Supplementary Materials

Design and preparation of magnetically-oriented poly(Styr-co-MMA)-3MPS capped Fe(ZnO) hybrid microspheres for ion exchange removal of toxic pollutants from wastewater

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S1. Materials and Methodology

S1.1. Materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99.8%), zinc chloride hexahydrate ($ZnCl_2 \cdot 6H_2O$, 99.9%), chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$, 99.8%), toluene ($C_6H_5CH_3$, 99.8%), oxalic acid ($H_2C_2O_4$, 99%), 3-methoxysilylpropyl methacrylate (3-MPS, 99%), ethylenediamine (EDA, 99%), dimethylformamide (DMF, 98%), styrene (99%), methyl methacrylate (MMA, 99%), polyvinyl alcohol (PVA, 99%) and fluorescein (95%) were purchased from Sigma-Aldrich. Benzoyl peroxide (BPO, 75%) was obtained from DaeJung Chemicals. Among other chemicals, sulphuric acid, hydrochloric acid, sodium chloride, phosphorus pentoxide, sodium carbonate and sodium bicarbonate were of analytical grade and employed as such without purification. The monomeric styrene (Styr) and methyl methacrylate (MMA) were washed with NaOH (5% w/v) followed by distilled water and redistilled under reduced pressure before polymerization.

S1.2. Synthesis of magnetic poly(Styr-co-MMA)-3MPS capped Fe(ZnO) hybrid microspheres

The polymeric microspheres of magnetic ZnO were synthesized in three distinct steps. Initially, Fe-doped ZnO were prepared by reported sol-gel method with some modifications (Scheme S1, Step 1) [14, 15]. The equimolar solutions of $FeCl_3 \cdot 6H_2O$ and $ZnCl_2 \cdot 6H_2O$ were gradually mixed together and stirred at 70 ^oC to ensure thorough mixing of the two solutions. Oxalic acid dihydrate (0.2 M) was added drop wise to the stirring solution and the whole mixture was refluxed at 70 ^oC for 1 hr. The obtained gel was dried under vacuum for 3 days and calcined at 650 ^oC in a muffle furnace. In the second step, silane-coated Fe(ZnO) were obtained by following the reported procedure of Bach *et al.*,[16]. The 3-methoxysilylpropyl methacrylate (5 mL) was added drop wise to the already dispersed

Fe(ZnO) (2 g, 25 mL) at 40 °C under constant stirring. The solution mixture was kept on stirring for 3 hr, then filtered and washed with deionized water/ethanol. The obtained product was oven dried at 60 °C for 3 hr (Scheme S1, Step 2). The third step involved the copolymerization of 3MPS-Fe(ZnO) nanoparticles with styrene and methyl methacrylate using oil-water suspension polymerization (Scheme S1, Step 3) [17, 18]. For this purpose, pretreated styrene (20 mL) and methyl methacrylate (10.6 mL) monomers were mixed at room temperature with silane-coated Fe(ZnO) (1.0 g) and stirred for 60 min to ensure the uniform mixing of oil-phase components. Afterwards, the aqueous phase consisting of polyvinyl alcohol (0.625 g) and NaCl (3.0 g) was gradually added to the oil phase while maintaining the temperature of 70 °C along with continuous N_2 flow. The benzoyl peroxide (0.3 g) was added as an initiator after 30 min of stirring, and the reaction was continued for 8 hr until the white precipitates were formed. The contents of the flask were filtered, washed, dried in the oven at 60 °C for 6 hr, and ground to a fine powder.

S1.3. Ion exchange functionalization of magnetic poly(Styr-co-MMA)-3MPS capped Fe(ZnO) hybrid microspheres

The functionalization of co-polymerized silane-modified magnetic ZnO was carried out according to the reported methods [19, 20]. For anion exchange functionalization (MFZPI) (Scheme S1, Step 4a), the procedure involved the addition of EDA/DMF (20 mL each) to the poly(Styr-co-MMA)-3MPS capped Fe(ZnO) and stirred for 6 hr at 70 °C. The EDA functionalized microspheres were separated, washed to remove excess DMF and dried for 6 hr at 70 °C. The dried sample was ground to a fine powder. The cation exchange polymer (SMFZPI) was prepared by sulphonation of EDA poly(Styr-co-MMA)-3-MPS-Fe(ZnO) (Scheme S1, Step 4b) [21, 22]. In this process, H_2SO_4 (50 mL) and P_2O_5 (100 g) were magnetically stirred at 40 °C. After 60 min, aminated polymer microspheres MFZPI (2.0 g) was added, and stirring was continued for the next 30 min. Then grayish-black precipitates of SMFZPI were separated by adding ice cubes (1.0 g) in the reaction mixture. The obtained product was filtered, washed and dried in an oven at 40 °C for 72 hr.

S1.4. Physicochemical analysis

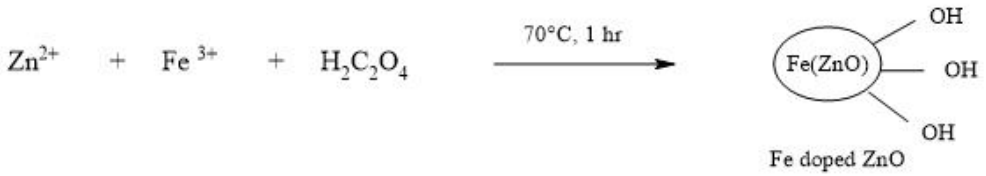
The physiochemical characterization of ion-exchange sorbents, i.e. MFZPI and SMFZPI was carried out by potentiometric titrations, also known as Boehm's titrations that predict the total acidic/basic concentration groups on the sorbent surface. The sorbents were dissolved in NaOH, Na_2CO_3, $NaHCO_3$, and HCl and allowed for the neutralization of ions [21]. The total acidic and basic groups on the sorbent's surface were determined by titrating against HCl (0.1 M) and NaOH (0.1 M) that counterbalance the unbound ions on the surface.

S1.5. Characterization

The synthesized materials were characterized using various analytical techniques. The functional group determination was carried out using Agilent Technologies Cary 630 FTIR spectrometer (Agilent Santa Clara, USA). UV-Vis spectrophotometer (Perkin Elmer λ-35, Waltham, MA, USA) provided the absorption spectral studies of fabricated materials. SEM and EDX analysis for the morphological study was done by FEI Nova Nano SEM 450, Oxford INCA X'ACT EDX, with 5000-100,000x magnifications at room temperature (298K). The structural aspects of the synthesized microspheres were studied by crystallographic data obtained from a powdered X-ray diffractometer (PXRD, Bruker D8 Advance Cu Radiation Ni filter). The thermal stability of magnetic polymer composites were obtained by using a simultaneous DSC-TGA Q600 thermal analyzer. A vibrating scanning magnetometer (VSM) (Cryogenic-free VSM with ETO) was used for the determination of magnetic properties of the magnetic polymer composites. The atomic absorption spectrophotometer (Perkin Analyst, 100 with Cr(III) torch) was used for the determination of Cr(III) adsorption.

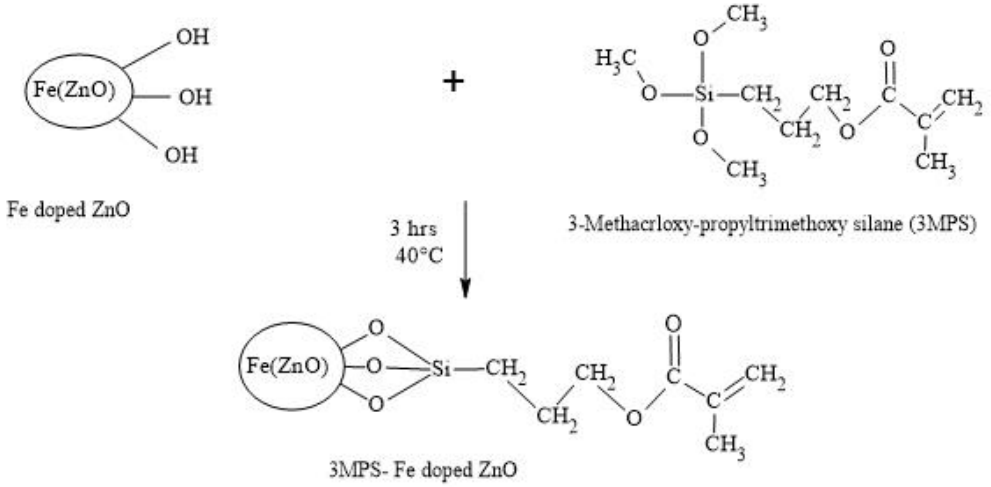
The adsorption capacity of fluorescein was measured by a visible spectrophotometer (Vis-spectrophotometer 721 Lab precision single light beam wavelength (360-1000 nm)).

Step 1: **Sol-gel synthesis of magnetic particles:**



Fe doped ZnO

Step 2: **Coating of magnetic nanoparticles with 3-methacryloxy-propyltrimethoxy silane (3-MPS)**

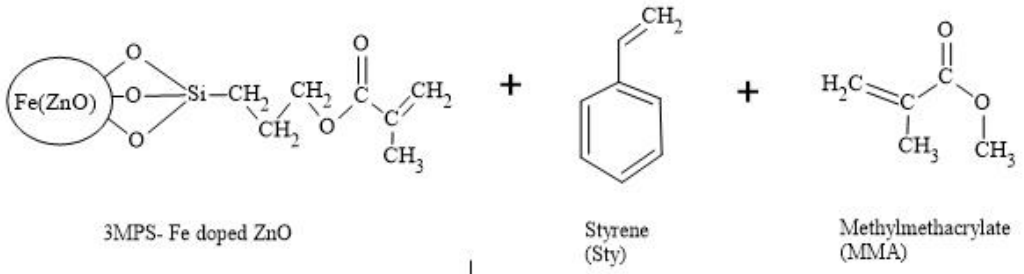


Fe doped ZnO

3-Methacrloxy-propyltrimethoxy silane (3MPS)

3MPS- Fe doped ZnO

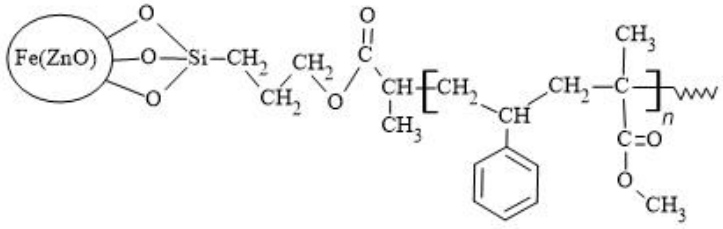
Step 3: Polymerization Reaction of 3-MPS coated Fe-doped ZnO composites:



3MPS- Fe doped ZnO

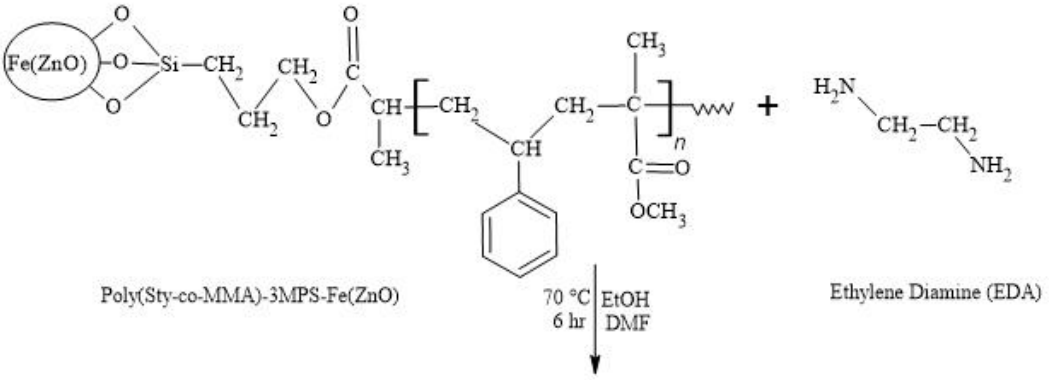
Styrene (Sty)

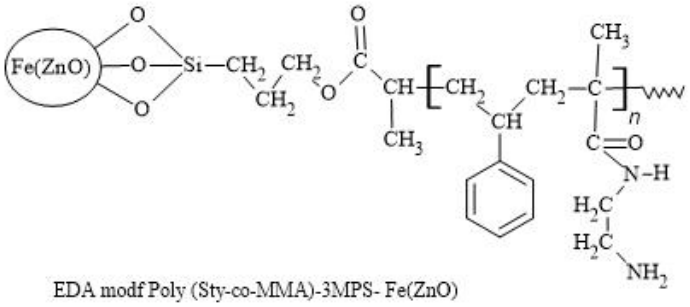
Methylmethacrylate (MMA)



Poly (Sty-co-MMA)-3MPS-Fe(ZnO)

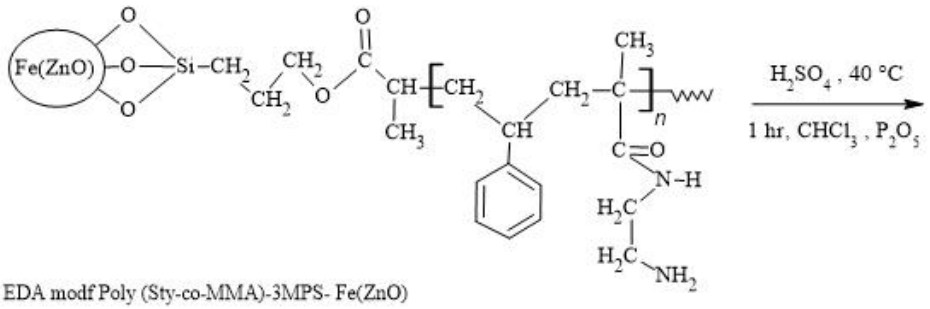
Step 4 (a): **Ethylene diamine functionalization of 3-mps-Fe(ZnO)-Styr-co-MMA**



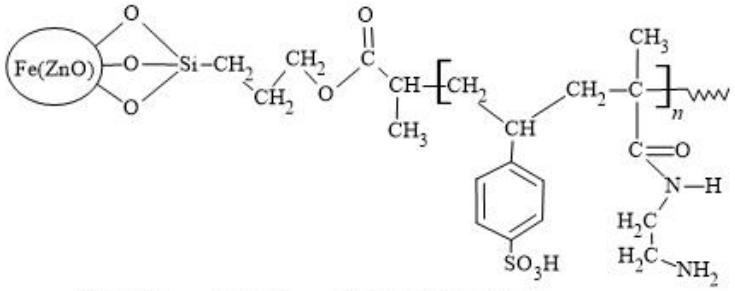


EDA modf Poly (Sty-co-MMA)-3MPS- Fe(ZnO)

Step 4 (b): **Sulphonation of EDA modified 3-mps-Fe(ZnO)-Styr-co-MMA**



EDA modf Poly (Sty-co-MMA)-3MPS- Fe(ZnO)



Sulph, EDA modf Poly (Sty-co-MMA)-3MPS-Fe(ZnO)

Scheme S1. The schematic illustration of the series of steps involved in the synthesis of co-polymerized magnetic ZnO microspheres and their functionalization.

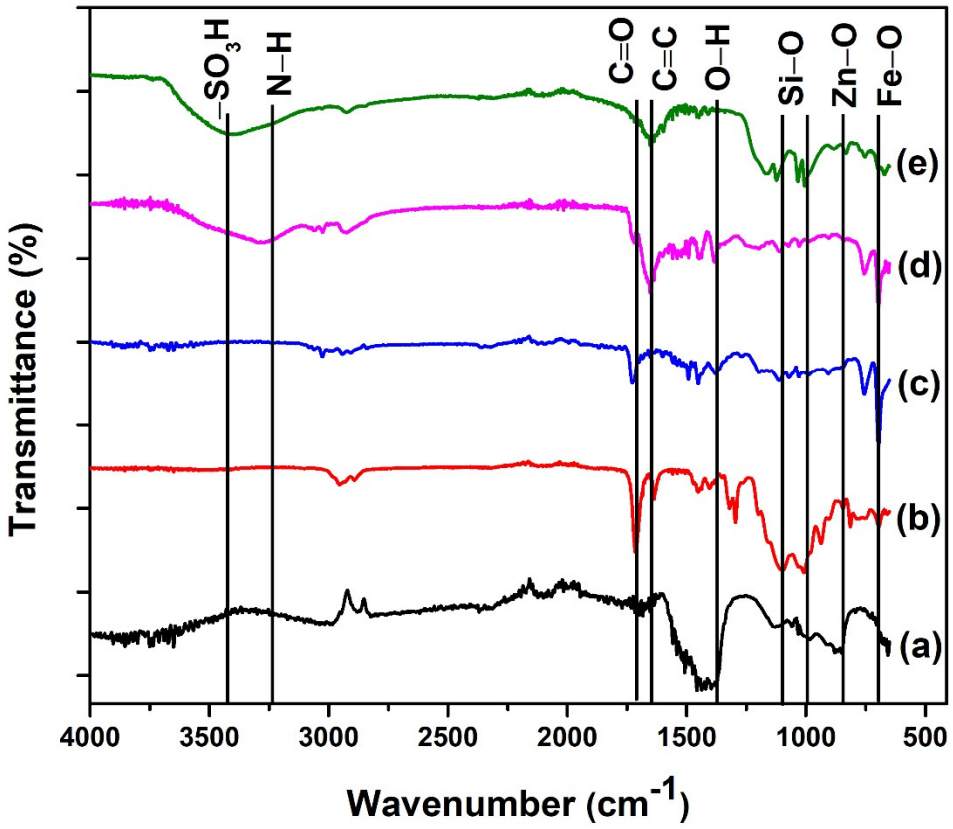


Figure S1. FTIR spectra of (a) Fe(ZnO), (b) 3-MPS-Fe(ZnO), (c) Poly(styr-co-MMA)-3MPS-Fe(ZnO), (d) EDA-Poly(styr-co-MMA)-3MPS-Fe(ZnO) (MFZPI), and (e) Sulphonated-EDA-Poly(styr-co-MMA)-3MPS-Fe(ZnO) (SMFZPI).

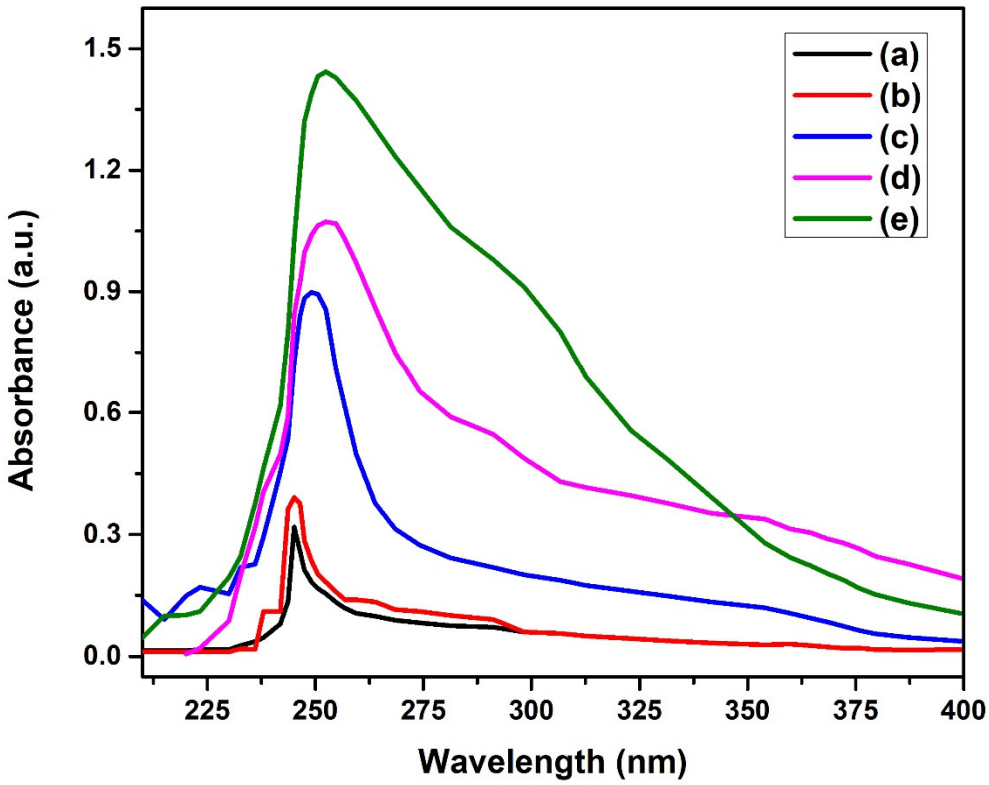


Figure S2. UV-Vis spectra of (a) Fe(ZnO), (b) 3-MPS-Fe(ZnO), (c) Poly(styr-co-MMA)-3MPS-Fe(ZnO), (d) EDA-Poly(styr-co-MMA)-3MPS-Fe(ZnO) (MFZPI), and (e) Sulphonated-EDA-Poly(styr-co-MMA)-3MPS-Fe(ZnO) (SMFZPI).

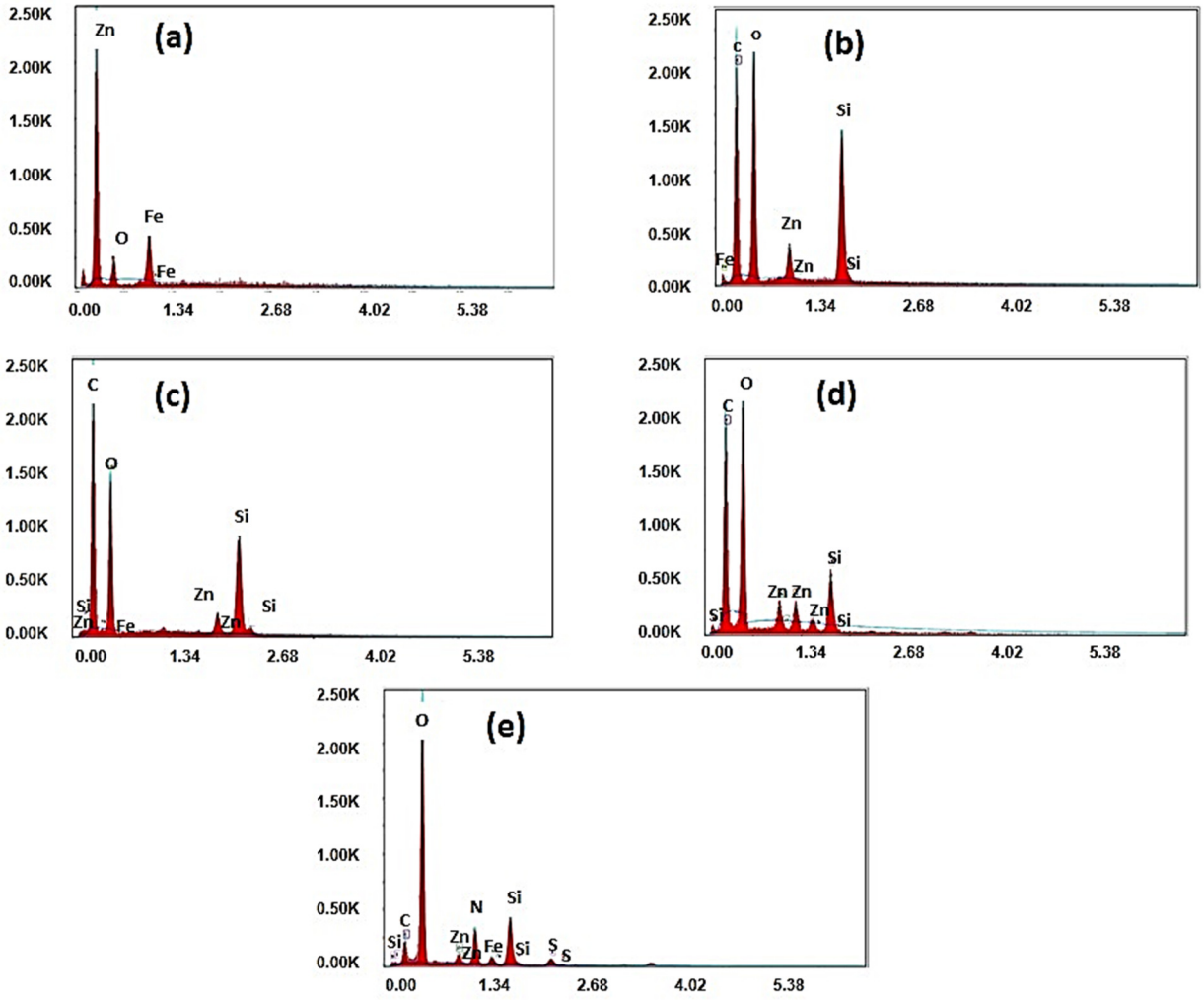


Figure S3. EDX profiles of (a) Fe(ZnO), (b) 3-MPS-Fe(ZnO), (c) Poly(styr-co-MMA)-3MPS-Fe(ZnO), (d) EDA-Poly(styr-co-MMA)-3MPS-Fe(ZnO) (MFZPI), and (e) Sulphonated-EDA-Poly(styr-co-MMA)-3MPS-Fe(ZnO) (SMFZPI).

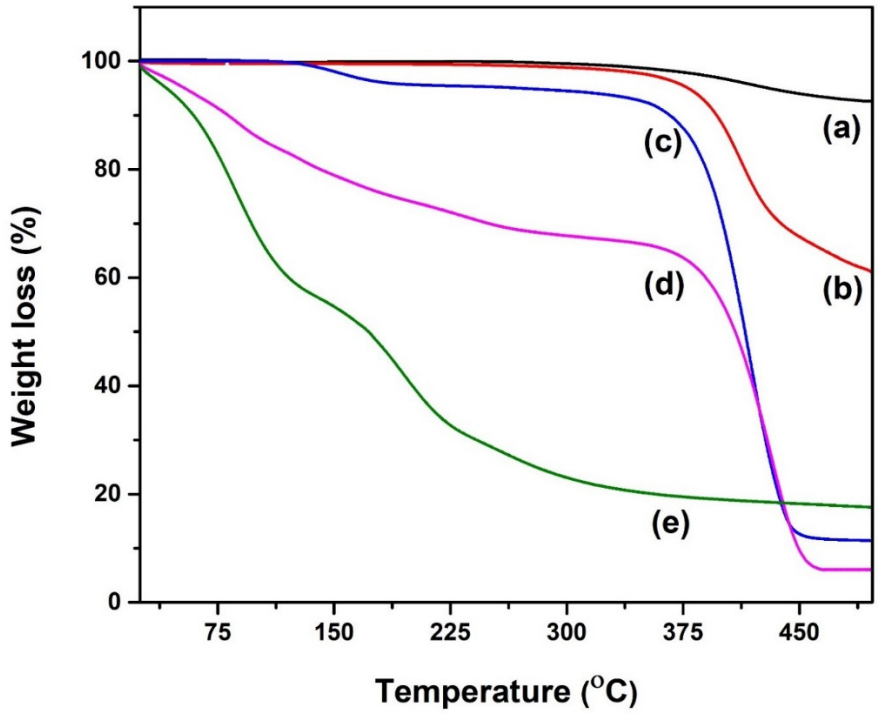


Figure S4. Thermogravimetric curves of (a) Fe(ZnO), (b) 3-MPS-Fe(ZnO), (c) Poly(styr-co-MMA)-3MPS-Fe(ZnO), (d) EDA-Poly(styr-co-MMA)-3MPS-Fe(ZnO) (MFZPI), and (e) Sulphonated-EDA-Poly(styr-co-MMA)-3MPS-Fe(ZnO) (SMFZPI).

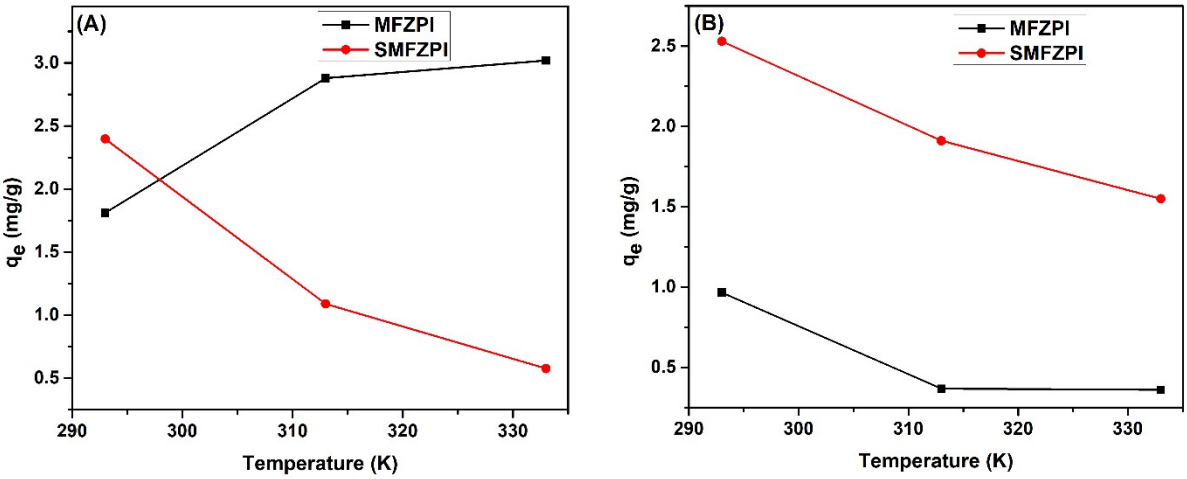


Figure S5. The influence of temperature (293-333K) on the sorption capacity of MFZPI and SMFZPI against (A) Cr(III), and (B) Fluorescein (initial concentration = 10 mg/L, and sorbent dose = 30 mg).