Supplementary material

Thiol functionalized TiO_2 microspheres and Fe(0) nanoparticles loaded polymeric hydrogel for selective recovery of Cr(III) and Cr(VI) from aquatic medium

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Uptake capacity calculation:

The uptake capacity was calculated by using the equation (S1)

$$Q_e = (C_i - C_f)\, v/m \qquad \text{(S1)}$$

Where Q_e uptake capacity in $\mu g g^{-1}$, C_i and C_f are the initial and final concentration in $\mu g mL^{-1}$, v is the volume of the metal ion solution in mL and m is the mass of the sorbent in g.

Thermo-gravimetric analysis (TG) of the SH-TiO_2-MS and SH-TiO_2-MS-Ca-Alg beads:

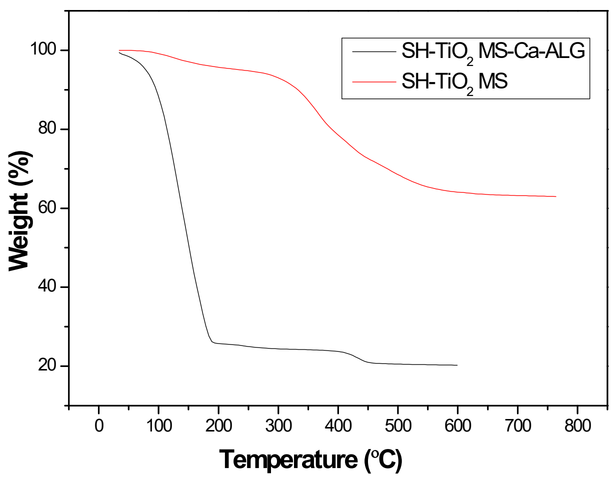

Fig. S1: TG of SH-TiO2 MS and SH-TiO_2-MS-Ca-Alg beads

Isotherm study:

Langmuir and Freundlich isotherms are two most widely used isotherm models for studying the interaction between sorbing medium and the sorbate. In Langmuir isotherm, it is assumed that there is only monolayer coverage on the surface of adsorbent whereas Freundlich model takes into consideration multilayer adsorption. Mathematically, Langmuir isotherm model is expressed as:

$$Q_e = Q_0 b C_e/(1 + b C_e) \quad \text{(S2)}$$

where Q_e is the equilibrium concentration of adsorbate ion in sorbent and Ce is equilibrium concentration of Cr(III)/Cr(VI) in solution. Q_0 is the maximum adsorption capacity, b is the Langmuir binding constant. The Langmuir isotherm assumes that the free energy of adsorption does not depend on the surface coverage.
Freundlich model is expressed as:

$$Q_e = k C_e^{1/n} \quad \text{(S3)}$$

Freundlich isotherm model assumes that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solutions is not constant at different solution concentrations. The constants of k and n in the Freundlich model are related to the strength of the adsorptive bond and the bond distribution.
The isotherm plots are given below:

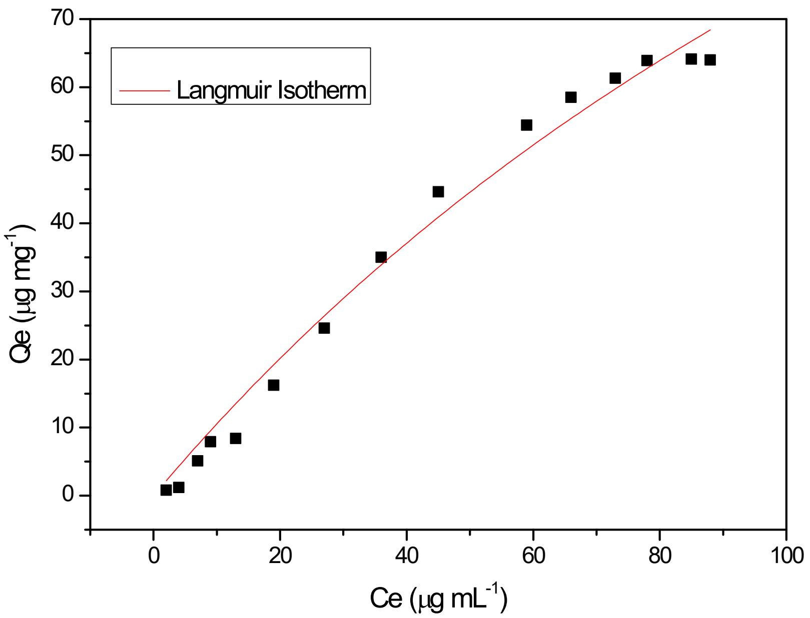

Fig. S2: Langmuir isotherm fitting for Cr(III) uptake by SH-TiO_2-MS-Ca-Alg beads

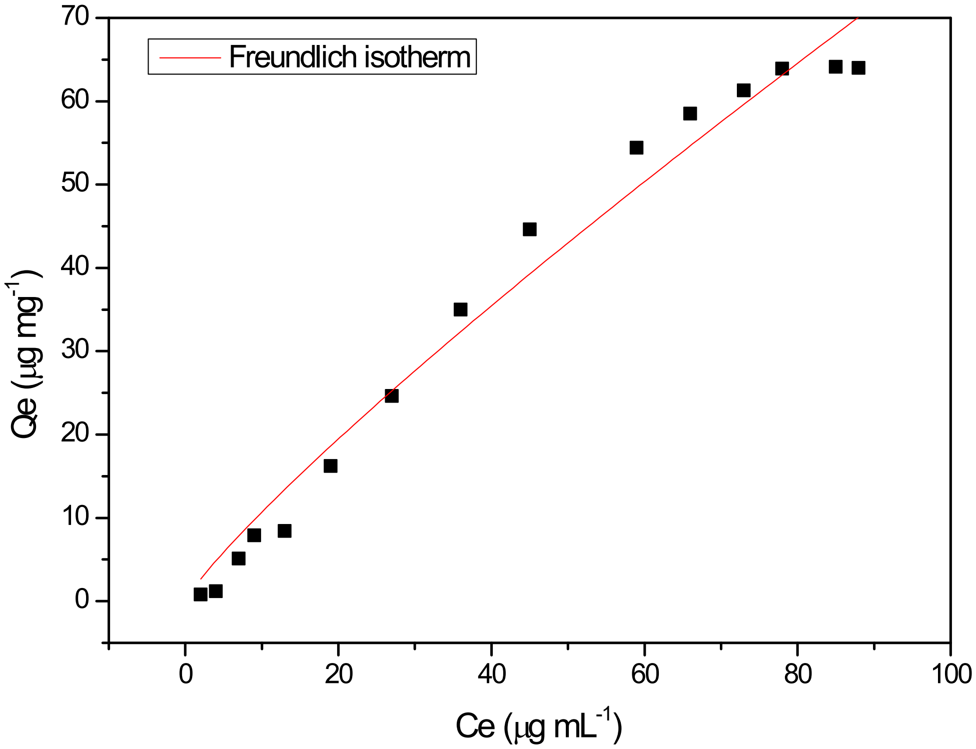

Fig. S3: Freundlich isotherm fitting for Cr(III) uptake by SH-TiO_2-MS-Ca-Alg beads

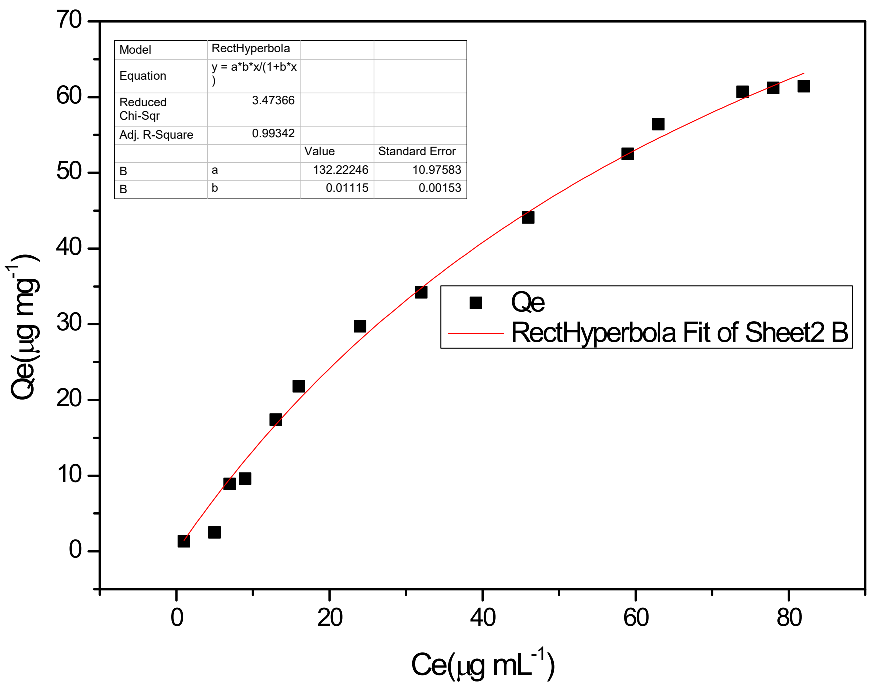

Fig. S4: Langmuir isotherm fitting for Cr(VI) uptake by Fe(0)-SH-TiO_2-MS-Ca-Alg beads

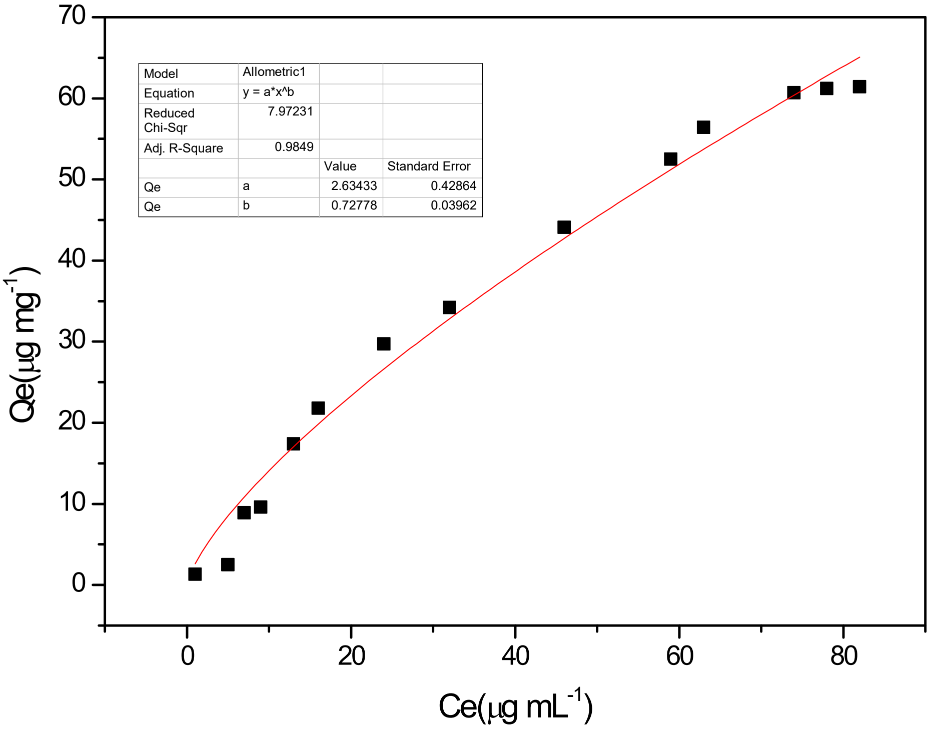

Fig. S5: Freundlich isotherm fitting for Cr(VI) uptake by Fe(0)-SH-TiO_2-MS-Ca-Alg beads

Kinetics study:

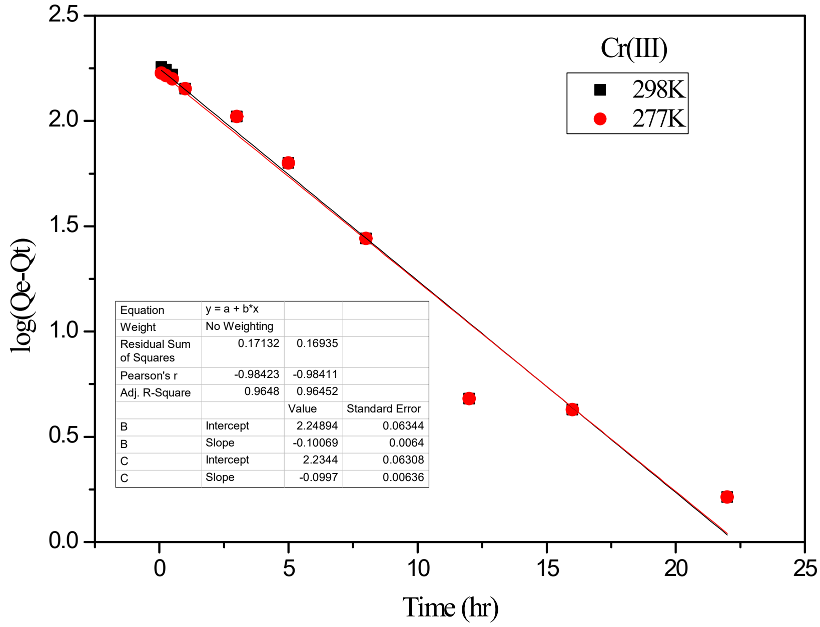

Fig. S6: Pseudo 1st order kinetic fitting for Cr(III) uptake by SH-TiO_2-MS-Ca-Alg beads

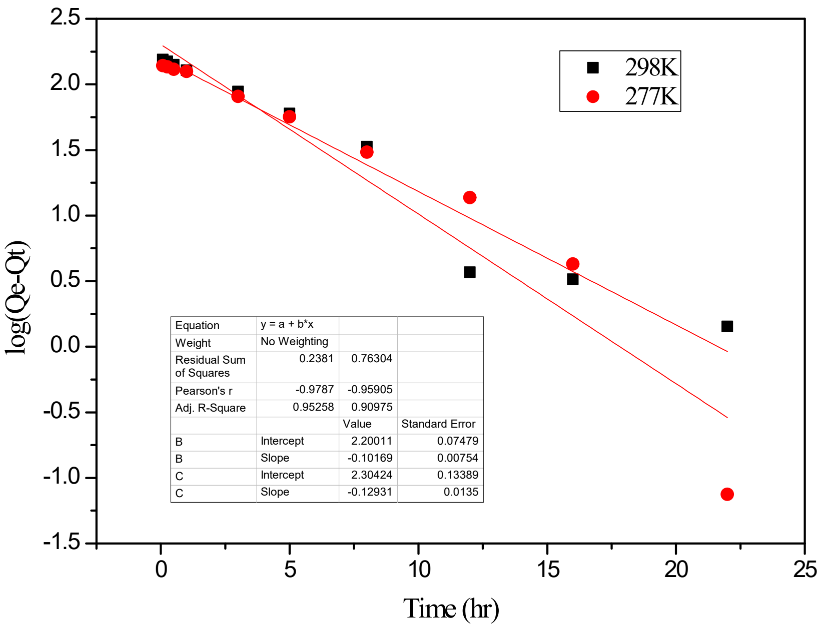

Fig. S7: Pseudo 1st order kinetic fitting for Cr(VI) uptake by Fe(0)-SH-TiO_2-MS-Ca-Alg beads

Table S1: Uptake study using regenerated beads

For reusability, used beads were taken and eluted using 1:1 mixture of 15 % thiourea and 4 N HNO_3. The regenerated beads were washed with demineralized water and utilized for 5 consecutive cycles with about 20% overall reduction in the Cr(III) and Cr(VI) recovery. Conditions maintained were 0.1 μgmL^{-1} concentration; 24h equilibration time; pH 2-3; number of beads 20. Removal efficiency (%) of Cr(III) and Cr(VI) using regenerated SH-TiO_2MS-Ca-Alg and Fe(0)-SH-TiO_2-MS-Ca-Alg beads are shown here (Table S1).

Number of cycle	**% uptake of Cr (III) using SH-TiO_2-MS-Ca-Alg beads**	**% uptake of Cr (VI) using Fe(0)-SH-TiO_2-MS-Ca-Alg beads**
1	92.8	91.2
2	89.3	88.6
3	82.5	80.1
4	78.3	77.4
5	75.7	74.2