



Application of hybrid MOF composite in extraction of f-block elements: Experimental and computational investigation

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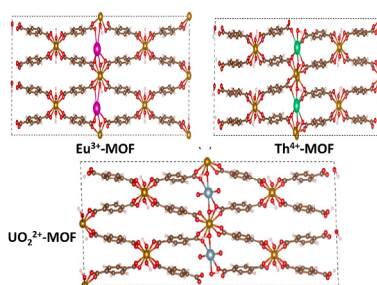
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HIGHLIGHTS

- Hybrid metal-organic framework composites for extraction of U, Th and Eu.
- Sorption followed Langmuir isotherm.
- Sorption process was found to be endothermic, and spontaneous.
- Sorption predominantly followed Pseudo 2nd order rate kinetics.
- DFT calculation on MOF-f element interactions.

GRAPHICAL ABSTRACT



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ABSTRACT

An attempt was made to understand the sorption behaviour of UO_2^{2+} , Th^{4+} and Eu^{3+} on novel hybrid metal-organic framework composites, FeBDC@CoBDC . The XRD pattern revealed the composite nature of the hybrid MOF materials, while FTIR and Raman spectroscopic analyses evidenced the presence of different functional moieties. The thermal stability of the hybrid MOF composites was investigated through thermogravimetric analysis. The sorption predominantly followed Langmuir isotherm with sorption capacity of 189 mg g^{-1} , 224 mg g^{-1} and 205 mg g^{-1} for UO_2^{2+} , Th^{4+} and Eu^{3+} respectively. The sorption proceeded through chemisorption following pseudo 2nd order rate kinetics. The processes were found to be thermodynamically favourable and endothermic in nature. However, they were entropically driven. Multiple contacts of complexing agents were necessary for quantitative elution of f-elements from loaded MOF. The MOF showed moderate stability towards radiation exposure. DFT calculation was used for the optimization of structures, estimation of bond length and estimation of binding energy. In hybrid MOF composites, the Fe atom was having six coordination with 4 O atoms of BDC moieties and 2 O atoms of $-\text{OH}$ groups. The O atoms of BDC and $-\text{OH}$ groups were coordinated to Eu, Th and U atoms during their sorption.

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1. Introduction

Nuclear energy is considered to be one of the viable sources to meet the ever-increasing global energy demand (Zinkle and Was, 2013; Schaffer, 2013). However, the public acceptability and industrialization of nuclear energy largely depend on the safe management of the highly radio-toxic waste generated during different steps of nuclear activities (Wattal, 2013; Raj et al., 2006). Separation Science and technology plays a pivotal role in meeting the criteria of efficient and selective separation of f-block elements (Grimes et al., 2014; Hu et al., 2020). These f-block elements can exist in different oxidation states and hence highly complex in nature. The solvent extraction is the most widely applied separation scheme in the nuclear establishment, wherein the complexing ability of f-block elements was utilized. The extractant molecule having suitable functional groups diluted in organic solvents is the main step for efficient as well as selective separation of f-block elements (Dam et al., 2007; Berthon et al., 2001; Nash, 2006; Modoloa et al., 2014). Therefore, finding proper function groups/extractants was the centre of attraction in separation science about nuclear establishment. However, with public awareness of the use of volatile organic solvents, not suitable for the environment; there was an urge to find out 'green' solvents like ionic liquid potential alternatives to VOCs (Priya et al., 2016; Singh et al., 2016; Pandey et al., 2021a; Das et al., 2021). Reports are also available demonstrating the task-specific application of ionic liquid by suitable functionalization (Pathak et al., 2021; Sengupta et al., 2014). Solid-phase extraction/sorption has also been utilized as a potential separation scheme for the efficient separation of f-block elements. Inorganic ion exchange materials, porous materials, activated carbon-based materials, silica and zeolite-based porous substances, magnetic nanomaterials and their composites, functionalized carbon nanotubes (multi/single wall), laminar structured graph oxides and their associated hybrid materials are some of the potential choices of sorbent materials showing very good extraction of different oxidation states of f-block metal ions (Han et al., 2010; Wu et al., 2014; Patil et al., 2019; Gupta et al., 2019, 2021a; Sengupta and Gupta, 2017). Metal-organic framework (MOF) is one of the porous materials that have been introduced recently for separation of f-block elements from aqueous medium due to some of their favourable properties including high BET, uniform pore, functionalized, oxygen-rich pore wall, having coordinating unsaturated sites, and structural diversity (Viltres et al., 2020; Zhang et al., 2017; Gilhula et al., 2019). Though nowadays, MOF is considered to be one of the technologically advanced materials, widely applied in a variety of fields including gas separation and storage, catalysis, energy applications and storage materials, drug delivery and other bio-medical applications, sensors, magnetism etc (Kirchon et al., 2018; Ding et al., 2019; Yu et al., 2017; Chaikittisilp et al., 2013; Liua et al., 2021); the reports on the application of MOF in nuclear establishment for separation of radio-toxic f-block elements are only very few. The efficacy of such MOF materials in f-element separation largely influenced by the following facts: The MOF must exhibit sufficient chemical, thermal as well as radiological stability; the pore size of the MOF must be large enough to accommodate the f-block ions either in aquated form or in dehydrated form; inside the pore structure of MOF, binding sites must be available to coordinate to the f-block metal ions.

Phosphorylurea functionalized MOF, UiO-68 showed highly efficient sorption of uranyl ion and is the first report on the application of MOF in actinide extraction (Carboni et al., 2013). Acylamide, carboxyl, coumarin functionalities have been introduced to Zn based MOF, Zn-MOF-74 and reported to extract uranyl ion (Zhang et al., 2016). Hafnium based MOF was reported to extract UO_2^{2+} , Th^{4+} from moderately acidic aqueous feed and Pu and Np from 4 M HNO_3 overcoming the limitation of lower stability of MOF at acidic conditions (-ping Xiong et al., 2019). This MOF also showed excellent radiolytic stability. Amino functionalized MOF was reported to adsorb uranyl ion with a capacity of 350 mg g^{-1} (Bai et al., 2015). Eu incorporated multifunctional MOF has been reported to have fluorescence sensing

capability along with the ability to degrade the dyes after sorption (Meng et al., 2015). EDTA modified MOF, UiO-66-EDTA was reported to be suitable for separation of Eu^{3+} , Hg^{2+} and Pb^{2+} with the capacity of 195.2, 371.6 and 357.9 mg g^{-1} , respectively (Wua et al., 2019). Zr^{4+} based MOF showed chemical sensing application towards the sorption of Cr^{6+} (Rapti et al., 2017). Pu^{4+} augmented MOF has also been synthesized recently demonstrating control of Pu^{4+} coordination under hydrolysis-prone conditions (Hastings et al., 2020).

Given this, hybrid MOF composites based on Fe and Co metals have been employed for the sorption of f-block metal ions. UO_2^{2+} has been chosen for hexavalent, Th^{4+} has been chosen for tetravalent ion and Eu^{3+} has been chosen for the trivalent f-block metal ion. 1,4-benzene dicarboxylic acid has been utilized as functional moieties associated with the present hybrid MOF composites. To understand the sorption mechanism Langmuir, Dubinin-Radushkevich (D-R), Freundlich and Temkin isotherms models were utilized (Sengupta et al., 2017; Gupta et al., 2017; Gupta and Sengupta, 2017a), while Lagergren first order, intra-particle diffusion and Pseudo 2nd order kinetics models were employed to understand the kinetics of the sorption (Kumar et al., 2016, 2017a, 2017b; Kishor et al., 2017). The thermodynamic parameters including change in Gibbs's energy, enthalpy and entropy associated with the sorption processes were estimated. Density Functional Theory (DFT) calculation was carried out to have a theoretical insight into the nature of bonding/coordination between f-block elements and MOF moieties, optimized structural parameters etc. The reusability and the stability of the MOF have been investigated in terms of performance deterioration of gamma-irradiated MOF and elution behaviour of f-block metal ions from the loaded MOF.

2. Experimental

2.1. Materials

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, terephthalic acid (H_2BDC), N,N'-dimethyl formamide (DMF), and ethanol were procured from Sigma Aldrich. All chemicals were of analytical grade and used without any further purification. Oxalic acid and ethylene diamine tetra acetic acid (EDTA) were purchased from Thomas Baker Chemical limited, Mumbai and Na_2CO_3 was bought from Qualigensfine Chemicals, India, respectively. Suprapure HNO_3 and CertiPUR® solutions were bought from E-Merck, Darmstadt, Germany. Deionized water (DI) was used throughout the experiment. For the preparation of U and Th stock solutions, high purity U_3O_8 and ThO_2 powder, obtained from the Inter laboratory Comparison experiments involving different laboratories from the Department of Atomic Energy, India were taken. For the U stock solution, the U_3O_8 powder was allowed to dissolve in concentrated nitric acid under an IR lamp. Then the solution was evaporated to dryness for five times. Finally, the stock solution was made in a 1 M HNO_3 medium. Similarly, for ThO_2 , concentrated HNO_3 was added along with 1–2 drops of HF. This F^- ion helped in the dissolution of high purity ThO_2 into nitric acid. In this case also, repeated evaporation to dryness was done. This is an essential step to remove all the F^- ion. Finally, 1 M HNO_3 medium was kept in Th stock solution.

2.2. Instrumentation

Fourier-Transform Infrared (FTIR) spectrum was collected on a PerkinElmer spectrometer, USA at 4 cm^{-1} resolution. Powdered X-ray diffraction (PXRD) pattern was recorded with a Bruker D8Advance Diffractometer, USA with $\text{CuK}\alpha$ radiation. Raman spectrum was recorded with an XRD Raman Microscope spectrometer (Thermo Fisher Scientific, USA). A 780 nm excitation line in backscattering geometry through a 10X objective lens was used to excite the sample with a power of 6 mW (5 s of exposure time and 20 scans). The thermal stability of the MOF composite was evaluated by thermogravimetric analysis (TGA, T A Instruments, Q5000 IR model, USA) at a heating rate of $10^\circ \text{C min}^{-1}$

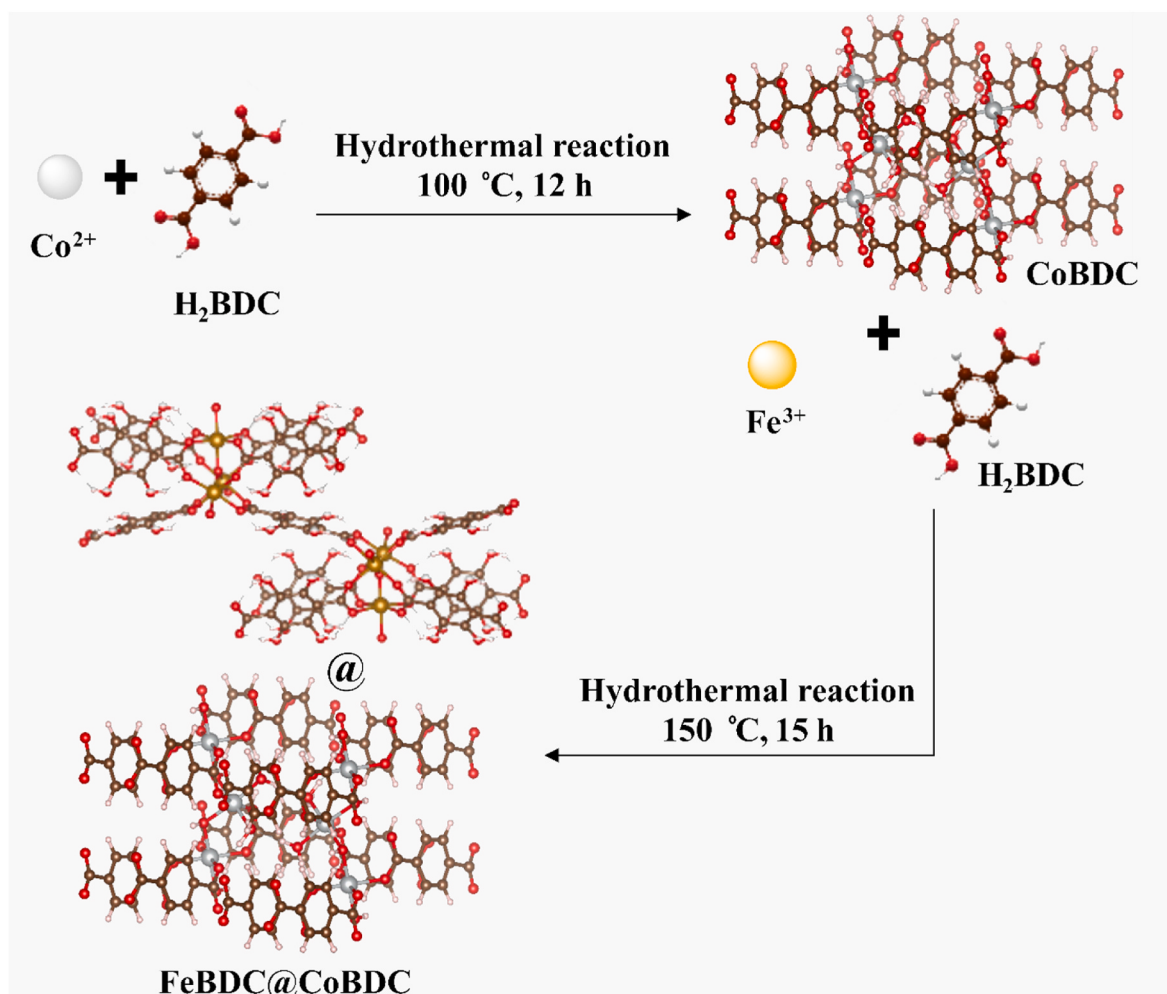


Fig. 1. The synthesis and the structure of the hybridMOF composite.

under N_2 flow. Energy-dispersive X-ray fluorescence spectroscopy (EDXRF) (procured from Jordan Valley, Israel, Model No: EX-3600 M) was used for the analysis of UO_2^{2+} , Th^{4+} and Eu^{3+} metal ion in aqueous solutions. The Si(Li) detector (resolution 139 eV, energy range 1–40 keV) with a 12.5 mm Be window was utilized for the detection system. ^{60}Co gamma chamber BARC, India was used for MOF irradiation at different gamma exposure. To achieve different gamma dose, the time of irradiation was varied. A thermostated temperature-controlled water bath bought from Lab Enterprise, Mumbai, India, was utilized for the sorption experiments. The shaking in a water bath can be achieved in the temperature range of 20 °C–90 °C with an accuracy of $\pm 0.5^\circ\text{C}$. The phase separation was carried out using a variable frequency centrifuge machine purchased from Lab Enterprise, Mumbai, India. 1200 RPM was used for centrifugation.

2.3. Synthesis of metal-organic framework

Synthesis of CoBDC: H_2BDC (996 mg, 1 mmol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1746 mg, 1 mmol) were dissolved in 30 mL of DMF. The solution was placed in a Teflon-lined stainless-steel autoclave and heated for 12 h at 100 °C. The product was washed with DMF and methanol and dried at 60 °C for 12 h to yield CoBDC MOF.

Synthesis of FeBDC@CoBDC: CoBDC (350 mg) was dispersed in a mixed solution of DMF (90 mL), deionized water (6 mL), and ethanol (6 mL) under ultrasonication for 10 min. To it, H_2BDC (330 mg) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (808 mg) were added sequentially under vigorous stirring to form a homogeneous suspension. The resulting blend was transferred

into a Teflon-lined steel autoclave and heated for 15 h at 150 °C. The product was washed with DMF and methanol and dried at 60 °C for 12 h to yield FeBDC@CoBDC.

2.4. Separation experiments

The sorption experiments were carried out using metal ion (UO_2^{2+} , Th^{4+} and Eu^{3+}) in an aqueous phase with an initial concentration of 1 mg mL^{-1} . 100 mg of sorbent was allowed to equilibrate with 5 mL of an aqueous solution containing the metal ions together. In the case of establishing extraction profile, the aqueous phase pH was allowed to vary in the range of pH 1 to pH6. Both the phases were allowed to equilibrate for 2 h at 300 K. After that, 2 min centrifugation was done for complete phase separation. Suitable aliquots from the supernatant were collected for the determination of U, Th and Eu in the aqueous phase after separation. Since the initial concentration was also known, therefore, amount adsorbed on the MOF can be evaluated. The K_d values were estimated based on the equation below (Curtis et al., 2004)

$$K_d = \frac{(C_0 - C_e) V}{C_e m} \quad (1)$$

where, C_0 and C_e are the concentration of U, Th and Eu at $t = 0$ and equilibrium. The V denotes the volume, whereas m denotes the weight of MOF under consideration. For isotherm analyses, the amount of MOF was varied from 25 mg to 200 mg, while the aqueous phase pH was kept at 1. The equilibration was done for 2 h at 300 K. After 2 min of centrifugation; the supernatant was taken for the estimation of f-block

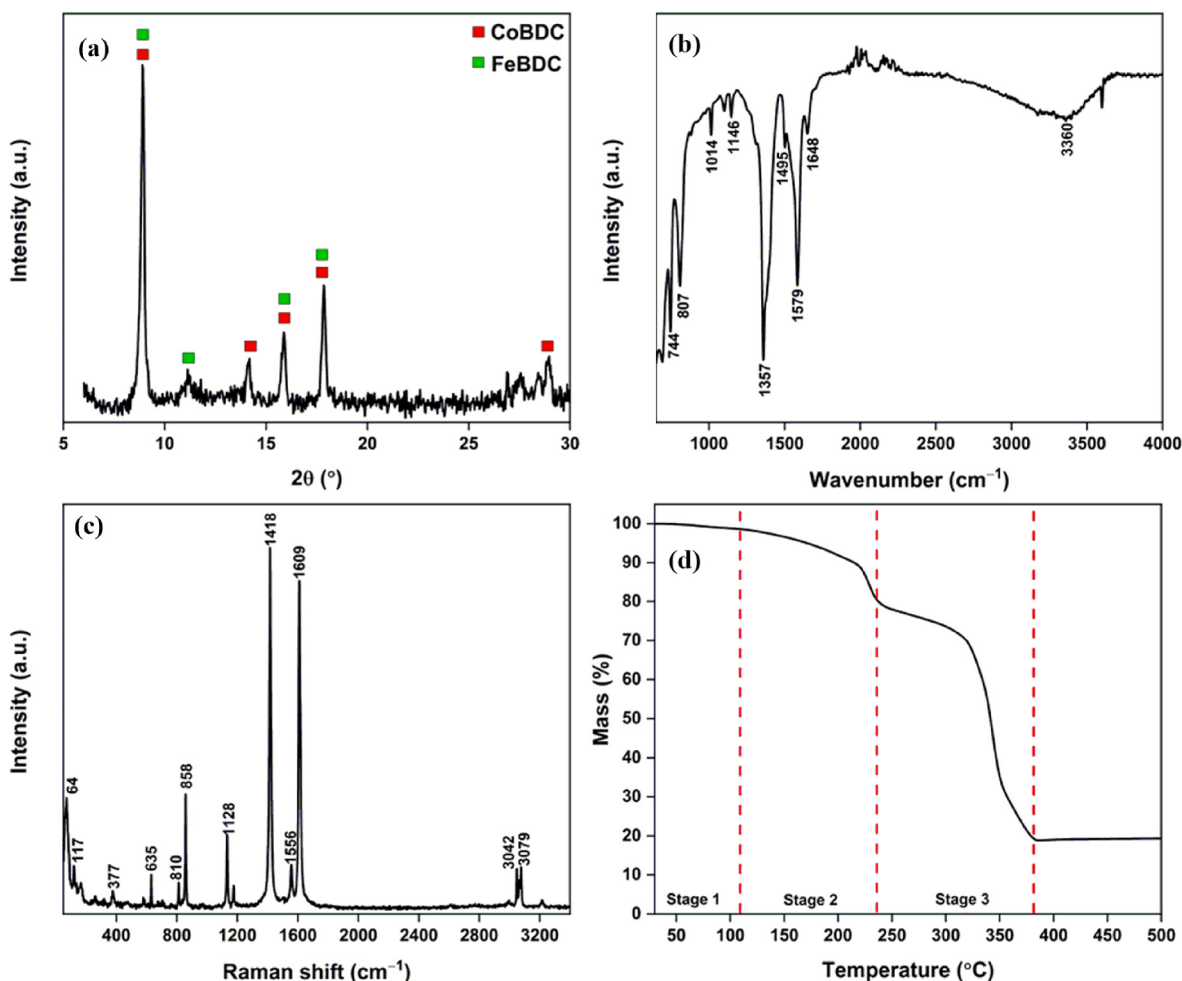


Fig. 2. (a) PXRD pattern; (b) FTIR spectrum; (c) Raman spectrum; (d) TGA profile of FeBDC@CoBDC.

metal ions. In the case of the kinetics experiment, the time of equilibration was varied from 5 min to 4 h, whereas the time of centrifugation was kept at 2 min, the pH of the feed solution was kept 1 and the initial concentration of U, Th and Eu were 1 mg mL^{-1} . The temperature was kept at 300 K 100 mg of MOF was allowed to equilibrate with 5 mL of an aqueous solution. The reusability of MOF was carried out in two-phase. For understanding the radiolytic stability of the MOF, the material was subjected to the gamma chamber to get the dose for a finite amount of time. Then, with the irradiated MOF, sorption experiments were carried out taking U, Th, Eu together in a 5 mL aqueous solution with pH 1. 100 mg of irradiated MOF was used for equilibration. Likewise, 2 h of equilibration followed by 2 min of centrifugation was done and subsequently, the EDXRF method was employed for the estimation of f-block elements from the supernatant. The elution experiment was carried out in two steps: the first step consisted of the sorption of metal ions from pH 1, at 300 K, whereas in the second step, the elution experiment was carried out. 100 mg of loaded MOF was allowed to equilibrate with 5 mL of an aqueous solution of sodium carbonate, oxalic acid and EDTA at 10 mM concentration for 30 min. After, 2 min centrifugation, the phase separation was achieved. Subsequently, the aqueous phase was analyzed for the determination of U, Th and Eu, simultaneously by EDXRF. To calculate the thermodynamic parameters, the sorption experiments were carried out at a different temperature in the range of 30°C to 60°C. The extraction experiment was carried out from pH 1, 5 mL aqueous solution containing the metal ions together. 100 mg of MOF was used for the same. The equilibration and centrifugation time was kept at 2 h and 2 min, respectively.

2.5. Computational methodology

The generalized gradient approximation (GGA) based Perdew-Burke-Ernzerhof (PBE) density functional (Perdew et al., 1992, 1996, 1998) calculations were performed using Vienna Ab-initio Simulation Package (VASP) (Kresse and Furthmüller, 1996; Kresse and Hafner, 1993). The ionic cores were represented by projector augmented wave (PAW) potentials (Blöchl, 1994; Kresse, 1999). The spin polarization calculations with kinetic energy cut off of 500 eV was used. The Monkhorst-Pack special k-points was used for integration in the Brillouin zone (Monkhorst and Pack, 1976). The electron self-consistency and force convergence thresholds are kept at $1 \times 10^{-5} \text{ eV}$ and $5 \times 10^{-3} \text{ eV/Å}$ respectively. The MIL-53-(Fe) unit cell with C2/c space group symmetry was optimized using a $1 \times 3 \times 3$ k points mesh. The optimized lattice parameter values are $a = 20.809 \text{ Å}$, $b = 7.206 \text{ Å}$, $c = 6.681 \text{ Å}$ and $\beta = 113.01(\text{deg})$, respectively. These values are closer to the earlier reported experimental values (Devic et al., 2010). Further, a $2 \times 1 \times 1$ supercell with $1 \times 3 \times 3$ k-point mesh was used to study the complexation of Eu^{3+} (septet spin multiplicity), Th^{4+} and UO_2^{2+} ions.

3. Results and discussion

3.1. Synthesis of MOF composite

The MOF synthesized is a hybrid MOF composite with Fe-MOF deposited on the surface of CoBDC with weak interaction. As such the interaction with a substrate on these hybrid materials could be independent of both the MOFs. So actinide adsorption onto hybrid can be

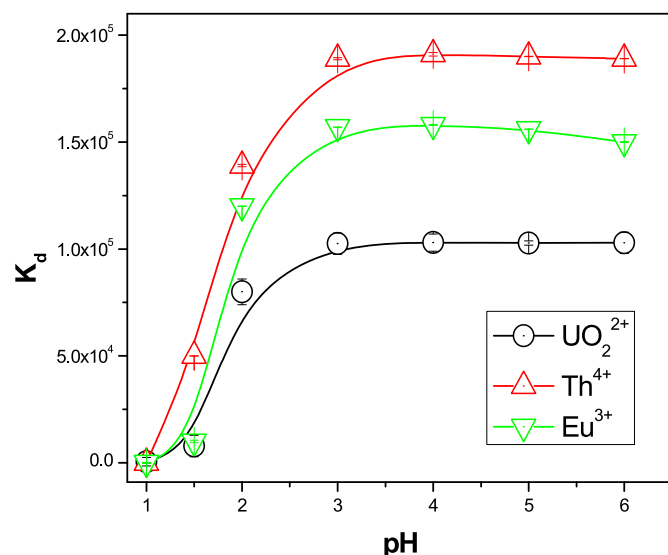


Fig. 3. The variation in partition coefficient values for UO_2^{2+} , Th^{4+} and Eu^{3+} as a function of the pH of aqueous feed solution.

simulated as actinide adsorption onto two separate MOFs, i.e., MIL-53 (Fe) and CoBDC. Fig. 1 presents the schematic illustration of the synthesis process and the structure of the hybrid MOF composite.

3.2. Characterization

The PXRD pattern of FeBDC@CoBDC is shown in Fig. 2a. The peaks at 8.9° , 11.1° , 15.8° , and 17.8° (marked as green squares) were assigned to the reported iron terephthalate MOF, MIL-88B(Fe) (MIL: Materials Institute Lavoisier) (Cho et al., 2011). The peaks at 8.9° , 14.2° , 15.8° , 17.8° , and 29.0° (marked as red squares) were assigned to the reported CoBDC MOF (Gupta et al., 2021b). The PXRD analysis confirmed the formation of the FeBDC@CoBDC composite. The FTIR spectrum of composites is shown in Fig. 2b. The band at 3360 cm^{-1} was assigned to the stretching vibrations of O–H in adsorbed water molecules. The bands at 1648 and 1495 cm^{-1} were assigned to the acid C=O and C=C stretching vibrations, respectively. The symmetric and asymmetric O–C–O stretching vibrations were observed at 1357 and 1579 cm^{-1} , respectively. The in-plane C–H bending modes were observed at 1146 and 1014 cm^{-1} . The out-of-plane C–H bending modes were observed at 807 and 744 cm^{-1} (Gupta et al., 2021c). The Raman spectrum of composite is shown in Fig. 2c. The band at 64 cm^{-1} was due to the closed MOF system as observed in the Raman spectrum of the reported DUT-8 (Ni) MOF. The bands at 117 and 377 cm^{-1} were assigned to the Co–O/Fe–O vibrations (Ryder et al., 2014). The aromatic C–H bonds were characterized by bands at 635 and 858 cm^{-1} , whereas the band at 1128 cm^{-1} was assigned to the bonds between two sp^2 -hybrid C atoms of benzene rings and carboxylate groups. The absorption band for ν_{as} (–COO[–]) and ν_{s} (–COO[–]) of the ligand coordinated to the metal centres were observed at 1609 and 1418 cm^{-1} , respectively (Sun et al., 2018; Nguyen et al., 2019). The bands at 3042 and 3079 cm^{-1} were due to the C–H stretching (Ryder et al., 2014). The TGA profile of the composite is depicted in Fig. 2d. The mass loss in stage 1 (30 – 110°C) was due to the evaporation of physically adsorbed water molecules. The mass loss in stage 2 (110 – 230°C) was assigned to the loss of physically adsorbed solvent (DMF/ethanol/methanol) and chemically bound water molecules. In stage 3 (230 – 380°C), the mass loss was due to the thermal breakdown of the coordination bonds and the loss of organic linkers. Thus, MOF composite was thermally stable up to 300°C (Banerjee et al., 2012).

3.3. Separation of tetra, hexa and trivalent f block elements

3.3.1. Extraction profile at various pH of the feed

Fig. 3 is the variation in K_d values as a function of pH of the aqueous phase. For all three cases, the K_d values were found to increase with an increase in the pH of the medium. The enhancement was found to be steeper up to pH 2. In the range of pH 2 to pH 3, only marginal enhancement was noticed. However, beyond that plateau was observed for all the metal ions under consideration. At higher pH, the availability of H^+ ion will be reduced and hence there were lesser chances of protonation of the coordinating groups present in the MOF structure. The competition between H^+ and the f-block metal ion will also be reduced. So as a whole, the K_d values are expected to increase. However, beyond pH 3, the appearance of plateau revealed that a counteraction became prominent at a pH of more than 3. However, the actual reason is not known till now. It was also to be noted that, the K_d values for Th^{4+} were found to more than that of Eu^{3+} , which was found to be more than UO_2^{2+} . The charge on metal ion might play important role in the sorption of f-block elements on MOF.

3.3.2. Sorption isotherm

To understand the mechanism of sorption and to get more insight into the sorption processes, experimentally obtained data were subjected to different sorption isotherm models. The data were obtained by changing the relative concentration of either the metal ions or the amount of MOF in the sorption processes. The linear equations of Langmuir, Dubinin-Radushkevich (D-R), Freundlich and Temkin isotherms were employed to fit the experimental data and based on linear regression coefficient the best fit model was identified and it was concluded that the sorption mechanism followed through the best fit model. The Langmuir isotherm is associated with more ideal behaviour. According to it, the sorption proceeds through monolayer coverage. No neighbouring coordinating sites can influence on sorption process. Practically, all the coordinating sites should be far apart from each other. This model represents a homogeneous, simple sorption process. However, non-ideality and heterogeneity of sorbent surface have been introduced in the Freundlich isotherm model. This is originally an empirical model, widely applicable for gas sorption on a solid surface; however, fails to incorporate high-pressure sorption. The main approach of the Freundlich isotherm model is based on the fact that the sorption capacity depends on the adsorbed amount on the surface of the material, unlike Langmuir isotherm. The equation of this model was derived based on the micropore filling theory concept associated with sorption on charcoal type of materials. The heat of sorption of all metal ions reduces linearly with the enhancement in coverage of the sorbent surface, and sorption is characterized by a uniform distribution of binding energies are the main focus for the Temkin isotherm model. The linear equations of these isotherm models are as follows (Sengupta et al., 2017; Gupta et al., 2017; Gupta and Sengupta, 2017a)

$$\text{Langmuir isotherm model: } \frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \quad (2)$$

$$\text{Freundlich isotherm model: } \log q_e = \log k_F + \frac{1}{n} \log C_e \quad (3)$$

$$\text{Dubinin – Radushkevich isotherm model: } \ln q_e = \ln X_m - \beta \epsilon^2 \quad (4)$$

$$\text{Temkin isotherm model: } q_e = \frac{RT}{b} \ln AT + \frac{RT}{b} \ln C_e \quad (5)$$

where, q_e is the amount of f-block metal ion sorbed on MOF at equilibrium and C_e is the corresponding concentration. q_0 is the theoretical capacity of sorption of f-block metal ion on MOF. The k_F is the Freundlich isotherm constant, while A_T and b are equilibrium binding constant (L g^{-1}) and Temkin isotherm constant, respectively. X_m and β denote the capacity of MOF for sorption of f-block elements and the activity

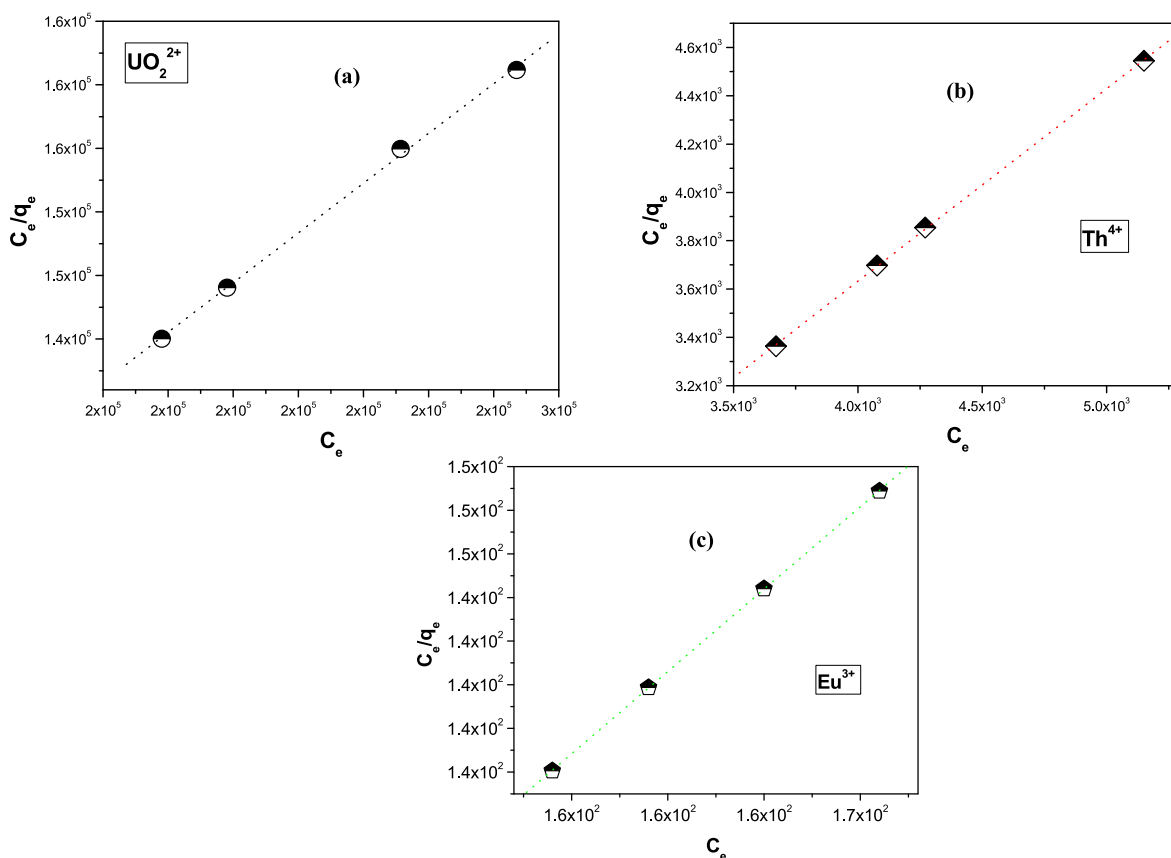


Fig. 4. Langmuir isotherm analyses for (a) UO_2^{2+} ; (b) Th^{4+} , (c) Eu^{3+} .

Table 1

Analytical results for linear regression on sorption isotherm.

Langmuir isotherm model			
f-block metal ion	q_0 (mg g^{-1})	B (L mol^{-1})	χ^2
UO_2^{2+}	189 ± 12	3.1 ± 0.2	0.9995
Th^{4+}	224 ± 20	3.9 ± 0.3	0.9989
Eu^{3+}	205 ± 15	3.8 ± 0.2	0.9998
Freundlich isotherm model			
f-block metal ion	n	K_f (mg g^{-1})	χ^2
UO_2^{2+}	11	177 ± 12	0.9566
Th^{4+}	29	217 ± 18	0.9723
Eu^{3+}	17	198 ± 16	0.9331
D-R isotherm model			
f-block metal ion	E (kJ mol^{-1})	X_m (mg g^{-1})	χ^2
UO_2^{2+}	10.2 ± 0.8	168 ± 10	0.9722
Th^{4+}	16.3 ± 0.9	230 ± 13	0.9810
Eu^{3+}	13.5 ± 0.5	212 ± 17	0.9922
Temkin isotherm model			
f-block metal ion	b (L mg^{-1})	A_T (L mg^{-1})	χ^2
UO_2^{2+}	80 ± 3	21 ± 2	0.9211
Th^{4+}	111 ± 7	29 ± 2	0.9018
Eu^{3+}	100 ± 6	25 ± 3	0.9322

coefficient associated with the sorption process, respectively. The sorption energy can be calculated from the term ζ as follows (Gupta et al., 2017; Gupta and Sengupta, 2017a).

$$E = \frac{1}{(2\zeta)^{0.5}} \quad (6)$$

Fig. 4 is showing the fitting of experimental data on Langmuir isotherm model, while Supplementary Fig. 1, Supplementary Fig. 2 and Supplementary Fig. 3 are showing the same for D-R isotherm, Temkin isotherm and Freundlich isotherm, respectively. Table 1 summarizes the estimated fitting parameters. Based on the linear regression analyses, it

can be concluded that the sorption of UO_2^{2+} , Th^{4+} and Eu^{3+} proceeded predominantly through Langmuir isotherm with regression coefficient values 0.9995, 0.9989 and 0.9998, respectively. The theoretical sorption capacity for these metal ions on MOF was estimated as 189 mg g^{-1} , 224 mg g^{-1} and 205 mg g^{-1} , respectively. This trend was found to be similar as obtained for their K_d values. The linear regression coefficient values for D-R isotherm model analyses were also found to be very close as 1 (however, obviously poorer than Langmuir isotherm). The sorption energy values estimated from the D-R isotherm model were found to be 10.2 kJ mol^{-1} , 16.3 kJ mol^{-1} and 13.5 kJ mol^{-1} for UO_2^{2+} , Th^{4+} and Eu^{3+} , respectively. The higher sorption energy (more than 8 kJ mol^{-1}) indicates that the chemical interaction is predominating during sorption processes, i.e. this exercise indicates the predominance of chemisorption. The sorption energy values followed the same order as K_d values and sorption capacity values.

3.3.3. Kinetics of sorption

Fig. 5a represents the influence of time of equilibration on the K_d values for UO_2^{2+} , Th^{4+} and Eu^{3+} on MOF. This exercise was carried out to understand how fast the sorption processes are. The K_d values were found to enhance with an increase in time of contact. Initially, the enhancement was steeper, whereas beyond, initial 1 h, moderate enhancement was observed. Beyond 120 min of contact almost no change in K_d values was noticed. Therefore, 120 min is required to attain the equilibrium K_d values. The experimentally obtained data were subjected to fit into the linear equations of commonly employed models Fig. 5b-d. Based on linear regression coefficient values, the best-fitted kinetics model was identified and it was concluded that the sorption processes predominantly followed the same kinetics model. In the present case Lagergren first-order rate kinetics, Kinetics model based on Intra-particle diffusion and Pseudo 2nd order rate kinetics have been employed for understanding. In Lagergren first-order rate kinetics, the

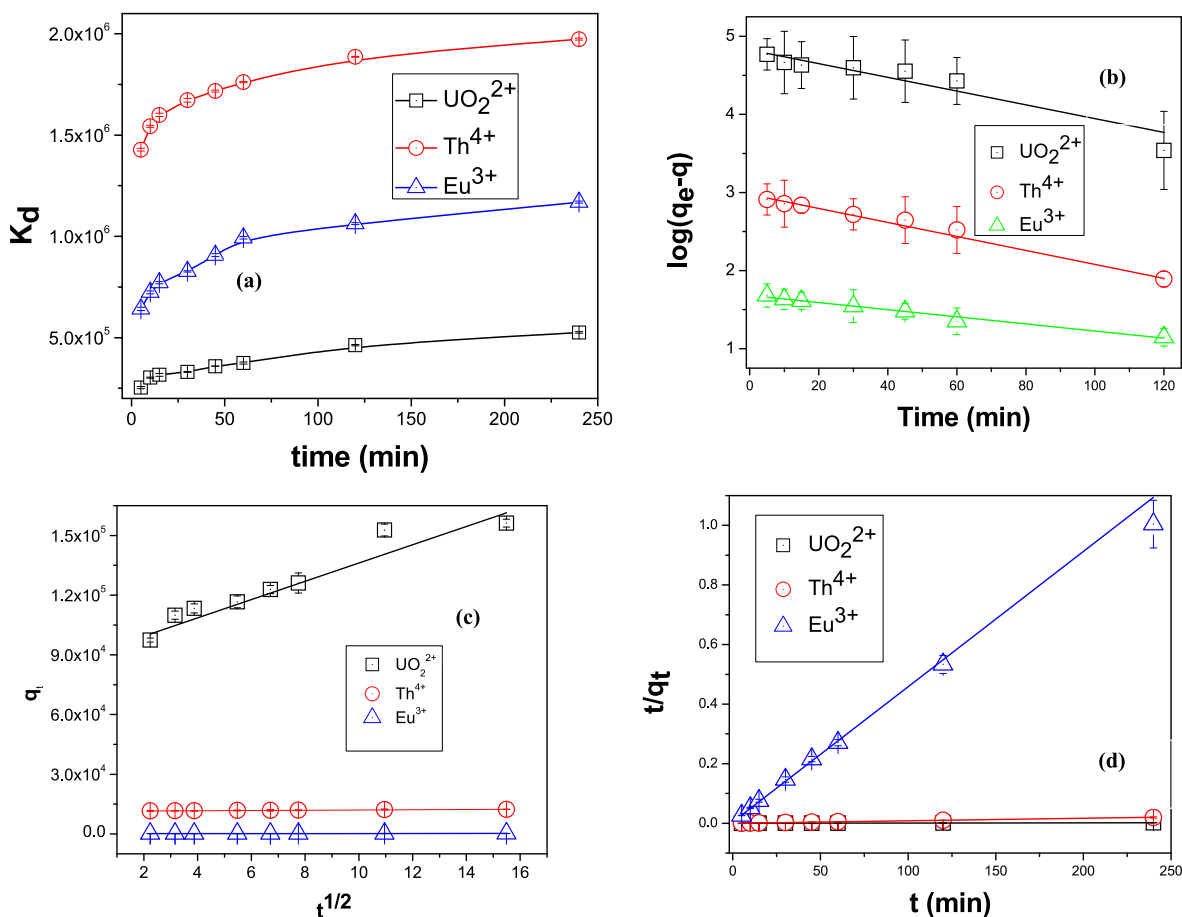


Fig. 5. (a) Influence of equilibration time (t) on partition coefficients for UO_2^{2+} , Th^{4+} and Eu^{3+} ; (b) Analyses of Lagergren first-order kinetics; (c) Analyses of Intra-particle diffusion model; (d) Analyses of Pseudo second-order model.

Table 2

The analyses of Lagergren 1st order kinetics, Intra-particle diffusion model and Pseudo 2nd order model.

Lagergren 1 st order kinetics			
f-block metal ion	k_1 (min ⁻¹)	q_e (mg g ⁻¹)	χ^2
UO_2^{2+}	0.019 ± 0.001	22 ± 2	0.9466
Th^{4+}	0.016 ± 0.002	39 ± 3	0.9610
Eu^{3+}	0.018 ± 0.001	27 ± 3	0.9830
Intra-particle diffusion model			
f-block metal ion	k_p (mg g ⁻¹ min ⁻¹)	C (mg g ⁻¹)	χ^2
UO_2^{2+}	194 ± 8	23 ± 2	0.9055
Th^{4+}	150 ± 9	47 ± 5	0.9722
Eu^{3+}	203 ± 11	37 ± 3	0.9756
Pseudo 2 nd order model			
f-block metal ion	k_2 (mg g ⁻¹ min ⁻¹)	q_e (mg g ⁻¹)	χ^2
UO_2^{2+}	$(6.01 \pm 0.23) \text{E}-05$	31 ± 3	0.9935
Th^{4+}	$(5.14 \pm 0.37) \text{E}-05$	52 ± 4	0.9990
Eu^{3+}	$(5.73 \pm 0.44) \text{E}-05$	46 ± 4	0.9989

Table 3

The thermodynamic parameters for sorption of UO_2^{2+} , Th^{4+} and Eu^{3+} on MOF.

Metal	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)
UO_2^{2+}	$-(2.21 \pm 0.2)$	4.9 ± 0.3	0.023 ± 0.001
Th^{4+}	$-(5.28 \pm 0.4)$	3.7 ± 0.4	0.030 ± 0.002
Eu^{3+}	$-(4.47 \pm 0.4)$	4.8 ± 0.5	0.031 ± 0.003

rate of change of f-block metal ion uptake on MOF with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time. For most of the sorption processes, the

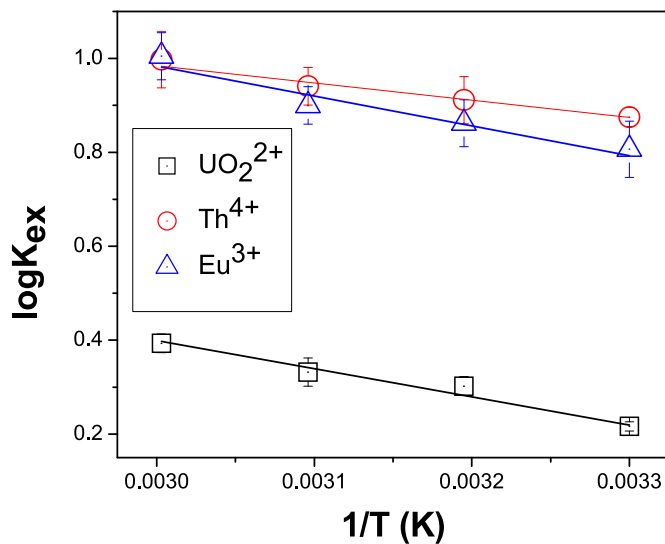


Fig. 6. The influence of temperature on the sorption of tetra, hexa and tri valent f-block elements using MOF.

initial stage proceeded through this mechanism. An intra-particle diffusion kinetics model is characterized by a rate of diffusion and maybe predominating after the initial stages of the adsorption. The mass of MOF taken, the size of MOF particles and the initial concentration of f-block metal ion used for sorption highly influenced the rate constants of

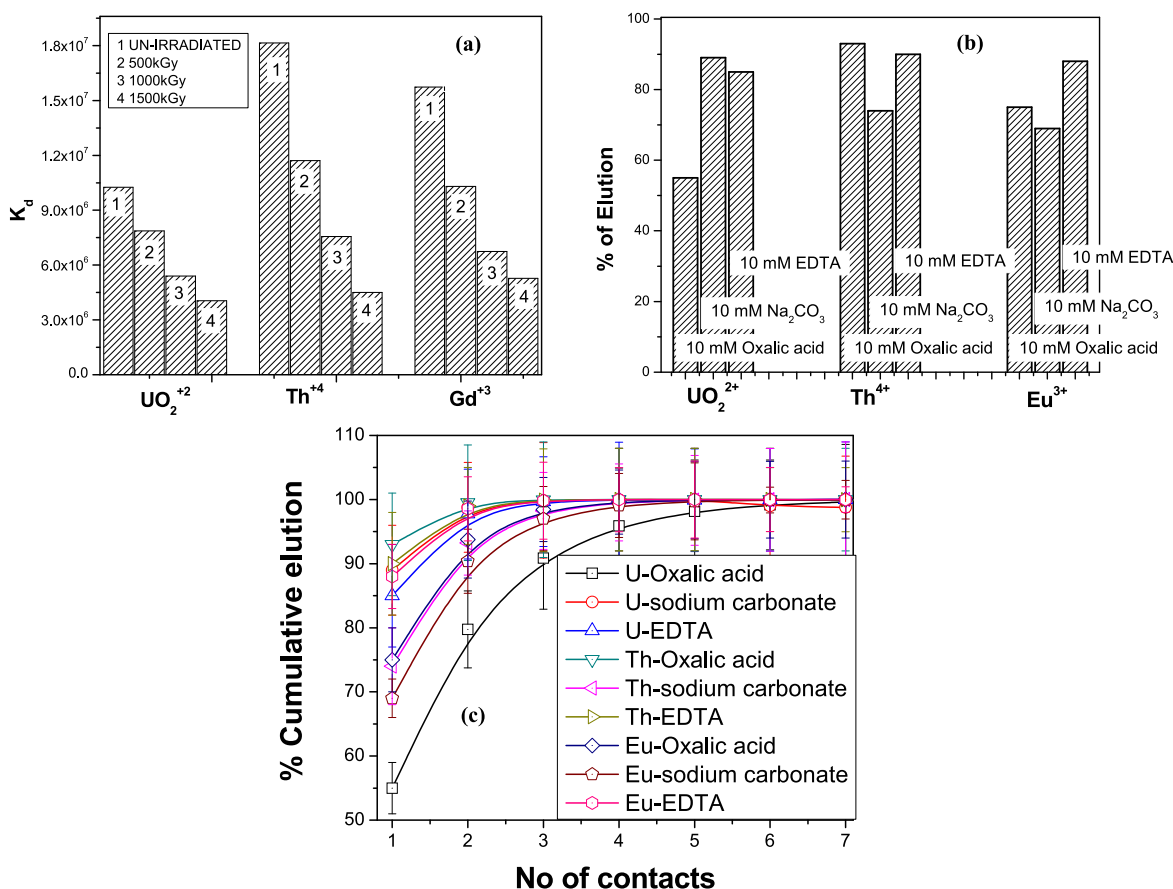


Fig. 7. (a) Deterioration in sorption performance of the MOF irradiated in gamma field for the sorption of tetra, hexa and trivalent f-block elements; (b) Elution of UO_2^{2+} , Th^{4+} and Eu^{3+} from loaded MOF using 10 mM Oxalic acid, Na_2CO_3 and EDTA solution.

the sorption processes. The pseudo-second-order kinetic model is applicable mainly for chemisorption. According to the model, chemical interaction is part of the rate-determining step. Based on this kinetics model the sorption capacity of MOF material played an important role. The linear equation for these models are as follows (Kumar et al., 2016, 2017a, 2017b; Kishor et al., 2017)

$$\text{Lagergren 1st order kinetics model: } \log(q_e - q_t) = \log q_e - \frac{k_L t}{2.303} \quad (7)$$

$$\text{Intra particular diffusion model: } q_t = k_{IPD} t^{1/2} + A \quad (8)$$

$$\text{Pseudo 2nd order kinetics model: } \frac{t}{q_t} = \frac{1}{k_{2nd} q_e^2} + \frac{t}{q_t} \quad (9)$$

q_t and q_e are the amount of f-block elements adsorbed on MOF at time t and equilibrium. k_L , k_{IPD} , and k_{2nd} are the rate constants for Lagergren 1st order kinetics, Intra particle diffusion model and Pseudo 2nd order kinetics model, respectively. Fig. 5 (b), (c) and (d) showed the fitting of experimentally obtained data on the linear equations of those kinetics models respectively. Table 2 summarizes the parameters obtained on curve fitting. Based on the linear regression coefficient values ($\chi^2_U = 0.9935$, $\chi^2_{Th} = 0.9990$ and $\chi^2_{Eu} = 0.9989$); the sorption kinetics were found to predominantly follow pseudo 2nd order kinetics with rate constant values $k_2^U \sim 6.01E-05 \text{ mg g}^{-1} \text{ min}^{-1}$, $k_2^{Th} \sim 5.14E-05 \text{ mg g}^{-1} \text{ min}^{-1}$, and $k_2^{Eu} \sim 5.73E-05 \text{ mg g}^{-1} \text{ min}^{-1}$, respectively. From the rate constant values, it is clear that the sorption of UO_2^{2+} is the fastest among the three metal ions followed by Eu^{3+} and Th^{4+} . However, the rate constant values are only marginally different. Hence, overall there was not much difference in the sorption rates for UO_2^{2+} , Th^{4+} and Eu^{3+} on MOF.

3.3.4. Thermodynamics of sorption

The Vant Hoff equation correlates the equilibrium constant for the sorption (K_{ex}) with the change in entropy (ΔS) and change in enthalpy (ΔH) due to sorption of metal ions on MOF as follows (Chen et al., 2003; Lima et al., 2020)

$$\ln K_{ex} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)$$

The equilibrium constant was also employed for the estimation of change in Gibb's energy during sorption as follows

$$\Delta G = -RT \ln K_{ex} \quad (11)$$

However, the thermodynamic parameters ΔG , ΔH and ΔS are interconnected using the equation below

$$\Delta G = \Delta H - T\Delta S \quad (12)$$

Table 3 summarizes the ΔG , ΔH and ΔS values for the sorption of U, Th and Eu on MOF. The negative ΔG values revealed that the sorption processes are thermodynamically favourable i.e. spontaneous in nature. The equilibrium constant values were found to decrease with a decrease in temperature, i.e. at high temperature, the sorption processes are favoured, whereas at a lower temperature the sorption processes are thermodynamically less favourable [Fig. 6]. The enthalpy values were found to decrease with sorption, i.e. the processes were endothermic in nature. The overall change in enthalpy can be broadly divided into three-step contributions. In the first step, energy needs to be given to the metal ions to dehydrate either partially or fully (ΔH_1). Similarly, energy will also be given to the MOF to acquire the preferred configuration to coordinate/capture the f-block ions (ΔH_2). In the subsequent step heat energy will be released when metal ions get coordinated/capture on

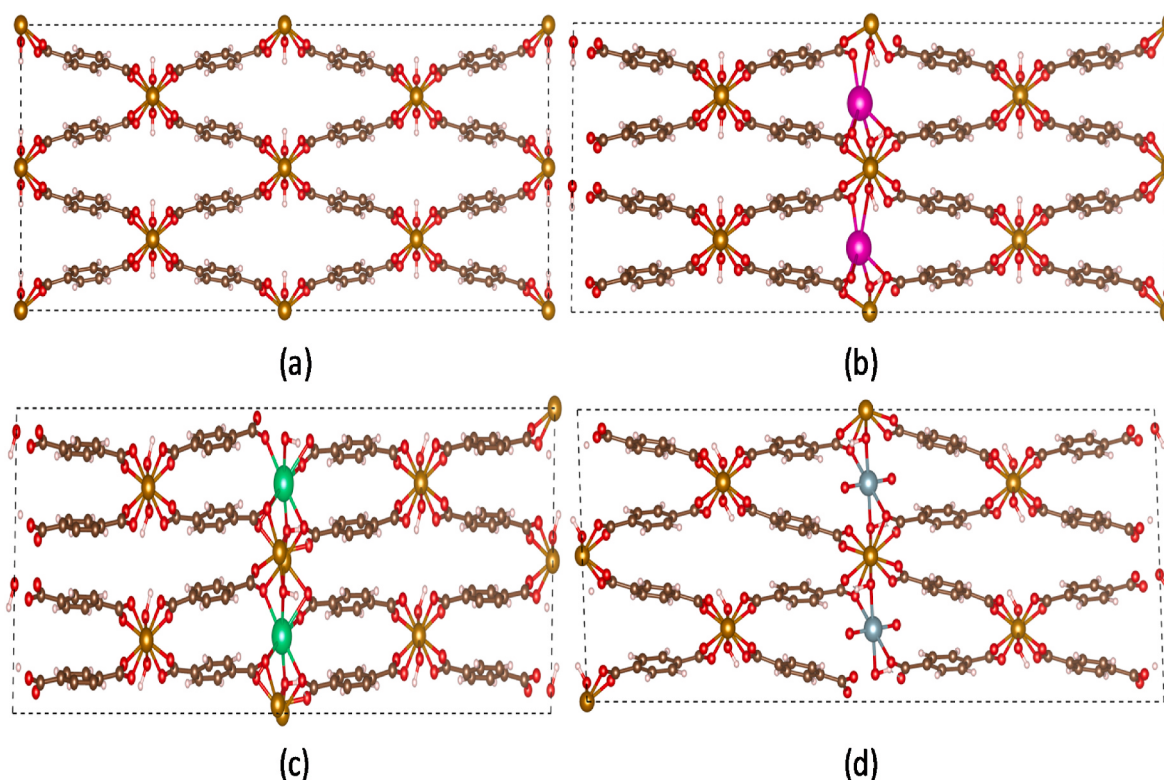


Fig. 8. Optimized structures of (a) MIL-53(Fe) (b) MIL-53(Fe) - Eu^{3+} (c) MIL-53(Fe) - Th^{4+} and (d) MIL-53(Fe) - UO_2^{2+} ; Carbon, oxygen, hydrogen, iron, europium, thorium and uranium atom are shown as deep brown, red, pale pink, brown, deep pink, lime green and light blue balls respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table:4

Calculated Binding Energy (B.E) values of Eu^{3+} , Th^{4+} and UO_2^{2+} with MIL-53(Fe) in the gas phase.

S. No	Complexation reaction	B.E (eV)
1	$\text{MIL-53(Fe)} + \text{Eu}^{3+} \rightarrow \text{MIL-53(Fe)} - \text{Eu}^{3+}$	-34.72
2	$\text{MIL-53(Fe)} + \text{Th}^{4+} \rightarrow \text{MIL-53(Fe)} - \text{Th}^{4+}$	-48.38
3	$\text{MIL-53(Fe)} + \text{UO}_2^{2+} \rightarrow \text{MIL-53(Fe)} - \text{UO}_2^{2+}$	-18.17

MOF (ΔH_3). The first two steps require heat energy, while the third step releases energy. For present case, $\text{mod}(\Delta H_1 + \Delta H_2) > \text{mod}(\Delta H_3)$. The enthalpy values were found to increase on sorption, hence there was the formation of inner-sphere complexes between f-block elements and MOF. The processes were entropically driven. Though sorption brings the two different identities to be attached, and hence resulting reduction in entropy, however, for inner-sphere complex release of a huge amount of water molecules resulted in overall enhancement in entropy of the system. The modulus of ΔG values were found to follow the trend $\text{Th}^{4+} > \text{Eu}^{3+} > \text{UO}_2^{2+}$, which is similar to that obtained in K_d values of the metal ions.

3.3.5. Recyclability: radiation damage and elution

The effect of gamma irradiation on the separation performance of the MOF has been investigated as shown in Fig. 7 (a). During the processing of radiotoxic materials, the MOF has to encounter lots of radiation coming out of the radiotoxic isotopes to be processed. Depending upon the nature of isotopes, MOF can experience high energy emission in the form of gamma rays or high energy particle emission in the form of α and β rays. During passage of gamma ray through a medium, it deposits energy and there might be three ways gamma rays can interact with the medium namely 1: Photoelectric effect; 2: pair production and 3: Compton effect. In photoelectric effect, if the deposited energy quanta is more than the work function of the most loosely bound electron of the

medium, then those electron will be knocked off from the system and depending upon the excess energy, the electrons will acquire the equivalent kinetics energy. All these three types of interaction can lead to either excitation or ionization of the medium. In molecular level, if the deposited energy is more than the bond energy, then there is a possibility that the bond can break and homogeneous cleavage can lead to the generation of radicals. Since radicals are highly unstable, they can immediately combine among themselves or can undergo some radical based chemical reaction leading to completely different functionalities. If the functional groups or coordinating sites get modified due to this, there is a chance of deterioration in expected performance. In view of this; in the present section, an attempt was made to mimic the dose and subjected to the MOF. The modification if occurs in MOF might have some influence on the separation performance. On 500 kGy irradiation, the K_d values for UO_2^{2+} , Th^{4+} and Eu^{3+} were found to become 76.7%, 64.6% and 65.6% of their original K_d values, respectively. On 1000 kGy irradiation, they became 52.7%, 41.7% and 42.8% of their original K_d values, respectively; whereas it further drastically reduced to 39.5%, 24.8% and 33.5%. This exercise revealed that a significant performance deterioration has been encountered due to gamma irradiation of 1500 kGy dose. Up to 500 kGy, the deterioration might be acceptable, while beyond that it is not worth using this MOF. Further investigation is necessary to find out the MOF having a high degree of radiation stability.

Fig. 7 (b) represents the elution characteristics of UO_2^{2+} , Th^{4+} and Eu^{3+} from the loaded MOF. This exercise is necessary for terms of understanding the reusability of the MOF in several consecutive cycles. 10 mM oxalic acid, sodium carbonate and EDTA in an aqueous solution were employed as an eluting solution for this exercise (Hashmi et al., 2021; SenguptaJayabun et al., 2016; Pahan et al., 2020; Pandey et al., 2021b, 2021c; Gupta and Sengupta, 2017b). In single contact of 10 mM oxalic acid, 55% of U, 93% of Th and 75% of Eu were found to be eluted from loaded MOF, while with 10 mM sodium carbonate solution 89% U, 74% of Th and 69% of Eu got eluted. 10 mM of EDTA was found to elute

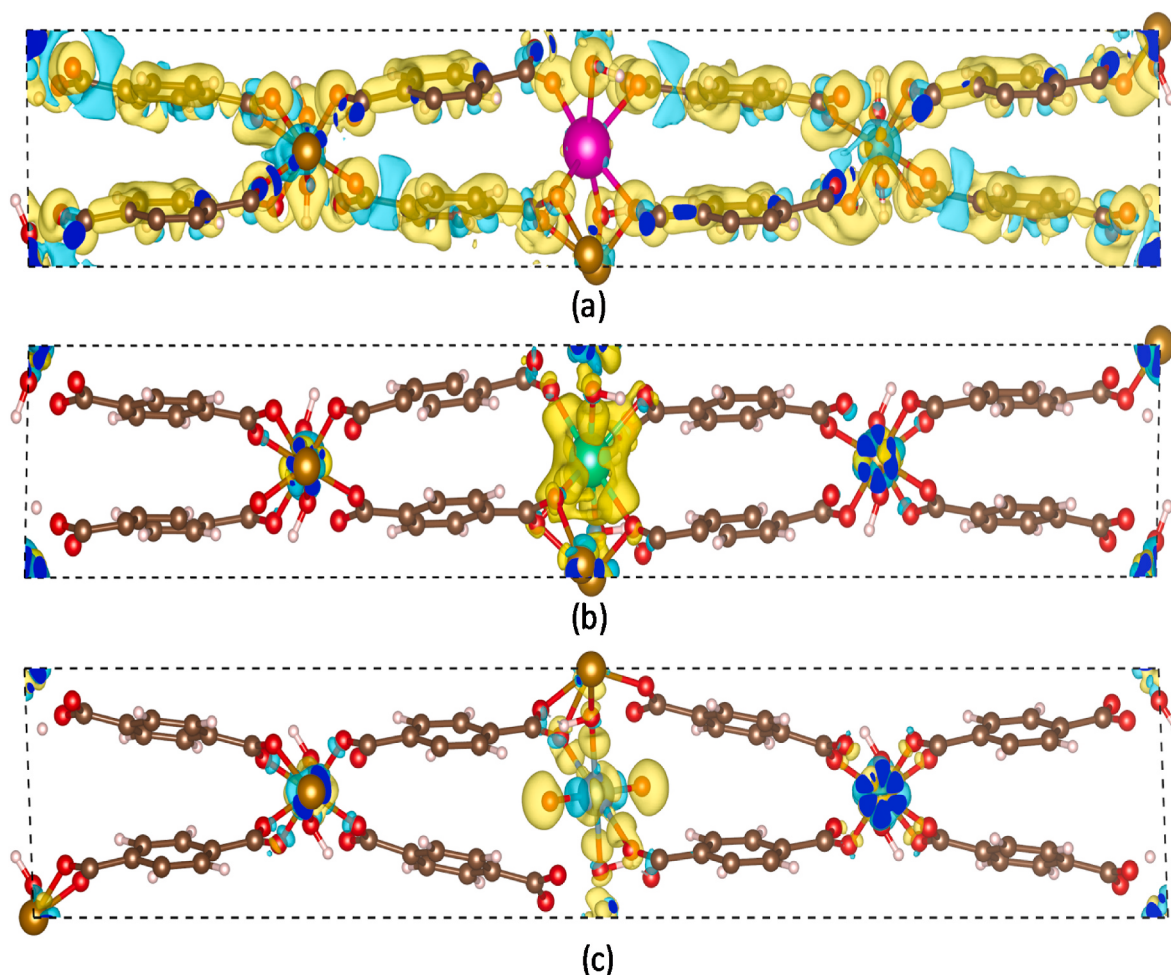


Fig. 9. Differential charge densities of (a) MIL-53(Fe)-Eu³⁺; isosurface was set to $\pm 0.03 \text{ e } \text{\AA}^{-3}$ (b) MIL-53(Fe)-Th⁴⁺; isosurface was set to $\pm 0.01 \text{ e } \text{\AA}^{-3}$ and (c) MIL-53(Fe)-UO₂²⁺; isosurface was set to $\pm 0.01 \text{ e } \text{\AA}^{-3}$. Here yellow corresponds to loss and blue corresponds to gain of electron density. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 5

Comparative evaluation of sorption behaviour of actinides at different oxidation states on a variety of sorben materials.

Sorbent	Metal ion	K _d	Isotherm	Kinetics	Reference
FeBDC@CoBDC MOF	UO ₂ ²⁺	1×10^5	Langmuir	Pseudo 2 nd order	Present investigation
	Th ⁴⁺	2×10^5			
	Eu ³⁺	1.4×10^5			
Amide functionalized CNT	UO ₂ ²⁺	2×10^3	Langmuir	Pseudo 2 nd order	SenguptaJayabun et al. (2016)
	Th ⁴⁺	1×10^4			
Rhizopus arrhizus dead biomass	Pu ⁴⁺	6×10^3	Langmuir	Pseudo 2 nd order	Kishor et al. (2017)
	PuO ₂ ²⁺	4×10^3			
CoFe ₂ O ₄ /Graphene oxide nano composite	UO ₂ ²⁺	60%	Fruendlich	Pseudo 2 nd order	Gupta et al. (2021a)
	Th ⁴⁺	90%			
	Gd ³⁺	88%			
poly(amidoamine) dendrimer functionalize MWCNT	NpO ₂ ⁺	1.6×10^3	Langmuir	Pseudo 2 nd order	Alqadami et al. (2017)
	Pu ⁴⁺	1.2×10^4	Langmuir	Pseudo 2 nd order	Sengupta et al. (2017)
Diglycolamide functionalized CNT	PuO ₂ ²⁺	1.7×10^4			
	Am ³⁺	2.8×10^4			
	Th ⁴⁺	5.87×10^4			
Hafnium phosphonates MOF	UO ₂ ²⁺	5.09×10^3	Langmuir	Pseudo 2 nd order	-ping Xiong et al. (2019)
	Th ⁴⁺	10.3 mg g^{-1}			
Fe ₃ O ₄ @AMCA-MIL(Al)	Th ⁴⁺	10.3 mg g^{-1}	Langmuir	Pseudo 2 nd order	Alqadami et al. (2017)
	UO ₂ ²⁺	14.8 mg g^{-1}			

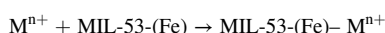
85% of U, 90% of Th and 88% of Eu. This exercise revealed two facts: 1.10 mM solution of oxalic acid, sodium carbonate and EDTA was found to be the best for Th⁴⁺, UO₂²⁺ and Eu³⁺, respectively; 2. Multiple contacts are required for quantitative elution of the loaded metal ions from the MOF [Fig. 7 (c)].

3.4. Computational analyses

The optimized structures of MIL-53(Fe), MIL-53(Fe)-Eu³⁺, MIL-53(Fe)-Th⁴⁺ and MIL-53(Fe)-UO₂²⁺ are presented in Fig. 8 (MIL stands for Materials Institute Lavoisier). The metal ions were incorporated in

the pores of MIL-53(Fe). In the case of MIL-53(Fe), the Fe atom is having six coordination with 4 O atoms of BDC and 2 O atoms of –OH groups. Further, in the case of MIL-53(Fe)-Eu³⁺, MIL-53(Fe)-Th⁴⁺ and MIL-53(Fe) – UO₂²⁺ it is observed that the O atoms of BDC and –OH groups are coordinated to Eu, Th and U atoms. In the case of MIL-53(Fe)-Eu³⁺, coordination of six is observed for Eu. The average Eu–O distance of 2.397 and 2.436 Å were observed with O atoms of BDC and –OH groups. Further, in the case of MIL-53(Fe)-Th⁴⁺, coordination of eight is observed for Eu (six from BDC and two from –OH). The average Th–O distance of 2.478 and 2.500 Å were observed with O atoms of BDC and –OH groups. In continuation, six coordination was observed in the case of MIL-53(Fe) – UO₂²⁺ for U (two O from uranyl, two from BDC and two from –OH). The U–O distances are 2.386, 2.420, 1.808 Å respectively for BDC, –OH and UO₂²⁺.

Further, the binding energy (B.E) values are evaluated for the complexation of metal ions with MIL-53(Fe) as



$$B.E = E_{\text{MIL-53(Fe)-}M^{n+}} - E_{M^{n+}} - E_{\text{MIL-53(Fe)}}$$

where, $E_{\text{MIL-53(Fe)-}M^{n+}}$, $E_{M^{n+}}$, $E_{\text{MIL-53(Fe)}}$ represents the total energy values of metal ion complex, metal ion and MIL-53(Fe) respectively.

From the calculated values of B.E (Table 4), it is observed that the Th⁴⁺ ions bind stronger than Eu³⁺ and UO₂²⁺ ions. This observation is in line with the experimental observation. Whereas experimentally it is observed that UO₂²⁺ ion binds stronger than Eu³⁺ ion and vice versa was observed in the theoretical findings. This may be attributed to the solvent effects. In the present paper, we have not considered the solvent effects which is beyond the scope of our work. In the future, the effect of nitrate ions and solvent will be considered.

Further, to have a better understanding of the complexation of metal ions the differential charge densities of MIL-53(Fe)-Eu³⁺, MIL-53(Fe)-Th⁴⁺ and MIL-53(Fe) – UO₂²⁺ were evaluated and plotted in Fig. 9. From Fig. 9 it is observed that there is a charge loss on the O atoms of the BDC and –OH groups which is due to the interaction of metal ion (Eu, Th and U ions) and O atoms.

3.5. Comparative evaluation of sorption behaviour

Table 5 summarizes the sorption behaviour of actinides and lanthanides at different oxidation states on a variety of sorbent materials. The f-block elements mainly exist as tetra, tri, hexa and penta valent oxidation states. Based on chemical potential the trend in getting coordinated varies as tetravalent > trivalent > hexavalent > pentavalent. In case of pentavalent and hexavalent oxidation states, the actinides exist as actinyl ions. Similar trend was also seen in present case and the other investigations reported in literature. Except for diglycolamide functionalized carbon nanotubes; where due to preorganization of the coordinating sites; trivalent f-block metal ion showed better extractability. Most of the sorption processes were found to be predominantly followed by Langmuir isotherm model, whereas pseudo 2nd order rate kinetics were found to be predominated during sorption processes. The sorption efficiency values for UO₂²⁺ as well as Th⁴⁺ were found to be atleast five times better than the other reports shown in Table 5.

4. Conclusion

A hybrid MOF composite, having Fe-MOF deposited on the surface of the nanosheets of CoBDC has been synthesized for sorption of UO₂²⁺, Th⁴⁺ and Eu³⁺ from an aqueous pH feed solution. The presence of sp²-hybrid C atoms of benzene rings, closed MOF system carbonyl moieties and carboxylate groups have been evident from FTIR and Raman spectra of the MOF. The XRD pattern revealed the existence of hybrid MOF composites. At higher pH, the K_d values were found to be more than that at lower pH with the trend K_dTh > K_d^{Eu} > K_d^U. To understand the sorption mechanism Langmuir, Dubinin-Radushkevich (D-R), Freundlich

and Temkin isotherm models have been utilized revealing the sorption processes proceeded through chemical interaction using monolayer coverage without the influence of neighbouring sites. Pseudo 2nd order rate kinetics model was found to fit well with the experimental data. The processes were found to be spontaneous, endothermic with overall enhancement in entropy. Aqueous complexing agents and multiple contacts are required for quantitative elution of metal ion loaded on MOF. The structure optimization and bond energy calculation were carried out by DFT calculation. For MOF-Eu complex, six coordination of Eu having Eu–O distance 2.397 and 2.436 Å; For MOF-Th complex, eight coordination of Th with average Th–O distance of 2.478 and 2.500 Å and for MOF-U six coordination of U with U–O distances 2.386, 2.420, 1.808 Å were estimated. Though these MOF composites showed high efficiency in the sorption of f-block elements, however, their radiation stability is not very good.

Declaration of competing interest

There is no conflict of interest to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2021.132232>.

Credit author statement

Gauri Salunkhe; Separation experiment; Arijit Sengupta; Conceptualization, writing, editing, reviewing the manuscript and supervision of separation experiments; Anil Boda: DFT calculation; Roxana Paz; Characterization of MOF; Nishesh Kumar Gupta; Synthesis of MOF; Carolina Leyva; Characterization of MOF; Rohit Singh Chauhan; Reviewing and editing the manuscript; Sk. Musharaf Ali; DFT calculation and supervision.

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