Triphenylamine-functionalized magnetic microparticles as a new adsorbent coupled with high performance liquid chromatography for the analysis of trace polycyclic aromatic hydrocarbons in aqueous samples

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## **Supplementary Materials**

### 2. Experimental

### 2.6 HPLC-FLD analysis

Table S-1 Optimized fluorescent detection program used for PAHs determination

| Time(min) | Excitation(nm) | Emission(nm) | PAH determined |  |
|-----------|----------------|--------------|----------------|--|
| 0.0-14.0  | 250            | 400          | Ant            |  |
| 14.0-16.2 | 280            | 460          | FlA            |  |
| 16.2-24.0 | 273            | 390          | Pyr, Chr       |  |
| 24.0-32.0 | 294            | 430          | BbF, BkF       |  |

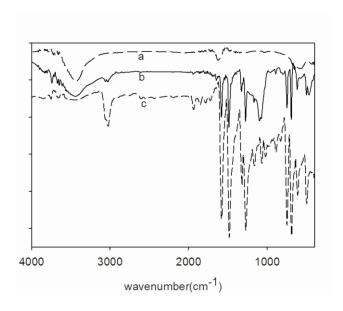
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#### 3. Results and discussion

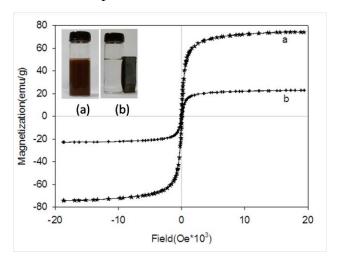
## 3.1 Characterization of prepared products

Figure S-1 FTIR spectroscopy of Fe<sub>3</sub>O<sub>4</sub>(a), Fe<sub>3</sub>O<sub>4</sub>/SiO<sub>2</sub>/TPA composite microspheres (b), and TPA (c).



### 3.2 Magnetic properties of prepared products

Figure S-2 Magnetization curves of  $Fe_3O_4$  nanoparticles (a) and  $Fe_3O_4/SiO_2/TPA$  composite (b). Inset shows the photographs of the dispersion (1) and separation (2) process of  $Fe_3O_4/SiO_2/TPA$  composite.



# 3.4 Analytical method validation

Table S-2 Comparative data of the represented method with C-18 SPE cartridge (n = 5)

| Analyte | Spiked      | Recovery           | (%)   | RSD (%)       |      |  |
|---------|-------------|--------------------|-------|---------------|------|--|
|         | $(\mu g/L)$ | Present study C-18 |       | Present study | C-18 |  |
| Ant     | 0.10        | 90.01              | 93.82 | 4.52          | 2.55 |  |
| FlA     | 0.20        | 87.87              | 94.36 | 2.86          | 3.10 |  |
| Pyr     | 0.20        | 85.67              | 89.58 | 1.15          | 2.96 |  |
| Chr     | 1.50        | 100.58             | 86.41 | 3.98          | 1.72 |  |
| BbF     | 0.08        | 103.02             | 89.70 | 1.83          | 4.75 |  |
| BkF     | 0.02        | 101.80             | 90.63 | 2.69          | 3.05 |  |

## 3.5 Application to real water samples

Table S-3 Analytical results of the proposed MSPE method for the determination of PAHs in real water samples (n = 5)

|         | Spring water       |     | Tap water      |     | River water    |      |
|---------|--------------------|-----|----------------|-----|----------------|------|
| Analyte | Detected           | RSD | Detected       | RSD | Detected       | RSD  |
|         | concentrations     | (%) | concentrations | (%) | concentrations | (%)  |
|         | (ng/L)             |     | (ng/L)         |     | (ng/L)         |      |
| Ant     | n.d. <sup>a)</sup> | -   | n.d.           | -   | 2.47           | 2.73 |
| FlA     | n.d.               | -   | n.d.           | -   | n.d.           | -    |
| Pyr     | n.d.               | -   | n.d.           | -   | n.d.           | -    |
| Chr     | n.d.               | -   | n.d.           | -   | n.d.           | -    |
| BbF     | n.d.               | -   | n.d.           | -   | n.d.           | -    |
| BkF     | n.d.               | -   | n.d.           | -   | 0.38           | 3.92 |

a) Not detected

Table S-4 Comparative data of the represented method with other methods in literatures

|                     | Present study | Ref. <sup>18</sup> | Ref. <sup>31</sup>    | Ref. <sup>32</sup> | Ref. <sup>33</sup> | Ref. <sup>34</sup>   |
|---------------------|---------------|--------------------|-----------------------|--------------------|--------------------|----------------------|
| Pretreatment method | MSPE          | MSPE               | C30-SPE <sup>a)</sup> | SPME <sup>b)</sup> | SBSE <sup>c)</sup> | MWCNTs <sup>d)</sup> |
| Analytical method   | HPLC-FLD      | GC-MS              | GC-MS                 | GC-MS              | HPLC-FID           | GC-MS                |
| LODs (ng/L)         | 0.04-3.8      | 14.1-70.0          | 30.0-210.0            | 0.32-2.2           | 0.2-1.5            | 2.0-5.3              |
| Recoveries (%)      | 82.5-104.7    | 83.6-119.1         | 79.0-115.0            | 78.8-100.7         | 60.1-86.8          | 74.5-105.0           |

- a) C30 solid phase extraction
- b) Solid phase microextraction
- c) Stir bar sorptive extraction
- d) Multi-walled carbon nanotubes