**Liquid chromatographic determination of per- and polyfluoroalkyl substances in environmental river water samples**

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Supplementary data

Table S1:Parameter and levels used in screening (fractional factorial design).

|  |  |  |  |
| --- | --- | --- | --- |
| parameters | Minimum | Central | Maximum |
| pH | 4 | 6.5 | 9 |
| Mass of sorbent (mg) | 5 | 12.5 | 20 |
| Eluent volume(µL) | 500 | 750 | 1000 |
| Extraction time (min) | 10 | 20 | 30 |
| Elution time(min) | 10 | 20 | 30 |

Table S2: The design matrix and respective analytical response

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  |  | Parameters | | | | %R | | |  |
| Runs | Pt | pH | MA (mg) | ET (min) | ELT (min) | EV (Ul) | PFOA | PFTeDA | PFDA | PFOS |
| 1 | 1 | 4 | 5 | 10 | 30 | 1000 | 78.4 | 77.5 | 79.3 | 81.4 |
| 2 | 1 | 9 | 5 | 10 | 10 | 500 | 34.5 | 43.5 | 28.4 | 43.7 |
| 3 | 1 | 4 | 20 | 10 | 10 | 1000 | 95.7 | 93.4 | 94.7 | 96.1 |
| 4 | 11 | 9 | 20 | 10 | 30 | 500 | 60.6 | 62.8 | 52.7 | 59.8 |
| 5 | 1 | 4 | 5 | 30 | 30 | 500 | 95.6 | 91.6 | 94.5 | 96.7 |
| 6 | 1 | 9 | 5 | 30 | 10 | 1000 | 24.3 | 39.3 | 23.7 | 23.4 |
| 7 | 1 | 4 | 20 | 30 | 10 | 500 | 97.9 | 96.3 | 95.7 | 98.1 |
| 8 | 1 | 9 | 20 | 30 | 30 | 1000 | 61.3 | 19.4 | 63.1 | 65.2 |
| 9 | 0 | 6.5 | 12.5 | 20 | 20 | 750 | 81.6 | 76.3 | 80.9 | 81.4 |
| 10 | 0 | 6.5 | 12.5 | 20 | 20 | 750 | 78.5 | 75.2 | 81.8 | 79.7 |
| 11 | 0 | 6.5 | 12.5 | 20 | 20 | 750 | 81.7 | 74.7 | 83.8 | 82.1 |
| 12 | 0 | 6.5 | 12.5 | 20 | 20 | 750 | 81.6 | 74.2 | 79.5 | 82.3 |

Table S3: CCD matrix and respective analytical response

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Runs | Parameters | | | %R | | | |
| Runs | pH | MA (mg) | ELT (min) | PFOA | PFTeDA | PFDA | PFOS |
| 1 | 4 | 5 | 10 | 79.1 | 99.6 | 92.3 | 78.3 |
| 2 | 4 | 5 | 30 | 94 | 102.4 | 99 | 93.5 |
| 3 | 4 | 20 | 10 | 4 | 100.6 | 95.5 | 104.8 |
| 4 | 4 | 20 | 30 | 105.9 | 101.3 | 97.2 | 118.9 |
| 5 | 9 | 5 | 10 | 120.1 | 55.7 | 72.9 | 57.7 |
| 6 | 9 | 5 | 30 | 58.3 | 32.3 | 53.2 | 70.3 |
| 7 | 9 | 20 | 10 | 71 | 45.7 | 56.5 | 60.2 |
| 8 | 9 | 20 | 30 | 60.8 | 70.1 | 71.6 | 53.5 |
| 9 | 3.1 | 12.5 | 20 | 54.1 | 96.8 | 88 | 103.2 |
| 10 | 9.9 | 12.5 | 20 | 104.2 | 60.3 | 45 | 42.5 |
| 11 | 6.5 | 2.4 | 20 | 42.9 | 69. | 52.2 | 59.8 |
| 12 | 6.5 | 22.6 | 20 | 60.4 | 95.7 | 99.5 | 110 |
| 13 | 6.5 | 12.5 | 6.5 | 111.1 | 41.1 | 28.1 | 28.1 |
| 14 | 6.5 | 12.5 | 33.5 | 28.3 | 108 | 101.2 | 72 |
| 15(C) | 6.5 | 12.5 | 20 | 73.2 | 73.2 | 96.9 | 77,1 |
| 16 (C) | 6.5 | 12.5 | 20 | 98.1 | 98.1 | 80.2 | 89,9 |
| 17(C) | 6.5 | 12.5 | 20 | 76.8 | 76.8 | 94.1 | 93.6 |

Table S4: Global concentrations of PFASs in comparison with the current study

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Country | | Concentrations (ng/L) | | | | |  |
|  | PFOA | | PFTeDA | PFDA | PFOS | Refs | |
| Australia | 39.9 | | 40 | 4.3 | 25.5 | [62] | |
| China | 12.0 | | < 18 | 10.9 | 14.4 | [60] | |
| Germany | 8.4 | | ND | 2.0 | 4.3 | [61] | |
| Netherlands | 1.78 | | 1.26 | 2.71 | ND | [63] | |
| China | 87.5 | | ND | 95.3 | 89.3 | [56] | |
| United States | 0.0070 | | ND | ND | 0.037 | [58] | |
| Australia | 71.1 | | ND | ND | 26.3 | [57] | |
| South Africa | 41.8 | | 10.4 | ND | 38.3 | [64] | |
| South Africa | 62.0 | | ND | 32.1 | 12.4 | [59] | |
| South Africa | 34.5 | | 4.2 | ND | ND | [65] | |
| South Africa | 314 | | 182 | ND | ND | [66] | |
| South Africa | 3.6-42.3 | | 0-9.28 | 0-11.2 | 0.51-38.2 | This study | |

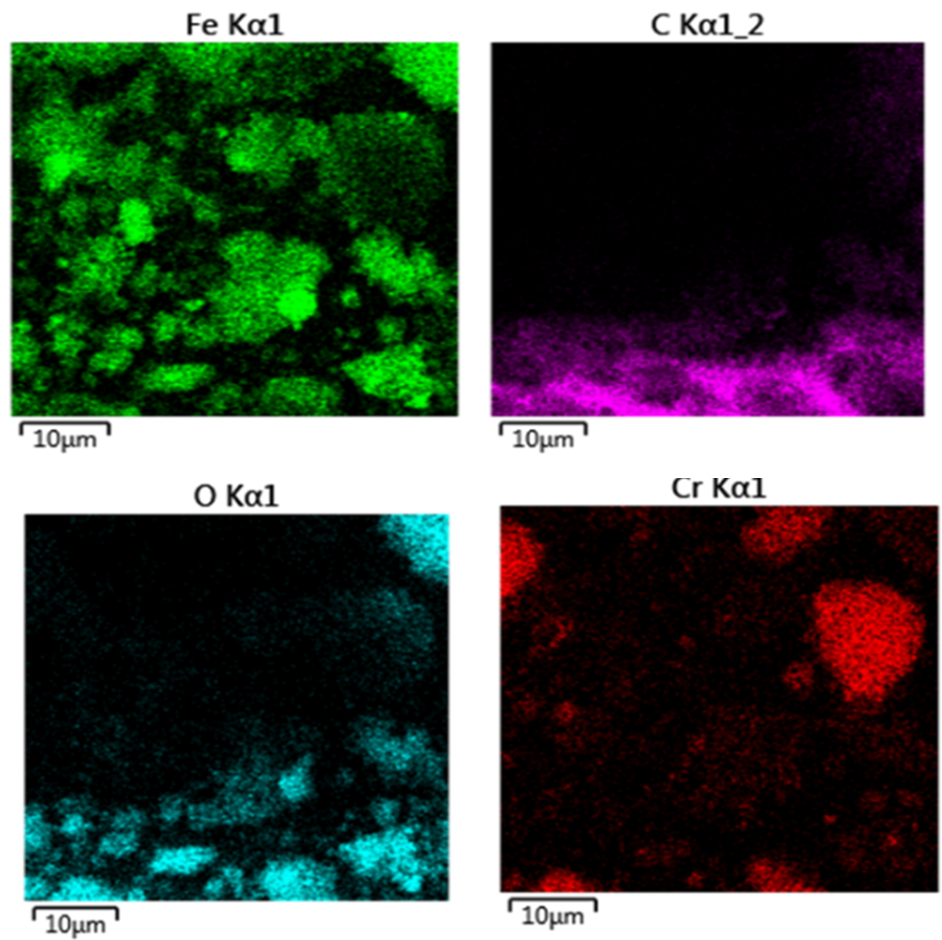


Figure S1: Element distribution from EDS mapping

Diagram

Description automatically generated

Figure S2: XRD of (a) MIL-101 (Cr), (b) Fe3O4 and (c)Fe3O4@MIL-101(Cr).

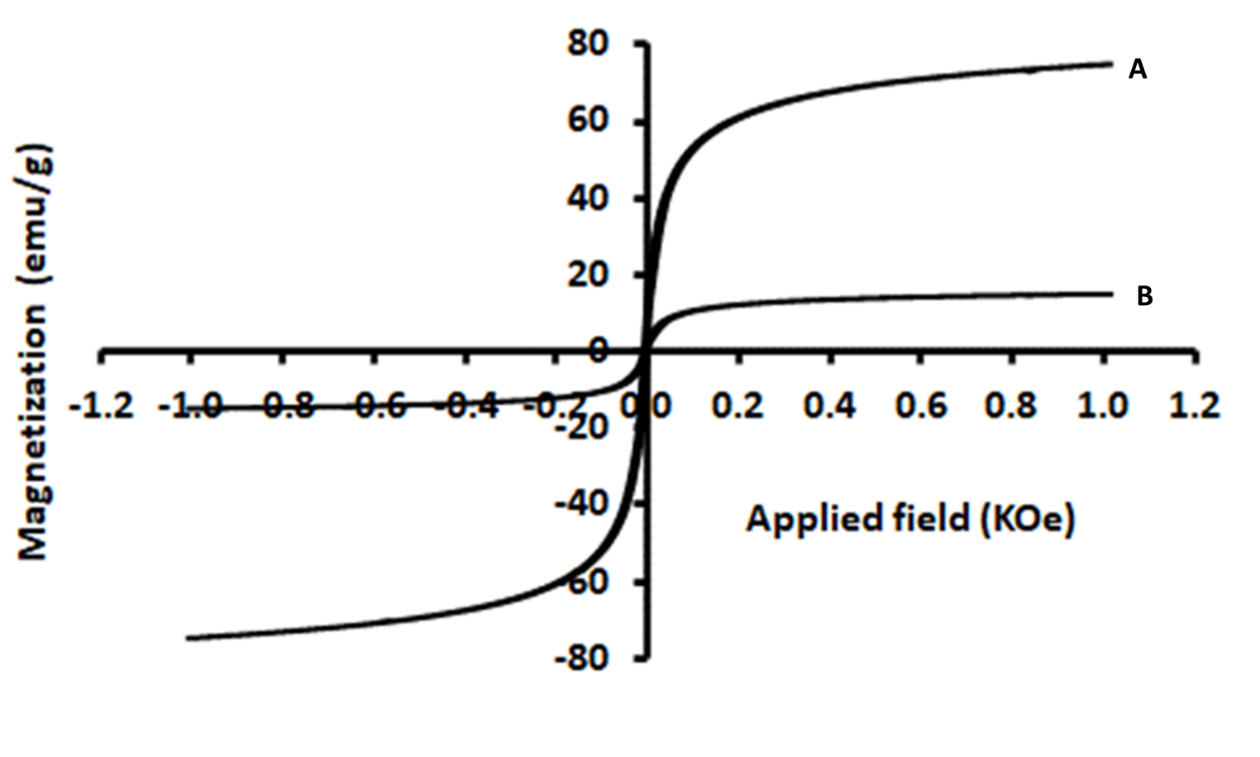


Figure S3: Vibrating sample magnetometry (VSM) of (A)Fe3O4 and (B) Fe3O4@MIL-101(Cr)

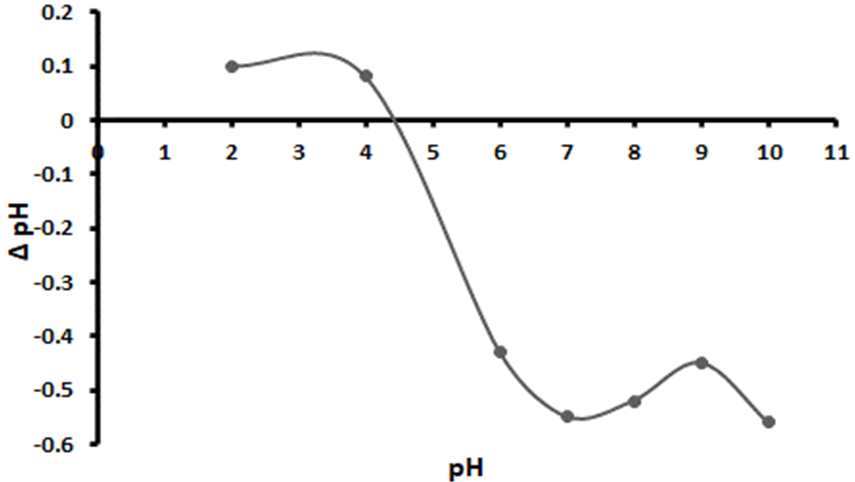


Figure S4: Point of zero charge

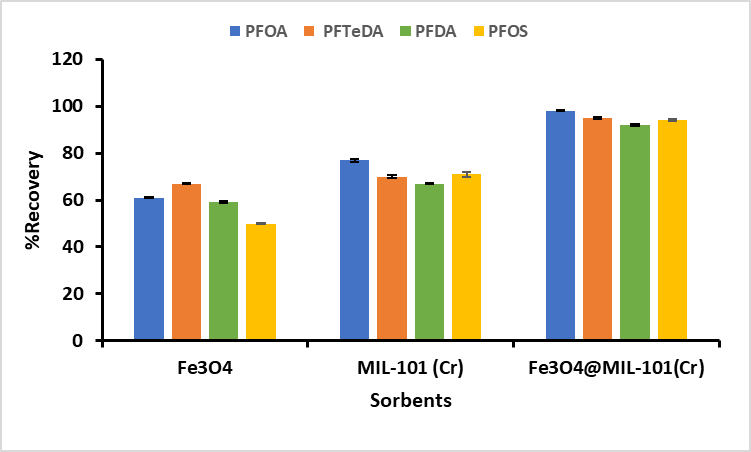


Figure S5: Selection of adsorbent material

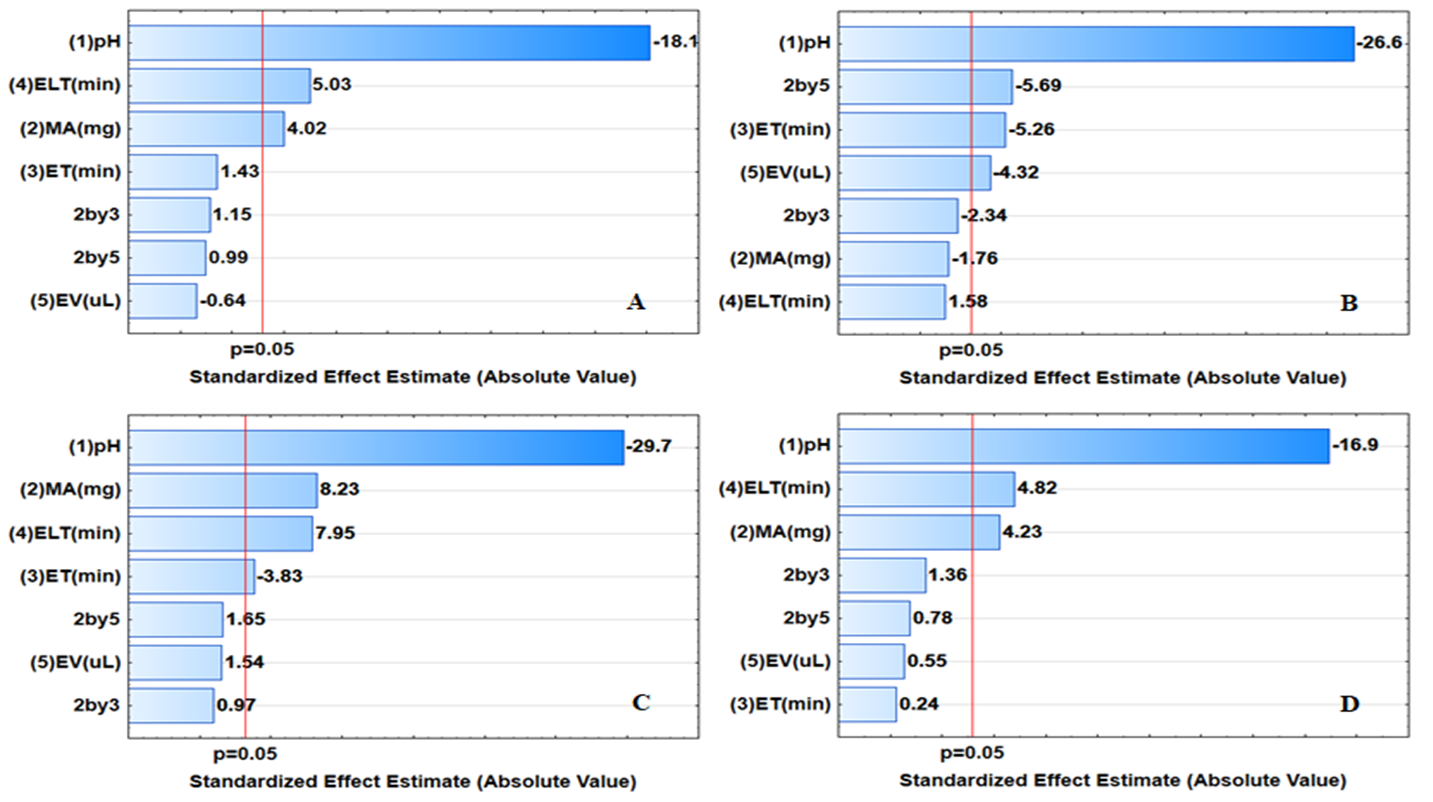


Figure S6: Pareto charts of standardised effects: (A) PFDA, (B) PFOA (C)) PFOS and (D) PFTeDA. ELT (min: Elution time, ET (min): Extraction time, MA (mg): Mass of adsorbent, EV (uL): Eluent volume. 2by3: Interaction between MA and ET, 2by5: interaction between MA and EV.

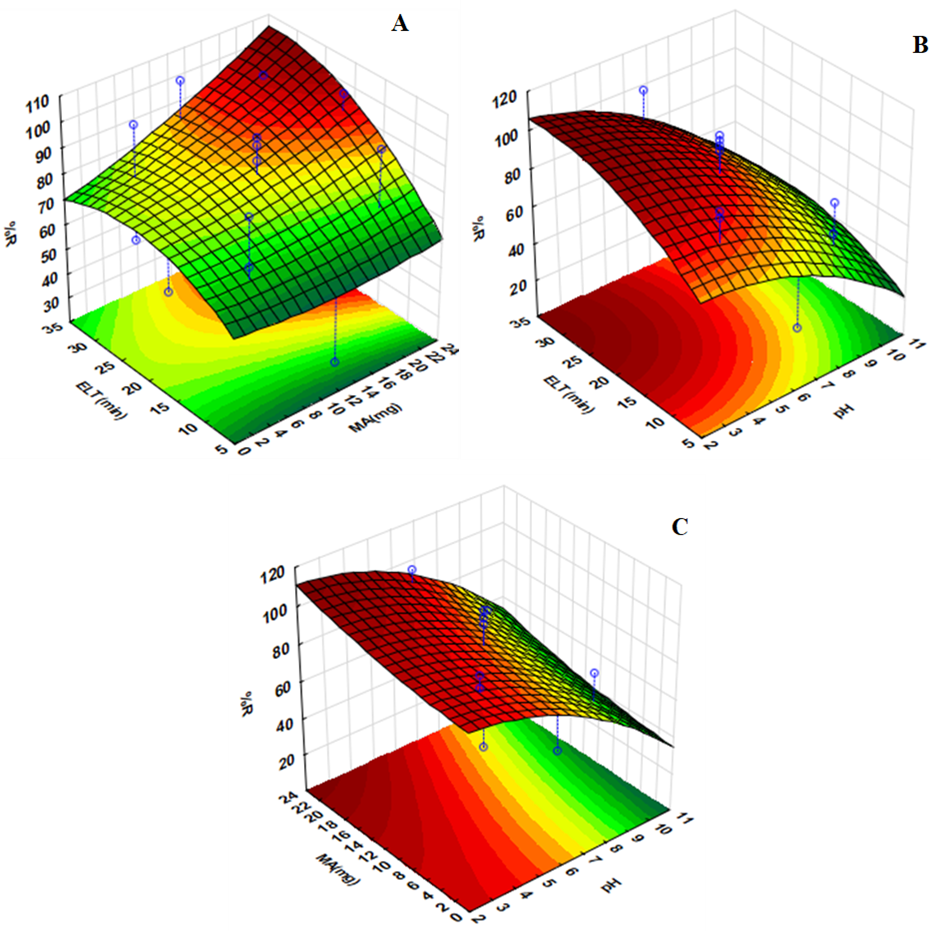
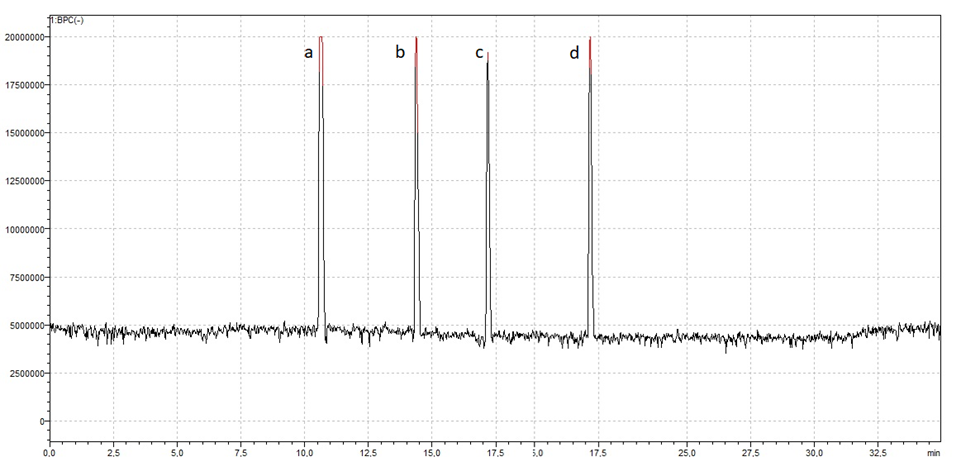
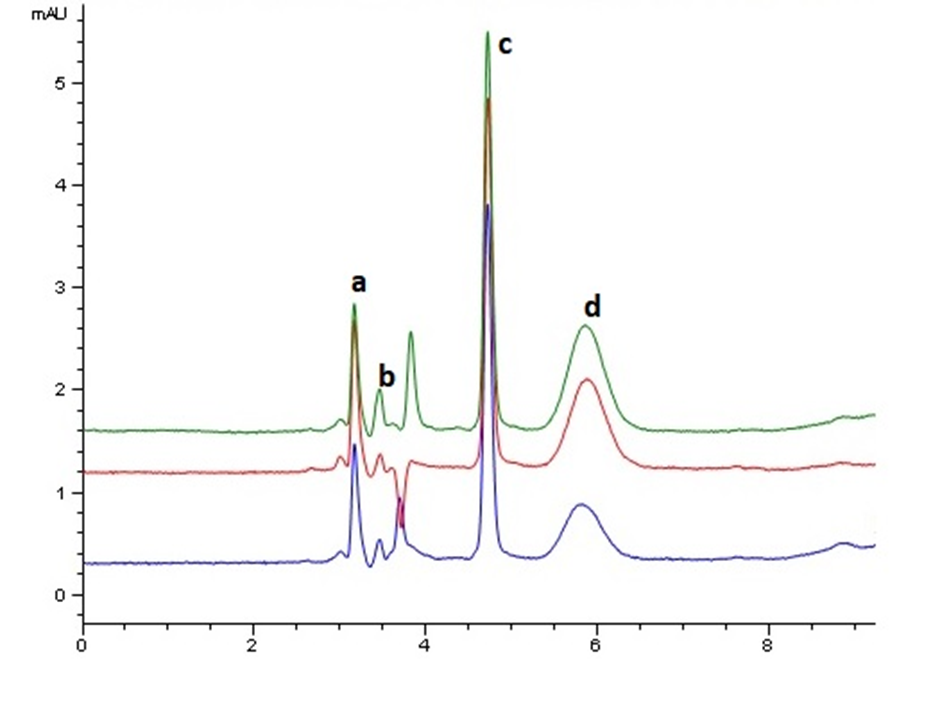


Figure S7: 3D response surface plots of (A) the interactive effect of elution time (ELT) and mass of adsorbent (MA) (B) the interactive effect of ELT and pH, and (C) the interactive effect of MA and pH.



Figure S8: Liquid chromatography peaks: (a) PFOS, (b) PFDA, (c) PFTeDA and (d) PFOS (Apies River water sample)



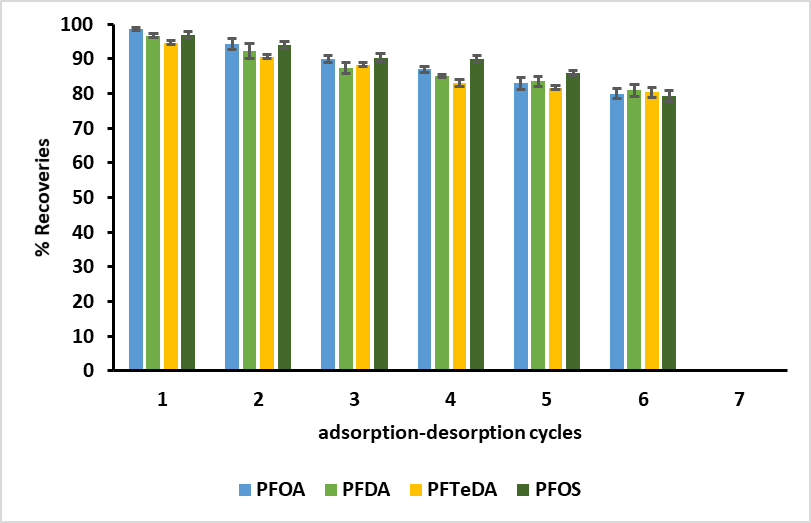


Figure S11: Reusability of Fe3O4@MIL-101(Cr) nanocomposite.