Magnetic Nano-adsorbent integrated with Flow-injection System for Trace Analysis of Multiple Heavy Metals

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Electronic Supplementary Information

Power X-ray Diffraction Measurement

Fig. S-1 shows the powder X-ray diffraction (PXRD) patterns of the pristine MNPs and MNPs-PAA, respectively. The PXRD characteristic peaks (2θ =30.26, 35.45, 43.3, 53.5, 57.12, 62.65°) for iron oxide (Fe_3O_4 or γ -Fe_2O_3), which were marked with respective indices (220), (311), (400), (422), (511), (440), appeared in both samples. The average crystallite size revealed from peak broadening was about 8 nm (and 4 nm) for pristine MNPs (and MNPs-PAA) according to Scherrer equation.[1]

$$D = \frac{0.9\,\lambda}{\beta \cos\theta}$$

where D is the average crystallite size (nm), λ is the wavelength of X-rays (CuKα : λ = 0.1540 nm), θ is the Bragg diffraction angle, and β is the full width at half maximum (FWHM in radians).

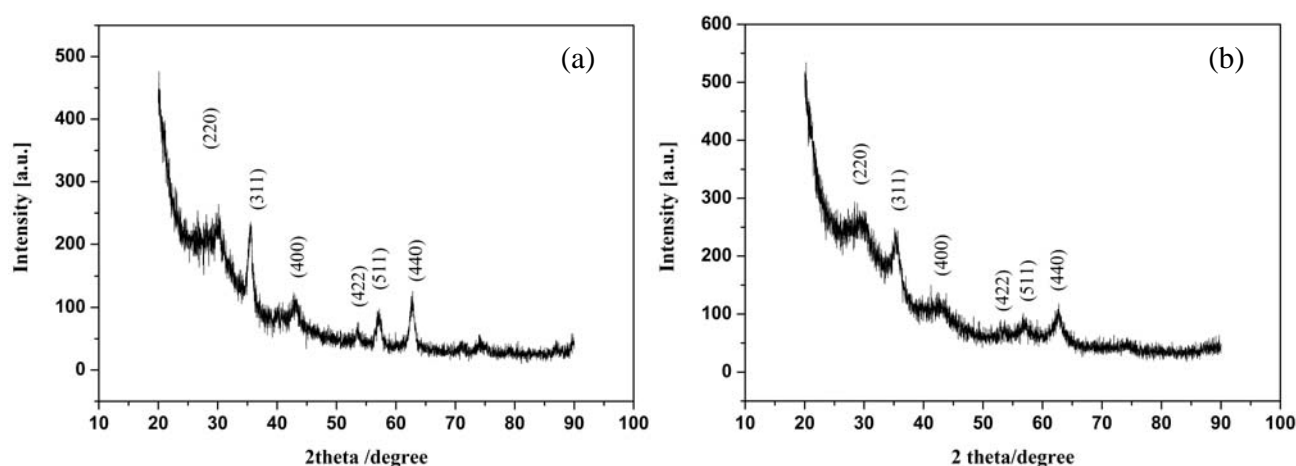**Fig. S-1** The powder X-ray diffraction (PXRD) patterns of (a) pristine MNPs, and (b) MNPs-PAA. The peaks are indexed to JCPDS card No. 19-0629.

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Estimation of Total Surface Area Per Unit Volume (Table S-1)

1. The number of MNPs-PAA in one cm^3 is 8×10^8 particles (5-nm particle size; non-porous material). The surface area of one MNPs-PAA is 78.5 nm^2. The total surface area per unit volume is 6.3×10^{20} nm^2 cm^{-3}.

2. The number of Amberlite XAD-4 in one cm^3 is 4096 particles (640-μm particle size; porous material 10-nm pore size; assuming 100 % porosity). The surface area of one XAD-4 is 5.14×10^{12} nm^2, which is based on $\sim 1.63 \times 10^{10}$ pores present in one XAD-4 (surface area of one 10-nm pore is 314 nm^2). The total surface area per unit volume is 2.1×10^{16} nm^2 cm^{-3}.

3. The number of C_{18} in one cm^3 is 9×10^9 particles (4.81-μm particle size; porous material 8-nm pore size; assuming 100 % porosity). The surface area of one C_{18} is 2.89×10^8 nm^2, which is based on $\sim 1.44 \times 10^6$ pores present in one C_{18} (surface area of one 8-nm pore is 200.96 nm^2). The total surface area per unit volume is 2.6×10^{18} nm^2 cm^{-3}

Table S-1. Comparison of specific surface area and relevant properties in different adsorbents

Adsorbent	Particle size (nm)	Specific surface area ($m^2 g^{-1}$)	Pore size (nm)	Total surface area per unit volume ($nm^2 cm^{-3}$)[a]
MNPs-PAA	5-10	120	2.7	6.3×10^{20}
Amberlite XAD-4[b]	6.4×10^5	831	6~20	2.1×10^{16}
C_{18}[c]	4.8×10^3	187	8	2.6×10^{18}

[a] Calculations were based on non-porous MNPs-PAA and 100 % porosity in XAD-4 and C_{18}.

[b] The specific surface area and pore size data were from reference[2] and manufacturing company.

[c] The particle size, specific surface area, and pore size data were from reference.[3]
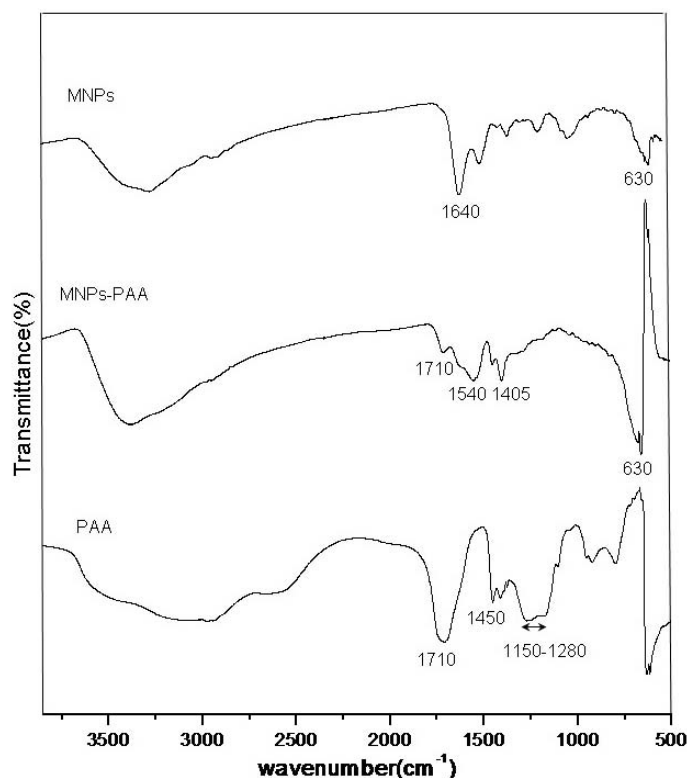
FT-IR Measurements

Fig. S-2 The FT-IR spectra of pristine MNPs, MNPs-PAA, and PAA.

Comparing the FT-IR spectra of pristine MNPs, MNPs-PAA, and PAA shown in Fig. S-2, characteristic absorption band at 630 cm^{-1} ascribed to Fe-O bond was expectedly present in both pristine MNPs and MNPs-PAA spectra. Similarly, characteristic bands at 3200 and 3400 cm^{-1} ascribed to N-H stretching vibrations of amine and amide were present in pristine MNPs and MNPs-PAA spectra. The absorption bands at 1500 and 1640 cm^{-1} characteristic of N-H bending vibration were present in the pristine MNPs spectrum only. Weak absorption bands at 1405, 1540, and 1710 cm^{-1} were present in the MNPs-PAA spectrum. The 1710 cm^{-1} band in PAA and MNPs-PAA spectra was ascribed to C=O from the carboxylic groups in PAA. On contrast, absorption bands at 1405 and 1540 cm^{-1} present in MNPs-PAA spectrum only were presumably the outcome of acid-base binding between the PAA and the MNPs

to form carboxylate groups. Previous study ascribed 1405 and 1540 cm^{-1} bands to COO^{-} anti-symmetric and COO^{-} symmetric vibrations, respectively.[4, 5] Thus, the bidentate bonding of the carbonyl groups to the most outer Fe atoms of MNPs could be demonstrated. Other characteristic absorption bands of PAA such as 1150-1280 cm^{-1} (aliphatic acid), 1400-1450 cm^{-1} (C-O stretch, deformation vibration of OH)[1]

are also present in MNPs-PAA spectrum.
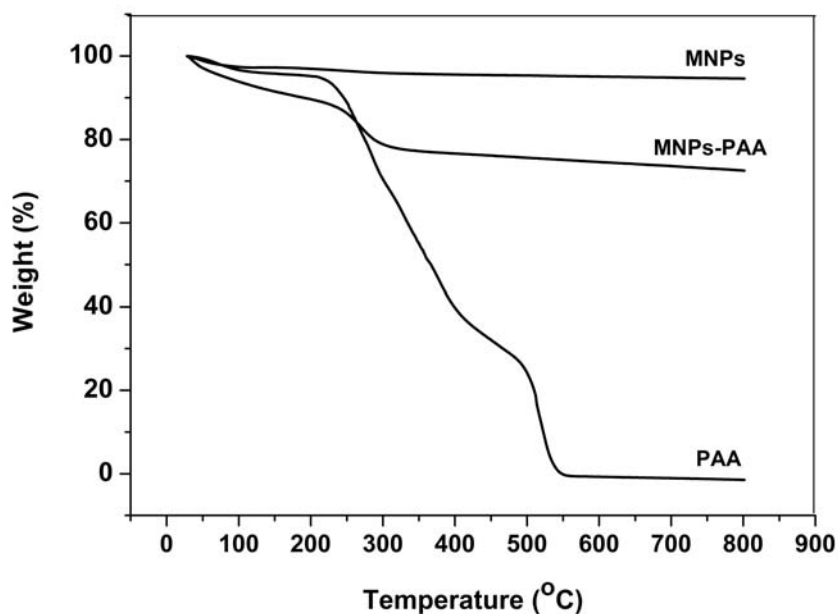
TGA Measurements

Fig. S-3 The TGA curves of pristine MNPs, MNPs-PAA and PAA

Fig. S-3 shows the TGA curves of pristine MNPs, MNPs-PAA and PAA. For pristine MNPs, there are not significant weight lose. The PAA oligomer and MNPs-PAA simultaneously show the significant weight loses at two stages on contrast. The first stage of degradation is below 250 ℃ contributing to the decompositions of free carboxyl groups and dehydration. The second stage of degradation is 250 ℃-800 ℃ attributing to the decompositions of polymer backbone.[6] The weight lose of MNPs-PAA due to dehydration is 2 % and 18 % for degradation of free carboxyl groups and polymer backbone. From the results of TGA analysis, 0.22 g PAA existing on 1 g MNPs would be presumed.

The estimated number of –COOH per unit area was 9.02×10^{11} molecules cm^{-2}, which was based on average particles size of 5 nm and 28 AA molecules per one PAA molecule.

References

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