

## Supplementary Information

### **A potential threat from biodegradable microplastics: mechanism of cadmium adsorption and desorption in the simulated gastrointestinal environment**

Jiang Timing<sup>1,3</sup>, Wu Xiang<sup>1,2\*</sup>, Yuan Shushan<sup>1,3\*</sup>, Lai Changfei<sup>1,3</sup>, Bian Shijie<sup>1,3</sup>, Yu Wenbo<sup>1,3</sup>, Liang Sha<sup>1,3</sup>, Hu Jingping<sup>1,3</sup>, Huang Liang<sup>1,3</sup>, Duan Huabo<sup>1,3</sup>, Shi Yafei<sup>4</sup>,  
Yang Jiakuan<sup>1,3,5</sup>

1. School of Environmental Science & Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
2. School of Resources and Environmental Science, Hubei University, Wuhan 430062, China
3. Hubei Provincial Engineering Laboratory for Solid Waste Treatment Disposal and Recycling, Wuhan 430074, China
4. School of Civil Engineering, Architecture and Environment, Hubei University of Technology, Wuhan 430068, China
5. State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China

\* Corresponding author: Prof. Shushan Yuan, E-mail: [yuanss@hust.edu.cn](mailto:yuanss@hust.edu.cn), Tel.: +86-27-87792207; Assoc. Prof. Xiang Wu, E-mail: [xiangwu@hubu.edu.cn](mailto:xiangwu@hubu.edu.cn), Tel.: +86-27-88661699-8210.

## Text S1 Adsorption kinetics and isotherms models

The adsorption kinetics models are presented as Eqs. (S1)–(S4) (Lagergren, 1898; Boyd et al., 1947; Weber and Morris, 1963; Ho and McKay, 2000):

$$\text{Pseudo-first-order model} \quad q_t = q_e(1 - e^{-k_1 t}) \quad (\text{S1})$$

$$\text{Pseudo-second-order model} \quad q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (\text{S2})$$

$$\text{Intraparticle diffusion model} \quad q_t = k_p t^{0.5} + C_i \quad (\text{S3})$$

$$\text{Film diffusion model} \quad B_t = -\ln\left(1 - \frac{q_t}{q_e}\right) - 0.4977 \quad (\text{S4})$$

where  $q_t$  (mg/g) is the amount of adsorbed Cd(II) on adsorbents (i.e., MPs) at time  $t$  (h);  $q_e$  (mg/g) is the amount of adsorbed Cd(II) on MPs at the equilibrium;  $k_1$  ( $\text{h}^{-1}$ ) and  $k_2$  ( $\text{g} \cdot \text{mg}/\text{h}$ ) are the equilibrium rate constant of Pseudo-first-order and Pseudo-second-order models, respectively;  $C_i$  is the constant of intraparticle diffusion model;  $B_t$  is the Boyd constant.

The adsorption isotherms models are presented as Eqs. (S5)–(S7) (Freundlich, 1907; Langmuir, 1918; Hu and Zhang, 2019):

$$\text{Langmuir model} \quad \frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{1}{q_m} C_e \quad (\text{S5})$$

$$\text{Freundlich model} \quad \ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (\text{S6})$$

$$\text{Dubbin-Radushkevich model} \quad \ln q_e = \ln q_m - k_{DR} \left[ RT \ln \left( 1 + \frac{1}{C_e} \right) \right]^2 \quad (\text{S7})$$

where  $C_e$  (mg/L) is the equilibrium concentration of Cd(II) in solution;  $q_m$  (mg/g) is the maximum Cd(II) adsorption capacity of adsorbents (i.e., MPs);  $k_L$  (L/mg) is the Langmuir constant associated with the adsorption rate;  $k_F$  (mg/g) and  $n$  were the Freundlich constants indicating the adsorption capacity and heterogeneity of adsorbents, respectively;  $k_{DR}$  (kJ/mol) is the Dubbin-Radushkevich constant;  $R = 8.314$  K/(mol·K);  $T$  (K) is the absolute temperature.

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**Table S1** Physical characteristics of the original PLA, PP, and PA microplastics (MPs).

MP types	PLA	PP	PA	
BET surface area (m <sup>2</sup> /g)	4.90	4.16	3.18	
Total pore volume ( $\times 10^{-3}$ cm <sup>3</sup> /g)	8.56	8.81	7.97	
Crystallinity (%)	40.85	30.99	27.46	
	V <sub>2–10 nm</sub>	67.16	59.96	69.34
	V <sub>10–20 nm</sub>	1.61	15.03	16.22
Percentage of pore volume (> 2 nm, %)	V <sub>20–50 nm</sub>	4.82	11.99	6.79
	V <sub>&gt;50 nm</sub>	10.41	13.02	7.65

**Table S2** Parameters of film diffusion model for adsorption of Cd(II) on PLA, PP, and PA microplastics (MPs).

Parameters	MPs		
	PLA	PP	PA
Intercept value ( $B_{t=0}$ )	0.10	-0.092	-0.13
$R^2$	0.961	0.955	0.947

**Table S3** Parameters of intraparticle diffusion model for adsorption of Cd(II) on PLA, PP, and PA microplastics (MPs).

	Parameters	MPs		
		PLA	PP	PA
First stage	$k_{p1}$ (mg/(g·h <sup>0.5</sup> ))	0.21	0.057	0.15
	$C_i$	0.020	0.005	0.057
	$R^2$	0.965	0.952	0.873
Second stage	$k_{p2}$ (mg/(g·h <sup>0.5</sup> ))	0.038	0.028	0.14
	$C_i$	0.232	0.039	0.049
	$R^2$	0.955	0.997	0.944
Third stage	$k_{p3}$ (mg/(g·h <sup>0.5</sup> ))	0.031	0.005	0.021
	$C_i$	0.545	0.153	0.311
	$R^2$	0.985	0.863	0.972

**Table S4** C 1s component peaks for the PP microplastics (MPs) before and after Cd(II) adsorption.

Core level	Assignment	Before Cd(II) adsorption			After Cd(II) adsorption		
		Binding energy (eV)	Area	Component percentage (%)	Binding energy (eV)	Area	Component percentage (%)
C 1s	C-C/C-H	284.79	314389	100.00	284.78	145923	98.53
	C-O/C=O	N.D.	N.D.	N.D.	288.67	2174	1.47

Notes: N.D.: Not detected.

**Table S5** C 1s, O 1s, and N 1s component peaks for the PA microplastics (MPs) before and after Cd(II) adsorption.

Core level	Assignment	Before Cd(II) adsorption			After Cd(II) adsorption		
		Binding energy (eV)	Area	Component percentage (%)	Binding energy (eV)	Area	Component percentage (%)
C 1s	C–C/C–H	284.67	84236	54.90	284.68	75670	44.91
	C–N	285.49	53145	34.65	285.36	72586	43.09
	O=C–N	287.98	15995	10.45	287.77	20186	12.00
O 1s	C=O	530.81	44898	64.35	530.80	601733	86.12
	C–O–H	532.49	24843	36.65	532.67	9681	13.88
N 1s	C–N	399.52	23567	100.00	399.17	23565	100.00

**Table S6** Peak assignments of FTIR spectral features of the PLA, PP, and PA microplastics (MPs) (Oliveira et al., 2014; Ma et al., 2021; Liu et al., 2022).

MPs Type	Wavenumbers (cm <sup>-1</sup> )	Peak assignments
PLA	2997, 2945	C–H stretching vibration
	1748	C=O stretching vibration
	1383, 1358	–CH <sub>3</sub> asymmetrical deformation vibration
	1266	C=O bending vibration
	1180	C–O–C stretching vibration
	1128	C–C stretching vibration
	1083	C–O asymmetric vibration
	871	C–COO stretching vibration
PP	2950	–CH <sub>3</sub> asymmetrical stretching vibration
	2917	–CH <sub>2</sub> – asymmetrical stretching vibration
	2867	–CH <sub>3</sub> symmetrical stretching vibration
	2837	–CH <sub>2</sub> – symmetrical stretching vibration
	1455	–CH <sub>2</sub> – bending vibration
	1376	–CH <sub>3</sub> symmetrical deformation vibration
	1156	–CH <sub>3</sub> wagging vibration
	973	–CH <sub>3</sub> rocking vibration
PA	3296	–NH stretching vibration
	2932	–CH <sub>2</sub> – asymmetrical stretching vibration
	2867	–CH <sub>2</sub> – symmetrical stretching vibration
	1632	amide I band (– <u>CO</u> –NH–) bending vibration
	1533	amide II band (–CO– <u>NH</u> –) bending vibration
	1463	–CH <sub>2</sub> – bending vibration
	1274	amide III band (C–N) bending vibration

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**Table S7** The comparison of Cd(II) adsorption capacities on microplastics (MPs) of different polymers between the present and previous studies.

MPs type	MPs Treatment	Size range (mm)	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Crystallinity (%)	Initial Cd(II) concentration (mg/L)	Dosage (g/L)	pH	q <sub>m</sub> (mg/g)	Reference
PLA	Washed and dried	0.1–0.2	4.899	0.00856	40.85	10–200	10	6.00	0.64±0.04	The present study
PA	Washed and dried	0.1–0.2	3.181	0.00797	27.46	10–200	10	6.00	0.96±0.07	The present study
PA	Washed and dried	0.05358	9.51	0.09	33.35	20–140	10	6.0	1.70	(Zhou et al., 2020)
PA	Virgin	N.A.	10.059	N.A.	19.75	2–40	10	N.A.	0.3396	(Li et al., 2019; Li et al., 2021)
PA	Aged	N.A.	30.597	N.A.	28.03	2–40	10	N.A.	2.13	(Li et al., 2021)
PA	Aged	N.A.	22.209	N.A.	48.82	2–40	10	N.A.	0.02574	(Li et al., 2021)
PA	Aged	N.A.	21.287	N.A.	15.24	2–40	10	N.A.	0.5435	(Li et al., 2021)
PP	Washed and dried	0.1–0.2	4.159	0.00881	30.99	10–200	10	6.00	0.22±0.03	The present study
PP	Ultrasonic cleaning and dried	0.347	1.74	0.0230	42.9	1–50	4	7.0	0.323±0.017	(Li et al., 2022)
PP	Immersed in HCl, washed and dried	< 0.074	0.348	N.A.	N.A.	N.A.	2	N.A.	0.3610	(Guo et al., 2020)
PP	Virgin	N.A.	N.A.	N.A.	N.A.	2–15	10	N.A.	0.1992	(Li et al., 2019)
PP	No treatment	< 0.1	0.2335	0.000856	N.A.	0.025–0.100	0.5	N.A.	0.0133	(Liu et al., 2022)
PE	Immersed in HCl, washed and dried	< 0.074	0.173	N.A.	N.A.	N.A.	2	N.A.	0.3663	(Guo et al., 2020)
PE	Virgin	N.A.	28.944	N.A.	24.72	2–40	10	N.A.	0.2345	(Li et al., 2019)
HDPE	HCl washed and dried	0.1–0.154	N.A.	N.A.	N.A.	1–5	28.57	7.06	0.0305	(Wang et al., 2019)
LPE	No treatment	< 0.28	1.3	N.A.	38.1	0.1–50	2	6.5	0.345±0.029	(Zou et al., 2020)
HPE	No treatment	< 0.28	3.1	N.A.	77.9	0.1–50	2	6.5	0.242±0.018	(Zou et al., 2020)

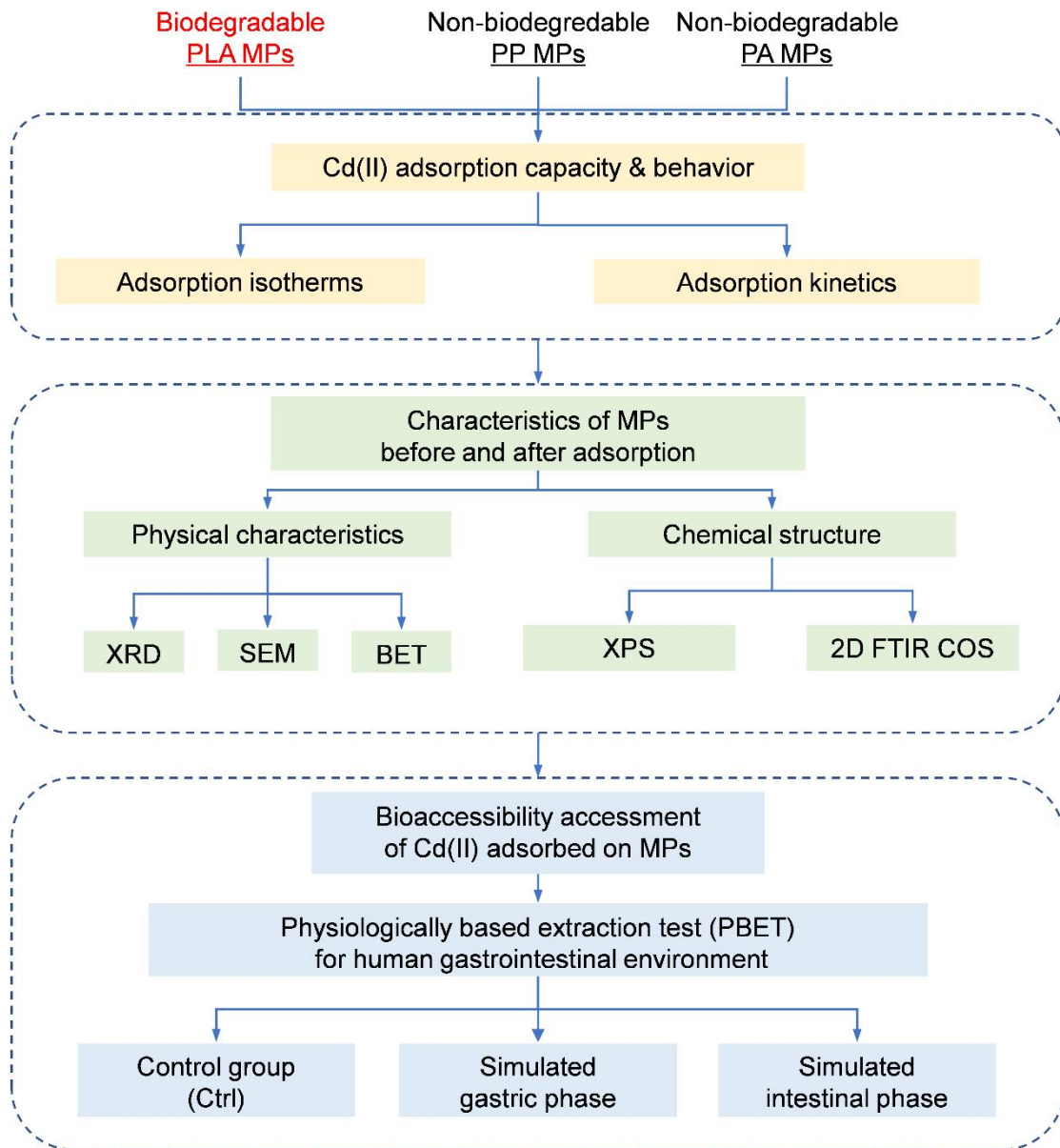
PS	Ultrasonic cleaning and dried	0.319	0.46	0.007	3.27	1–50	4	7.0	0.314±0.028	(Li et al., 2022)
PS	Immersed in HCl, washed and dried	< 0.074	0.508	N.A.	N.A.	N.A.	2	N.A.	0.4049	(Guo et al., 2020)
PS	Washed and dried	0.06238	4.13	0.044	4.12	20–140	10	6.0	0.763	(Zhou et al., 2020)
PS	No treatment	N.A.	N.A.	N.A.	N.A.	0.1–2	0.5	4.0	0.020154	(Lang et al., 2020)
PS	Fenton aging for 1–7 h	N.A.	N.A.	N.A.	N.A.	0.1–2	0.5	4.0	0.16863–0.23872	(Lang et al., 2020)
PS	H <sub>2</sub> O <sub>2</sub> aging for 1–7 h	N.A.	N.A.	N.A.	N.A.	0.1–2	0.5	4.0	0.04402–0.07690	(Lang et al., 2020)
PS	Washed and freeze-dried	N.A.	N.A.	N.A.	10 <sup>-4</sup>	0.1–2	N.A.	N.A.	0.106	(Mao et al., 2020)
PS	UV aging for 3 months	N.A.	N.A.	N.A.	10 <sup>-4</sup>	0.1–2	N.A.	N.A.	0.161–0.175	(Mao et al., 2020)
PS	Virgin	N.A.	28.944	N.A.	N.A.	2–40	10	N.A.	0.0699	(Li et al., 2019)
PS	No treatment	< 0.1	0.7215	0.001793	N.A.	0.025–0.100	0.5	N.A.	0.0171	(Liu et al., 2022)
PVC	No treatment	< 0.28	8.9	N.A.	N.A.	0.1–50	2	6.5	1.748±0.505	(Zou et al., 2020)
PVC	Immersed in HCl, washed and dried	< 0.074	0.836	N.A.	N.A.	N.A.	2	N.A.	0.05348	(Guo et al., 2020)
PVC	Washed and dried	0.05997	5.29	0.051	6.25	20–140	10	6.0	1.041	(Zhou et al., 2020)
PVC	Virgin	N.A.	N.A.	N.A.	N.A.	2–15	10	N.A.	0.2222	(Li et al., 2019)
PS	No treatment	< 0.1	0.7399	0.002480	N.A.	0.025–0.100	0.5	N.A.	0.0438	(Liu et al., 2022)
ABS	Washed and dried	0.05439	3.58	0.026	27.15	20–140	10	6.0	0.65±0.02	(Zhou et al., 2020)
PET	Washed and dried	0.06573	1.95	0.025	3.34	20–140	10	6.0	0.25±0.01	(Zhou et al., 2020)
CPE	No treatment	< 0.28	2.3	N.A.	N.A.	0.1–50	2	6.5	7.485±1.544	(Zou et al., 2020)

Notes: N.A.: not available; HDPE: high-density PE; LPE: PE with low crystallinity degree; HPE: PE with high crystallinity degree; PVC: polyvinyl chloride; CPE: Chlorinated PE.

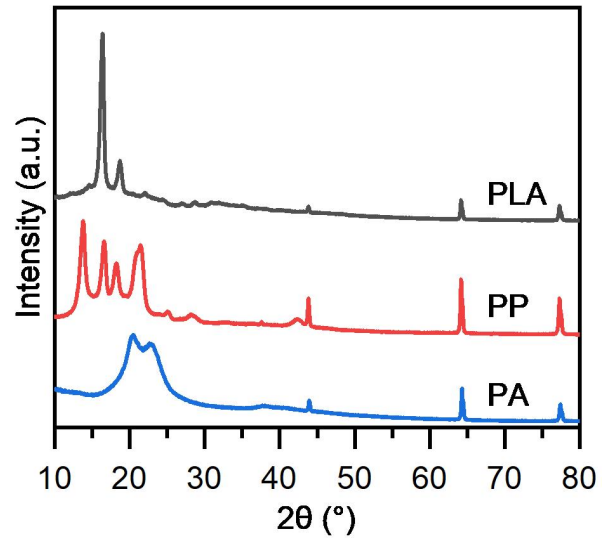


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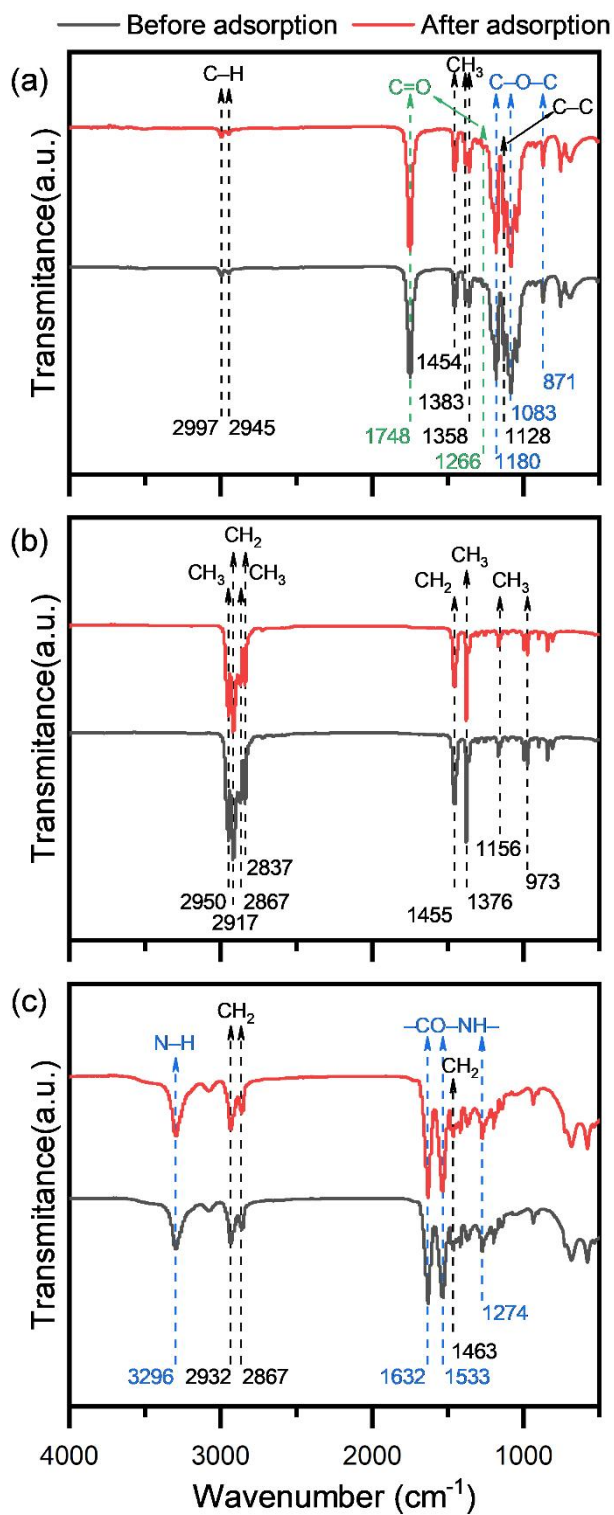
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**Fig. S1** The schematic of this study.



**Fig. S2** XRD patterns of the original PLA, PP, and PA microplastics (MPs) samples.



**Fig. S3** FTIR spectra of the examined microplastics (MPs) before and after Cd(II) adsorption: (a) PLA, (b) PP, and (c) PA.