

Supplemental Information

The adsorption behavior of imidacloprid pesticide on polar microplastics under environmental conditions: Critical role of photo-aging

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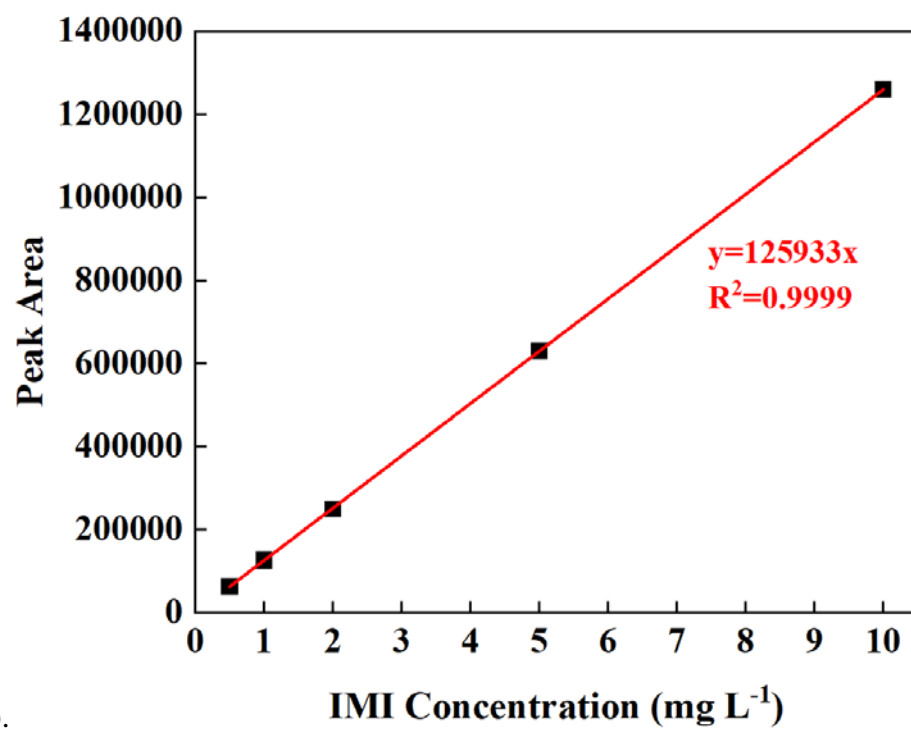
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Text S1. Relevant information on the characterization analysis methods of MP samples.

Scanning electron microscopy (SEM, S-4800, Hitachi, Japan) was used to characterize the surface morphology and particle size of the MPs. Contact angle / surface tension measuring instrument (JY-82B, Kruss DSA, Germany) was used to characterize the static contact angle of the MP, with deionized water as medium.

The surface functional groups of MPs were characterized by Fourier transform infrared spectroscopy (FTIR, Tensor-27, Bruker, Germany), and the carbonyl index was calculated. The MPs were pressed with potassium bromide and tested on the computer. The wave number range was 400 cm^{-1} ~4000 cm^{-1} . X-ray photoelectron spectroscopy (XPS, AlK α , Thermo Fisher Scientific, U.S.A.) was used to characterize the elemental composition and chemical state of various compounds on the surface of MPs. The energy of the monochromatic alka source is 1486.6 eV. The chemical bond information on the surface of MPs was obtained by fitting the high-resolution energy spectra of different orbitals (C 1s, N 1s and O 1s).

The zeta potential of MPs at different pH was characterized by Malvern laser particle sizer (Nano ZS90, Malvern Panalytical, U.K.). Fluorescence spectrophotometer (F-7000, Hitachi, Japan) was used to characterize the effect of dissolved organic matter and humic acid (HA) extracted from the MPs on the fluorescence characteristics of IMI adsorbed by the MPs. The excitation light source of the fluorescence spectrophotometer is an arc lamp (150 W), and the voltage of the photomultiplier tube is 700 V. the excitation wavelength (E_x) and the emission wavelength (E_m) range of the fluorescence spectrophotometer is set to be 200 nm~450 nm and 250 nm~550 nm, respectively. The step length is set to 5 nm, and the scanning speed is set to 12000 $\text{nm}\cdot\text{min}^{-1}$ (Jin et al.,



2021).

Figure S1. Standard curve of IMI concentration.

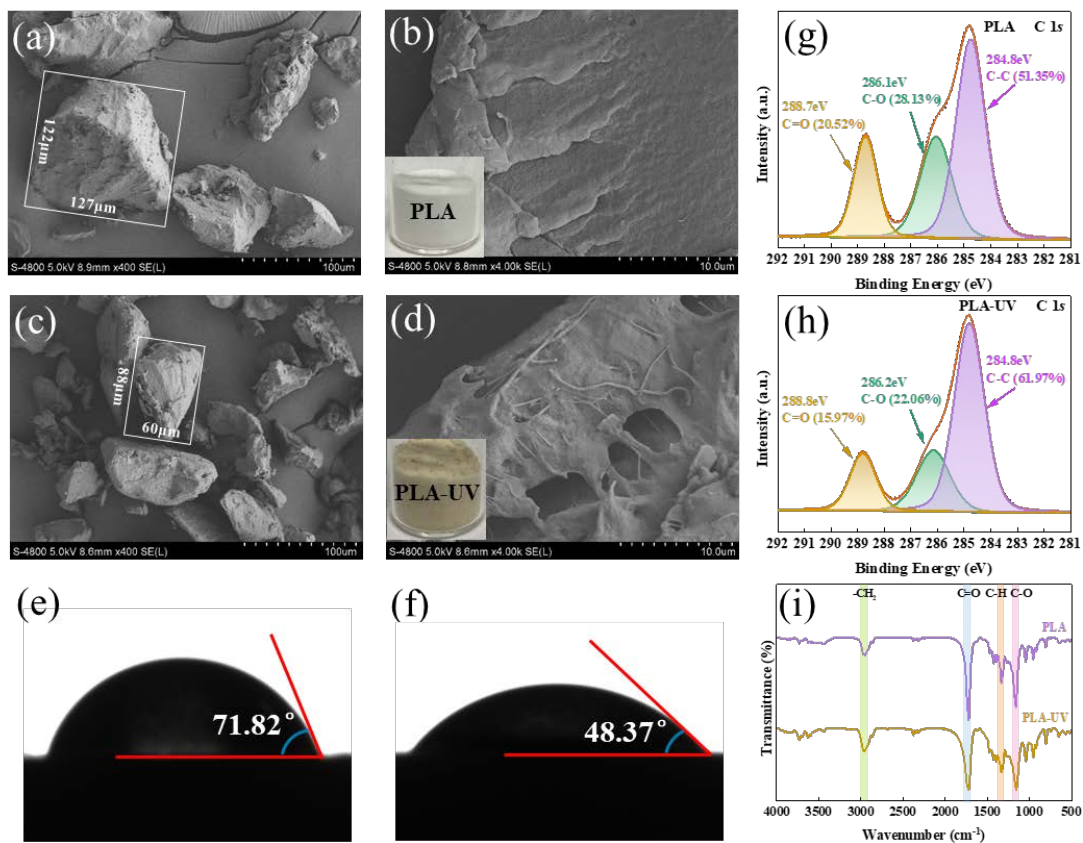


Figure S2. Characteristics of MP samples. SEM images of (a-b) pure PLA MPs and (c-d) photo-aging PLA-UV MPs; (e-f) Contact angles of PLA and PLA-UV MPs; (g-h) XPS C 1s spectra of PLA and PLA-UV MPs; (i) FTIR spectra of PLA and PLA-UV MPs.

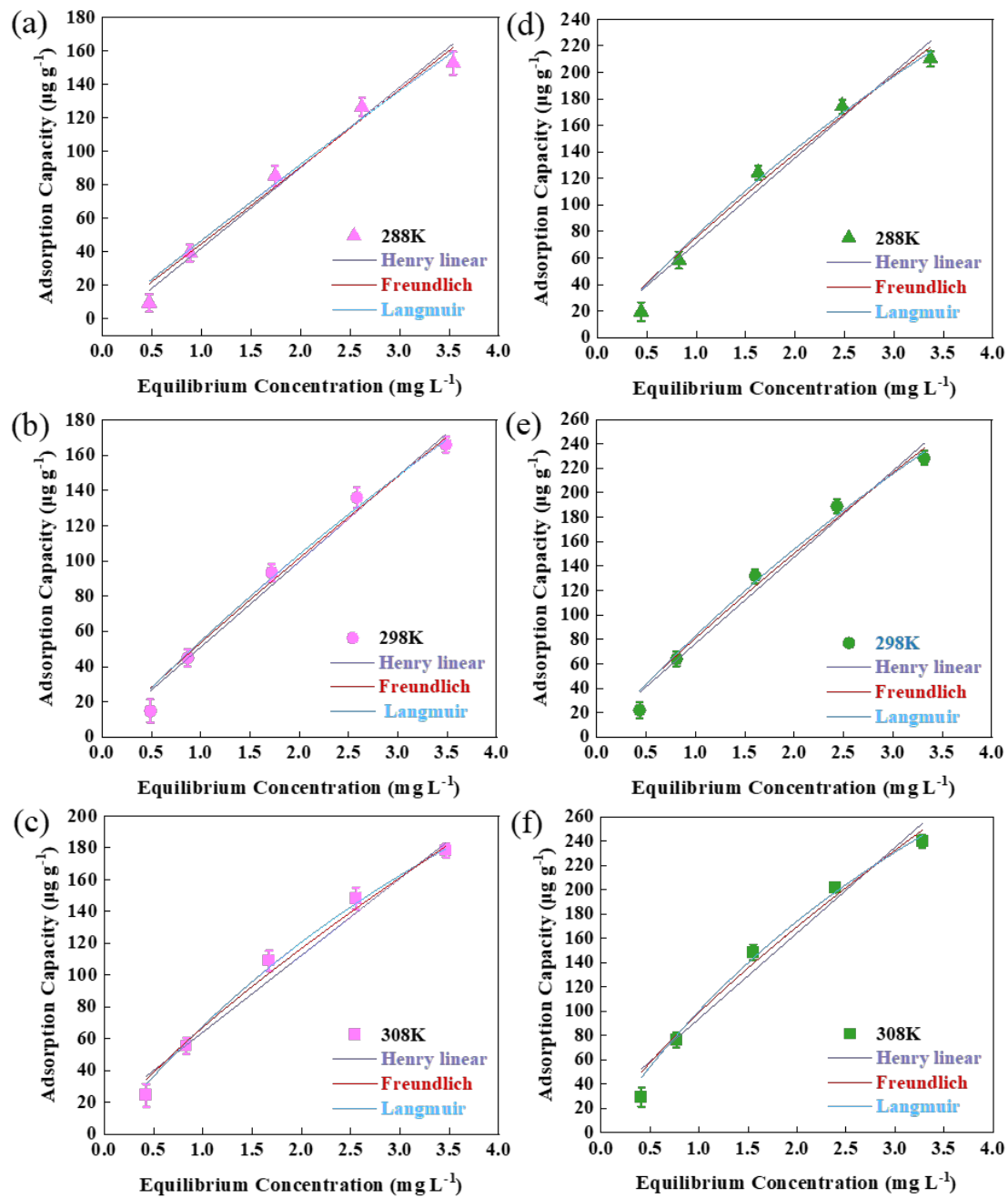


Figure S3. Sorption isotherms of IMI onto (a-c) PLA MPs, (d-f) PLA-UV MPs based on Henry linear, Freundlich, and Langmuir models in different temperatures.

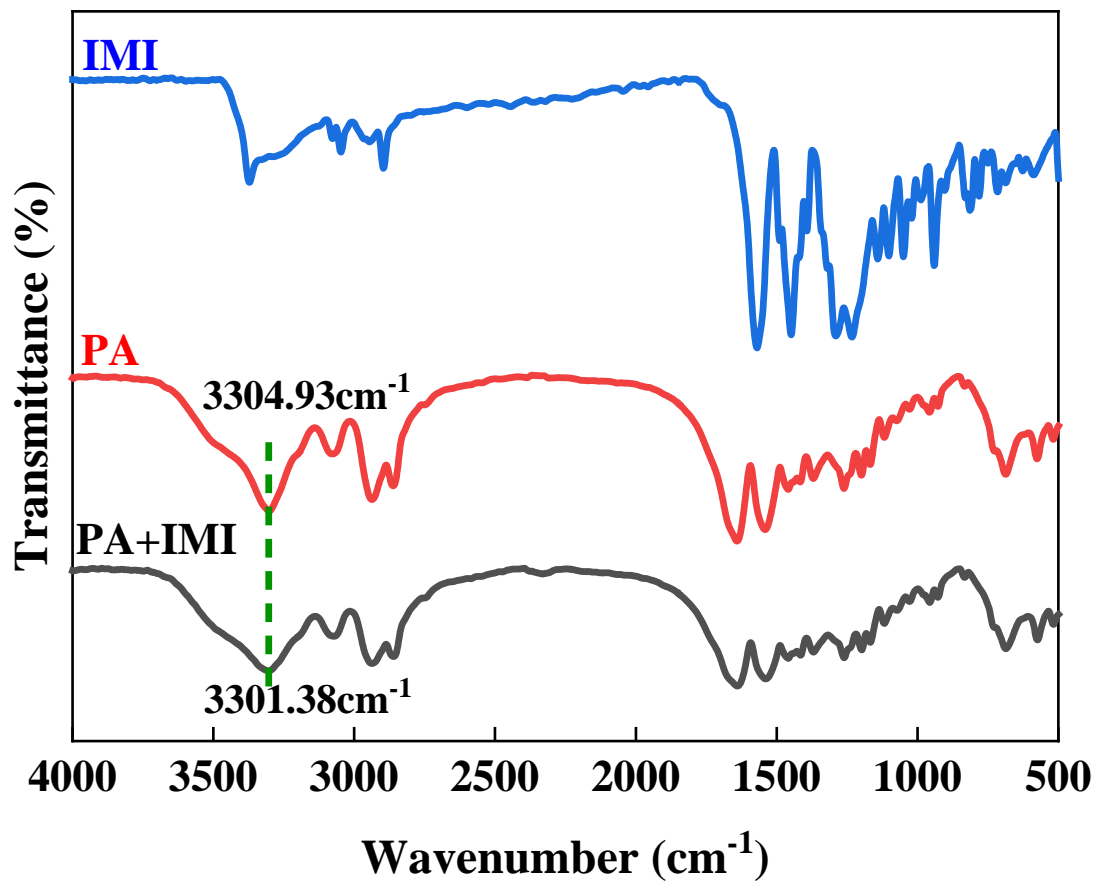


Figure S4. FTIR spectra of PA MPs before and after adsorption of IMI.

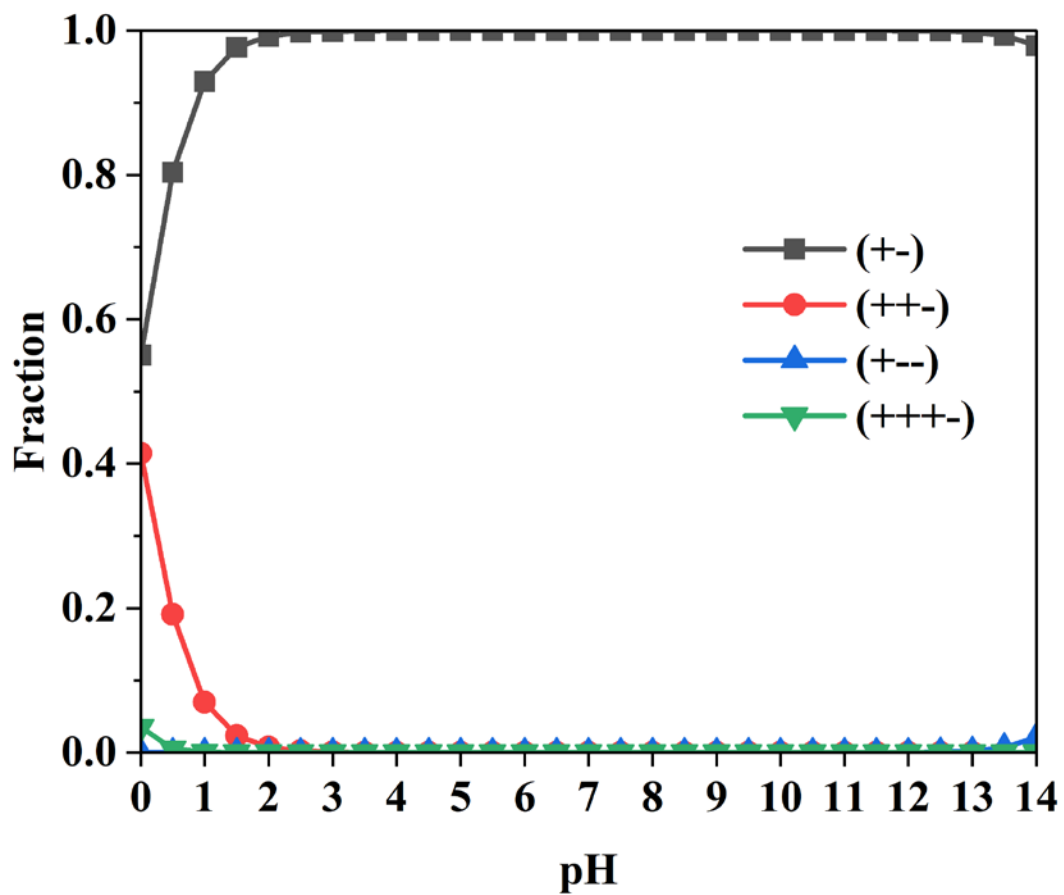


Figure S5. Speciation distribution of IMI under different pH conditions.

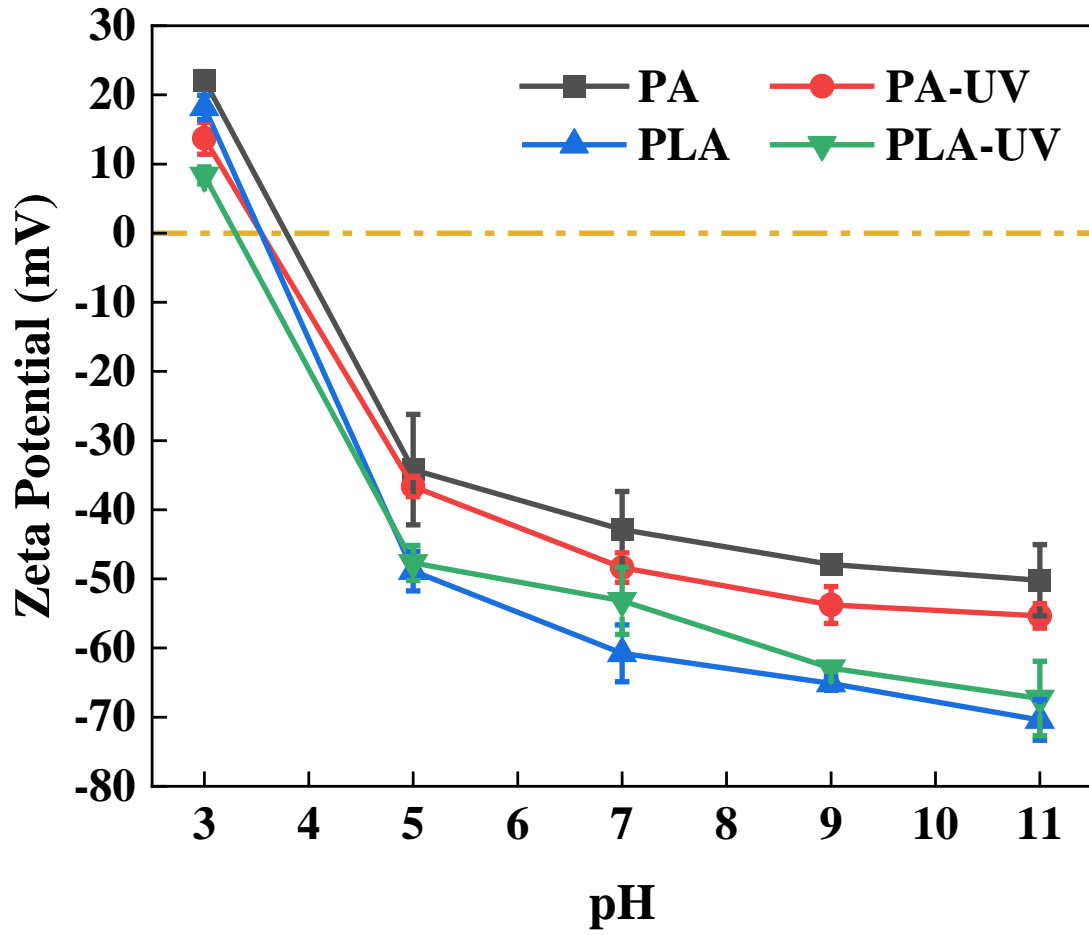


Figure S6. Zeta potential of four kinds of MPs in different pH solutions.

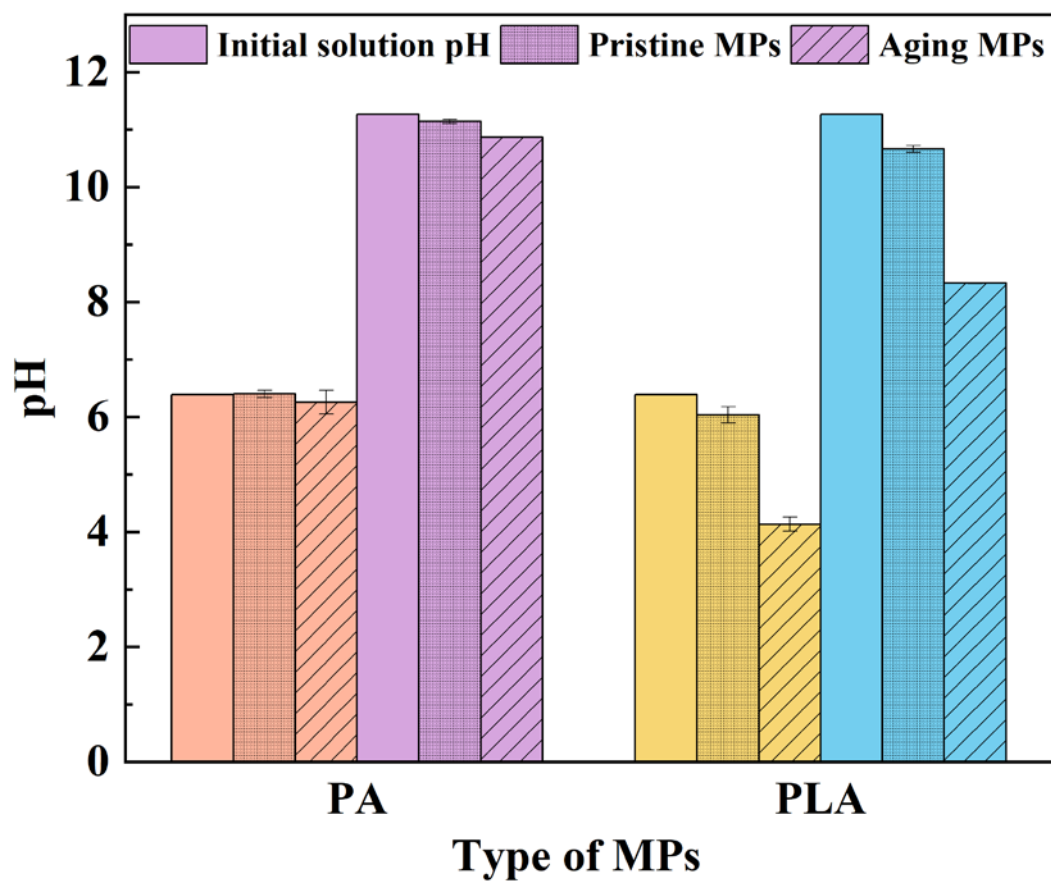


Figure S7 Solution pH before and after adsorption of IMI by MPs.

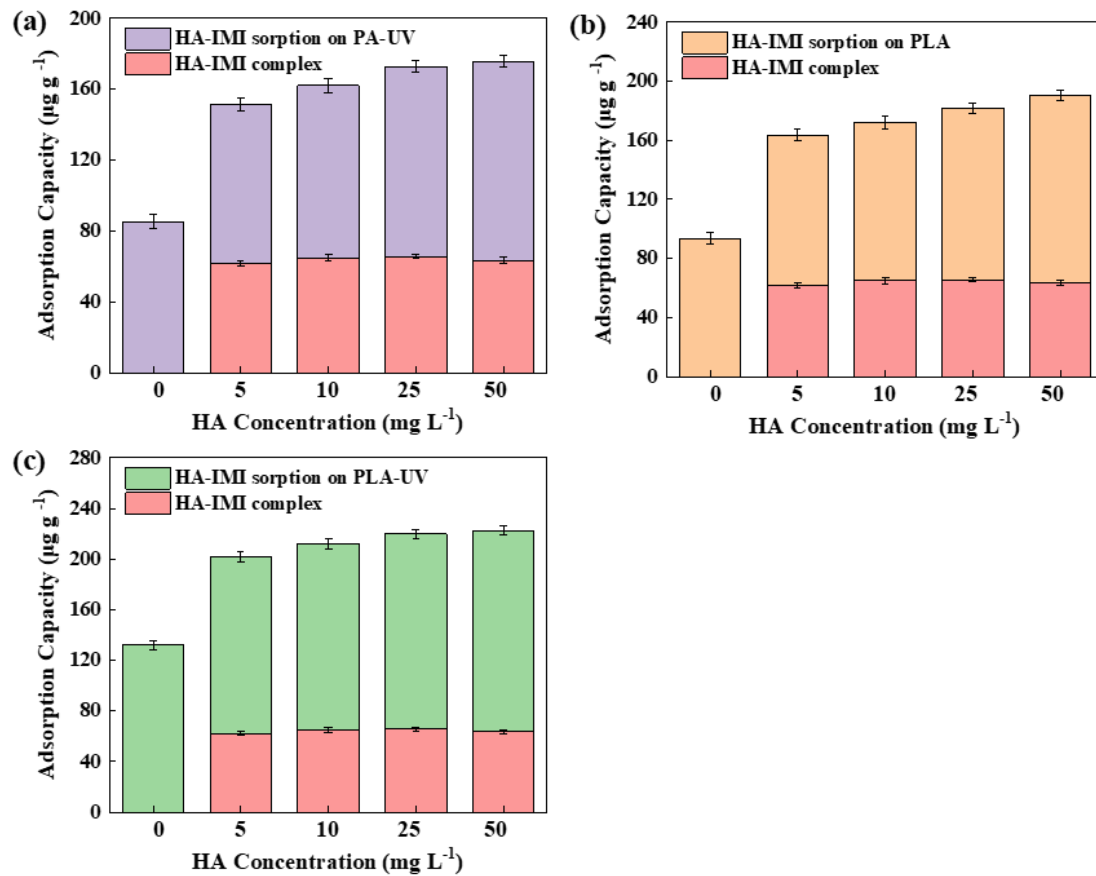


Figure S8. The adsorption of 2 mg L⁻¹ IMI onto 3 g L⁻¹ (a) PA-UV MPs; (b) PLA MPs; (c) PLA-UV MPs with 0-50 mg L⁻¹ HA.

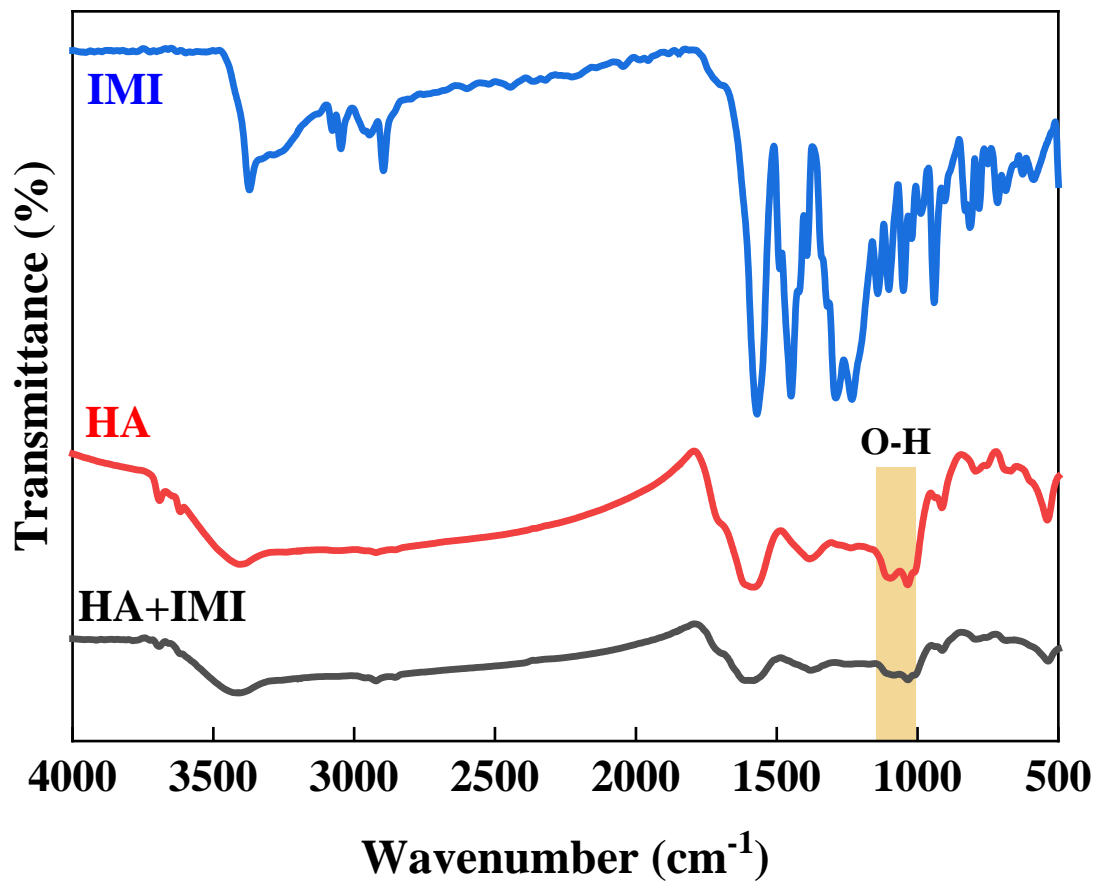
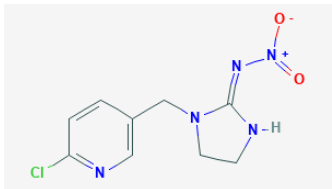


Figure S9. FTIR spectra of the reaction between IMI and HA.

Table S1. Characteristics of IMI in this study.

Contaminant	Structure*	Molecular Formula*	Molecular Weight (g mol ⁻¹)*	p <i>K_a</i> *	log <i>K_{ow}</i> *
IMI		C ₉ H ₁₀ ClN ₅ O ₂	255.7	p <i>K_{a1}</i> = 1.6; p <i>K_{a2}</i> = 11.1	0.6 at 21 °C

* Values were compiled from PubChem Database [<https://pubchem.ncbi.nlm.nih.gov/>].

Table S2. Molar content of each element in samples measured by XPS.

	C (%)	O (%)	N (%)
PA	76.4	11.3	12.3
PA-UV	74.7	14.2	11.1
PLA	69.8	30.2	-
PLA-UV	74.3	25.7	-

Table S3. Parameters of the adsorption kinetic models of IMI on PA and PLA MPs.

	Pseudo-first-order model			Pseudo-second-order model			Boyd model
	k_1	q_e	R^2	k_2	q_e	R^2	R^2
PA	0.2042	105.0	0.9888	0.0020	118.4	0.9974	0.9871
PA-UV	0.1754	85.0	0.9342	0.0024	94.2	0.9860	0.9564
PLA	0.2028	131.0	0.9736	0.0017	145.8	0.9957	0.9798
PLA-UV	0.2201	93.0	0.9697	0.0026	103.1	0.9913	0.9809

Table S4. Parameters of the adsorption isotherm models of IMI on PA, PA-UV, PLA, and PLA-UV MPs.

		Henry linear		Freundlich			Langmuir		
		k_D	R^2	k_F	n	R^2	k_L	q_{max}	R^2
PA	288K	53.2716	0.9987	57.6736	0.9523	0.9999	0.0328	1842.4	0.9889
	298K	53.3098	0.9995	68.9728	0.8521	0.9985	0.0776	936.1	0.9855
	308K	51.5883	0.9987	82.7513	0.7142	0.9961	0.2193	453.6	0.9765
PA-UV	288K	34.5325	0.9674	45.0332	0.8265	0.9978	0.0574	760.8	0.96112
	298K	38.7151	0.9762	51.8159	0.8140	0.9940	0.1310	451.3	0.98841
	308K	44.4685	0.9925	61.5414	0.8099	0.9936	0.1391	510.2	0.9870
PLA	288K	48.0001	0.9745	44.7510	0.9575	0.9697	0.0156	2042.9	0.9702
	298K	45.5869	0.9784	53.4734	0.9258	0.9822	0.0540	1062.0	0.9863
	308K	70.7342	0.9709	80.9291	0.8949	0.9780	0.0828	1083.5	0.9849
PLA-UV	288K	64.3422	0.9609	75.5233	0.8772	0.9712	0.0950	888.8	0.9806

298K	70.7342	0.9709	80.9291	0.8949	0.9780	0.0828	1083.5	0.9849
308K	70.5911	0.95339	98.8965	0.7782	0.9750	0.1773	665.3	0.9890

References

JIN B C, LIN Z H, LIU W Y, Xiao Y, Meng Y, Yao X L, Zhang T T (2021). Spatiotemporal variations of dissolved organic matter in a typical multi-source watershed in northern China: A fluorescent evidence. *Environmental Science and Pollution Research*, 29: 20517-20529.