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Post COVID-19 pandemic: Disposable face masks as a potential vector of antibiotics in freshwater and seawater

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HIGHLIGHTS

• DFMs act as a potential vector of antibiotics in the freshwater and seawater systems.
• Higher sorption and desorption of antibiotics on DFMs in freshwater than in seawater.
• The log Kow of antibiotics can be used as an indicator of sorption affinity on DFMs.
• Solution pH plays a critical role in the antibiotics sorption and desorption process.
• Hydrophobic interaction regulates the sorption of the antibiotics onto the DFMs.

GRAPHICAL ABSTRACT

ABSTRACT

With the outbreak and widespread of the COVID-19 pandemic, large numbers of disposable face masks (DFMs) were abandoned in the environment. This study first investigated the sorption and desorption behaviors of four antibiotics (tetracycline (TC), ciprofloxacin (CIP), sulfamethoxazole (SMX), and triclosan (TCS)) on DFMs in the freshwater and seawater. It was found that the antibiotics in the freshwater exhibited relatively higher sorption and desorption capacities on the DFMs than those in the seawater. Here the antibiotics sorption processes were greatly related to their zwitterionic species while the effect of salinity on the sorption processes was negligible. However, the desorption processes were jointly dominated by solution pH and salinity, with greater desorption capacities at lower pH values and salinity. Interestingly, we found that the distribution coefficient (Kd) of TCS (0.3947 L/g) and SMX (0.0399 L/g) on DFMs was higher than those on some microplastics in freshwater systems. The sorption affinity of the antibiotics onto the DFMs followed the order of TCS > SMX > CIP > TC, which was positively correlated with octanol-water partition coefficient (log Kow) of the antibiotics. Besides, the sorption processes of the antibiotics onto the DFMs were mainly predominated by film diffusion and partitioning mechanism. Overall, hydrophobic interaction regulated the antibiotics sorption processes. These findings would help to evaluate the environmental behavior of DFMs and to provide the analytical framework of their role in the transport of other pollutants.

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1. Introduction

With the outbreak of the COVID-19 pandemic, citizens around the world are urged to the necessary use disposable face masks (DFMs), especially in public places (Li et al., 2021b). According to the World Health Organization (WHO) estimated, 89 million DFMs were used globally every day to prevent the widespread of the COVID-19 pandemic and its impact could last for decades (WHO, 2020). In the long run, DFMs will remain a...
necessary product to prevent the spread of the COVID-19 pandemic, hence the huge increase in global DFMs production, which will continue to increase in the coming years (Chowdhury et al., 2021; Fernández-Arribas et al., 2021).

Unfortunately, more than 10 million DFMs are abandoned in the environment each month due to poor handling and management (Adyel, 2020; Chen et al., 2021b). Once DFMs enter the environment, their impact on the environment is inevitable (Patrício Silva et al., 2021). For example, DFMs can act as carriers of some pollutants (Anastopoulos and Pashalidis, 2021) and viruses (Mol and Caldas, 2020) in the environment, which likely exacerbates the widespread of those pollutants. Ioannidis et al. (2021) highlighted that the DFMs could act as radionuclide (UR-232 and Ra-226) carriers even at ultra-trace concentrations. At solution pH 7, the distribution coefficients (Kd) values for Ra-226 ranged between 80 and 130 L/kg and for U-232 from 60 to 590 L/kg. Besides, Liu and Mabury (2021) and Fernández-Arribas et al. (2021) reported that DFMs were a potential source of synthetic phenolic and organophosphate antioxiyants to the environment. Recently, DFMs releasing numerous microplastics (< 5 mm) into the aquatic environment have been reported, greatly increasing microplastics pollution in the environment (Chen et al., 2021b; Fadare and Okofio, 2020; Li et al., 2021b; Ma et al., 2021; Morgana et al., 2021; Shen et al., 2021). It is estimated that 2.37 million tons of plastic waste from improperly disposed of DFMs enter the oceans each year in 46 coastal countries (Chowdhury et al., 2021). The increase in DFMs waste is recognized as a new source of contamination directly related to the COVID-19 pandemic (Sullivan et al., 2021). However, information regarding the underlying roles of DFMs in the environment is extremely lacking.

Antibiotics, as a kind of the emerging pollutants in natural aqueous environments, play an irreplaceable role in the treatment of human and animal diseases as well as aquaculture and land-based agriculture (Li et al., 2021c; Nguyen et al., 2021). According to Zhang et al. (2015), about 92,700 tons of antibiotics were used in China in 2013, of which 53,800 tons of antibiotics were released into the environment. Therefore, antibiotics were often detected in surface water, groundwater, and coastal water (Jurado et al., 2019; Li et al., 2020; Xie et al., 2019). Importantly, the residual antibiotics in the environments resulted in the generation and spread of antibiotic-resistant genes and antibiotic-resistance bacteria, posing a potential threat to ecological functions and even human health (Samanic et al., 2021; Zhao et al., 2021).

Considering that the environmental impact of DFMs remains largely underestimated and the increasing antibiotic contamination. The objectives of this study were to (1) investigate the sorption and desorption behaviors of tetracycline (TC), ciprofloxacin (CIP), sulfamethoxazole (SMX), and trimethoprim (TCS) onto DFMs in the freshwater and seawater systems through batch-type experiments; (2) elucidate the effects of environmental factors include salinity and pH on the sorption and desorption processes; (3) reveal the interaction mechanisms between DFMs and the antibiotics. Overall, our main purpose is to highlight that DFMs could act as a carrier of antibiotics in the environment. To the best of our knowledge, this is the first report on the potential role of DFMs as a vector of antibiotics in the freshwater and seawater systems.

2. Materials and methods

2.1. Materials and chemicals

We purchased DFMs from a Chinese e-commerce platform (JD. COM). The DFMs were chosen because they were the No. 1 sales on the platform in June and July 2021. Details of the DFMs were supplied in Table S1. Ciprofloxacin (CIP, ≥ 98%) and sulfamethoxazole (SMX, 98%) were purchased from Shanghai Aldadin Bio-Chem Technology Co. Ltd., China. Triclosan (TCS, 99%) was purchased from Shanghai Yuanye Biological Technology Co., Ltd., China. Tetracycline (TC, 98%) was purchased from Tianjin Xienai Biological Technology Co., Ltd., China. The physicochemical properties of the four antibiotics are summarized in Table S2. All the other chemicals used were analytical grade or higher purity.

2.2. Experimental procedures

The ultrapure water used was prepared from a Milli-Q water purification system (Milli-Q Reference, China). The freshwater was prepared by ultrapure water containing 0.01 M NaCl and the solution pH was adjusted to 7. To overcome the effects of analysis and seasonal variation of natural seawater in organic matter, we used artificial seawater instead of natural seawater to prepare repeatable seawater solutions of known components. Herein, the artificial seawater was prepared according to the previous paper (Mathew et al., 2016), as shown in Table S3, which was almost imitated natural seawater. The 100 mg/L stock solutions of TC were directly prepared in the ultrapure water and the artificial seawater. For SMX stock solutions (100 mg/L), 5 mL methanol was added to enhance their solubility in the above background solutions. The accurately weighed 0.1 g TCS was completely dissolved in 10 mL methanol to obtain a TCS stock solution (10 g/L). Because CIP is soluble in dilute hydrochloric acid solutions, the CIP stock solutions (100 mg/L) were prepared with ultrapure water or the artificial seawater and 1% methanol at pH 3.5 (Perniafel et al., 2011). The solution pH was adjusted using HCl or NaOH. All the stock solutions were stored in brown reagent bottles at 4 °C for no longer than 7 days. In this study, the final methanol concentration used in sorption experiments was maintained at <0.1% (v/v) to avoid co-solvent effects during the experiments.

All the antibiotics solutions with different concentrations were obtained by dilution of the pre-prepared stock solutions with different background solutions (the freshwater or the seawater). Batch sorption and desorption experiments were conducted at 25 °C and 150 rpm by a constant temperature air oscillator under dark conditions (Fang et al., 2019).

2.2.1. Sorption/desorption kinetics and isotherms

For sorption kinetics, a DFM (3.1228–3.2665 g) was put into a 250 mL brown glass reagent bottle with a lid. And then, 5 mg/L antibiotics (TC, CIP, SMX, and TCS) solutions with 200 mL volume were added to the flasks. Herein, the solution pH was adjusted to 7 (the freshwater system) or 8.18 (the seawater system) based on the different research backgrounds, respectively. The solution was collected at given time intervals (0.5, 1, 2, 4, 6, 12, 24, 36, 48, and 60 h), and the samples were stored in the dark at 4 °C until further analysis. For sorption isotherms, the initial concentrations of the four antibiotics of 1, 3, 5, 10, 20, 30, and 50 mg/L were used. According to different research systems, the freshwater or the seawater was selected as background correspondingly. All the other conditions (e.g., solution pH, DFM dosage, antibiotics solution volume) and operations were the same as those in kinetics experiments. The equilibration time for subsequent experiments was set to 36 h based on foregoing kinetic experiments.

Desorption experiments were implemented uniformly as the sorption experiments. Specifically, the DFMs in the sorption kinetic experiments (the initial concentration of antibiotics was 5 mg/L) were taken out at the sorption equilibrium, dried at room temperature, and then transferred to a 250 mL brown reagent flask. Next, 200 mL of the freshwater or the seawater was added to the flask. The solution was collected at given time intervals (0.5, 1, 2, 4, 6, 12, 24, 36, 48, and 60 h).
2.3. Characterization and analytical methods

The DFMs are mainly composed of four parts, namely outer layer, middle layer, inner layer, and ear band. Therefore, the DFMs were disassembled into four parts for the following characterization. The functional groups of DFMs with and without antibiotics sorbed were identified by Fourier transform infrared spectroscopy with attenuated total reflection equipment (ATR-FTIR, Bruker Vertex 70 V, Germany). The water contact angles of DFMs were measured by a contact angle goniometer (JY-82B Kruss DSA, Germany). X-ray diffraction (XRD, Ultima IV, Japan) was utilized to analyze the crystal structure and morphology of the DFMs. The surface morphology and elements of DFMs with and without antibiotics sorbed were characterized using a scanning electron microscope equipped with energy dispersive X-ray analysis (SEM-EDX, FEI NANO 450, USA).

The TC, CIP, SMX, and TCS concentrations were detected by UV/Vis spectrophotometer (Agilent 8453, USA) at a wavelength of 356, 277, 275, and 282 nm, respectively.

2.4. Mathematical models and data analyses

The amounts of antibiotics sorbed onto the DFMs were calculated according to Eq. (1):

\[ Q_t = \frac{V(C_0 - C_t)}{m} \]

in which \( Q_t (\mu g/g) \) and \( C_t (\mu g/L) \) are the sorption capacities and concentrations of adsorbates at time \( t \), respectively; \( C_0 (\mu g/L) \) is the initial concentration of antibiotics; \( m (g) \) is the weight of DFMs, and \( V (L) \) represents the volume of antibiotics solution. When the sorption reaches equilibrium, \( C_e = C_t \), \( Q_e = Q_t \), where \( C_e (\mu g/L) \) and \( Q_e (\mu g/g) \) are the antibiotics concentrations and sorption capacities at equilibrium, respectively.

Details of the mathematical models and the statistical parameters for the antibiotics sorption onto the DFMs (i.e., intra-particle diffusion, Boyd, Langmuir, Freundlich, and Linear models) are shown in the Supplementary Information.

3. Results and discussion

3.1. Characterization of DFM

The photographs, SEM images, EDX spectra, contact angles, and XRD spectra of the outer layer, middle layer, inner layer, and ear ribbon of the DFMs are shown in Fig. 1. From the SEM images, we can observe that the outer layer, middle layer, inner layer, and ear ribbon of the DFMs are composed of many cylindrical fibers, which may provide sufficient sorption sites for pollutants. The contact angles of the outer layer, middle layer, inner layer, and ear ribbon of the DFMs are 112.62°, 126.05°, 116.66°, and 119.39°, respectively, which indicates that the surface of DFMs exhibits a high hydrophobicity. Hereby, some antibiotics may be sorbed onto the DFMs through hydrophobic interaction in aquatic environments (Li et al., 2019). Xu et al. (2018a) pointed out that TC could be sorbed on the hydrophobic surface of microplastics through hydrophobic interaction. Xu et al. (2018b) also found that the sorption mechanism between SMX and hydrophobic microplastics was the hydrophobic interaction. As shown in EDX spectra, only C elements appear in the outer layer, middle layer, and inner layer, while the ear ribbon presents C and O elements (H elements can not be displayed in EDX spectra). Further, we confirm that the outer layer, middle layer, and inner layer are composed of polypropylene (PP) while the ear ribbon is made of polyethylene terephthalate (PET) through the XRD (Fig. 1) (Li et al., 2018; Silvia et al., 2021; Usman et al., 2021) and FTIR spectra (Fig. S1) (Munoz et al., 2021; Shen et al., 2021). Besides, FTIR was employed to analyze the changes of the surface functional groups of the DFMs before and after the antibiotics sorption. As can be seen in Fig. 1. The photographs, SEM images, EDX spectra, contact angle, and XRD spectra (from left to right) of outer layer, middle layer, inner layer, and ear ribbon of the DFMs (from top to bottom).
Fig. S1, the peaks at 2955–2835 cm\(^{-1}\) represent the CH stretching vibrations of aliphatic structures (–CH\(_2\), –CH\(_3\), and –CH\(_2\)-CH\(_2\)) (Charles et al., 2009). The peaks at 1000–720 cm\(^{-1}\) are ascribable to the CH vibration out of plane (Muñoz-González et al., 2009). The peaks at 1507–1336 cm\(^{-1}\) are assigned to CC stretching (Chang et al., 2009). For the ear ribbon (PET fibers), the peaks at roughly 1717 and 1246 cm\(^{-1}\) are attributed to the CH and CH stretching of –COOH (Park et al., 2005).

For the sorption of antibiotics onto the DFMs, no new peaks appeared or disappeared, which indicates that the sorption process is dominated by physical force (Anastopoulos et al., 2021).

### 3.2. Sorption kinetics

Fig. 2 (a & b) shows the temporal profiles of sorption amounts of the antibiotics onto the DFMs in the freshwater and seawater. It is found that the antibiotics sorption onto the DFMs increased promptly within 6 h, and then gradually increased or decreased until the sorption reach equilibrium (about 36 h). The sorption capacities of the DFMs fluctuated slightly after the sorption reach equilibrium, which possibly indicates that the interaction force between the antibiotics and the DFMs is relatively weak (Yu et al., 2020a). Besides, the antibiotics sorption capacities of the DFMs vary greatly in both the freshwater and seawater systems, with greater sorption capacities in the freshwater. Differences in salinity and solution pH might be the key factors causing the different sorption capacity. The sequence of the sorption capacity is in order of TCS > SMX > CIP > TC. This result indicates that the sorption behaviors onto the DFMs can be affected by the properties of antibiotics (Li et al., 2018). Chen et al. (2020) also found that the sorption affinity of MnFe\(_2\)O\(_4\)@cellulose activated carbon for six typical antibiotics followed chloramphenicol > sulfadimethoxine > sulfamethizole > sulfamethazine > SMX > TC, which was dependent on the molecular structures or sizes of the antibiotics. In general, the sorption affinity will be positively correlated with the log \(K_{\text{ow}}\) of antibiotics if hydrophobic distribution plays an important role in the sorption process (Li et al., 2018). As shown in Fig. 3, the correlation between \(Q_e\) and log \(K_{\text{ow}}\) of the antibiotics in the freshwater and seawater systems displays the excellent linear (Adj.\(R^2\) = 0.9443 (\(p = 0.01875\)) and 0.8539 (\(p = 0.04993\)), further confirming that the sorption processes are dominated by hydrophobic interaction (Choi and Lee, 2017; Hüffer and Hofmann, 2016). Li et al. (2018) pointed out that microplastics exhibited relatively stronger sorption capacity for CIP than that for TC due to the larger log \(K_{\text{ow}}\) value of CIP. Wu et al. (2019) also found that the adsorption capacities for five bisphenol analogs on PVC microplastics were in order of bisphenol AF > bisphenol B > bisphenol A > bisphenol F > bisphenol S, which was linear with the log \(K_{\text{ow}}\) of these bisphenol analogs.

Furthermore, intraparticle diffusion and Boyd (film diffusion) models were employed to investigate the diffusion behaviors of the antibiotics’ sorption processes. In general, intraparticle diffusion model assumes that the sorption process is proceeded by sorbate diffusion into the internal particles (Wang et al., 2020). The Boyd model assumes that the sorption process is mainly controlled by intraparticle diffusion if the data in the Boyd plot are linear and pass through the origin, otherwise, film diffusion is the rate-limiting step of the sorption process (Boyd et al., 1947). The plots of fitting intraparticle diffusion model (\(Q_e\) versus \(t^{1/2}\)) are displayed in Fig. 4, and the related parameters of \(K_{\text{ad}}\), \(C_i\), and Adj.\(R^2\) are given in
3.3. Sorption isotherms

Fusion is the main diffusion mechanism in the sorption processes. The sorption processes of the antibiotics are mainly dominated by partitioning (Jensen et al., 2013). Overall, we conclude that the antibiotics sorption onto the DFMs involves multiple diffusion processes, among which film diffusion is the main diffusion mechanism in the sorption processes.

3.4. Influence of solution pH and salinity on the sorption processes

The solution pH is a critical parameter in different aqueous solutions, which can influence the proton state and sorption performance of antibiotics. As shown in Fig. 6 (a, c, e, g), the TC, CIP, and SMX can form three species (zwitterion, cation, and anion) due to protonation and deprotonation, while TCS can only form zwitterion and anion. Interestingly, it can be clearly observed that the sorption capacities \( Q_e \) of the four antibiotics in the freshwater and seawater systems follow the order of TCS > SMX > CIP > TC, which is positively correlated with the log \( K_{ow} \) values of the antibiotics. The sorption capacities of the antibiotics onto the DFMs in the seawater system are significantly lower than those in the freshwater system, which may be related to the difference in salinity and solution pH in these water systems as above mention (Li et al., 2018). Furthermore, the sorption isotherms of the antibiotics onto the DFMs appear the same growth trend, that is, the equilibrium sorption capacities increased linearly with the increase of the initial concentration of the antibiotics. Therefore, the fitting curves of sorption isotherms based on linear model are shown in Fig. 2 (c & d). In addition, the fitted Linear, Freundlich, and Langmuir parameters are listed in Table S5. The experimental data fitted Linear, Freundlich, and Langmuir isotherm models well according to the higher values of \( Adj.R^2 \) (0.9025–0.9997). Whereas, the \( n_f \) values of Freundlich model are approximately equal to 1 and the \( K_f \) values of Langmuir model are extremely close to 0, which indicates that the Freundlich and Langmuir equations tend to be Linear equation. Therefore, the sorption processes of the antibiotics onto DFMs in the freshwater and seawater are best described by Linear model, which implies that the sorption processes are predominated by partitioning mechanism (Liu et al., 2019; Wang et al., 2018). As shown in the SEM-EDX mapping (Fig. 5), some elements that only appear in the antibiotics in contrast to the DFMs, such as N and O elements of TC, were evenly sorbed onto the DFMs, which further suggests that the partitioning play a crucial role in the sorption processes. The distribution coefficient \( (K_d) \) value represents the sorption affinity between the antibiotics and DFMs (Lin et al., 2021b). As summarized in Table S5, the \( K_d \) values of the antibiotics in the freshwater and seawater system are in order of TCS (0.3947 L/g) > SMX (0.0399 L/g) > CIP (0.0114 L/g) > TC (0.0014 L/g) and TCS (0.3924 L/g) > SMX (0.0018 L/g) > TC (0.0011 L/g) > CIP (0.0005 L/g), respectively. This result implies that the TCS exhibits a relatively higher affinity to be sorbed onto the DFMs, which may be related to the hydrophobic nature of antibiotics mentioned above. Considering that plastic fibers (PP and PET) are the main components of the DFMs, here we summarize some \( K_d \) values of antibiotics sorbed onto microplastics in Table 1. It is noteworthy that the \( K_d \) values of SMX (0.0399 L/g) and TCS (0.3947 L/g) sorption onto the DFMs in the freshwater system are higher than those onto some microplastics (e.g., PP, PS, and PET) (Li et al., 2019; Guo et al., 2019). Therefore, the sorption abilities of the DFMs as the antibiotics carriers in the environment should not be underestimated.

Table S4. As shown in Fig. 4, the sorption processes of the antibiotics onto the DFMs are divided into two or three stages (multi-linear plots), which likely suggests that multiple sorption behaviors (e.g., film diffusion, intraparticle diffusion, and dynamic equilibrium) exist in the sorption processes (Fierro et al., 2008; Wang et al., 2020). Generally, the foremost linear stages are related to the film transport (the boundary layer diffusion), and the subsequent linear stages represent intraparticle diffusion and/or sorption dynamic equilibrium (Wang et al., 2020; Wu et al., 2019; Zhang et al., 2018a). Here the extending line of the second stage deviates from the origin, that is the \( C_i \neq 0 \) (Table S4), which indicates that the films diffusion and intraparticle diffusion are concurrently operating in the whole sorption process of the antibiotics onto the DFMs (Alkurdi et al., 2021; Martins et al., 2015). The Boyd plots are procured by plotting \( B_i \) versus \( f \). As shown in Fig. S2, the Boyd plots of TC, CIP, SMX, and TCS sorption appear non-linear but close to the origin, which attests that the sorption processes of the antibiotics are mainly dominated by film diffusion (Cáceres-Jensen et al., 2013). Overall, we conclude that the antibiotics sorption onto the DFMs involves multiple diffusion processes, among which film diffusion is the main diffusion mechanism in the sorption processes.

3.3. Sorption isotherms

The dynamics equilibrium relationship between the antibiotics and the DFMs in the freshwater and seawater systems is displayed in Fig. 2 (c & d). Like the above kinetics analyses, the antibiotics sorption capacities of the DFMs in both the freshwater and seawater systems follow the order of TCS > SMX > CIP > TC, which is positively correlated with the log \( K_{ow} \) values of the antibiotics. The sorption capacities of the antibiotics onto the DFMs in the seawater system are significantly lower than those in the freshwater system, which may be related to the difference in salinity and solution pH in these water systems as above mention (Li et al., 2018). Furthermore, the sorption isotherms of the antibiotics onto the DFMs appear the same growth trend, that is, the equilibrium sorption capacities increased linearly with the increase of the initial concentration of the antibiotics. Therefore, the fitting curves of sorption isotherms based on linear model are shown in Fig. 2(c & d). In addition, the fitted Linear, Freundlich, and Langmuir parameters are listed in Table S5. The experimental data fitted Linear, Freundlich, and Langmuir isotherm models well according to the higher values of \( Adj.R^2 \) (0.9025–0.9997). Whereas, the \( n_f \) values of Freundlich model are approximately equal to 1 and the \( K_f \) values of Langmuir model are extremely close to 0, which indicates that the Freundlich and Langmuir equations tend to be Linear equation. Therefore, the sorption processes of the antibiotics onto DFMs in the freshwater and seawater are best described by Linear model, which implies that the sorption processes are predominated by partitioning mechanism (Liu et al., 2019; Wang et al., 2018). As shown in the SEM-EDX mapping (Fig. 5), some elements that only appear in the antibiotics in contrast to the DFMs, such as N and O elements of TC, were evenly sorbed onto the DFMs, which further suggests that the partitioning play a crucial role in the sorption processes. The distribution coefficient \( (K_d) \) value represents the sorption affinity between the antibiotics and DFMs (Lin et al., 2021b). As summarized in Table S5, the \( K_d \) values of the antibiotics in the freshwater and seawater system are in order of TCS (0.3947 L/g) > SMX (0.0399 L/g) > CIP (0.0114 L/g) > TC (0.0014 L/g) and TCS (0.3924 L/g) > SMX (0.0018 L/g) > TC (0.0011 L/g) > CIP (0.0005 L/g), respectively. This result implies that the TCS exhibits a relatively higher affinity to be sorbed onto the DFMs, which may be related to the hydrophobic nature of antibiotics mentioned above. Considering that plastic fibers (PP and PET) are the main components of the DFMs, here we summarize some \( K_d \) values of antibiotics sorbed onto microplastics in Table 1. It is noteworthy that the \( K_d \) values of SMX (0.0399 L/g) and TCS (0.3947 L/g) sorption onto the DFMs in the freshwater system are higher than those onto some microplastics (e.g., PP, PS, and PET) (Li et al., 2019; Guo et al., 2019). Therefore, the sorption abilities of the DFMs as the antibiotics carriers in the environment should not be underestimated.

![Fig. 3. Correlation between the \( Q_e \) and octanol-water partition coefficients (log \( K_{ow} \)) of the four antibiotics in the freshwater (a) and seawater (b).](image-url)
Fig. 4. Intraparticle diffusion plots for TC (a, b), CIP (c, d), SMX (e, f), and TCS (g, h) sorption onto DFMs in the freshwater (left column) and the seawater systems (right column).
Hereby, we conclude that the sorption capacities of the antibiotics onto the DFMs in the seawater are lower than those in the freshwater mainly due to the influence of the solution pH. Similar results were reported by Li et al. (2018) who studied that antibiotics sorption onto microplastics in freshwater and seawater.

Furthermore, the influence of NaCl content on the sorption process was also investigated. As seen in Fig. S3, with the increase of NaCl concentration from 0% to 3.5%, no significant variation is observed in the sorption capacities of the four antibiotics sorption onto the DFMs. This result indicates that the interaction mechanisms between the four antibiotics and the DFMs are not dominated by cation exchange and electrostatic interaction (Wang et al., 2015; Xu et al., 2018a; Yu et al., 2020a). Meanwhile, it further highlights that hydrophobic interaction likely plays a decisive role in the antibiotics sorption process (Lin et al., 2021a). Similar findings have also been reported in previous studies on the sorption behavior between plastics fibers and antibiotics (Li et al., 2019; Lin et al., 2021a, 2020; Xu et al., 2018a, 2018b; Zhang et al., 2018b). The result also confirms that solution pH can be regarded as a key factor for the antibiotics sorption in the freshwater and seawater.

### 3.5. Desorption behaviors of the four antibiotics from the DFMs

Desorption kinetics of TC, CIP, SMX, and TCS from the DFMs in the freshwater and seawater systems are shown in Fig. S4. All the desorption process increased drastically during the first 2 h and then reached dynamic equilibrium within 12 h. Fig. 7 summarizes the desorption rate (%) for the release of the antibiotics from the DFMs in the freshwater and seawater, and the results show two interesting phenomena. On the one hand, the desorption rate of TC, CIP, SMX, and TCS in the freshwater is 23.58%, 23.17%, 21.75%, and 12.9%, respectively, which is inversely proportional to the log $K_{ow}$ of the four antibiotics. Razanajatovo et al. (2018) suggested that high desorption rates of propranolol and sertraline were due to hydrophobic interactions with PE microplastics. Besides, more hydrophobic antibiotics (e.g., TCS and SMX with higher log $K_{ow}$) can be more easily

### Table 1

Comparison of $K_d$ (L/g) between the results of this work and others found in the literatures.

| Types of plastics (size) | TC     | CIP    | SMX    | TCS    | Medium | References |
|-------------------------|--------|--------|--------|--------|--------|------------|
| PP and PET (DFMs)       | 0.0014 | 0.0114 | 0.0399 | 0.3947 | Freshwater | This work  |
| PP and PET (DFMs)       | 0.0011 | 0.0005 | 0.0018 | 0.3924 | Seawater  |            |
| PP (75–180 μm)          | 0      | 0.0571 | NM     | NM     | Freshwater | (Li et al., 2018) |
| PP (75–180 μm)          | 0      | 0      | NM     | NM     | Seawater  |            |
| PE (125 μm)             | 0.0670 | NM     | NM     | NM     | Freshwater | (Yu et al., 2020a) |
| PS (74 μm)              | 0.0580 | NM     | NM     | NM     | Freshwater | (Yu et al., 2020b) |
| PVC (74 μm)             | 0.0550 | NM     | NM     | NM     | Freshwater | (Yu et al., 2020b) |
| PS (~ 75 μm)            | 0.2100 | NM     | NM     | NM     | Freshwater | (Lin et al., 2019) |
| aged PS (~ 75 μm)       | 0.3180 | NM     | NM     | NM     | Seawater  |            |
| PVC (~ 75 μm)           | 0.2150 | NM     | NM     | NM     | Freshwater | (Lin et al., 2019) |
| aged PVC (~ 75 μm)      | 0.2510 | NM     | NM     | NM     | Seawater  |            |
| Aged PS (0.5–2 mm)      | 0.0328 | NM     | NM     | Freshwater | (Guo and Wang, 2019) |
| PP (100–150 μm)         | 0      | 0.0309 | NM     | NM     | Freshwater | (Guo et al., 2019) |
| PET (100–150 μm)        | 0      | 0.0222 | NM     | NM     | Freshwater | (Guo et al., 2019) |
| PP (63–125 μm)          | 0      | 0.0010 | NM     | Freshwater | (Puckowski et al., 2021) |
| PE (~ 150 μm)           | 0.5917 | NM     | NM     | Freshwater | (Xu et al., 2018b) |
| PS (106.9 μm)           | 0.1600 | NM     | NM     | Freshwater | (Li et al., 2019) |
| PCV (~ 1 μm)            | 1.3500 | NM     | NM     | Freshwater | (Ma et al., 2019) |
| PCV (100 μm)            | 1.0500 | NM     | NM     | Freshwater | (Ma et al., 2019) |
| PE (~ 225 μm)           | 0.0000 | NM     | NM     | Freshwater | (Chen et al., 2021a) |
| PS (~ 225 μm)           | 0.2600 | NM     | NM     | Freshwater | (Gao et al., 2018) |
| PP (~ 75 μm)            | 0.9413 | NM     | NM     | Freshwater | (Gao et al., 2018) |

Note: Abbreviations: PP (Polypropylene); PET (Polypropylene Terephthalate); PS (Polystyrene); PVC (Polyvinyl Chloride); PE (Polyethylene); NM (Not mentioned).
entrapment in the inner spaces of the DFMs due to hydrophobic interactions, but this is not energetically conducive to their subsequent desorption behaviors in freshwater (Wu et al., 2020). However, less hydrophobic antibiotics (e.g., TC and CIP) seem less likely to enter the internal field of the DFMs and then surface sorption onto the DFMs. Therefore, the desorption processes of TC and CIP from the DFMs are more reversible than that of

Fig. 6. The species fraction of TC (a), CIP (c), SMX (e), and TCS (g) as function of solution pH (left column); Influence of pH on the sorption of TC (b), CIP (d), SMX (f), and TCS (h) onto DFMs (right column).
The desorption processes were jointly dominated by solution pH and salinity, with greater desorption rates in the seawater than those in the freshwater. The antibiotics sorption processes were comprehensively studied. Results revealed that the antibiotics exhibited different sorption behaviors in the freshwater and seawater.

4. Conclusions

Herein, the sorption and desorption behaviors of the four antibiotics (TC, CIP, SMX, and TCS) on DFMs in the freshwater and seawater were comprehensively studied. Results revealed that the antibiotics exhibited relatively higher sorption and desorption capacities on the DFMs in the freshwater than those in the seawater. The antibiotics sorption processes were greatly related to their zwitterion species while the effect of salinity on the sorption processes was negligible. However, the desorption processes were jointly dominated by solution pH and salinity, with greater desorption capacities at lower pH values and salinity. The log \( K_{\text{d}} \) of the antibiotics could be used as an indicator parameter to the sorption affinity between the DFMs and the antibiotics. Besides, the sorption processes of the antibiotics on the DFMs were mainly predominated by film diffusion and partitioning mechanism, and hydrophobic interaction regulated the sorption processes. Results from this study provided new insights into the interaction mechanisms between the DFMs and the antibiotics, which would help to evaluate the environmental behavior of DFMs and to provide the analytical framework of their role in the transport of other pollutants. We also advocated for strengthening the responsible regulation of DFMs, especially during the COVID-19 pandemic. It was noted that some oxygen-containing functional groups and biofilms might be presented on the surface of DFMs due to their long-term exposure to the aquatic environment. Therefore, future studies should be considering the influence of changes in DFMs surface in the natural environment on the migration and fate of pollutants.

**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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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.153049.

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