Supporting Information

Cooperative Molecular Interactions Based Highly Efficient Capturing of Ultrashort- and Short-Chain Emerging PFAS using Multifunctional Nanoadsorbents

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Methods

All the chemicals such as Ferrous sulfate heptahydrate, Potassium Nitrate, Sodium hydroxide, Polyethylenimine (PEI) ethylenediamine branched, nonafluoro-1-butanesulfonyl chloride, Triethylamine, N, N-Dimethylformamide anhydrous (DMF) were purchased from Sigma-Aldrich and were used without further purification.

Synthesis of acid functionalized magnetic nanoparticle.

Carboxy acid functionalized magnetic nanoparticles were prepared from ferric chloride and 1,6-hexanedioic acid using co-precipitation method as we and others have reported before [34-39]. In brief, 2.703 g (10 mmol) of $FeCl_3.6H_2O$ and 0.994 g (4.24 mmol) of $FeCl_2.6H_2O$ were dissolved in 50 ml of water. After that the mixture was kept under nitrogen atmosphere and heated at 80°C. In the next step, 10 ml of 20% ammonia solution was added slowly into the reaction mixture and kept for another half an hour. Finally, 2 ml aqueous solution of 1,6-Hexanedioic acid (0.37 gm/ml) was added slowly to the reaction mixture. Then the solution was continuously refluxed at 200oC for six hours. The obtained black precipitate of Fe3O4 nanoparticles were then thoroughly washed with water several times and separated from supernatant using neodymium magnet. After fresh synthesis, magnetic nanoparticles were characterized using tunneling electron microscopy (TEM) (JEOL-2100 PLUS), as reported in Figure S1.

Synthesis of F-PEG-CH_2COOH functionalized magnetic nanoparticle.

F-PEG-CH_2COOH [Poly(ethylene glycol) containing fluorine and carboxylic acid functionalized magnetic nanoparticles were prepared from ferric chloride and F-PEG-CH_2COOH using co-precipitation method as we and others have reported before [34-39]. In brief, 2.703 g (10 mM) of $FeCl_3.6H_2O$ and 0.994 g (4.24 mM) of $FeCl_2.6H_2O$ were dissolved in 50 ml of water. After that the mixture was kept under nitrogen atmosphere and heated at 80°C. In the next step, 6 ml of ammonia solution was added slowly into the reaction mixture and kept for another half an hour. Finally, 5 ml aqueous solution of F-PEG-CH_2COOH was added slowly to the reaction mixture. Then the solution was continuously refluxed at 200°C for six hours. The obtained black precipitate of F-PEG-CH_2COOH functionalized Fe_3O_4 nanoparticles were then thoroughly washed with water several times and separated from supernatant using neodymium magnet. After fresh synthesis, magnetic nanoparticles were characterized using tunneling electron microscopy (TEM) (JEOL-2100 PLUS), as reported in Figure S6.

Determining removal efficiency for short-chain and ultrashort chain PFAS like GenX, PFHxS, PFBS and PFPrS using LC-MS

For the determination of the removal amount for short-chain and ultrashort chain PFAS like GenX, PFHxS, PFBS and PFPrS using NFBS and PEI-conjugated multifunctional magnetic nanoadsorbents, PFAS and nanoadsorbent were stirred for different times. To determine the time dependent separate efficiency and kinetics, 1 mL aliquot was taken at each predetermined time intervals. After that the aliquots were centrifuged for 15 minutes. In the next step the supernatant was analyzed using LCMS to determine the residual GenX, PFHxS, PFBS and PFPrS concentration. For this purpose, we have used LC-MS (Agilent technologies) [10-20] and the X Bridge-C18 column (4.6mm×250mm) from Agilent Technologies [10-20]. For the analysis we have used negative ionization (ESI-) mode[10-20]. For the processing the data we have used the MassLynx workstation[10-20]. We have also

performed control experiments to account for the losses of GenX, PFHxS, PFBS and PFPrS during handling. For this purpose, we have performed experiments under identical conditions, where NFBS and PEI-conjugated multifunctional magnetic nanoadsorbents are absent.

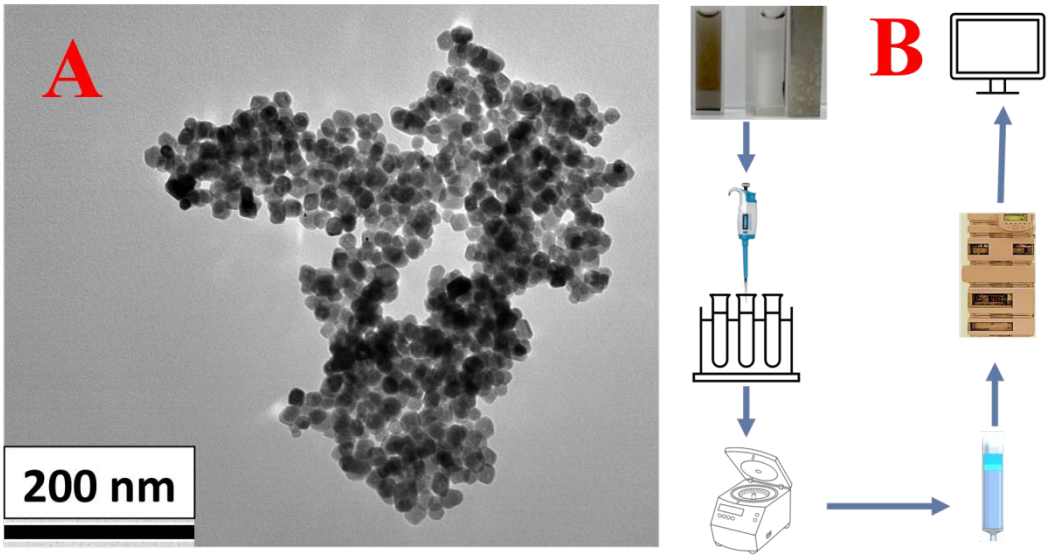

Figure S1. A) TEM image from acid functionalized - Fe_3O_4 magnetic nanoparticles show the shape is spherical and size is 25 ± 4 nm. B) The scheme shows the experimental setup and procedure we have used to determine the removal efficiency and capturing kinetics.

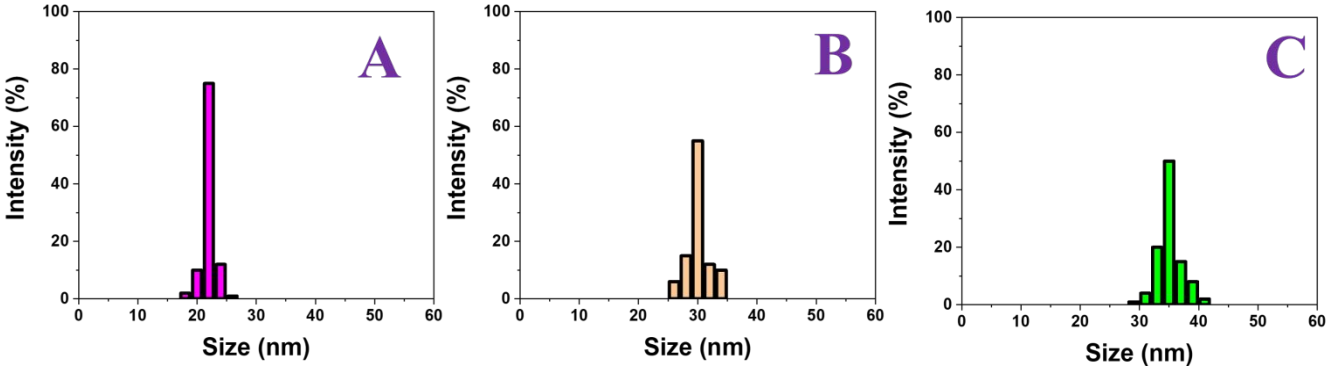

Figure S2. A) Particle size distribution histogram of Fe_3O_4 magnetic nanoparticles without PEI. B) Particle size distribution histogram of PEI attached Fe_3O_4 magnetic nanoparticles. C) Particle size distribution histogram of PEI and NFBS attached Fe_3O_4 magnetic nanoparticles.

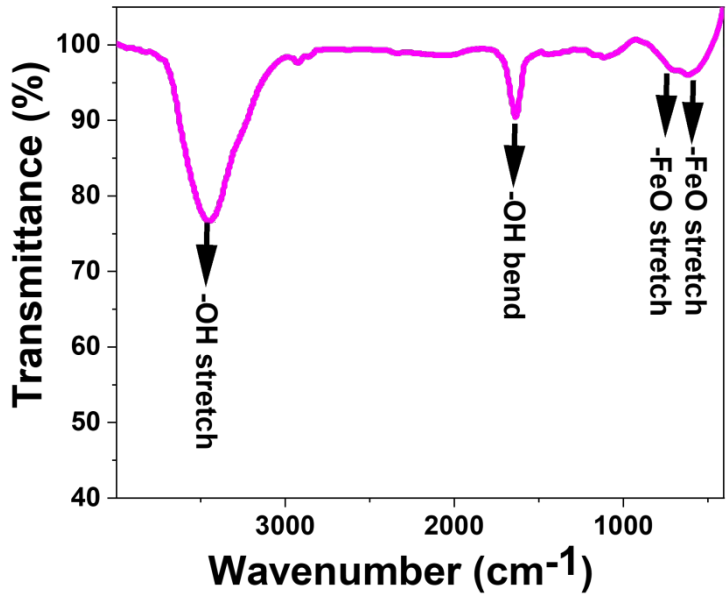

Figure S3: FTIR spectra from Fe_2O_3 nanoparticles without PEI shows the presence of –OH stretch, -OH bend, -Fe-O stretch peaks.

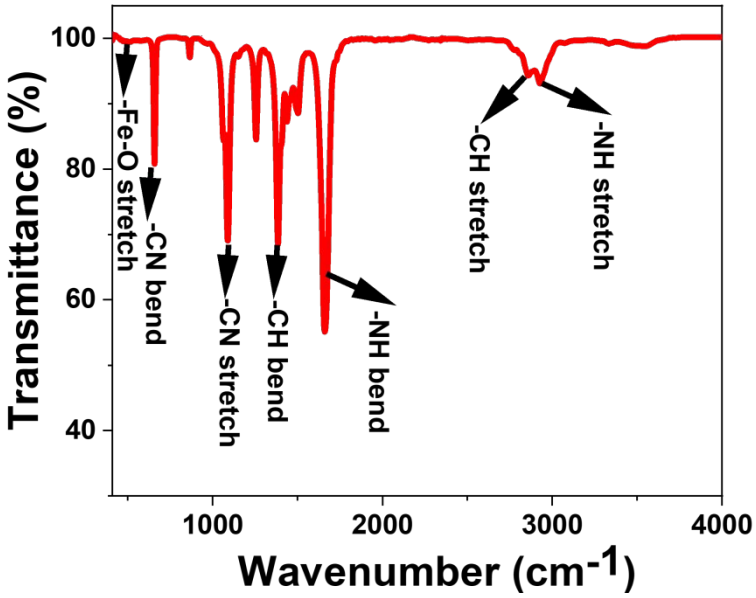

Figure S4: FTIR spectra from PEI attached Fe_2O_3 nanoparticles shows the presence of –NH stretch, -CH stretch, -NH bend, -CH bend, -CN stretch, -CN bends, Fe-O stretch peaks.

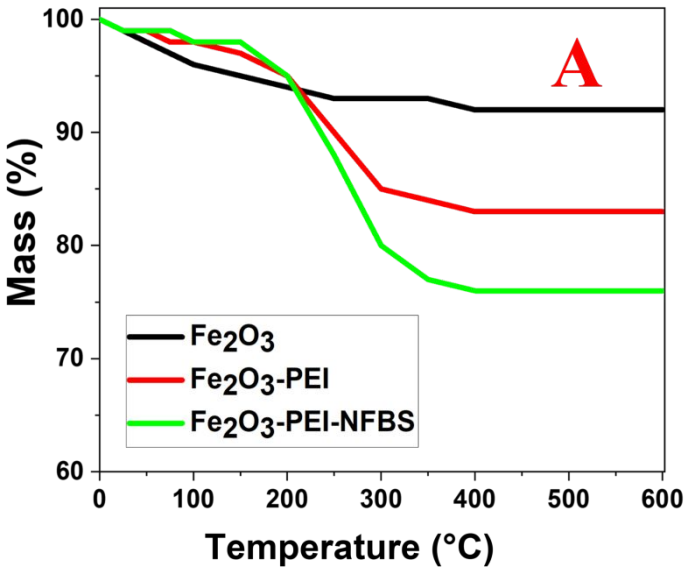

Figure S5: A): TGA curve shows percentage (%) of weight loss during thermal decomposition from Fe_2O_3 nanoparticles without PEI, PEI attached Fe_2O_3 nanoparticles, NFBS and PEI attached Fe_2O_3 nanoparticles.

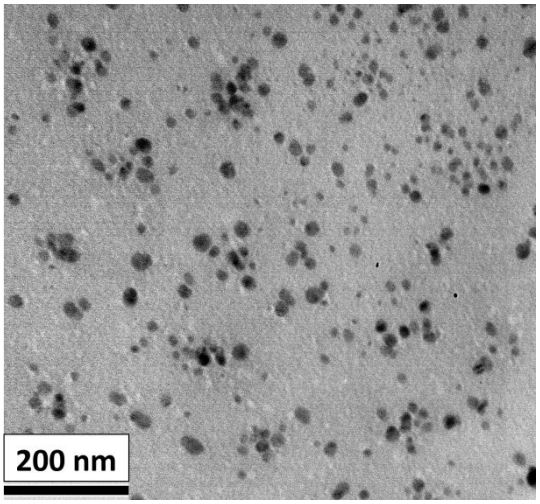

Figure S6. TEM image from F-PEG-CH_2COOH functionalized - Fe_3O_4 magnetic nanoparticles.

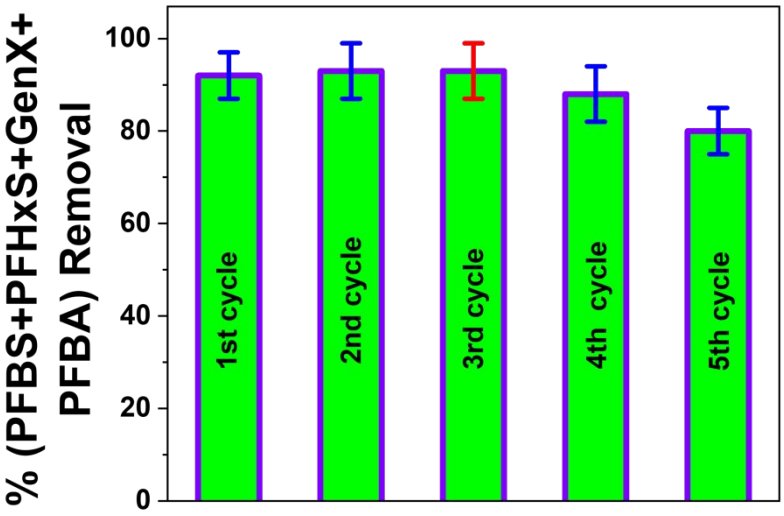

Figure S7: Plot shows how the removal efficiency of nanoadsorbent for PFAS samples containing the mixture of 0.25 µg/L of each of the short chain PFBS, PFHxS, GenX, and PFBA varies with different cycles.