Supporting Information for

Interaction of disposable face masks (nano)microplastics with antibiotics: performance and mechanisms

Ting Zhang[1],Xi Chen[1,2],Angrui Jiang[1,2], Jingfan Qi[1,2], Zhaoyang You[1, *], Kinjal J. Shah[1,*]

[1]College of Urban Construction, Nanjing Tech University, Nanjing, 211800, China

[2]Yangtze River Innovation Center for Ecological Civilization, Nanjing, 211800, China

2.7 Sorption models and data analyses

The adsorption of pollutants by (nano)microplastic in solution is a complex process that can be controlled through the following steps: first, the spreading of the pollutants into the surrounding boundary layer; The second is film transport, in which pollutants diffuse through the liquid film around the microplastic; The third point is the diffusion and adsorption of pollutants between microplastic particles. In this study, in-particle diffusion and Boyd's model were applied to determine the diffusion mechanism in the adsorption system.

Pseudo-first reaction kinetic model (PFO) [1]:

$$Q_t = Q_{e,1}\left(1 - e^{-K_1 t}\right) \tag{1}$$

The parameters in the formula are expressed as follows: Q_t represents the adsorption capacity at a certain time, mg/g; $Q_{e,1}$ represents the adsorption amount at equilibrium reaction, mg/g; K_1 is a quasi-first-order rate constant, h^{-1}; t stands for adsorption time, h.

Pseudo-second-order kinetic model (PSO) [2]:

$$Q_t = \frac{K_2 Q_{e,2}^{2} t}{1 + K_2 Q_{e,2}} \quad (2)$$

In the formula, K_2 is the rate constant of the pseudo-second-order kinetic model, g/mg·h; The other parameters are the same as those of the pseudo-first-order dynamics model.

Intra-particle diffusion[3]：

$$Q_t = k_{id} t^{0.5} \quad (3)$$

Where, kid is the intra particle diffusion constant (mg/g·$h^{1/2}$), and its value can determine the different stages of mass decline of adsorbed material. C_i is a parameter related to the thickness of the microplastic boundary layer, μg/g.

- Boyd membrane diffusion model equation [4]:

$$F(t) = \frac{q}{q_e} = 1 - \left(\frac{6}{\pi^2}\right) \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) exp\left(-n^2 B_t\right) \quad (4)$$

- Simplified conversion is obtained:

$$B_t = -\ln\left(1 - \frac{Q_t}{Q_e}\right) - 0.4977 \quad (5)$$

Where F is the fraction that reaches equilibrium at different times t; Bt is Boyd constant; Qe represents the equilibrium adsorption capacity of the antibiotic, μg/g. Calculate the value of Bt based on the value of each Qt, and then plot it against t. By applying the Fourier transform, then integrating as follows:

$$For\ Fvalues > 0.85 \Rightarrow B_t = -\ln(1 - F) - 0.4977 \quad (6)$$

$$For\ Fvalues < 0.85 \Rightarrow B_t = -\ln(\sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 F}{3}}) \quad (7)$$

Where, qt (μg/g) is the adsorption value of pollutants on microplastics at time t (h); qe (μg/g) is the equilibrium adsorption capacity; Kid ((μg/ (g·h0.5)) is a parameter related to the phase i diffusion rate. Ci (μg/g) is a parameter related to the thickness of the (nano)microplastic boundary layer, and Bt is Boyd constant.

The adsorption isotherm model is as follows:

Langmuir model[5]：

$$Q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{8}$$

Freundlich model[4]:

$$Q_e = K_f C^{1/n} \tag{9}$$

Where, qe is the equilibrium adsorption capacity of antibiotics,μg/g; Ce is the equilibrium concentration of antibiotics,mg/L; qmax is the maximum adsorption capacity of antibiotics in Langmuir model (μg/g). KL is the parameter of Langmuir's model,L/mg; n is the linear exponent in Freundlich's model; Kf is the parameter of the Freundlich model, (μg/g)/(mg/L).

Reference:

[1]Zhou Z, Sun Y, Wang Y, et al. Adsorption behavior of Cu(II) and Cr(VI) on agedmicroplastics in antibiotics-heavy metals coexisting system[J]. Chemosphere, 2022,291:132794.DOI:10.1016/j.chemosphere.2021.132794.

[2]Ho Y S, McKay G. The kinetics of sorption of divalent metal ions onto sphagnum moss peat[J]. Water research (Oxford), 2000,34(3):735-742.DOI:10.1016/S0043-1354(99)00232-8.

[3]Lin L, Yuan B, Hong H, et al. Post COVID-19 pandemic: Disposable face masks as a potential vector of antibiotics in freshwater and seawater[J]. Science of The Total Environment, 2022,820:153049.DOI:10.1016/j.scitotenv.2022.153049.

[4]Wang J, Guo X. Adsorption kinetic models: Physical meanings, applications, and solving methods[J]. J Hazard Mater, 2020,390:122156.DOI:10.1016/j.jhazmat.2020.122156.

[5] Lin L, Yuan B, Zhang B, et al. Uncovering the disposable face masks as vectors of metal ions (Pb(II), Cd(II), Sr(II)) during the COVID-19 pandemic[J]. Chemical Engineering Journal, 2022,439:135613.DOI:10.1016/j.cej.2022.135613.

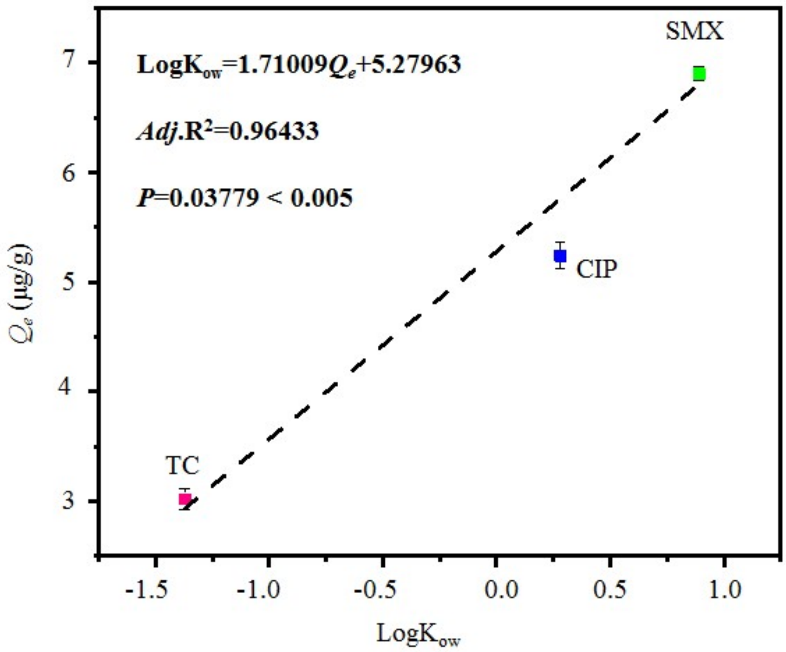


Fig.**S1** Linear relationship between Q_e and octanol-water partition coefficient (log Kow) of three antibiotics in pure water

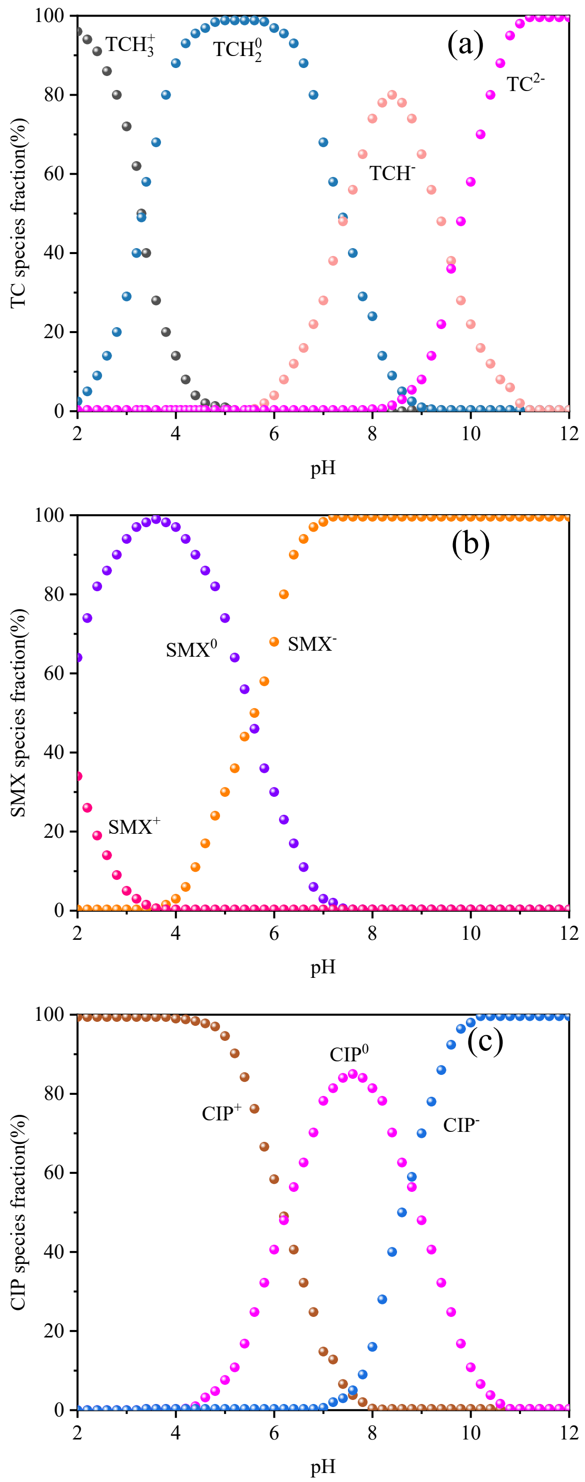


Fig. S2. Change of species fraction of TC (a), SMX (b), CIP (c) with pH value of solution

Table S1
Physicochemical properties of tested antibiotics

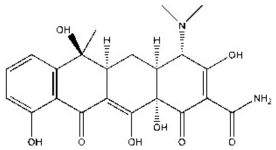
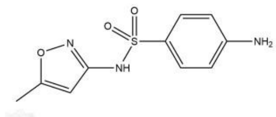
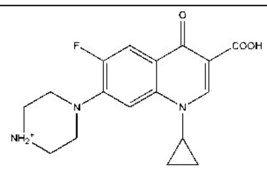
Antibiotics	Molecular formula	structure	Log Kow	pKa
Tetracycline (TC)	$C_{22}H_{24}N_2O_8$		-1.37	pKa1 = 3.3 pKa2 =7.7 pKa3 = 9.7
Sulfamethoxazole (SMX)	$C_{10}H_{11}N_3O_3S$		0.89	pKa1 = 1.6 pKa2 =5.7
Ciprofloxacin (CIP)	$C_{17}H_{18}FN_3O_3$		0.28	pKa1 = 6.1 pKa2 = 8.7

Table S2 Pseudo-first-order kinetic and pseudo-second-order kinetic parameters of antibiotics adsorbed by (nano)microplastics in masks

Antibiotic	Parametric					
	Pseudo-first-order dynamics			Pseudo-second-order dynamics		
	$K_1(h^{-1})$	$Q_{e,1}$(ug/g)	*Adj*.R^2	K_1(g/(ug/h))	$Q_{e,2}$(ug/g)	*Adj*.R^2
Origin outer						
SMX	3.152	1.494	0.739	0.073	6.942	0.937
CIP	6.555	0.374	0.867	0.009	6.281	-18.810
TC	4.263	1.538	0.827	0.728	3.286	0.913
Aged outer						
SMX	3.111	1.851	0.840	0.849	3.252	0.918
CIP	6.562	0.205	0.811	0.055	7.013	0.926
TC	3.741	2.042	0.257	0.605	4.134	0.682
Origin middle						
SMX	2.973	0.413	0.220	0.277	3.149	0.820
CIP	9.585	0.268	0.899	0.022	11.858	0.950
TC	4.123	1.525	0.569	0.432	4.392	0.856
Aged middle						
SMX	3.189	0.234	0.498	0.143	3.418	0.735
CIP	9.445	0.275	0.955	0.029	10.533	0.979
TC	4.455	1.416	0.929	0.558	4.617	0.806
Origin inner						
SMX	2.582	1.757	0.172	0.711	2.760	0.685

CIP	5.899	0.685	0.912	0.105	6.889	0.947
TC	3.677	1.564	0.700	1.738	3.772	0.813
Aged inner						
SMX	2.598	0.744	0.009	0.737	2.754	0.686
CIP	7.677	0.147	-0.511	0.117	0.799	0.953
TC	4.213	1.660	0.621	0.557	4.446	0.813

Table S3

Intraparticle diffusion parameters of antibiotics adsorbed by microplastics in masks

Antibiotic	Intraparticle diffusion model parameters								
	First stage			Second stage			Third stage		
	K_{id} (μg/(g·h$^{0.5}$))	C_i (μg/g)	$Adj.R^2$	K_{id} (μg/(g·h$^{0.5}$))	C_i (μg/g)	$Adj.R^2$	K_{id} (μg/(g·h$^{0.5}$))	C_i (μg/g)	$Adj.R^2$
Origin outer									
SMX	2.2970	0.2797	0.9613	0.5295	5.4073	0.9936	-0.6571	13.3270	0.9452
CIP	1.8429	0.5408	0.9690	-0.1194	4.3206	0.7347	0.3810	1.8974	0.7242
TC	1.6937	-0.8209	0.9754	0.5759	0.8044	0.9544	0.5202	-0.0829	0.7289
Aged outer									
SMX	6.6024	-0.4785	0.9393	0.7126	10.2598	0.8933	-	-	-
CIP	3.1155	0.6420	0.8966	0.4240	5.5756	0.9198	-0.1536	8.4434	0.7249
TC	3.5535	0.3571	0.9189	0.5857	4.6493	0.9409	-0.2925	9.7059	0.9965
Origin middle									
SMX	4.1134	-1.6346	0.8518	1.2451	0.7628	0.9881	-0.3101	8.5756	0.3381
CIP	2.0258	1.2696	0.9057	1.4532	1.7765	0.9203	0.3562	6.4334	0.7478
TC	0.9048	0.4688	0.8508	-0.0471	3.2129	0.2947	-	-	-
Aged middle									
SMX	3.9667	1.2735	0.8489	-0.1605	9.8510	0.9987	0.5697	6.3141	0.8571
CIP	1.2489	1.2011	0.7079	0.3841	2.6712	0.8690	-0.1497	5.3951	0.6631
TC	3.8863	-1.1702	0.9326	-0.1844	6.4757	0.6672	0.4387	3.5292	0.7925
Origin inner									
SMX	2.5417	0.8721	0.9149	-0.3053	8.7798	0.4278	-0.8251	14.3439	0.8214

CIP	1.9752	0.1579	0.5792	0.2216	2.8499	0.8496	-	-	-
TC	4.7802	-1.9806	0.9861	1.3444	0.1925	0.8139	-0.1083	4.5061	0.9780
Aged inner									
SMX	3.6740	2.3337	0.9699	0.2602	11.6269	0.4264	-	-	-
CIP	2.2664	1.7643	0.8768	0.4106	6.5092	0.2303	0.8345	3.8468	0.8917
TC	2.6716	1.1051	0.9740	-0.3244	9.6888	0.9979	0.3479	6.3339	0.8530

Table S4

Isothermal model parameters of microplastic adsorption data on origin and aging masks of antibiotics

Antibiotic	Freundlich model			Langmuir model		
	K_F(L/g)	n_f	*Adj.R*^{2}	K_L(L/μg)	Q_m(μg/g)	*Adj*.R^2
			Origin outer			
TC	0.0259	1.5825	0.9454	1049.5941	3.0822E-5	0.9485
SMX	0.2189	1.6612	0.8994	81.2873	1.8957E-4	0.8244
CIP	0.0473	1.3324	0.9714	128.4477	5.7648E-5	0.9592
			Aged outer			
TC	0.1279	1.7568	0.9667	30.7448	2.7102E-4	0.9084
SMX	0.1140	1.2526	0.9736	391.4255	7.6058E-5	0.9884
CIP	0.0079	1.0310	0.9890	16138.7045	3.7616E-7	0.9886
			Origin middle			
TC	1.8687E-4	0.8315	0.7876	209006.0912	5.6054E-9	0.7856
SMX	9.1318E-5	0.6759	0.9858	2.0377E6	3.5590E-9	0.9583
CIP	0.1132	1.5200	0.9525	77.3341	1.5181E-4	0.9249
			Aged middle			
TC	0.0025	1.0029	0.9542	9635.3583	2.5652E-7	0.9542
SMX	0.0880	1.2526	0.9732	298.4014	7.8425E-5	0.9879
CIP	5.0016E-4	0.7776	0.9916	229565.1148	2.7440E-8	0.9659
			Origin inner			
TC	0.0162	1.3489	0.9475	21.8272	1.5420E-4	0.951

SMX	0.0251	1.1300	0.9832	468.7538	2.2474E-5	0.9799
CIP	0.0865	1.3783	0.9342	147.3713	8.1695E-5	0.9171
			Aged inner			
TC	0.0194	1.2559	0.9823	66.3926	7.3366E-5	0.9897
SMX	0.0382	1.1053	0.9744	28969.8989	5.7467E-7	0.9688
CIP	0.0705	1.2742	0.9744	212.6909	8.0515E-5	0.9866