Adsorbing nanoplastics through high-resilience lignin-polyurethane foam

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Methods to prevent plastic contamination from all plasticware used, statistical analysis procedures, and quality assurance/quality control (QA/QC) protocols.

(1) Handling of plastic contamination from plasticware

To minimize plastic contamination from the plasticware used in the experiments, we took the following precautions:

Selection of high-quality plasticware: We used plasticware from well-known and reliable suppliers. For example, the NPs was purchased from Sigma-Aldrich, and other plastic containers were from suppliers with a good reputation for low-leaching plastic products.

Pre-cleaning procedures: All plasticware was thoroughly cleaned before use. We first rinsed the plasticware with deionized water multiple times, followed by soaking in a mild detergent solution for at least 24 hours. Then, we rinsed them again with deionized water until the pH of the rinse water was neutral. Finally, the plasticware was dried in a clean environment to prevent re-contamination.

Control experiments: We conducted control experiments without adding the target NPs. These control experiments were carried out under the same conditions as the main experiments, using the same plasticware. By analyzing the results of the control experiments, we could detect and quantify any potential plastic contamination from the plasticware. If any contamination was detected, we adjusted our experimental results accordingly.

(2) Addition of statistical analysis

We have added comprehensive statistical analysis to our study to strengthen the reliability of our conclusions:

Kinetic analysis: For the adsorption kinetics of NPs on the polyurethane foam, we used the pseudo - first - order and pseudo - second - order kinetic models. We calculated the reaction rate constants ($k_1$and k_2) and the correlation coefficients (R^2) for each model. The higher R^2 value of the pseudo-second-order kinetic model indicated that this model was more suitable for describing the adsorption process, suggesting that the adsorption mainly proceeded via chemical adsorption.

Isotherm analysis: In the adsorption isotherm study, we used the Langmuir and Freundlich isotherm models. We calculated the Langmuir constants (K_L, q_m) and the Freundlich constants ($1/n$, K_F) and their corresponding correlation coefficients (R^2). The better R^2value of the Langmuir model indicated that the adsorption process was a single-molecular layer adsorption.

Thermodynamic analysis: We calculated several thermodynamic parameters, including the standard enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS). These parameters were calculated using the equilibrium constant (K_L) from the Langmuir isotherm in the Van't Hoff equation. The negative values of ΔH and ΔG and the positive value of ΔS provided important information about the nature of the adsorption process, such as its exothermic and spontaneous characteristics.

(3) QA/QC protocol in the methods

We have established a strict QA/QC protocol in our experimental methods:

Calibration of instruments: All instruments used in the experiments were calibrated regularly according to the manufacturer's instructions. For example, the fluorescence spectrophotometer used to measure the NPs concentration was calibrated using standard solutions of known concentrations before each measurement. The zeta potential analyzer and the mercury porosimeter were also calibrated to ensure accurate and reliable data collection.

Replicate experiments: We conducted replicate experiments for each set of conditions. For example, in the adsorption experiments, we repeated each experiment at least three times. By calculating the mean and standard deviation of the replicate results, we could assess the reproducibility of our experiments. If the standard deviation was too large, we repeated the experiments to ensure the reliability of the data.

Quality control samples: We used quality control samples in our experiments. For example, we prepared a standard solution of NPs with a known concentration and analyzed it periodically during the experiments. By comparing the measured results of the quality control samples with the known values, we could monitor the accuracy and precision of our analytical methods.

We believe that these improvements have enhanced the quality and reliability of our study. Thank you again for your constructive comments.

The method for calculating adsorption efficiency is:

$$\eta = q_n / q_0 \times 100\%$$

Among them, q_0 is the amount of NPs adsorbed by the PUF during the first adsorption, and q_n is the amount of NPs adsorbed by the PUF during the nth adsorption.

Table S1 Various adsorbents for the remediation of MNPs via adsorption.

Absorbents	MNP types	MNP size	Adsorption capacity	References
Magnetic corncob biochar	PVC	325 nm	22.59 mg/g	[S1]
CuNi carbon material	PS	0.1 μm	83.1 mg/g	[S2]
Corncob-derived mesoporous biochar	PS	100 nm	56.02 mg/g	[S3]
Bagasse-derived biochar	PS	500 nm	44.9 mg/g	[S4]
Chitin sponge material	PS	1 μm	5.898 mg/g	[S5]
Untreated coffee grounds	PS	100 nm	4 mg/g	[S6]
Biodegradable sponge	PS	1 μm	10.87 mg/g	[S7]
MgAl layered double hydroxides	PS	100 nm	6.08 mg/g	[S8]
Mesoporous metal	PS	100 nm	6.08 mg/g	[S9]

organic frameworks				
Magnetic activated biochar-zeolite	PS	15 μm	736 mg/g	[S10]
Dialdehyde-modified and cationic aerogel	PS	1 μm	145.05 mg/g	[S11]
MOF-545	PA	3.2 μm	294.6 mg/g	[S12]
Chitosan-based sponge	PS	1 μm	0.26 mg/g	[S13]
ZIF-8/sodium alginate	PVC	5 μm	282 mg/g	[S14]
Cellulose nanocrystal-based Pickering foams	PS	1 μm	300 mg/g	[S15]
Sodium alginate ultralight sponge	PS	5 μm	329.85 mg/g	[S16]
Chitin sponges	PS	1 μm	99.74 mg/g	[S17]
Filamentous algae and their magnetic biochar	PS	1 μm	176.99 mg/g	[S18]
Mg/Zn modified magnetic biochar	PS	1 μm	98.52 mg/g 99.21 mg/g	[S19]
PU-Ln (20%)	PS	70-80nm	38.06mg/g	Our work

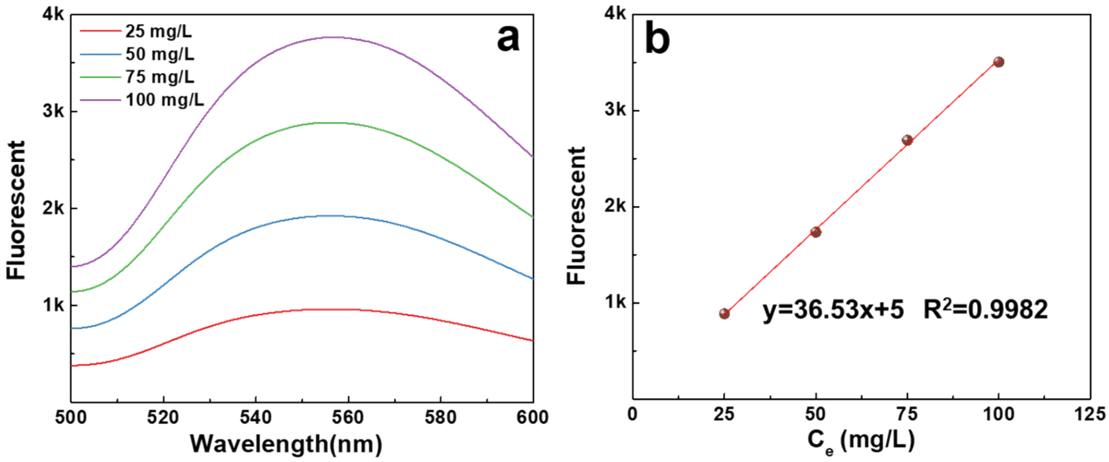

Fig. S1 Fluorescence spectrum of nanoparticles (NPs), (b) Standard curve of NPs.

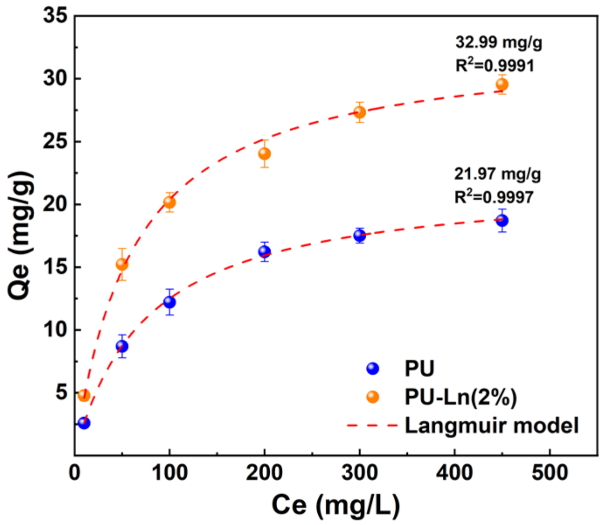

Fig. S2 Adsorption isotherms of PU and PU–Ln (2%) for NPs (pH = 7, dosage = 2.5g/L, adsorption time = 6 h).

Table S2 Langmuir isotherm constants for the adsorption of NPs over PU and PU-Ln (2%) foam.

Samples	K_L	Q_m(mg/g)	R^2
PU	0.01319	21.97	0.9997
PU-Ln (0.2%)	0.01619	32.99	0.9984

The adsorption capacities of the PU and PU-Ln (2%) foams were significantly influenced by pHs (Fig. 6). Especially in the pH range of 6~8, the adsorption capacities of both PU and PU-Ln (2%) showed the significant change, which implied the surface properties of PU and PU-Ln (2%) experienced an obvious mutation when the pHs of solution changed from acidic to alkaline. In this regard, to evaluate the contribution of lignin on the adsorption capacity of PU-Ln (2%), the neutrality condition (pH=7) should be considered to exclude the effect of the changes of the surface properties of PU and PU-Ln (2%). As shown in the Fig. S2 and Table S2, the Q_m of PU and PU-Ln (2%) in pH=7 were ~33mg/g and 22 mg/g, respectively. Thus, the contribution of 2% lignin to the adsorption capacity was approximately 11 mg/g, corresponding to the 50% increment compared with the PU foam. Such a result directly indicated the importance of the trace lignin in notably boosting the adsorption capacity of polyurethane foam.

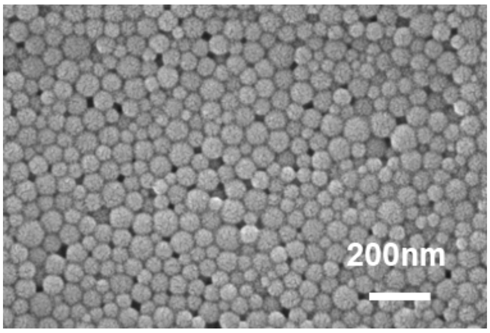

Fig. S3 SEM characterization of NPs.

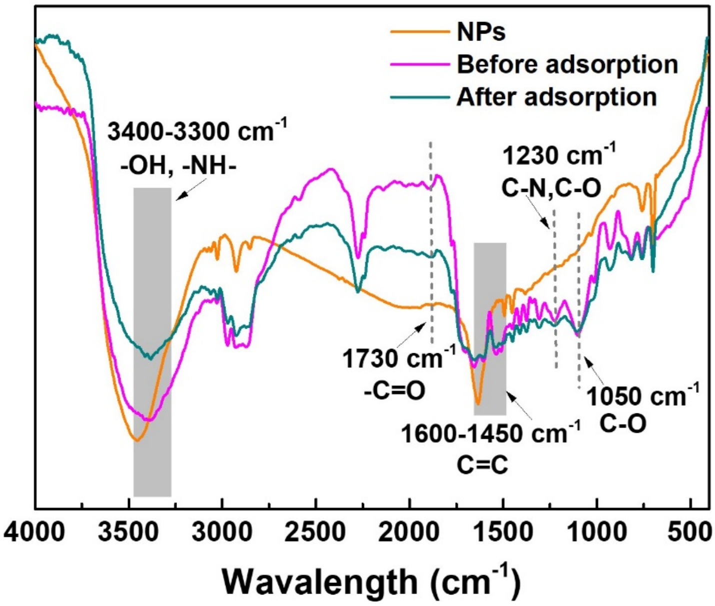

Fig. S4 FT-IR spectra of PU-Ln (2%) before and after adsorbing NPs.

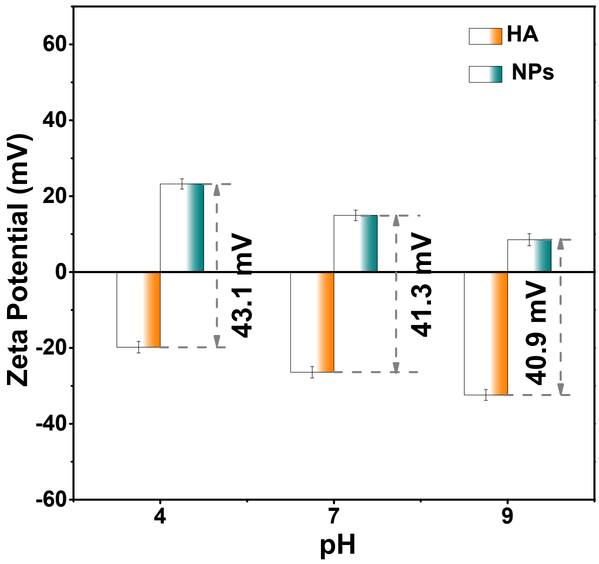

Fig. S5 The potential difference between HA and NPs under different pH conditions.

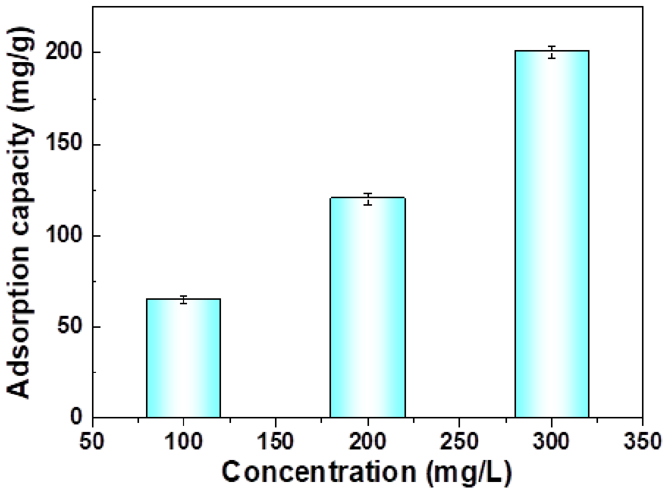

Fig. S6 The adsorption capacity of PU-Ln (2%) for MPs. Condition: pH=8, T=298 K.

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