition, and enhanced contaminant transport. *Environ. Sci. Technol.* 52, 1704–1724. <https://doi.org/10.1021/acs.est.7b05559>.
- Aristilde, L., Sposito, G., 2010. Binding of ciprofloxacin by humic substances: A molecular dynamics study. *Environ. Toxicol. Chem.* 29, 90–98. <https://doi.org/10.1002/etc.19>.
- Ashiq, A., Sarkar, B., Adassooriya, N., Walpita, J., Rajapaksha, A.U., Ok, Y.S., Vithanage, M., 2019. Sorption process of municipal solid waste biochar-montmorillonite composite for ciprofloxacin removal in aqueous media. *Chemosphere* 236, 124384. <https://doi.org/10.1016/j.chemosphere.2019.124384>.
- Bolan, N.S., Adriano, D.C., Kunhikrishnan, A., James, R., Senesi, N., 2011. Dissolved organic matter: biogeochemistry, dynamics, and environmental significance in soils. *Adv. Agronomy* 110, 1–75. <http://dx.doi.org/10.1016/B978-0-12-385531-2.00001-3>.

- Chen, W., Ouyang, Z.Y., Qian, C., Yu, H.Q., 2018. Induced structural changes of humic acid by exposure of polystyrene microplastics: A spectroscopic insight. *Environ. Pollut.* 233, 1–7, <https://doi.org/10.1016/j.envpol.2017.10.027>.
- Dias Murbach, H., Jaques Ogawa, G., Azevedo Borges, F., Romeiro Miranda, M.C., Lopes, R., Roberto De Barros, N.G.u., Guedes Mazalli, A.V., Gonçalves Da Silva, R., Ferreira Cinman, J.L., De Camargo Drago, B., et al., 2014. Ciprofloxacin release using natural rubber latex membranes as carrier. *Int. J. Biomater.* <https://doi.org/10.1155/2014/157952>.
- Guo, X., Chen, C., Wang, J., 2019. Sorption of sulfamethoxazole onto six types of microplastics. *Chemosphere* 228, 300–308, <https://doi.org/10.1016/j.chemosphere.2019.04.155>.
- Guo, X., Pang, J., Chen, S., Jia, H., 2018. Sorption properties of tylosin on four different microplastics. *Chemosphere* 209, 240–245, <https://doi.org/10.1016/j.chemosphere.2018.06.100>.
- Guo, X., Wang, J., 2019. The chemical behaviors of microplastics in marine environment: A review. *Mar. Pollut. Bull.* 142, 1–14, <https://doi.org/10.1016/j.marpolbul.2019.03.019>.
- Guo, X., Wang, X., Zhou, X., Kong, X., Tao, S., Xing, B., 2012. Sorption of four hydrophobic organic compounds by three chemically distinct polymers: Role of chemical and physical composition. *Environ. Sci. Technol.* 46, 7252–7259, <https://doi.org/10.1021/es301386z>.
- Heinrich, P., Hanslik, L., Kämmer, N., Braunbeck, T., 2020. The tox is in the detail: technical fundamentals for designing, performing, and interpreting experiments on toxicity of microplastics and associated substances. *Environ. Sci. Pollut. Res. Int.*
- Hüffer, T., Hofmann, T., 2016. Sorption of non-polar organic compounds by micro-sized plastic particles in aqueous solution. *Environ. Pollut.* 214, 194–201, <https://doi.org/10.1016/j.envpol.2016.04.018>.
- Jalali, M., Majeri, M., Najafi, S., 2019. Kinetic release and fractionation of cobalt in some calcareous soils. *J. Geochemical Explor.* 204, 131–141, <https://doi.org/10.1016/j.jgexplo.2019.02.006>.
- Jiang, W.T., Chang, P.H., Wang, Y.S., Tsai, Y., Jean, J.S., Li, Z., Krukowski, K., 2013. Removal of ciprofloxacin from water by birnessite. *J. Hazard. Mater.* 250–251, 362–369, <https://doi.org/10.1016/j.jhazmat.2013.02.015>.
- Kumar, M., Ram, B., Sewwandi, H., Sulfikar, R., Chaminda, T., 2020. Treatment enhances the prevalence of antibiotic-resistant bacteria and antibiotic resistance genes in the wastewater of Sri Lanka, and India. *Environ. Res.* <https://doi.org/10.1016/j.envres.2020.109179>.
- Laganà, P., Caruso, G., Corsi, I., Bergami, E., Venuti, V., Majolino, D., La Ferla, R., Azzaro, M., Cappello, S., 2019. Do plastics serve as a possible vector for the spread of antibiotic resistance? First insights from bacteria associated to a polystyrene piece from King George Island (Antarctica). *Int. J. Hyg. Environ. Health* 222, 89–100, <https://doi.org/10.1016/j.ijheh.2018.08.009>.
- Lee, H., Shim, W.J., Kwon, J.H., 2014. Sorption capacity of plastic debris for hydrophobic organic chemicals. *Sci. Total Environ.* 1545, <https://doi.org/10.1016/j.scitotenv.2013.08.023>, 470–471–1552.
- Li, C., Busquets, R., Campos, L.C., 2020. Assessment of microplastics in freshwater systems: A review. *Sci. Total Environ.* 707, 135578.
- Li, S., Liu, H., Gao, R., Abdurahman, A., Dai, J., Zeng, F., 2018b. Aggregation kinetics of microplastics in aquatic environment: Complex roles of electrolytes, pH, and natural organic matter. *Environ. Pollut.* 237, 126–132, <https://doi.org/10.1016/j.envpol.2018.02.042>.
- Li, J., Zhang, K., Zhang, H., 2018a. Adsorption of antibiotics on microplastics. *Environ. Pollut.* 237, 460–467, <https://doi.org/10.1016/j.envpol.2018.02.050>.
- Lin, G., Hu, T., Wang, S., Xie, T., Zhang, L., Cheng, S., Fu, L., Xiong, C., 2019. Selective removal behavior and mechanism of trace Hg(II) using modified corn husk leaves. *Chemosphere* 225, 65–72, <https://doi.org/10.1016/j.chemosphere.2019.03.006>.
- Lin, L., Tang, S., Wang, X., Sun, X., Han, Z., Chen, Y., 2020. Accumulation mechanism of tetracycline hydrochloride from aqueous solutions by nylon microplastics. *Environ. Technol. Innov.* 100750.
- Liu, F. fei, Liu, G. zhou, Zhu, Z. lin, Wang, S. chun, Zhao, F. fei, 2019a. Interactions between microplastics and phthalate esters as affected by microplastics characteristics and solution chemistry. *Chemosphere* 214, 688–694, <https://doi.org/10.1016/j.chemosphere.2018.09.174>.
- Liu, X., Lu, S., Liu, Y., Meng, W., Zheng, B., 2017. Adsorption of sulfamethoxazole (SMZ) and ciprofloxacin (CIP) by humic acid (HA): Characteristics and mechanism. *RSC Adv.* 7, 50449–50458, <https://doi.org/10.1039/c7ra06231a>.
- Liu, P., Zhan, X., Wu, X., Li, J., Wang, H., Gao, S., 2020. Effect of weathering on environmental behavior of microplastics: Properties, sorption and potential risks. *Chemosphere* 242, <https://doi.org/10.1016/j.chemosphere.2019.125193>.
- Liu, G., Zhu, Z., Yang, Y., Sun, Y., Yu, F., Ma, J., 2019b. Sorption behavior and mechanism of hydrophilic organic chemicals to virgin and aged microplastics in freshwater and seawater. *Environ. Pollut.* 246, 26–33, <https://doi.org/10.1016/j.envpol.2018.11.100>.
- Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., Kaminuma, T., 2001. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. *Environ. Sci. Technol.* 35, 318–324, <https://doi.org/10.1021/es0010498>.
- Maya, M.T., Gonçalves, N.J., Silva, N.B., Morais, J.A., 2001. Simple high-performance liquid chromatographic assay for the determination of ciprofloxacin in human plasma with ultraviolet detection. *J. Chromatogr. B Biomed. Sci. Appl.* 755, 305–309, [https://doi.org/10.1016/S0378-4347\(01\)00126-8](https://doi.org/10.1016/S0378-4347(01)00126-8).
- Morét-Ferguson, S., Law, K.L., Proskurowski, G., Murphy, E.K., Peacock, E.E., Reddy, C.M., 2010. The size, mass, and composition of plastic debris in the western North Atlantic Ocean. *Mar. Pollut. Bull.* 60, 1873–1878, <https://doi.org/10.1016/j.marpolbul.2010.07.020>.
- Naidu, R., Bolan, N.S., Kookana, R.S., Tiller, K.G., 1994. Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *Eur. J. Soil Sci.* 45, 419–429, <https://doi.org/10.1111/j.1365-2389.1994.tb00527.x>.
- Oldak, D., Kaczmarek, H., Buffeteau, T., Sourisseau, C., 2005. Photo- and bio-degradation processes in polyethylene, cellulose and their blends studied by ATR-FTIR and raman spectroscopies. *J. Mater. Sci.* 40, 4189–4198, <https://doi.org/10.1007/s10853-005-2821-y>.
- Ram, B., Kumar, M., 2020. Correlation appraisal of antibiotic resistance with fecal, metal and microplastic contamination in a tropical Indian river, lakes and sewage. *Npj Clean Water.* <https://doi.org/10.1038/s41545-0200050-1>.
- Rios, L.M., Moore, C., Jones, P.R., 2007. Persistent organic pollutants carried by synthetic polymers in the ocean environment. *Mar. Pollut. Bull.* 54, 1230–1237, <https://doi.org/10.1016/j.marpolbul.2007.03.022>.
- Sarici Özdemir, Ç., 2018. Adsorptive removal of methylene blue by fruit shell: Isotherm studies. *fullerenes nanotub. Carbon Nanostruct.* 26, 570–577, <https://doi.org/10.1080/1536383X.2018.1472083>.
- Seidensticker, S., Zarfl, C., Cirkpa, O.A., Fellenberg, G., Grathwohl, P., 2017. Shift in mass transfer of wastewater contaminants from microplastics in the presence of dissolved substances. *Environ. Sci. Technol.* 51, 12254–12263, <https://doi.org/10.1021/acs.est.7b02664>.
- Shen, X.C., Li, D.C., Sima, X.F., Cheng, H.Y., Jiang, H., 2018. The effects of environmental conditions on the enrichment of antibiotics on microplastics in simulated natural water column. *Environ. Res.* 166, 377–383, <https://doi.org/10.1016/j.envres.2018.06.034>.
- Stasinakis, A.S., 2012. Review on the fate of emerging contaminants during sludge anaerobic digestion. *Bioresour. Technol.* 121, 432–440, <https://doi.org/10.1016/j.biortech.2012.06.074>.
- Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M.A., Jonsson, S., Björn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., et al., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. *Philos. Trans. R. Soc. B* 364, 2027–2045, <https://doi.org/10.1098/rstb.2008.0284>.
- Tourinho, P.S., Kočí, V., Loureiro, S., van Gestel, C.A.M., 2019. Partitioning of chemical contaminants to microplastics: Sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation. *Environ. Pollut.* 252, 1246–1256, <https://doi.org/10.1016/j.envpol.2019.06.030>.
- Wagner, M., Lambert, S., 2018. Freshwater microplastics - the handbook of environmental chemistry vol. 58. *Freshw. Microplastics Handb. Environ. Chem.* 302, <https://doi.org/10.1007/978-3-319-61615-5>.

- Wang, H., Shen, H., Shen, C., Li, Y.N., Ying, Z., Duan, Y., 2019. Kinetics and mechanism study of mercury adsorption by activated carbon in wet oxy-fuel conditions. *Energy Fuels* 33, 1344–1353, <https://doi.org/10.1021/acs.energyfuels.8b03610>.
- Wang, F., Shih, K.M., Li, X.Y., 2015. The partition behavior of perfluorooctanesulfonate (PFOS) and perfluorooctanesulfonamide (FOSA) on microplastics. *Chemosphere* 119, 841–847, <https://doi.org/10.1016/j.chemosphere.2014.08.047>.
- Wang, W., Wang, J., 2018. Comparative evaluation of sorption kinetics and isotherms of pyrene onto microplastics. *Chemosphere* 193, 567–573, <https://doi.org/10.1016/j.chemosphere.2017.11.078>.
- Wang, Y., Wang, X., Li, Y., Li, J., Wang, F., Xia, S., Zhao, J., 2020. Biofilm alters tetracycline and copper adsorption behaviors onto polyethylene microplastics. *Chem. Eng. J.* 392, 123808, <https://doi.org/10.1016/j.cej.2019.123808>.
- Wright, S.L., Thompson, R.C., Galloway, T.S., 2013. The physical impacts of microplastics on marine organisms: a review. *Environ. Pollut.* 178, 483–492, <https://doi.org/10.1016/j.envpol.2013.02.031>.
- Wu, J., Jiang, R., Lin, W., Ouyang, G., 2019. Effect of salinity and humic acid on the aggregation and toxicity of polystyrene nanoplastics with different functional groups and charges. *Environ. Pollut.* 245, 836–843, <https://doi.org/10.1016/j.envpol.2018.11.055>.
- Wu, C., Zhang, K., Huang, X., Liu, J., 2016. Sorption of pharmaceuticals and personal care products to polyethylene debris. *Environ. Sci. Pollut. Res.* 23, 8819–8826, <https://doi.org/10.1007/s11356-016-6121-7>.
- Xu, P., Ge, W., Chai, C., Zhang, Y., Jiang, T., Xia, B., 2019. Sorption of polybrominated diphenyl ethers by microplastics. *Mar. Pollut. Bull.* 145, 260–269, <https://doi.org/10.1016/j.marpolbul.2019.05.050>.
- Xu, B., Liu, F., Brookes, P.C., Xu, J., 2018a. Microplastics play a minor role in tetracycline sorption in the presence of dissolved organic matter. *Environ. Pollut.* 240, 87–94, <https://doi.org/10.1016/j.envpol.2018.04.113>.
- Xu, B., Liu, F., Brookes, P.C., Xu, J., 2018b. The sorption kinetics and isotherms of sulfamethoxazole with polyethylene microplastics. *Mar. Pollut. Bull.* 131, 191–196, <https://doi.org/10.1016/j.marpolbul.2018.04.027>.
- Zhan, Z., Wang, J., Peng, J., Xie, Q., Huang, Y., Gao, Y., 2016. Sorption of 3, 3', 4, 4'-tetrachlorobiphenyl by microplastics: A case study of polypropylene. *Mar. Pollut. Bull.* 110, 559–563, <https://doi.org/10.1016/j.marpolbul.2016.05.036>.
- Zhang, H., Wang, J., Zhou, B., Zhou, Y., Dai, Z., Zhou, Q., Chriestie, P., Luo, Y., 2018. Enhanced adsorption of oxytetracycline to weathered microplastic polystyrene: Kinetics, isotherms and influencing factors. *Environ. Pollut.* 243, 1550–1557, <https://doi.org/10.1016/j.envpol.2018.09.122>.
- Zuo, L.Z., Li, H.X., Lin, L., Sun, Y.X., Diao, Z.H., Liu, S., Zhang, Z.Y., Xu, X.R., 2019. Sorption and desorption of phenanthrene on biodegradable poly(butylene adipate co-terephthalate) microplastics. *Chemosphere* 215, 25–32, <https://doi.org/10.1016/j.chemosphere.2018.09.173>.