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 (Fe₃O₄ or γ-Fe₂O₃), 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.
1. The number of MNPs-PAA in one cm$^3$ is $8\times10^8$ 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 $6.3\times10^{20}$ 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 $5.14\times10^{12}$ nm$^2$, which is based on $\sim1.63\times10^{10}$ 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 $2.1\times10^{16}$ nm$^2$ cm$^{-3}$.

3. The number of C$_{18}$ in one cm$^3$ is $9\times10^9$ particles (4.81-μm particle size; porous material 8-nm pore size; assuming 100 % porosity). The surface area of one C$_{18}$ is $2.89\times10^8$ nm$^2$, which is based on $\sim1.44\times10^6$ 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 $2.6\times10^{18}$ nm$^2$ cm$^{-3}$.

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

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Particle size (nm)</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>Pore size (nm)</th>
<th>Total surface area per unit volume (nm$^2$ cm$^{-3}$)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNPs-PAA</td>
<td>5-10</td>
<td>120</td>
<td>2.7</td>
<td>$6.3 \times 10^{20}$</td>
</tr>
<tr>
<td>Amberlite XAD-4$^b$</td>
<td>$6.4 \times 10^5$</td>
<td>831</td>
<td>6-20</td>
<td>$2.1 \times 10^{16}$</td>
</tr>
<tr>
<td>C$_{18}$$^c$</td>
<td>$4.8 \times 10^3$</td>
<td>187</td>
<td>8</td>
<td>$2.6 \times 10^{18}$</td>
</tr>
</tbody>
</table>

$^a$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$^3$. 
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)$^{1}$
TGA Measurements

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 °C contributing to the decompositions of free carboxyl groups and dehydration. The second stage of degradation is 250 °C-800 °C attributing to the decompositions of polymer backbone. 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 x 10^{11} molecules cm^{-2}, which was based on average particles size of 5 nm and 28 AA molecules per one PAA molecule.

References