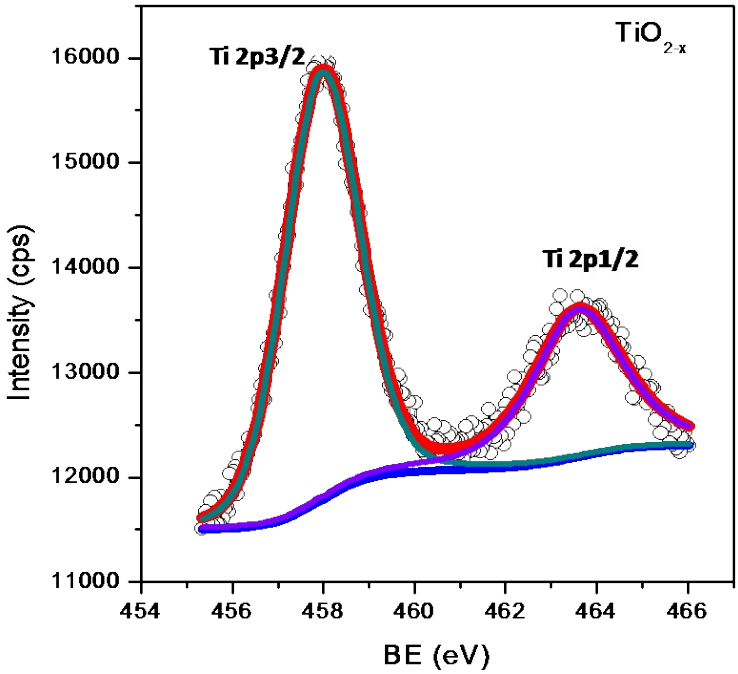
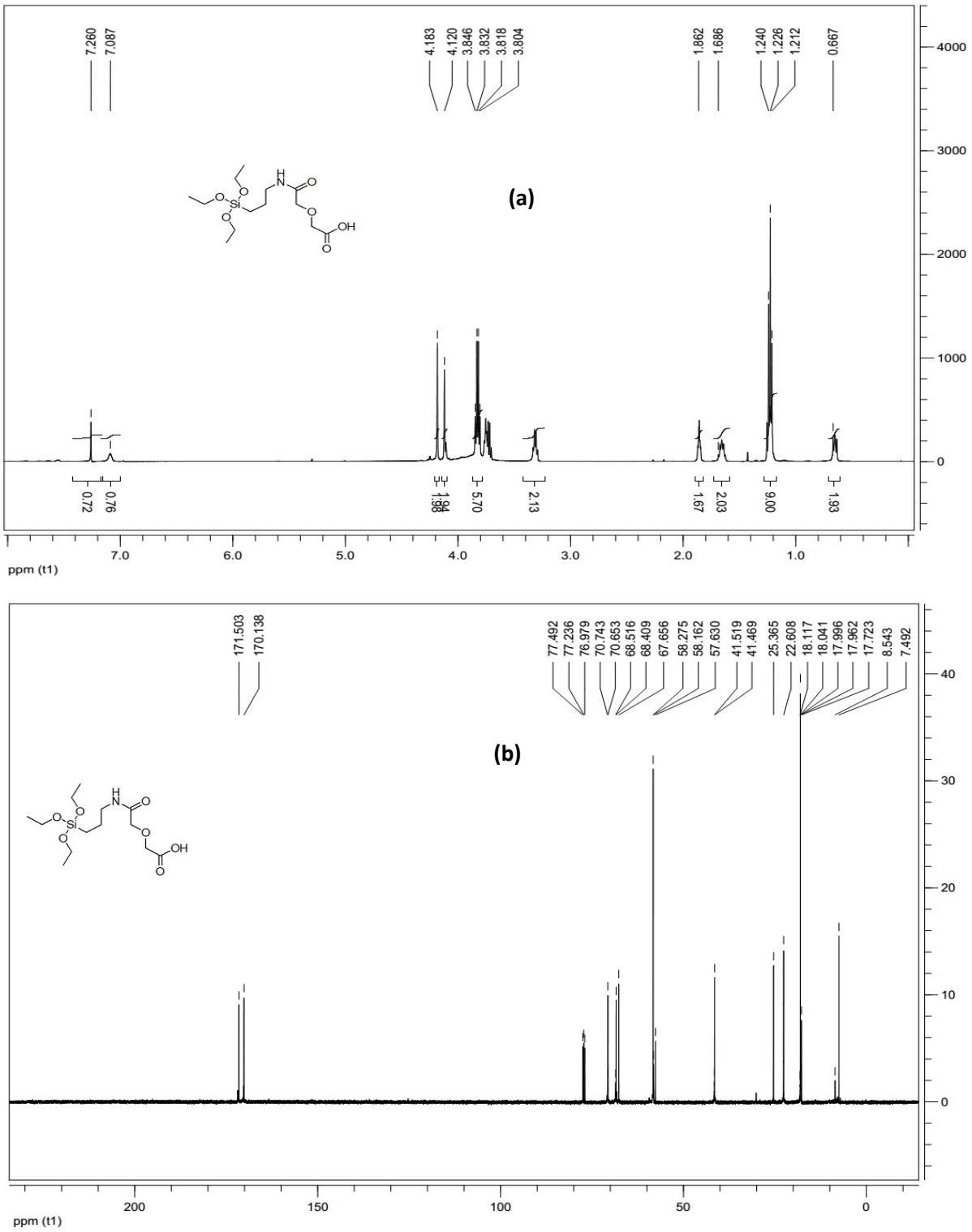
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

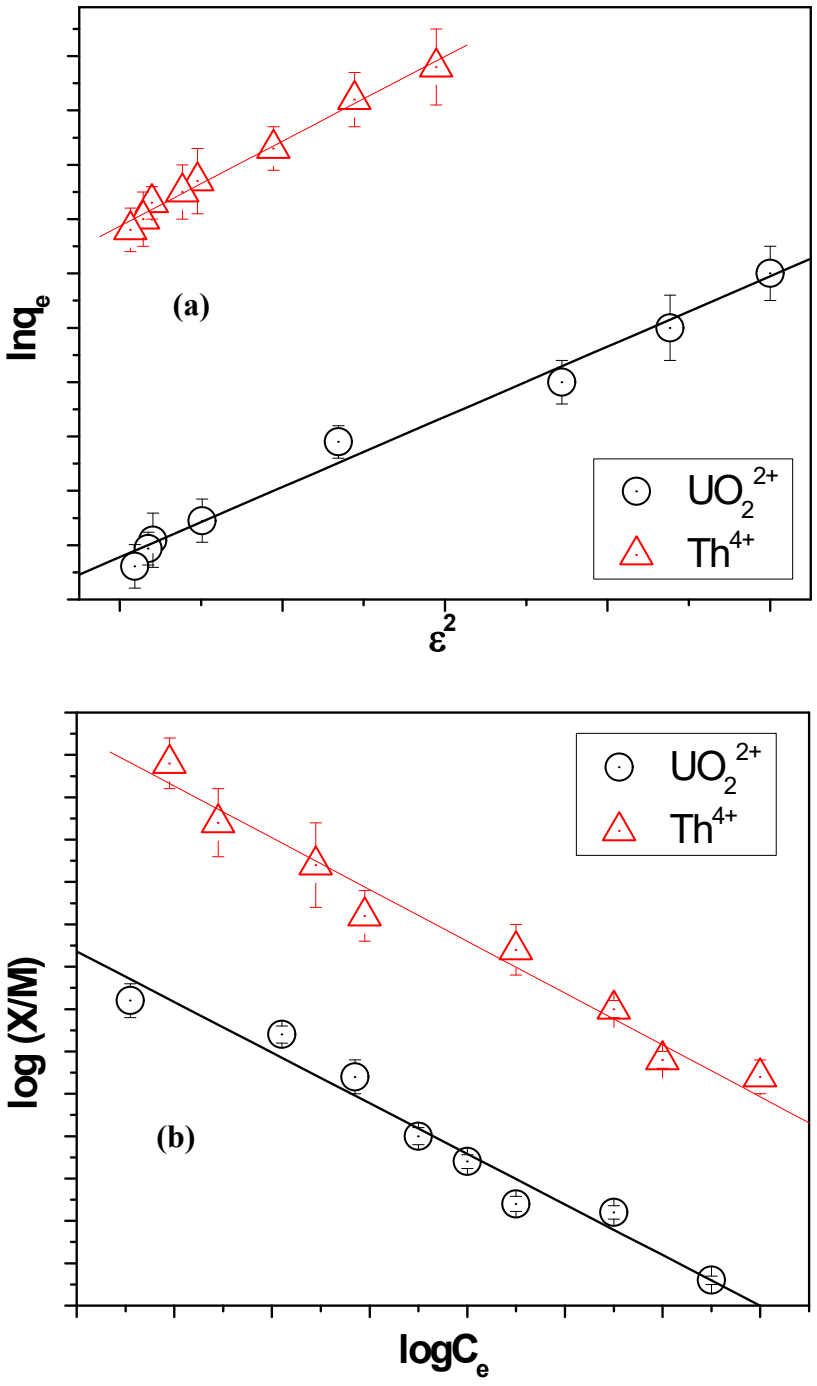

**Supporting Information**



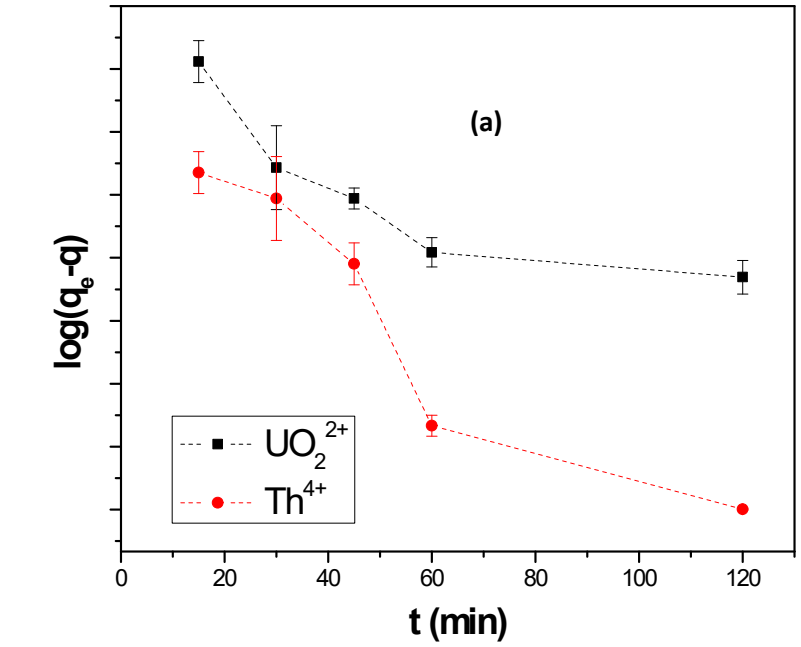

**SI Fig. 1**: XPS spectra for $TiO_2$ precursor for Ti peak

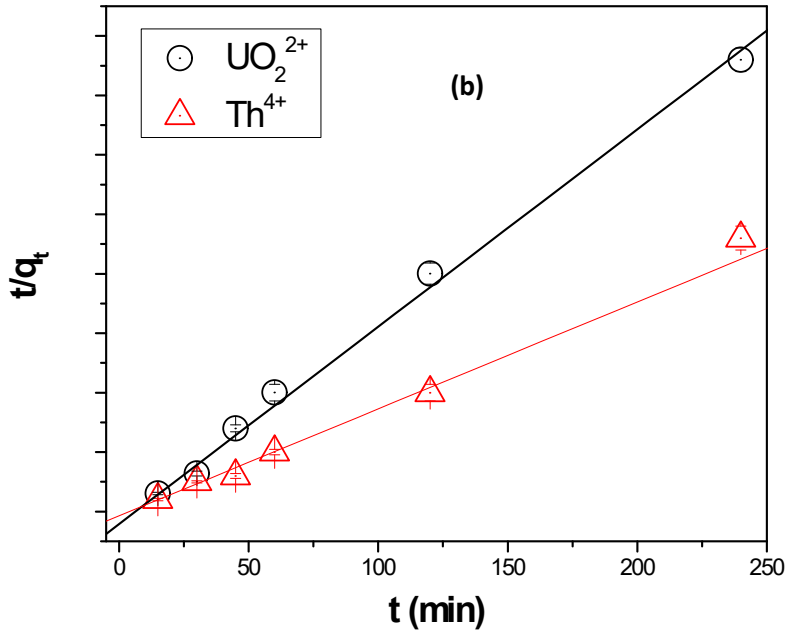



**SI Fig. 2**: (a) $^{1}$H-NMR spectra of SAPOGA (b) $^{13}$C-NMR spectra of SAPOGA

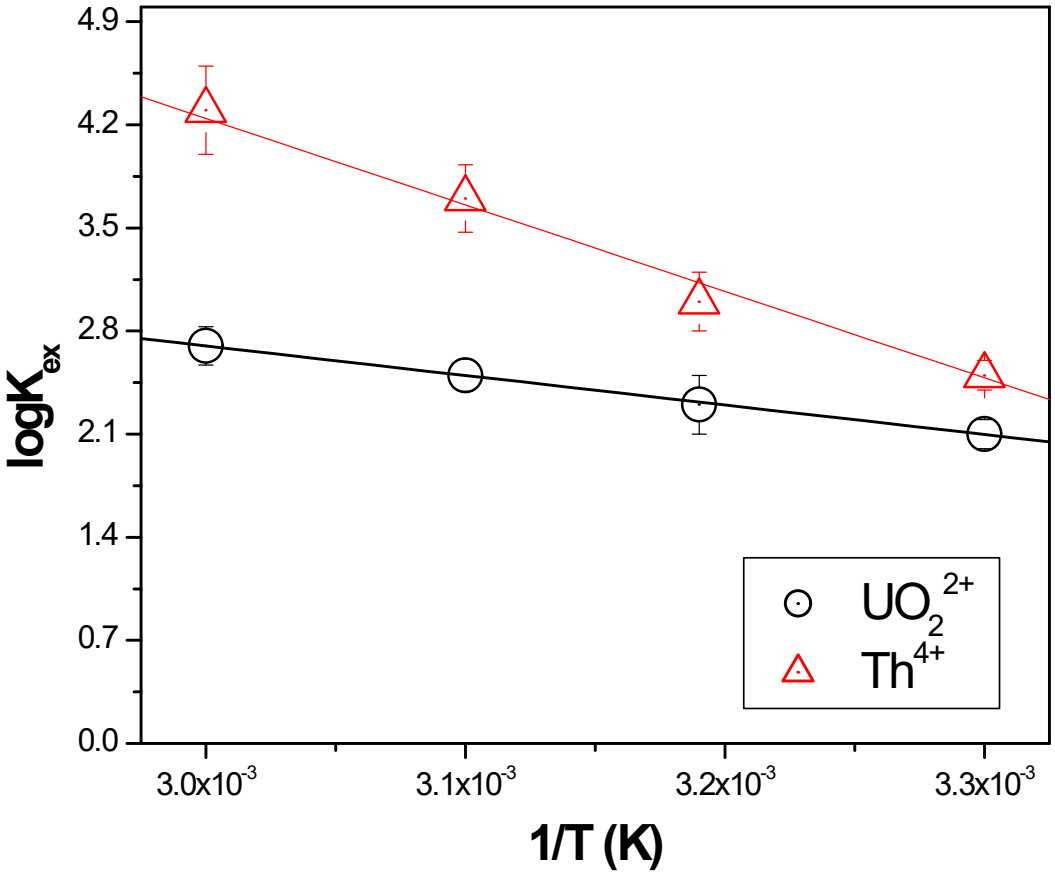



**SI Fig. 3**: The linear regression analysis for (a) Dubbin-Radushkevich (D-R) isotherm; and (b) Freundlich isotherm

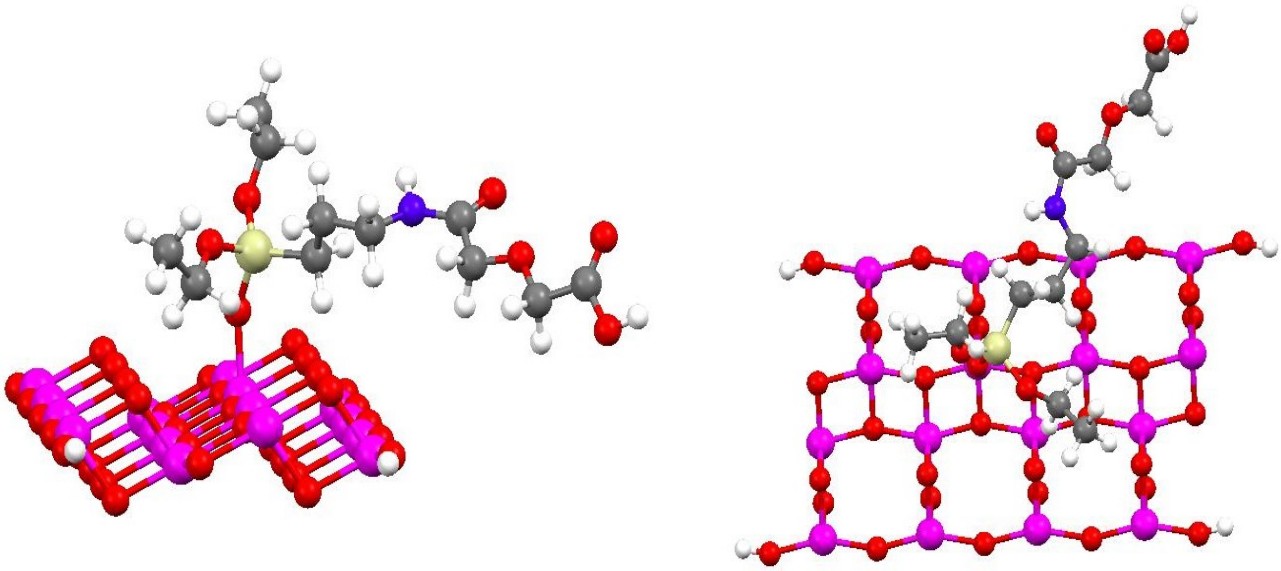


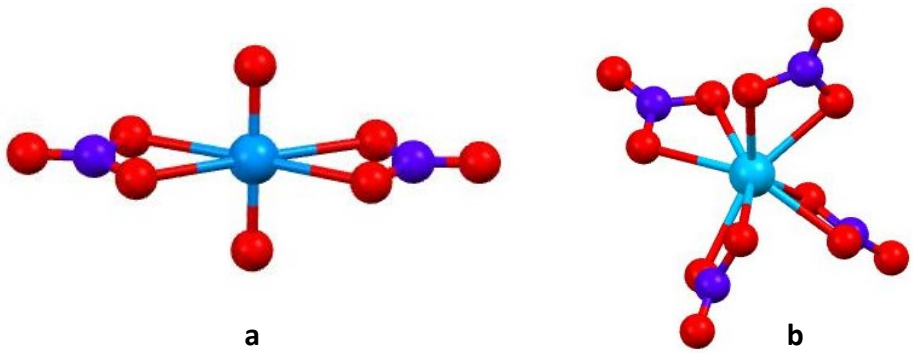

**SI Fig. 4**: Linear regression analysis for (a) Lagergren pseudo 1st order kinetics; (b) Pseudo 2nd order kinetics model



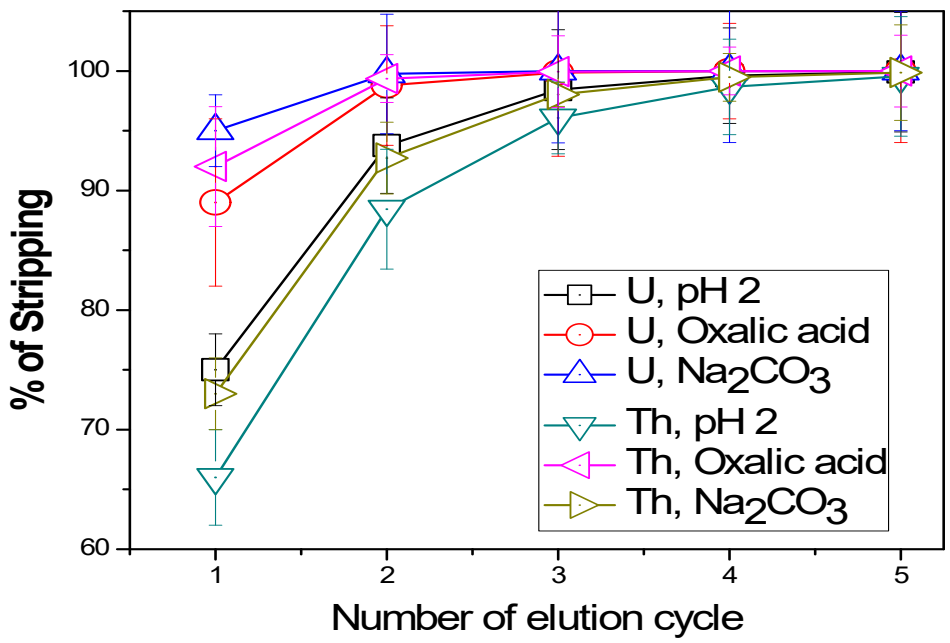

**SI Fig. 5**: The variation in conditional extraction constants for $UO_2^{2+}$ and $Th^{4+}$ on SAPOGA-$TiO_2$ as a function of reciprocal of absolute temperature



**SI Fig. 6**: The optimized structure for the sorbent SAPOGA-$TiO_2$




**SI Fig. 7**: The optimized structure of (a) $UO_2(NO_3)_2$ and (b) $Th(NO_3)_4$




**SI Fig. 8**: Cumulative % stripping of metal ions using multiple contacts of aqueous phase complexing agents

**SI Table.1**: Analytical results obtained by linear regression analysis of the experimentally obtained data using Langmuir, D-R, and Freundlich isotherm models

| | Langmuir | | | Dubinin-Radushkevich | | | Freundlich | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_e$ (mg/g) | b (l/mol) | $\chi^2$ | $x_m$ (mg/g) | E (kJ/mol) | $\chi^2$ | $K_f$(mmol/g) | n | $\chi^2$ |
| $UO_2^{2+}$ | 231 | 0.05 | 0.9989 | 200 | 15.7 | 0.9875 | 115 | 9 | 0.9890 |
| $Th^{4+}$ | 458 | 0.08 | 0.9972 | 381 | 19.0 | 0.9842 | 154 | 13 | 0.9867 |

**SI Table.2**: The linear regression analysis of the experimentally obtained data using Lagergren 1st order, Intra particle diffusion and Pseudo 2nd order kinetics models

| | Lagergren first order kinetics model | | | Intra particle diffusion model | | | Pseudo 2nd order model | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_e$ | $k_{ads}$ | $\chi^2$ | $k_p$ (mg $g^{-1}$ $min^{-1}$) | C | $\chi^2$ | $q_e$ (mg $g^{-1}$) | $k_2$ (mg $g^{-1}$ $min^{-1}$) | $\chi^2$ |
| $UO_2^{2+}$ | 66 | 0.08 | 0.7817 | 51 | 23 | 0.9997 | 88 | 5.8E-04 | 0.9973 |
| $Th^{4+}$ | 89 | 0.04 | 0.6866 | 48 | 29 | 0.9982 | 99 | 3.6E-04 | 0.9956 |

**SI Table.3**: Calculated structural parameters (bond length in Å) of complexes of $UO_2^{2+}$/$Th^{4+}$ ion with SAPOGA-$TiO_2$ in presence of nitrate ion.

| System | M-$O_{C=O}$ (Å) | M-$O_{ethereal}$ (Å) | M-$O_{NO3}$(Å) |
|---|---|---|---|
| UO2$(NO_3)_2$-L | 2.423, 2.593 | 2.835 | 2.442, 2.427, 2.504, 2.517 |
| Th$(NO_3)_4$-L | 2.441, 2.600 | 2.783 | 2.515, 2.519, 2.453, 2.480, 2.597, 2.578, 2.518 |

**SI Table.4**: Calculated value of Gibbs free energy (kcal/mol) in the gas and aqueous phase

| Equilibrium reaction | Free energy of adsorption (kcal/mol) | |
|---|---|---|
| | Gas phase | Aqueous phase |
| $[UO_2(H_2O)_5]^{2+}_{(aq)} + 2NO_3^-{}_{(aq)} + L_{(aq)} \longrightarrow UO_2(NO_3)_2\text{-}L_{(aq)} + 5H_2O$ | -312.5 | -30.2 |
| $[Th(H_2O)_{10}]^{4+}_{(aq)} + 4NO_3^-{}_{(aq)} + L_{(aq)} \longrightarrow Th(NO_3)_4\text{-}L_{(aq)} + 10H_2O$ | -915.1 | -83.7 |
| $UO_2(NO_3)_{2(aq)} + L_{(aq)} \longrightarrow UO_2(NO_3)_2\text{-}L_{(aq)}$ | -24.9 | -6.6 |
| $Th(NO_3)_{4(aq)} + L_{(aq)} \longrightarrow Th(NO_3)_4\text{-}L_{(aq)}$ | -87.8 | -36.8 |

**SI Table.5**: Calculated charge and orbital population using NBO analysis in aqueous phase at the B3LYP/TZVP level of theory.

| System | charge | s | p | d | f |
|---|---|---|---|---|---|
| $UO_2(NO_3)_2$-L | 1.803 | 4.17 | 11.77 | 11.46 | 2.78 |
| $Th(NO_3)_4$-L | 1.694 | 4.20 | 11.99 | 11.12 | 0.981 |
| $[UO_2(H_2O)_5]^{2+}$ | 2.088 | 4.14 | 11.75 | 11.38 | 2.61 |
| $[Th(H_2O)_{10}]^{4+}$ | 2.175 | 4.18 | 11.99 | 10.91 | 0.73 |
| $UO_2(NO_3)_2$ | 2.195 | 4.11 | 11.74 | 11.30 | 2.62 |
| $Th(NO_3)_4$ | 2.382 | 4.15 | 11.99 | 10.86 | 0.59 |

SI Table 6: Average value of Wiberg bond Indices for metal-ligand and metal nitrate bonding.

| System | M-O(-C=$O_{DGA}$) | M-O(-ether $O_{DGA}$) | M-O ($NO_3$) |
|---|---|---|---|
| $UO_2(NO_3)_2$-L | 0.334 | 0 | 0.461 |
| $Th(NO_3)_4$-L | 0.369 | 0.073 | 0.431 |