# Adsorption-based Separation and Recovery of Rare Earth Elements

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## Introduction

This chapter briefly covers different technologies involved in the adsorption-based separation of rare earth elements (REE – the 15 lanthanide elements of the periodic table with atomic numbers Z=51-71, plus scandium Z=21, and yttrium Z=39). The separation technologies include a wide range of materials from ion exchange resins (IERs), metal (hydro)oxides adsorbents, and solvent impregnated resins (SIRs) that have the extractant impregnated into solid support to the recent technologies of surface-functionalized adsorbents with complexing ligand chemically anchored on to the solid support and ion-imprinted polymers with specific recognition sites for the desired REEs.

The adsorption sites in these adsorbents are various surface functional groups or ligands which can adsorb REEs through different mechanisms, i.e., physical adsorption, electrostatic interaction, and/or surface complexation. The adsorbent's behavior depends on the chemistry and chemical properties of these functional groups or ligands (discussed in section 2). Additionally, the interaction of the surface sites and the REEs is controlled by the chemical properties of REEs, such as charge, ionic radius, coordination number, aqueous speciation, and the ability to form complexes with the ligand.

REEs occurs dominantly in trivalent oxidation state, have variable coordination numbers (CN 8–12 (Cotton & Harrowfield, 2012)), and have similar ionic radii between adjacent REEs (which decreases with increasing atomic number among lanthanides) (Nash, 1993). They are considered hard acid cations and interact strongly with hard anions such as hydroxide, alkoxide, carbonates, and phosphates and have strong complexes with organic ligands containing carboxylates and phosphonates (Johannesson et al., 1995; Noack et al., 2016; Pearson, 1963; Xie et al., 2014). More stable REE-ligand complexes are obtained with multidentate ligands like amino-poly(carboxylic acids) due to the high coordination number of REEs (Noack et al., 2016; Xie et al., 2014). These characteristics of REEs affect the extent, kinetics, and mechanism of the adsorption. In aqueous solutions, the pH of the solution controls the REEs speciation. REEs are predominantly cationic REE(III) in aqueous solution at acidic pH and REEs hydroxides at alkaline pH (Callura, 2018; Ramasamy, Repo, et al., 2017). At high pH, the primary mechanism of REEs uptake can be the surface precipitation of REEs as hydroxides instead of adsorption (Dardenne et al., 2002; Farley et al., 1985; Iftekhar, Ramasamy, et al., 2018; Piasecki & Sverjensky, 2008).

A measure of the adsorbent's effectiveness for separation and its performance can be obtained by conducting batch or column adsorption experiments. In batch adsorption, the frequently used characteristics are equilibrium adsorption capacity (q<sub>e</sub>) (eq. 1a), maximum adsorption capacity calculated using Langmuir isotherm (q<sub>m</sub>) (eq. 1e), % adsorption (eq. 1b), solid-liquid distribution (partitioning) coefficient (K<sub>d</sub>) (eq. 1c), and selectivity factor (SF) between element A and B (eq. 1d) in case of competitive adsorption or adsorption from a multi-element solution. These parameters are defined as follows:

$$q_e\left(\frac{\mathrm{mg}}{g}\right) = (C_0 - C_e) * V/m(1\mathrm{a})$$
Adsorption (%) =  $\frac{C_0 - C_e}{C_0} * 100$  (1b)  
 $K_d (\mathrm{ml}/g) = \frac{C_0 - C_e}{C_e} \frac{V}{m} (1\mathrm{c})$ 
SF  $(A/B) = \frac{Kd_A}{Kd_B}$  (1d)  
 $q_e\left(\frac{\mathrm{mg}}{g}\right) = q_m \frac{K_L C_e}{1 + K_L C_e}$  (1e)

where  $C_o$  and  $C_e$  are initial and equilibrium concentrations of the adsorbate in the solution in batch adsorption (mg/L), m is the mass of the adsorbent used (g), V is the total volume of the solution (L), q is the adsorption (in mg/g), and  $K_L$  is Langmuir isotherm constant (L/mg).

# Surface functional groups or ligands

The active components of an ion-exchange resin or adsorbent that interacts and binds the aqueous REEs species are the functional groups present on the surface. These functional groups can be active molecules of the polymeric ion exchange resins or ligands grafted on the solid support in functionalized adsorbents (shown in figure 1) or the existing functional groups of a naturally occurring surface, such as -O/-OH on the surface of a mineral oxide/hydroxide. They are involved in the uptake of REEs from solution through electrostatic interaction or surface complexation. The different functional groups can be classified based on the heteroatom bonded to the adsorbent surface (Yang et al., 2019). The common groups are O-containing-functional groups (e.g., -OH, -COOH, -C=O, and -C-O), S-containing functional groups (e.g.,  $-SO_3H$ , C-S, C=S, and S=O), P-containing functional groups (e.g.,  $-PO_2H_2$ ,  $-PO(OH)_2$ ), and N-containing functional groups (e.g.,  $-NH_2$ , -NH, -C=N and -C-N) (Figure 1). Additionally, ligands containing multiple types of functional groups are common, especially in chelating resins and functionalized adsorbents (Figure 1), resulting in wide variations in REE sorption chemistry (Hérès et al., 2018; Page et al., 2017; Trochimczuk & Alexandratos, 1994). Polyfunctional ligands can provide additional affinities (Alexandratos & Smith, 2004a). Also, the same functional group can have a higher or lower affinity for REEs based on its side group (Martell & Hancock, 1996; Zhu & Alexandratos, 2015).

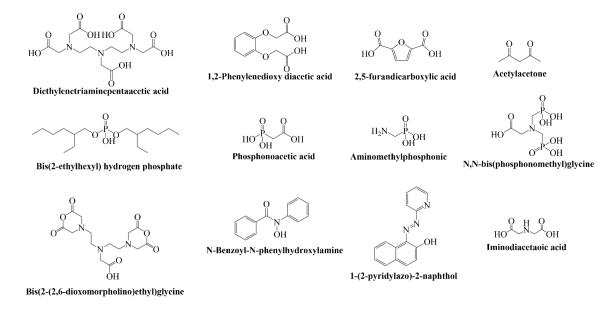


Figure 1: Different ligands used for REEs adsorption in chelating ion-exchange resins or grafted onto solid supports.

The most common functional groups used in ion-exchange and adsorption of REEs are carboxyl, found in both cation-exchangers (Bezzina et al., 2018; Shu et al., 2007; Xiong et al., 2011; Xiong, 2008) and various functionalized adsorbents (Figure 1) (Ahmed, Lee, et al., 2019; Callura et al., 2018; Noack et al., 2016; Polido Legaria, Rocha, et al., 2017; Ravi, Zhang, et al., 2018). The mechanism of REEs uptake by carboxyl-based adsorbents can be ion-exchange process in cation-exchangers or surface complexation in case of a chelating carboxyl-based surface ligand (e.g., complexation of REEs with diethylenetriaminepentaacetic acid (DTPA) functionalized adsorbent (Noack et al., 2016)). Many commercially available carboxyl-based cation exchange resins have been used for REEs extraction (Bezzina et al., 2018; Shu et al., 2007; Xiong et al., 2011; Xiong, 2008). Since carboxyl acid is a weak acid, its behavior is highly dependent on pH.

Sulfonic functional groups are the active component of the strongly acidic cation-exchange resins. The affinity of the counter-ion for the ion-exchanger depends on its charge and hydration radius (Harris & Lucy, 2015). REEs exist as triply charged positive ions in acidic aqueous solutions and hence have a high affinity to negatively charged sulfonic ions and can be separated from singly and doubly charged metal cations using interaction with sulfonic anion (Fritz & Garralda, 1963; Korkisch et al., 1967; Page et al., 2019; Strelow, 1960; Strelow et al., 1965). However, due to similar radii of adjacent Ln(III), selectivity for a particular Ln(III) is limited with sulfonic-acid cation-exchangers (Boyd, 1978; Strelow, 1960; Strelow et al., 1965; Strelow & Bothma, 1964). The sulfonic group is a strong acid; hence its behavior is mostly independent of pH.

Phosphorus-containing functional groups used for REEs sorption are organophosphoric acid, phosphonic acid  $(-PO(OH)_2)$ , and phosphonic ester  $PO(OR)_2$  based derivatives (Egawa et al., 1994; Ihara et al., 2001; Miklishanskii et al., 1968; Page et al., 2017). The ion-exchange resin containing phosphonic acid-based groups are considered weakly acidic cation-exchange resins similar to carboxyl-based ion-exchange resins and are dependent on pH. Additionally, P-based chelating ligands have been used as functional groups in different chelating resin (Callura et al., 2019; Hérès et al., 2018) and functionalized adsorbents (Figure 1) (Artiushenko, Kostenko, et al., 2020; Bertelsen et al., 2019; Callura et al., 2018; de Decker et al., 2016; Kavun et al., 2021; Noack et al., 2016; Ravi, Lee, et al., 2018; Z. Wang et al., 2002; X. Zheng et al., 2020).

Most common among N-containing functional groups is amine-based compounds. The REE sorption mechanism for amino-based sorbent is an ion-exchange process. These amino-based sorbents can be used to separate Th (IV) and U(IV), which form strong an ionic compounds with nitrate and phosphate (Jackson, 1954). Among REEs, Ce(IV) can form anionic nitrates, which can be separated from other REEs using amino-based resins or adsorbents (Zhu & Chen, 2011). Moreover, N-based ligands are used for surface complexation of REEs in chelating resin (Niu et al., 2021; Page et al., 2019) and other adsorbents (Figure 1) (de Decker et al., 2016; Lee et al., 2019; Ramasamy, Puhakka, Repo, Ben Hammouda, et al., 2018; Ramasamy, Repo, et al., 2017).

In naturally occurring oxidic adsorbents such as ferric hydroxide or silica oxide, the surface OH groups undergo protonation-deprotonation and produce surface charges which lead to electrostatic attraction of cations and anions present in the solution. They can electrostatically attract REEs cations resulting in the adsorption of REEs.

## Ion-exchange resins

Ion-exchange in the context of solid-phase extraction involves a reversible interchange of ions between a solid phase (or ion-exchanger) and the solution through electrostatic sorption and desorption to and from the ion-exchange material. The ion-exchangers are classified as cation or anion-exchanger based on the mobile exchangeable ions (i.e., counter-ions). Acidic cation-exchangers, introduced in 1944 by cross-linking polystyrene with 6-8% divinylbenzene, have cations as counterions and attract and bind cations, while anion exchanger, introduced later in 1948, can attract and bind anions from solution. Based on the physical form of the ion-exchanger, ion-exchangers can be classified as membranes, fibers, hydrogels, or resins. Ion-exchange resins (IERs), which represent the major class of ion-exchangers, are insoluble polymers with active-ion groups, commercially available as spherical beads or particles, and have been used to separate REEs mainly in chromatographic setup (Ehrlich & Lisichkin, 2017).

## Cation-exchange resins

**Strongly acidic cation-exchange resins:** Strongly acidic cation-exchange resins are formed by copolymerization of polystyrene and divinylbenzene and have sulfonic  $(SO_3^-)$  groups introduced to the benzene rings. There are many sulfonic  $(SO_3^-)$  group-based resins available under various trade names (e.g., Amberlite IR-120, Dowex 50WX), having different grain sizes, pore diameters, sorption capacities, degrees of cross-linking, and other characteristics (Ehrlich & Lisichkin, 2017). Sulfonic acid-based cation-exchangers have been used to separate REEs but are not very selective for a specific REE over the other.

In cation-exchange resins (CERs), the strength of cation binding depends on the charge and radius of the hydrated ion (Harris & Lucy, 2015). The electrochemical attraction increases with decreasing ionic radius for ions with the same charge. Within Ln(III), the ionic radius decreases with the increasing atomic number from La(III) (ionic radius: 103 pm) to Lu(III) (ionic radius: 86.1 pm), and thus the binding strength to cation-exchanger increases with atomic number. However, the use of strongly acidic cation-exchange resins for the separation of individual REEs in mineral acids, such as HCl,  $H_2SO_4$ , and HNO<sub>3</sub> is not selective due to similar ionic radius of adjacent Ln(III) (Boyd, 1978; Strelow, 1960; Strelow et al., 1965; Strelow & Bothma, 1964). The similar ionic radius of adjacent Ln(III) results in similar electrostatic attraction as evident by similar equilibrium constants for an ion-exchange reaction involving a strongly acidic cation-exchanger (3a). The ratio of the ion-exchange equilibrium constants of adjacent Ln(III) for reaction similar to (3a) does not exceed 1.1 (Boyd, 1978).

 $Ce^{3+} + LnR_3 = CeR_3 + Ln^{3+}$  (3a)

This limits the use of strongly acidic cation-exchange resins in individual REE separation from a solution containing a mix of different REEs. Still, these resins can be used for the separation of Ln(III) from other cations of lower or higher ionic charge (Fritz & Garralda, 1963; Korkisch et al., 1967; Page et al., 2019; Strelow, 1960; Strelow et al., 1965).

The separation of individual REEs increased with the use of complexing ligands as eluents for strongly acidic cation-exchanger (Boyd, 1978; B. Chen et al., 2017; Spedding et al., 1947, 1954; Strelow & Victor, 1990). The REE ions form complexes with the ligand. These REE-ligand complexes have less affinity for the exchanger than corresponding REE ions, which results in easier desorption of REE-ligand complex and a difference in relative REE desorption based on the stability of individual REE-ligand complex. With the same ligand, the relative concentration of different REE-ligand complexes depends on the ratio of their REE-ligand complex's stability constants. Since the ratio of stability constants of REE-ligand complexes (Karraker, 1961; Mackey et al., 1960; Schoeb, 1965; Suzuki et al., 1980; Wheelwright et al., 1953; Wood, 1993) of neighbor REEs is significantly higher than the ratio of ion-exchange constants (Boyd, 1978), better separation between REE is obtained during elution (Chen et al., 2017). The stability of REE-ligand complexes increases with the increasing atomic number for most complexing ligands, which leads to an order of elution from Lu(III) to Ln(III)) with complexing ligand as eluent (Karraker, 1961; Mackey et al., 1960; Schoeb, 1965; Suzuki et al., 1993) The different complexing ligands used as eluent for REEs schromatographic separation using strong acidic cation-exchangers are discussed later in the chapter (section 8.2).

The sulfonic cation-exchangers with complexing ligand eluents have been mainly used in the chromatographic separation of REEs (Ehrlich & Lisichkin, 2017). However, alternatively, in a batch adsorption process, Khawassek et al. (2019) used macroreticular sulfonic acid resin Dowex 50X8 to adsorb REEs from effluents solution collected from the hydrometallurgical process for El-Erediya mineralization. The maximum total REE uptake from leachate solution was 80 mg REEs/g. Similarly, strong acid resin Amberlite 200C Na and Amberlite 200C H showed high sorption efficiency (more than 99.8%) for La(III), Ce(III), and Nd(III) (Kołodyńska et al., 2019). Page et al. (2019) used strong acidic cation exchange resin, Lewatit MonoPlus SP 112, for La(III), Sm(III), and Er(III) adsorption in sulfate and chloride medium in the presence of competitive ions, such as Fe(III) and Al(III), and reported maximum adsorption capacity of 42 mg/g for Sm(III). The equilibrium constants for the ion-exchange reactions and the REEs selectivities were higher in the chloride medium than the sulfate medium. The ion-exchange equilibrium constants for competitive ions, Fe(III) and Al(III), were significantly lower in both media. A macro-porous strongly acidic CER, SQS-6, adsorbed 97.6% La(III) and 90.36% Nd(III) in 4.0 M H<sub>3</sub>PO<sub>4</sub> media with equilibrium capacities of 13.8 and 12.70 mg/g (in 8 M H<sub>3</sub>PO<sub>4</sub>), respectively (Abu Elgoud et al., 2019).

**Carboxylic acid-based cation-exchange resins:** Carboxylic acid-based cation-exchange resins can form complexes with REEs in addition to electrostatic interaction (Arnold & Hing, 1967; Kazantsev et al., 1974). The carboxylic functionalized cation-exchangers involve copolymerization of methacrylic acid or acrylic, or acrylonitrile, generally, with divinylbenzene. The type of carboxylic group on cation-exchanger affects the adsorption of REEs; for example, polyacrylic acid resin (Amberlite XE 89) showed lower selectivity for lanthanide than the polymethacrylic acid resin (Amberlite IRC 50) (Arnold & Hing, 1967).

Many macro-porous carboxylic cation-exchange resins such as D113, D155, D152, D151, and SQD-85 have been used for REEs adsorption in acetate medium. The macro-porous carboxylic acid resin D113 was used for adsorption of La (III) ( $q_m = 273.3 \text{ mg/g}$  (Shu et al., 2007)), Dy(III) ( $q_m = 292.7 \text{ mg/g}$  (Wang & Gao, 2007)), Nd(III) ( $q_m = 232.56 \text{ mg/g}$  (Xiong et al., 2011)) and Er(III) ( $q_m = 250 \text{ mg/g}$  (Xiong et al., 2009)). The separation coefficients for La (III) adsorption onto D113 were 2.29, 3.64, 4.27, and 0.627 against Ce(III), Gd(III), Er(III), and Y(III), respectively (Shu et al., 2007). With another carboxylic acid resin D152, the maximum adsorption capacities at pH 6.70 for different REEs were between 238 mg/g (for Er(III)) and 510 mg/g (for Sm (III)) (Xiong et al., 2008). Similarly, D155 was used for Ce(III) ( $q_m = 294 \text{ mg/g}$ ) and Gd(III) ( $q_m = 283 \text{ mg/g}$ ) (Xiong, 2008), SQD-85 for Yb(III) ( $q_m = 347.6 \text{ mg/g}$ ) (Xiong et al., 2011), D151 for Ce(III) ( $q_m = 392 \text{ mg/g}$ ) (Yao, 2010), and a gel-type weak acid resin (110) for Yb(III) ( $q_m = 265.8 \text{ mg/g}$ ) (Zheng & Xiong, 2011). Commercial resin Amberlite IRC86 (functional group: carboxylic acid, and Purolite S910 (functional group = amidoxime) were used in various buffer solutions (i.e., malic acid, formic acid, acetic acid, alanine, and lactic acid) for adsorption of REE in the presence of competitive Fe(III) and Al(III) ions (Bezzina et al., 2018). The use of a carboxylate buffered system allowed easy separation of REE from Fe(III) and Al(III) ions. The carboxylic resin IRC86 showed higher capacity for HREEs in acetic acid media at pH 4.4, showing preference order of Y(III) > Er(III) > Sm(III) > La(III).

The limitation of using carboxylic cation-exchange resins is that these resins operate in the weak acidic pH range (pH>3.5), posing additional challenges due to hydrolysis of REE ions and occurrence of other competitive cations such as Fe(III) (Ehrlich & Lisichkin, 2017; Kazantsev et al., 1974; Wood, 1993).

**P-containing cation-exchange resins:** The phosphorus-based ligand containing resins are considered part of the family of the weakly acidic cation-exchangers. Among different phosphorus-containing functional groups, phosphinic showed higher selectivity than phosphonic, with both showing higher selectivity than their respective oxidized derivatives (Egawa et al., 1994). Their Ln(III) distribution coefficient increased with increasing atomic number in general but with a plateau from Sm(III) to Ho(III). Macroreticular methylenephosphonic acid resin showed affinity series of Fe (III) ~ U(VI) ~ Mo(VI) > Bi(III) > AI(III) > Gd(III) > La(III) ~ V(V) > Pb(II) > Cd(II) > Cu(II) [?] Ca(II) [?] Ba(II) [?] Zn(II) > Mg(II) [?] Co(II) [?] Ni(II) (Jyo et al., 1997); whereas macroreticular phosphonic acid resin had affinity series of Mo(VI) [?] Fe(III) [?] U(VI) > Bi(III) [?] Lu(III) > Al(III) [?] Gd(III) > La(III) > Cr(III) > Pb(II) > Mn(II) [?] Cd(II) [?] Cu(II) > Ca(II) [?] Cu(II) [?] Cu(II) > Ca(II) [?] Cu(II) [?] Cu(I

Many different P-based cation-exchange resins used for REE adsorption involve different side-group with phosphorous. The P-based resin containing P(R)(O)OH (R = Et, Bu) and -P(O)(OR)OH (R = Et, Pr, Bu) were used for chromatographic separation of La, Pm, and Eu with increasing K<sub>d</sub> values with increase in atomic number (Miklishanskii et al., 1968). Among different adsorbents with phosphorus-containing ligands, the strength of metal ion binding is affected by electron density on the oxygen atom, the spacer connecting the phosphorous-containing ligand to the polymer matrix, and the hydrophilicity of its environment (Spiro D. Alexandratos & Hussain, 1998; Spiro D. Alexandratos & Zhu, 2005, 2008, 2015; Andrzej W. Trochimczuk & Alexandratos, 1994; X. Zhu & Alexandratos, 2014, 2015) The affinity for REEs increased with the introduction of hydroxyl or polyol into the spacer due to their stronger interaction with REEs (Alexandratos & Zhu, 2008).

Adsorbents containing di- and polyfunctional groups in addition to P-based groups have been studied for REE separation (Alexandratos & Natesan, 1999; Alexandratos & Hussain, 1995; Alexandratos & Smith, 2004b; Shumilova et al., 2012; Trochimczuk, 2000). The addition of a second functional group can enhance the behavior of the adsorbent, as in phosphorylated adsorbents, where the introduction of highly hydrophilic sulfonic acid eliminated intra-ligand hydrogen bonding, which reduced intra-ligand cooperation, and increased the accessibility of P-containing groups (Alexandratos & Smith, 2004b). Additionally, the sulfonic acid itself has an affinity for REE, which can increase REE adsorption (Ehrlich & Lisichkin, 2017). Bonding sulfonic acid groups to the phosphinated polystyrene matrix increased the Eu (III) distribution coefficient from 61.8 to 220.5 in a 1 N HNO<sub>3</sub> solution (Alexandratos & Hussain, 1995). Hérès et al. (2018) used Monophos and Diphonix resin, which had sulfonic groups together with alkylphosphonic groups for adsorption of REEs. The extraction efficiency of Monophos and Diphonix resin increasing ionic radius of REEs.

#### Anion-exchange resins

REE ions do not form anions with inorganic ligands thus are poorly adsorbed on the anion-exchange resins (Ehrlich & Lisichkin, 2017; Koodynska & Hubicki, 2012; J Minczewski et al., 1982). Still, Th(IV) and U(VI) can be separated from solution containing REEs using anion-exchange resins (AERs) as they form anion complexes with nitrate and phosphate (Ehrlich & Lisichkin, 2017; Koodynska & Hubicki, 2012). Among REEs, cerium (IV) can form negatively charged complexes with nitrate and can be adsorbed to the AERs, e.g., anion-exchanger containing N-methyl-imidazolium group (Zhu & Chen, 2011).

Anionic REE-ligand complexes can be formed by adding organic compounds (e.g., methanol (Faris & Warton, 1962), ethanol (Hubicki & Olszak, 1998), and propanol (Hubicki & Olszak, 2002)) to nitric acid. These anionic complexes can be separated using a strongly basic anion-exchange resin. Anionic REE-ligand complex

electrostatically binds to the positive anion-exchanger. Similarly, complexing ligands such as ethylenediaminetetraacetic acid (EDTA) and cyclohexane-1,2-diaminetetraacetic acid (CDTA) were used to form anionic REE-ligand complex for REEs separation using anion-exchange resins (Hubicka & Hubicki, 1986; Hubicka & Kołodyńska, 2004, 2008; Jerzy Minczewski & Dybczyński, 1962; Wódkiewicz & Dybczyński, 1968). Binary mixtures of Y-Nd, Sm-Tb, La-Nd, and Dy-Er were separated using frontal chromatography with EDTA as eluent using different Dowex anion-exchangers (Hubicka and Hubicki 1986). Strongly basic anion resin Dowex 1 and Dowex 2 were used to separate REE complex with N-hydroxyethylenediaminetriacetic acid (HEDTA) and with iminodiacetic acid (IDA) (Hubicka & Drobek, 1997, 1998, 1999). Similarly, REEs complexes with DCTA of the Ln(dcta)<sup>-</sup> type were chromatographically separated using different polyacrylate anion-exchangers (Amberlite IRA 68, Amberlite IRA 458, and Amberlite IRA 958) and different polystyrene anion-exchangers (Lewatit MonoPlus M 500, Lewatit MonoPlus M 600, Lewatit MonoPlus MP 64, Lewatit MonoPlus MP 500, and Lewatit MP 62) (Hubicka & Kołodyńska, 2004, 2008).

## Chelating ion-exchange resins

Chelating ion-exchange resins are equipped with ligands that form complexes with metal ions through their functional groups (Garg et al., 1999). Chelating ion-exchange resins used for REE separation contain iminodiacetate, aminomethylphosphonic, hydroxamine, and diamide (Ehrlich & Lisichkin, 2017; Koodynska & Hubicki, 2012). Many commercially available iminodiacetate based resins such as Amberlite IRC 718, Chelex 100, Dowex A-1 (Mathur & Khopkar, 1985; Schrobilgen & Lang, 1968), Duolite ES466, Lewatit TP 207 (Junior et al., 2021; Niu et al., 2021), and Purolite S930 Plus (Page et al., 2019) have been used for REE separation (Ehrlich & Lisichkin, 2017; Koodynska & Hubicki, 2012).

Iminodiacetic acid resins are also characterized by a very high selectivity for REE over the alkali and alkaline earth metals, often present in high concentrations in alternative REE resources (Ehrlich & Lisichkin, 2017; Koodynska & Hubicki, 2012; Page et al., 2017, 2019). An iminodiacetic acid resins, Purolite S930Plus, showed higher selectivity for REEs in the presence of high Na and Ca concentration than the sulfonic acid resin (SA), sulfonic-phosphonic resin (Purolite S957), and aminophosphonic resins (Purolite S950) (Page et al., 2017). However, the SA resin, Purolite S957, and Purolite S950 were tolerant towards REEs adsorption from acid solutions up to 0.5 M [H<sup>+</sup>], whereas iminodiacetic acid resins effectively adsorbed REE only at [H<sup>+</sup>] < 0.001 M. For the sulfonic acid resin, the selectivity was REE [?] Th > Fe [?] Al whereas for other resins it was Th [?] Fe [?] REE [?] Al. In another study with Purolite S930Plus, the resin selectively adsorbed La(III) over Mg(II) with a selectivity factor of 3046 in 1 M MgCl<sub>2</sub>, but the selectivity factor decreased to 453 and 240 in 0.5 M MgCl<sub>2</sub> + 0.5 M MgSO<sub>4</sub> and 1 M MgSO<sub>4</sub> medium, respectively (Page et al., 2019). Another iminodiacetic acid-based resin, TP207, showed adsorption capacity order of La(III) > Eu(III) > Y(III), with capacity of 0.73 mmol/g (or 101.5 mg/g) for La(III) at pH 4.0 (Niu et al., 2021).

The REEs extraction efficiency using different aminophosphonic resins (Tulsion CH-93, Purolite S940, Amberlite IRC-747, Lewatit TP-260) decreased with an increase in Z/IR (atomic number/ionic radius) from Sc up to a plateau of La, Nd, and Gd, with an increase and increased after that with Z/IR from Dy to Yb (Hérès et al., 2018). Concurrently, the extraction efficiency decreased with an increase in ionic radius (IR) in general, with a slight spike at Nd (III) and Pr(III). Another chelating ligand diglycolamic acid-containing polymeric adsorbent showed adsorption capacity ( $q_m$ ) of 0.113 mmol Dy/g (or 18.3 mg/g) and selectively adsorbed REEs at low pH values (Shinozaki et al., 2018). Other chelating ligands ethylenetriaminepentaacetic dianhydride (DTPADA), phos-phonoacetic acid (PAA), and N,N-bis(phosphonomethyl)glycine (BPG) containing polymers had maximum adsorption capacities of 2.9, 5.0, 3.0 mg/g, and respectively for a mixture of three REEs (Nd(III), Gd(III), and Ho(III) (Callura et al., 2019, 2021). N-based chelating resin, Dowex M 4195 with bis(2-pyridylmethyl) amine showed very low sorption (maximum 3.1%) for La(III), Ce(III), Nd(III) (Kołodyńska et al., 2019).

# **Inorganic** adsorbents

Inorganic adsorbents used for REEs adsorption include mineral oxides and hydroxides, clay minerals, and nanomaterials. Mineral oxides and hydroxides are adsorbents with reactive sites containing oxygens ( $O^{2-}$ ) or hydroxides (-OH) that interact with cations and anions. The mineral adsorbents used for REEs adsorption are silica, alumina, iron (hydro)oxides, Mn oxides, and TiO<sub>2</sub>.

Silica has been studied as an adsorbent for Gd(III), Y(III) (Kosmulski, 1997b), and Yb(III) (Marmier et al., 1999). These investigations focused on surface complexation modeling and % uptake and did not report maximum uptake in mg/g, distribution (partitioning) coefficient, or separation factor. Alumina was studied for adsorption of Gd(III), Y(III) (Kosmulski, 1997a), Yb(III) (Marmier et al., 1997), and Eu(III) (Wang et al., 2006). TiO<sub>2</sub> was studied for adsorption of Y(III) (Zhang et al., 2004), Nd(III) (Ridley et al., 2005; Zhang et al., 2004), and Eu(III) (Tan et al., 2009). The q<sub>m</sub> for Eu(III) was 1.5 mg/g with TiO<sub>2</sub> and 2.7 mg/g in the presence of fulvic acid (Tan et al., 2009).

Other researches involving inorganic adsorbents are Yb(III) adsorption on hematite (Marmier et al., 1997), La(III) onto hematite (Nicolas Marmier & Fromage, 1999), REEs onto Mn oxide, Fe oxy-hydroxide (Davranche et al., 2004, 2005; Ohta & Kawabe, 2001), and REEs on amorphous ferric hydroxide (Quinn et al., 2006, 2007). In addition to oxides and hydroxides, other minerals have been used as adsorbents as well. Adsorption of Nd(III) onto kaolinite (Aja, 1998), Ln(III) onto kaolinite and smectite (Coppin et al., 2002), Eu(III) onto montmorillonite (Kowal-Fouchard et al., 2004), REEs on kaolin (XIAO et al., 2016), REEs adsorption onto Kaolinite (Feng et al., 2021), and Eu(III) on halloysite and kaolinite (Zhou et al., 2022) are such studies involving inorganic mineral adsorbents. Kaolin showed a saturated adsorption capacity of 1.731, 1.587, and 0.971 mg/g for La(III), Nd(III), and Y(III), respectively (XIAO et al., 2016). Mosai et al. (2019) used natural zeolite and bentonite to recover REEs from aqueous solution and reported q<sub>m</sub> values of 0.09-0.24 mg/g and 1.07-2.87 mg/g for adsorption of different REEs onto zeolite and bentonite, respectively.

Most of the research mentioned above focuses on understanding the mechanism of REE adsorption onto the inorganic adsorbent and uses surface complexation models. The mechanism of adsorption is required for a better understanding of natural as well as engineered systems. However, since the adsorption capacity of these unmodified adsorbents is low (i.e., around 0.01-0.1 mmol/g) (Ehrlich & Lisichkin, 2017), it is impractical to employ these adsorbents for REE separation at an industrial scale.

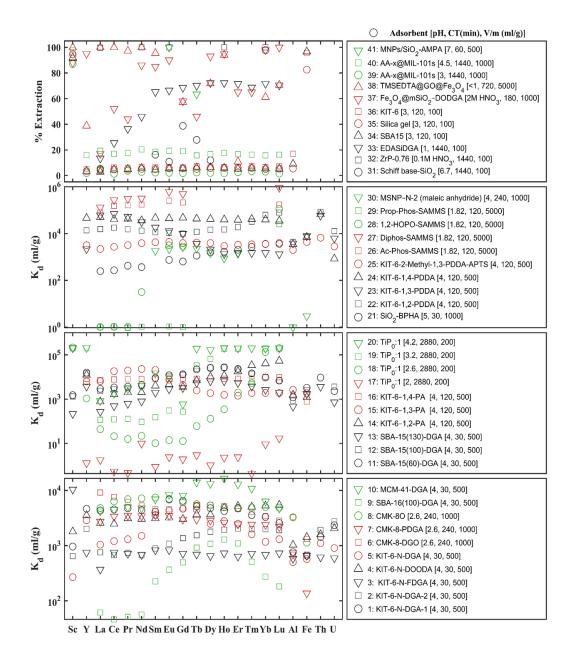


Figure 2: Distribution coefficient ( $K_d$ ) for various adsorbents. The legends include adsorbent with the experimental condition (pH, contact time (CT), and V/m ratio (volume of solution/mass of adsorbent)) Source for data: Adsorbents 1-2 (Florek et al., 2014), 3-5 (Florek et al., 2015), 6-8 (Perreault et al., 2017), 9-13 (Juère et al., 2016), 14-16 (Hu et al., 2017), 17-20(pH is equilibrium pH) (Zhang et al., 2018), 21 (Artiushenko, Ávila, et al., 2020), 22-25 (Hu et al., 2019), 26-29 (Yantasee et al., 2009), 30 (Zheng et al., 2015), 31 (Amarasekara et al., 2009), 32 (Veliscek-Carolan et al., 2014), 33 (Ogata et al., 2015b), 34-36 (Giret et al., 2018), 37 (Li et al., 2018), 38 (Barrak et al., 2019), 39-40 (Lou et al., 2019), 41 (Kostenko et al., 2019).

Nonetheless, there are some recent studies involving novel inorganic adsorbents that show promising results. Multiple Zirconium organophosphonate (ZrP) with different Zr:P ratios were prepared using low-temperature hydrothermal reactions of zirconium propoxide with amino tris(methylene phosphonic acid) (ATMP). The adsorbents showed selectivity for lanthanide elements over mono- and divalent metal ions. The sorption capacities of 37, 56, and 60 mg Eu/g were reported for ZrP-0.65, ZrP-0.71, and ZrP-0.76 (legend 32, Figure 2), respectively (Veliscek-Carolan et al., 2014). In another study, Attallah et al. (2016) synthesized a number of aluminum silicotitanates (ATS 1-31) and obtained 99% La (III) and Eu (III) adsorption. Inorganic titanium phosphate showed Sc(III) uptake capacities of 26.1, 8.25, and 3.3 mg/g for amorphous,  $\alpha$ -, and  $\gamma$ -TiP. respectively. In chromatographic separation using amorphous TiP, almost all Sc(III) were eluted using a mixed acid comprising of nitric and phosphoric acid, with Sc(III)/Fe(II) and Sc(III)/Al(III) enrichment factor of 9 and 265, respectively (Zhang, Koivula, et al., 2017). Titanium phosphate prepared from acidic wastewater of titanium dioxide achieved maximum Ce(III) adsorption capacity  $(q_m)$  of 158.0 mg/g and was selective for Ce in presence of Na, K, Ca, and Mg ions (Zhaowang Liu et al., 2021). Another inorganic adsorbent, layered titanium (IV) butyl phosphate (TiP), showed Dy(III) uptake of more than 25 mg/g and a maximum separation factor of 2065 for Dy(III)-Nd(III), 11.5 for Dy(III)-Tb(III), and around 25 for La(III)-Ce(III) in respective binary element solutions (Zhang et al. 2018). Adsorptions conducted at different pH resulted in selectivity for different Ln(III) with the highest distribution coefficient ( $K_d$ ) of around 10<sup>5</sup> ml/g (legend 17-20, Figure 2). The adsorbent TiP showed selectivity for Yb(III) and Lu(III) at pH 2.6. The distribution coefficient (K<sub>d</sub>) of different REEs measures the selectivity of the adsorbent for a particular REE in competitive adsorption (Figure 2).

With another inorganic adsorbent amorphous zirconium phosphate (am-ZrP), maximum adsorption of 27.5 mg/g and 38.3 mg/g for Nd and Dy were obtained (Xu et al., 2018). The SF for Dy(III)/Co(II), Nd(III)/Co(II), Dy(III)/Nd(III) were 1811, 958, and 1.9, respectively (Xu et al., 2018). A microporous titanosilicate, ETS 10, had adsorption capacities ( $q_m$ ) of 48.8, 68.1, 99.0, 124.7, and 122.7 mg/g, respectively for Y(III), Nd(III), Eu(III), Tb(III), and Dy(III) (Thakkar et al., 2019). Magnetic hydroxyapatite composite (CaHAP/NF) derived from calcium hydroxyapatite [Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>], and nickel ferrite [NiFe<sub>2</sub>O<sub>4</sub>] was synthesized by a coprecipitation method had capacities of 137.35 and 130.43 mg/g for Eu(III) and Tb(III) (Attia et al., 2019). Adsorbent synthesized through modification of titanium oxide modified with arsenate (4As-TiO<sub>2</sub>) and further doping with Nd (Nd/4As-TiO<sub>2</sub>) reached maximum capacities of 65 and 37 mg/g mg/g for Y(III) at pH 9, respectively with the possible mechanism of Y(III) surface precipitation in alkaline medium and Y(III) surface complexation in neutral medium (Vasylyeva et al., 2021).

Many metal-oxides based nanoparticles have been tested for REE adsorption. Fe(III)–Ti(IV) mixed oxide nanoparticles showed capacities of 229, 181, and 126 mg/g for Ce(III), Nd(III), and Gd(III), respectively (Metwally & Rizk, 2014). Nano maghemite showed Y(III) uptake capacity of 13.5 mg/g (Dubey & Grandhi, 2016). A magnetic nanoparticle (MNP)  $Co_xMn_{1-x}Fe_2O_4(x = 0.2)$  had adsorption capacity of 125 mg/g and 25 mg/g for La(III) and Ce(III) while  $Co_xMn_{1-x}Fe_2O_4(x = 0.8)$  had adsorption capacity of 189 mg/g and 294 mg/g for La(III) and Ce(III) (Ghobadi et al., 2017). In another study, MNP MnFe<sub>2</sub>O<sub>4</sub> prepared via co-precipitation and further modified with graphene oxide (MnFe<sub>2</sub>O<sub>4</sub>-GO) showed high capacities for La(III) and Ce(III) was 982 mg/g at pH 7, both higher than MnFe<sub>2</sub>O<sub>4</sub> (La(III) = 785 and Ce(III) = 770 mg/g) (Table 1). Other Magnetic nano-MnFe<sub>2</sub>O<sub>4</sub> composites with Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-chitosan showed similar high adsorption capacities (Liu et al., 2021) (Table 1). Other high-capacity REEs adsorbents are listed in Table 1 (adsorbents are discussed in their respective sections).

Table 1. Some adsorbents with high adsorption capacity $(q_m > 350 \text{ mg/g})$ for various REEs (III	Table 1. Some ads	sorbents with high	a dsorption	capacity (q <sub>n</sub>	$_{\rm m} > 350  {\rm mg/g}$	) for variou	ıs REEs (III).
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Adsorbent	Type of adsorbent	$q_m (mg/g)$ for REE(III)
D152	Carboxyl acid-CER	La: 486, Pr: 373, Nd: 453, Sm: 510, Gd: 391, Dy: 413, Lu:
D151	Carboxyl acid-CER	Ce: 392
$MnFe_2O_4$	Inorganic adsorbent	La: 785, Ce: 770
$MnFe_2O_4$ -GO	Inorganic adsorbent/ GO based	La: 1001, Ce: 982
TMO-nanowire	Inorganic adsorbent	La: 1111, Ce: 1000
$MnF_2O_4$ - $Al_2O_3$	Inorganic adsorbent	La: 885, Ce: 879
$MnFe_2O_4@SiO_2-CS$	Composite adsorbent	La: 1030, Ce: 1020

Adsorbent	Type of adsorbent	$q_m (mg/g)$ for REE(III)
SH-MCM-41	OMS based	La: 560.56, Gd: 467.60, Yb: 546.68
APHMSN	Functionalized mesoporous silica	Gd: 387.3
$\rm Fe_3O_4/MnO_2/rGO$	GO based	La: 1016, Ce: 981
GO@TiP-Sponge	GO based	Dy: 576.17
CNT/GO hybrid hydrosol	CNT-GO based	Gd: 534.76
ZIF-8	MOF	Dy: 430.4
ZIF-8	MOF	La: 385
HKUST	MOF	Ce: 353
ZnGA	MOF	Y: 377.02
Mg-Fe-LDH-Cyanex272	Metal based	La: 480,8
CMC-g-PAC hydrogel	Composite adsorbent	La: 381.72

CER: Cation-exchange resin, TMO: Transition metal oxide, GO: Graphene oxide, OMS: ordered mesoporous silica, APHMSN: Amino-phosphonic functionalized hollow mesoporous silica nanoparticle, CNT: Carbon nanotube, MOF: Metal-organic framework, LDH: Layered double hydroxide, CMC-g-PAC: carboxymethyl-cellulose grafted polyacrylic acid.

Magnetic nanoparticle CuFe<sub>2</sub>O<sub>4</sub> showed adsorption capacity of 51.02, 42.02, and 40.16 mg/g for Nd(III), La(III), and Ce(III), respectively (Tu & Johnston, 2018). Marwani et al. (2018) synthesized CeO<sub>2</sub>-CdO nanomaterial and used it for adsorption of Y(III) from a solution containing Co(II), Cu(II), Cr(III), Cr(VI), Pb(II), W(VI), Y(III) and Zn(II). The distribution coefficient (K<sub>d</sub>) for Y(III) reported was 17,743.90 ml/g with a capacity (q<sub>m</sub>) of 84.67 mg/g. Other nano adsorbents, nano-thorium (IV) oxide, and nano-zirconium oxide showed adsorption capacities of 10.5 mg/g and 18.0 mg/g for Y (III), respectively (Dubey & Grandhi, 2019). High adsorption capacities of 1111 for La(III) and 1000 mg/g for Ce(III) were obtained at pH 5 with transition metal oxide (TMO) nanowires synthesized via hydrothermal processing of a metal mix (Co, Fe, Ni) followed by pyrolysis (Sarmadi et al., 2021).

# Extractant immobilized materials

Extractants immobilized materials (EIMs) are a class of adsorbents in which the active component or extractant used to bind the target analyte separating it from its original medium is physically immobilized onto a solid support (Hidayah & Abidin, 2017). The active component or the extractant is a compound capable of ionic or complex interaction with the target metal ions. The active component is attached to the solid support's surface by physical adsorption, or it resides in a thin solvent layer covering the support surface, or it can be part of the bulk solvent filling the pores of the solid support. In literature, solvent impregnated resins (SIRs) is commonly used to identify adsorbent obtained when solvent extractant such as N,N-dimethylformamide (DMF), N,N,N',N'-Tetraoctyl diglycolamide (TODGA), and Cyanex-923 are infused onto solid support like silica or resin (Sun et al. 2009; Kabay et al. 2010; Zhu and Chen 2011). Another similar term, supported ionic liquid (SIL), describes adsorbents where ionic liquids are infused into the solid support (Bao et al., 2016; Zhu et al., 2012).

The separation processes involving EIMs have been termed as supported liquid extraction (SLE) or solidsupported liquid-liquid extraction (SLLE) (Florek et al., 2016; Hidayah & Abidin, 2017; Hu et al., 2018). Supported liquid extraction (SLE) is analogous to traditional liquid-liquid extraction (LLE), where target species are separated based on their relative solubilities in two different immiscible liquids, usually water and an organic solvent containing the extractant but instead of shaking the two immiscible phases together, the extractant is supported on a solid support and put in a column (or cartridge). The REEs containing solution is passed through, REEs ion gets adsorbed, and then eluent is used to desorb the adsorbed REEs species. In SLE, it is possible to achieve higher recovery due to the increase in surface area of interaction between the extractant and the target cations and increasing the diffusion rate through control of the porous structure of the support material. Other advantages over traditional LLE are less use of organic compounds, waste reduction, and lack of third phase formation (Florek et al., 2016; Hidayah & Abidin, 2017; Kabay et al., 2010).

The synthesis of EIMs (SIRs and SILs) involves modification of already synthesized polymers or other solid supports like silica or activated carbon using dry or wet methods. In the dry method, the active component is impregnated into support in excess using a volatile solvent then the excess amount is evaporated by heating, thus leaving the active component physically adsorbed to the support surface. In the wet method, support is impregnated with a solution of active component in a non-polar or weakly polar solvent followed by repeated washing with water, leaving a layer of the non-polar solution of the active component (Bao et al., 2016; Ehrlich & Lisichkin, 2017). Based on the types of solid support used for preparing, these adsorbents can be broadly divided into organic polymer-based support and inorganic supports.

## **Organic polymer-based supports**

Many researchers have used organic polymers as the solid support for solvent impregnated resins (SIRs) used for REEs uptake from solution. Relevant examples of polymer based SIRs include N,N,N'N' tetraoctyldiglycolamide (TODGA) and N,N,N'N' tetrakis-2-ethylhexyldiglycolamide (TEHDGA) impregnated Amberchrom CG-71 for REEs separation; tributyl phosphate infused Styrene–divinylbenzene to copolymer separate Am and Eu (Louis & Duyckaerts, 1984, 1985); 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) infused Amberlite XAD-7 for separation of Gd and Y mixtures (WAKUI et al., 1988); 8-Quinolinol (oxine) and 2-(2-(5 chloropyridylazo)-5-dimethylamino)-phenol (5ClDMPAP) immobilized Amberlite XAD-4 and XAD-7 each for preconcentration of Ce, La, and Pr (Masi & Olsina, 1993); Amberlite XAD-7 impregnated with binary mix of cobalt dicarbollide and dibutyl-N,N-diethylcarbamoylmethyl phosphonate (DB-DECMP) for Eu sorption (Svoboda et al., 1997); bis(2,4,4-trimethyl pentyl) phosphinic acid (Cyanex 272) (Wang et al., 1998), 1-hexyl-4-ethyloctyl hydrogen isopropylphosphonic acid (HEOPA) (Wang et al., 2002) , and bis(2,4,4-trimethylpentyl) monothiophosphinic acid (CL302, HL) (Jia et al., 2004) infused resin for HREEs separation.

Additional examples include PC88A infused styrene–divinyl benzene copolymer for Gd(III) and Tb(III) chromatographic separation (PARK et al., 2005), Octacarboxymethyl-C-methylcalix 4-resorcinarene impregnated Amberlite XAD-16 for La(III), Ce(III), and Y(III) preconcentration (Gok et al., 2007); XAD-4 infused with tri-n-octylmethylammonium chloride (Aliquat-336) in benzene for Ln(III) and Gd(III) (Elsofany, 2008); microporous polymer infused with phosphorus podands bearing two Ph<sub>2</sub>P(O)CH<sub>2</sub>C(O)NH for REEs (Turanov et al., 2008); Cyanex272- 2-ethylhexyl phosphoric acid-2-ethylhexyl ester (P507) impregnated resin for HREEs (Liao et al., 2010); TOPS-99 infused Amberlite XAD-4 to extracted Tb (Kumar et al., 2011),  $\beta$ -glycerophosphate impregnated Amberlite XAD 7 for La(III) (Gabor et al., 2016); di-(2-ethylhexyl)phosphinic acid (P227) impregnated XAD-7HP for HREEs (Yang et al., 2020); and HDEHP impregnated XAD-7 for REEs (Sert et al., 2021).

Lee et al. (2009) used trialkylphosphine-based (Cyanex 923), PC88A, and HDEHP for selective separation of La from Ce, Pr, Nd, and Sm, as well as from other concomitant metals in chloride medium. HDEHP provided the best separation with separation factors of 2.57, 3.63, 4.72, and 32.06 for Ce, Pr, Nd, and Sm over La (Lee et al., 2009, 2010b). The same adsorbent was used, followed by anion exchange and oxalate precipitation to obtain La<sub>2</sub>O<sub>3</sub> of more than 99.9998% purity (Lee et al., 2010a). Amberlite XAD-7 coated with  $\beta$ -glycerophosphate had q<sub>m</sub> of 33.8 mg/g for La (Gabor et al., 2016). Mondal et al. (2019) used N, N,N',N'-tetrakis-2-ethylhexyldiglycolamide (TEHDGA) impregnated XAD-7 resin to selectively adsorb REEs from coal fly ash solution containing Fe, Ca, Al, Mg, and Si with K<sub>d</sub> of 200-520 ml/g for REEs and 0.2-2.9 ml/g for impurities. Cyanex 272 impregnated Amberlite XAD-7 resin showed distribution coefficient in order of Gd > Eu > Sm > Nd > Pr > La with K<sub>d</sub> value for Gd and Eu as 208.1 and 156.4 ml/g (İnan et al., 2018). The SIR P227 infused XAD-7HP showed selectivity series of Fe > Lu > Tm > Zn > Mg > Ca > Ho > Co > Ni > Cu > Al (B. Yang et al., 2020). Another adsorbent, HDEHP-XAD-7 showed selectivity series Gd > Eu > Sm > Nd > Pr > La with separation factors achieved Gd/La separation factors of >140 (Sert et al., 2021).

The examples SILs with organic polymer include 1-octyl-3-methylimidazolium hexafluorophosphate  $(C8mim^+PF_6^-)$  containing Cyanex923 immobilized on XAD-7 for REE extraction (Sun et al., 2008), trialkylmethylammonium sec-nonylphenoxyacetate ([A336][CA-100]) impregnated on Amberlite XAD-7 (Sun et al., 2009), Trihexyl(tetradecyl) phosphonium mono-(2-ethylhexyl) 2-ethylhexyl phosphonate ([P<sub>66614</sub>][EHEHP]) and trioctylmethylammonium bis(2,4,4-trimethylpentyl) phosphonate ([N<sub>1888</sub>][BTMPP]) impregnated Amberlite XAD-7 (Zhao et al., 2016), betainium sulfonyl(trifluoromethanesulfonylimide) poly(styrene-co-divinylbenzene) [Hbet–STFSI–PS–DVB] impregnated Amberlite XAD-16 (Avdibegović et al., 2017), 1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl)imide ([Bmim][NTf2]) combined with N,N-dioctyldiglycolamic acid (DODGAA) and impregnated into Amberlite XAD7HP (Friend et al., 2020), and trihexyl (tetradecyl) phosphine bis (2,4, 4-trimethyl-amyl)–phosphonate (Cyphos IL 104) impregnated polymer membrane (Wang et al., 2020).

#### Inorganic supports

Inorganic supports mostly include silica-based polymers. In some cases, ordered mesoporous silica and carbon nanotubes have been used. Extractant bis(2- ethylhexyl) hydrogen phosphate (HDEHP) coated C18-hydrophobized silica was used for chromatographic separation of lanthanides (Sivaraman et al., 2002); 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester impregnated silica-based urea-formaldehyde (SiO<sub>2</sub>/UF) for Eu(III) and Nd(III) (Naser et al., 2015); HDEHP impregnated Polyethersulfone (PES) embedded with polyvinyl alcohol (PVA) and multiwalled carbon nanotubes (MWCNT) for Y(III) sorption (Yadav et al., 2015); and tetraoctyldiglycolamide impregnated Carbon inverse opals (C-IOP) for REEs (Turanov et al., 2015).

Cyanex 272 impregnated mesoporous silica MCM 41 was used for the extraction of lanthanides. The selectivity between light lanthanide (La(III)), medium lanthanide (Eu(III)), and heavy lanthanide (Lu(III)) followed the order of Lu(III) > Eu(III) > La(III) with separation factor of 61, 61 and 3504 for Lu(III)/Eu(III), Eu(III)/La(III) and Lu(III)/La(III), respectively (Mohammedi et al., 2019). Silica gel modified with 1- (-2-pyridylazo) naphthol (PAN) and acetylacetone (Acac) through solvent evaporation process was selective for Sc(III) against Fe(III) with selectivity factors of 5.79 and 8.95, respectively at pH 6 (Ramasamy, Puhakka, Repo, & Sillanpää, 2018). Magnetite nanoparticle was used as a support for coating di(2-ethylhexyl)phosphonate (HDEHP), bis(2,4,4-trimethylpentyl)phosphinic acid (CYANEX 272), and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (CYANEX 301) (Molina et al., 2019). These coated magnetite nanoparticles had q<sub>m</sub> of 6.6-8.3 mg/g for La(III), 7.7-8.7 mg/g for Pr(III), and 4.8-8.9 mg/g for Nd(III). The same extractant, HDEHP was infused into styrene-divinylbenzene copolymer immobilized silica particles (HDEHP-SiO<sub>2</sub>-P) for REEs adsorption (Shu et al., 2017, 2018; Zhang et al., 2019). The adsorption capacity (q<sub>m</sub>) of HDEHP-SiO<sub>2</sub>-P was 38.95 mg/g for Ce(III) and 52.84 mg/g for Gd(III) (Shu et al., 2017). In a different study, the HDEHP-SiO<sub>2</sub>-P had q<sub>m</sub> of 14.1 mg/g for Sc(III) with Sc(III) selectivity factor of >50 over other REEs (Zhang et al., 2019).

Inorganic solid supports infused with ionic liquids are mesoporous silica doped with binary IL mixtures (C8mim+PF6-/Cyphos IL 104 or C4mim+PF6-/Cyphos IL 104) (Liu et al., 2009), silica gel impregnated with N-PhenacylPyrNTf2 ionic liquid (Marwani & Alsafrani, 2013), silica doped with bifunctional ionic liquid trioctylmethylammonium 1-phenyl-3-methyl-4-benzoylpyrazol-5-onate ([A336]+[L]-) (Turanov et al., 2016), and MCM-41 silica impregnated with [Hbet–STFSI–PS–DVB] (Avdibegović et al., 2017). Among the SILs, trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos) entrapped in silica reached maximum adsorption capacities of 14.7 mg/g for Nd(III) and 19.8 mg/g at pH 4.0 (Mohamed et al., 2017). Ionic liquid (IL), 1-butyl-3-methylimidazolium bromide ([C4mim]+[Br]<sup>-</sup>) impregnated metal-organic framework (MOF) UiO-66 had a maximum Gd(III) adsorption capacity of 65 mg/g at pH 6 with Gd(III) selectivity in the presence of other metal ions (Na(I), Ca(II), Ma(II), Al(III), and Fe(III)) (Ahmed, Adhikary, et al., 2019).

The main limitation of SLEs is the gradual washout of the active component during operation (Bao et al., 2016). Possible solutions include the selection of highly hydrophobic and low soluble active components (Muraviev et al., 1998; Sparfel & Cote, 2004) and/or thorough washing of weakly adsorbed active components after their application onto the solid surface (Muraviev, 1998; Muraviev et al., 1998). Another method to prevent the leaking of the extractant from adsorbent grain is to coat a layer of polymer on the adsorbent, which acts as a semipermeable membrane or protective barrier for extractant while allowing the metal ion diffusion (Bao et al., 2016; Muraviev et al., 1998; Nishihama et al., 2013; Trochimczuk et al., 2004).

A protective barrier around the SIR was formed using polysulfone in dimethylformamide (DMF); however, loss of the adsorbed extractant [bis(2-ethylhexyl) hydrogen phosphate, bis- (2-ethylhexyl) hydrogen dithiophosphate, or bis(3- propylphenyl) dithiophosphate] still occurred (Muraviev et al., 1998). Better results were obtained with the coating of water-soluble polymer poly(vinyl alcohol) (PVA) precipitate onto SIR (Trochimczuk et al., 2004). The stability of the coating layer can be increased by cross-linking PVA with vinyl sulfone (Trochimczuk et al. 2004), boric acid (Yuan et al., 2010), and glutaraldehyde (Nishihama et al., 2013).

In general, EIMs (SIRs and SILs) can improve the performance of extractants by avoiding drawbacks of LLE, such as poor contact between the organic and aqueous phase, requirement of a large amount of extractant, emulsion formation, and formation of the third phase. The issue with SLEs is the stability of the active layer, which can wash out during operation. Moreover, the extractant layer may also be not uniform throughout the support surface, e.g., capillary forces may accumulate the extractant in narrow pores, a process enhanced in contact with an aqueous solution (Shenxu Bao et al., 2016). In addition, the complex nature of real-life REEs sources such as very acidic solutions can put extra pressure on these adsorbents, which can limit their industrial applications.

The adsorbents obtained through ligand functionalization to the surface of solid support using coupling agents provide an alternative to EIMs. The surface-functionalized adsorbents can be an alternative with better control of ligand distribution on the surface and better ligand and surface bonding and thus better stability, but however, they can be more resource intensive to produce.

# Surface-functionalized adsorbents

In this class of adsorbents, the active component or the extractant is chemically immobilized onto the surface of the solid support through chemical bonds. The active component is usually a complexing ligand containing specific functional groups that can selectively bind to the target REE. These adsorbents have been used for solid-phase extraction (SPE) of various elements. Solid-phase extraction (SPE) is similar in the process as the solid-liquid extraction (SLE); however, the extractant or the ligand is chemically immobilized onto the surface in SPE as opposed to physical immobilization in the case of SLEs (Florek et al., 2016; Hidayah & Abidin, 2017; Hu et al., 2018).

A typical ligand functionalized adsorbent involves solid support (e.g., silica, polymer beads, or carbon nanomaterials), coupling agent (e.g., silane), ligand containing a specific functional group (i.e., binding unit), and spacer between the coupling agent and the ligand (Pallavicini et al., 2014). Since the ligand is chemically bound to the surface, it is more robust than EIMs, provides better control of surface ligand distribution, and can work under extreme solution conditions. The surface-functionalized adsorbents used for REEs adsorption can be classified based on the type of solid support. Silica-based and carbon-based supports have been the primary focus for solid-phase extraction (SPE) of REEs; however, magnetic nanomaterials, metal-organic frameworks (MOFs), and other composite supports are gaining attention due to their various advantages.

#### Silica-based supports

Silica-based supports are popular for functionalized adsorbents used in SPE as they fulfill the requirements of good solid support: 1) They can have a large specific surface area (silica gel: usually 100-750 m<sup>2</sup>/g (Bhatnagar & Sillanpää, 2010), mesoporous silica >1000 m<sup>2</sup>/g (Meynen et al., 2009)), 2) are robust and reusable, 3) are easy to modify with functional groups, 4) have the possibility of shape control for various uses, and 5) show negligible swelling (Florek et al., 2016; Hu et al., 2018). Limiting factors affecting the use of silica as solid support are its tendency to lose the integrity of its porous structure under strong acidic conditions (El Mourabit et al., 2012; Florek et al., 2016) and its high dissolution rate in alkaline solution (Croissant et al., 2017; Crundwell, 2017).

Silica gel is a commonly used silica-based support. The other type of silica support is nano-porous silica material, further classified as macroporous (pore size>50 nm), mesoporous (pore size 2-50 nm), microporous (pore size< 2 nm), and hierarchically porous materials, which contain multiple levels of above porosities (Sun et al., 2016; Wan & Zhao, 2007). Mesoporous silica nanoparticles are gaining widespread attention in various fields due to uniform and tunable pore size, presence of internal and external pores, controlled morphology, and easy functionalization (Hu et al., 2018; Mehmood et al., 2017; Narayan et al., 2018).

#### Silica gel

Silica gel is the porous amorphous form of silicon dioxide (SiO<sub>2</sub>), composed of interconnected networks of microscopic pores. It can have a pore size of 2-25 nm. The surface silanol groups present in silica gel are used for attaching organofunctional alkoxysilane through the silanization process. The organofunctional alkoxysilane is used for attaching functional groups in a process known as grafting. The most commonly used silane are amino-propyl alkoxy silanes (3-aminopropyl triethoxysilane (APTES) and 3-aminopropyl trimethoxysilane (APTMS)) as they allow easy attachment of amino-poly(carboxylic acid) and other functional groups (Noack et al., 2016; Ramasamy, Khan, et al., 2017). Both the silica gel and silica gel with attached organo-silanes (e.g., 3-aminopropyl silica gel) are available commercially under various brands and have been functionalized further for adsorption of REEs (Asadollahzadeh et al., 2020; Callura et al., 2018; Noack et al., 2016; Ogata et al., 2014, 2015a; Ramasamy, Khan, et al., 2017; Ramasamy, Puhakka, et al., 2017).

Instead of surface modification of already prepared silica gel or 3-aminopropyl silica gel, co-condensation of tetra-alkoxy silane  $Si(OR)_4$  (generally, R = Me or Et) with silane coupling agent  $(RO)_3Si(CH_2)_3X$  (where R = Me or Et, X = complexing ligand group) have been used to obtain the required adsorbent (El-Nahhal & El-Ashgar, 2007).

Functional ligands grafted on the silica gel for REEs adsorption are 4-acylpyrazolone Schiff base (Amarasekara et al., 2009), diglycolamic acid (Ogata et al., 2014, 2015a, 2015b, 2016), 1-(-2-pyridylazo) naphthol (PAN) (Ramasamy, Puhakka, Repo, et al., 2018; Ramasamy, Repo, et al., 2017), acetylacetone (Ramasamy, Repo, et al., 2017), phosphonoacetic acid (PAA), N, N-bis(phosphonomethyl) glycine (BPG), diethylenetriaminepentaacetic dianhydride (DTPADA) (Callura et al., 2018; Noack et al., 2016), diethylenetriaminepentaacetic acid (DTPA) (Noack et al., 2016), diglycolamide (Zhe Liu et al., 2019) N-Benzoyl-N-phenylhydroxylamine (BPHA) (Artiushenko, Ávila, et al., 2020), amino-di(methylene-phosphonic) acid (Artiushenko, Kostenko, et al., 2020), N, N-dioctyldiglycolic acid (DODGA)(Li et al., 2020), polyhexamethylene guanidine and Arsenazo I or Arsenazo III (Losev et al., 2020), and bis(ethylhexyl)amido diethylenetriaminepentaacetic acid (Hovey et al., 2021).

The diglycolamic Acid -functionalized silica gel showed selectivity for HREEs with the highest adsorption capacity of 0.148 mmol/g (or 24.4 mg/g) for Ho(III) (Ogata et al., 2015a). Another adsorbent PANfunctionalized silica gel showed capacities of 82.72, 75.5, and 62.92 mg/g for La(III), Sc(III), and Y(III), respectively (Ramasamy, Puhakka, Repo, et al., 2018; Ramasamy, Repo, et al., 2017). The BPHA functionalized SiO<sub>2</sub> with adsorption capacities (q<sub>m</sub>) of 6.7 and 8.3 mg/g for Eu(III) and Tb(III), respectively, was selective for HREEs with K<sub>d</sub> values of 3500 ml/g for Lu(III) and Yb(III) each (legend 21, Figure 2) (Artiushenko, Ávila, et al., 2020).

#### Ordered mesoporous silicas

Ordered mesoporous materials have pore sizes of 2-50 nm with ordered arrangements of pores. Common ordered mesoporous silica materials are available as groups, defined as MCM (Mobil Composition of Matter) (e.g., MCM-41 (2d hexagonal, p6m), MCM-48 (cubic Ia3d), MCM-50 (lamellar)) (Beck et al., 1992; Florek et al., 2016; D. Kumar et al., 2001), SBA (Santa Barbara Amorphous), KIT (Korean Advanced Institute of Science and Technology), and COK (Centre for Research Chemistry and Catalysis). Within each mentioned group, there are different types of OMS with different pore symmetry, pore sizes, and pore volume (Beck et al., 1992; Florek et al., 2016; Hu et al., 2018; Huo et al., 1996; Trewyn et al., 2007).

Similar to surface functionalization of silica gel, the silica mesoporous can be functionalized through the reaction of organo-silanes with surface silanol group (grafting) or by co-condensation with tetra-alkoxy silane  $Si(OR)_4$  (generally, R = Me or Et) and tri-alkoxyorganosilanes (R'O)<sub>3</sub>SiRX (X = ligand) in the presence of a surfactant template (one-pot synthesis) (Florek et al., 2016; Hoffmann et al., 2006; Hu et al., 2018).

The abundance of silanol groups on the surface of silica (1-2 Si-OH per nm<sup>2</sup> on average (Ide et al., 2013)) allows for facile and efficient functionalization through grafting. The limitation of grafting manifests in the case of small pore size or narrow entrance of support and/or with a bulky size of the functional group. In such cases, the entrance may have a higher number of functional groups, or some smaller pores may lack functional groups due to pore blocking, resulting in an overall non-homogenous distribution (Hoffmann et al., 2006). The limitation of pore-blocking is not faced in co-condensation synthesis, and organic units are more homogeneously distributed than the grafting process (Hoffmann et al., 2006). However, in co-condensation, the concentration of ligands in the pore-wall tends to be lesser than the starting (R'O)<sub>3</sub>SiRX in the reaction mixture. Additionally, the degree of mesoscopic order of the OMS decreases in co-condensation with increasing concentration of (R'O)<sub>3</sub>SiRX in the reaction mixture, which leads to disordered products (Hoffmann et al., 2006). The increasing concertation of (R'O)<sub>3</sub>SiRX in the reaction mix favors homocondensation over co-condensation, thus reducing the homogeneity and mesoscopic order of the OMS. Another challenge with one-pot syntheses of OMS is removing the surfactant template after co-condensation without destroying the surface ligands (Hoffmann et al., 2006).

Mesoporous KIT-6 has been functionalized with ethylenediaminetetraacetic acid (EDTA) (Ravi, Zhang, et al., 2018), phenylenedioxy diamide (PDDA) (Hu et al., 2019), bidentate phthaloyl diamide (PA) (Hu et al., 2017), diglycolamide-based (Florek et al., 2014, 2015, 2020), furan-2,4-diamido-propyltriethoxysilane (Florek et al., 2015, 2020), and 3,6-dioxaoctanedioic acid (Florek et al., 2015, 2020) for REEs adsorption. Similarly, MCM-41 has been functionalized with titanium(IV) alkylphosphate (Wenzhong Zhang, Avdibegović, et al., 2017), diglycolylamide (Juère et al., 2016), and iminodiacetamide (Fryxell et al., 2011) and SBA15 has been functionalized with diglycolamide (DGA) (Juère et al., 2016), benzene-1,3,5-triamido-tetraphosphonic acid (BTATPA) (Ravi, Lee, et al., 2018), phosphoric acid (Zheng et al., 2020), and 1,4-phthaloyl diamido-propyltriethoxysilane (Ryu et al., 2021) for REEs adsorption. In case of unmodified SBA-15 and KIT-6, uptake of Sc(III) (KIT-6:  $q_m = 1.0 \text{ mg/g}$  (legend 36, Figure 2), SBA-15:  $q_m = 1.1 \text{ mg/g}$  (legend 34, Figure 2)) was achieved through adsorption to accessible surface silanols (Giret et al., 2018).

Diglycolylamide (DGA) was used as a common ligand for three different OMS solid supports, SBA-15, MCM-41, and SBA-16, to investigate the effect of silica support pore network structure (2D vs. 3D), pore shape (cylindrical vs. cage-like), and pore size on the adsorption of REE from synthetic samples of REEs and REEs with Al, Fe, Th and U ions (shown as legend 9-13, Figure 2) (Juère et al., 2016). The 2D hexagonal structure (SBA-15) has the advantage over the 3D cage-like structure of SBA-16 since the cage-like pore structure and narrow connectivity made SBA-16 more prone to pore blocking. The pore size of SBA-15 was tuned by varying aging temperatures during synthesis. The highest capacity of extraction was observed for SBA-15(80)–DGA (pore size, 5.2 nm), which was attributed to the presence of certain confinement of the targeted ions by SBA-15 material with a smaller pore (5-8 nm) (Juère et al., 2016). Functionalization of DGA onto MCM-41 (3.2 nm, 2D pore) resulted in the obstruction of the entrance of pore during grafting due to smaller pore size hence had lower extraction capacity (Juère et al., 2016).

The ligand immobilization on the surface of solid support can lead to reduced flexibility, which results in a more stable bite angle (angle formed by chelate ligands) and yields enhanced selectivity towards particular REE cations (Hu et al., 2018). The ligand DGA was functionalized onto KIT-6 by anchoring on both ends (KIT-6-N-DGA-1) or single-end (KIT-6-N-DGA-2) (Florek et al., 2014). KIT-6-N-DGA-1 had a higher extraction capacity for REEs (especially MREEs) than KIT-6-N-DGA-2 (ligand 1-4, Figure 2). The higher extraction capacity of KIT-6-N-DGA-1 was attributed to increased rigidity in the DGA ligand anchored on the surface at both ends, which increased the size-specific cavity (Hu et al., 2018). The presence of competitive ions did not affect  $K_d$  values (ligand 3-4, Figure 2). The separation factor between Eu (III) and Th(IV) was 6.3, and between Eu(III) and U(IV) was 3.4 for KIT-6-N-DGA-1 (Florek et al., 2014).

The effect of different bite angles of ligands on the selectivity of REEs was studied using DGA, 3,6dioxaoctanediamidopropyl (DOODA), and furan-2,4-diamidopropyl (FDGA) functionalized KIT-6 (Florek et al., 2015, 2020). The DOODA ligand has a smaller bite angle than DGA (Figure 3); hence showed a preference for smaller Ln(III) (Ho-Lu, legend 4-5, Figure 2) (Florek et al., 2015; Hu et al., 2018). Hu et al. (2017a) grafted phthaloyl diamide (PA) bearing different bite angles onto KIT-6 by varying the position (ortho, meta, and para) of the amide groups. The KIT-6-1,2-PA (ortho-position) with a smaller bite angle showed higher affinity for heavy Ln(III), which have smaller ionic radii (legend 14, Figure 2), whereas the KIT-6-1,3-PA showed selectivity for middle-size Ln(III) due to its larger bite angle (legend 15, Figure 2). KIT-6-1,4-PA did not show selectivity for a particular lanthanide (legend 16, Figure 2) due to the absence of any synergist action of the moieties (Hu et al., 2017, 2018). In another study, the bite angle of phenylenedioxy diamide (PDDA) functionalized modified KIT-6 was varied by using PDDA with amide at different positions (Hu et al., 2019). Results analogous to KIT-6-PA systems were obtained as adsorbent KIT-6-1,2-PDDA having the smallest bite angle (Figure 3) showed high affinity for heavy lanthanides (Tm(III), Yb(III), and (Lu(III)) with smallest ionic radii (legend 22, Figure 2), adsorbent KIT-6-1,3-PDDA with larger bite angle showed higher selectivity for light lanthanides (La(III), Ce(III), and Pr(III)) with larger ionic radii (legend 23, Figure 2). KIT-6-1.4 PDDA did not show selectivity (legend 24, Figure 2) and behaved similarly to KIT-6-1,4-PA.

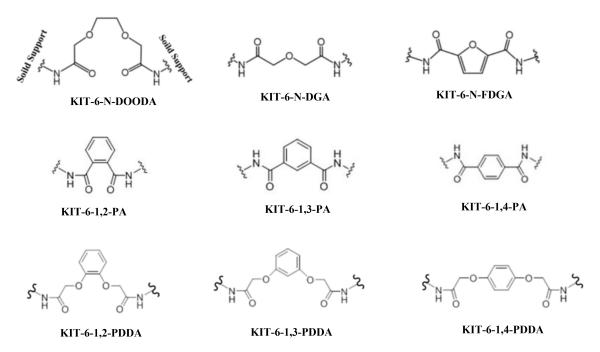


Figure 3: Different bite angles of the ligands grafted onto KIT-6 (modified after (Florek et al., 2015; Hu et al., 2017, 2019)). DOODA: 3,6-dioxaoctanediamidopropyl, DGA: diglycolylamide FDGA: furan-2,4-

diamidopropyl (Florek et al., 2015, 2020), PA: phthaloyl diamide (Hu et al., 2017, 2018) PDDA: phenylenedioxy diamide (Hu et al., 2019).

In other examples of functionalized ordered mesoporous silica used for REEs uptake, Dy(III) was selectively adsorbed from a solution of Cu(II), Dy(III), Fe(III), Nd(III), and Zn(II) using amino and carboxylic functionalized mesoporous silica having different pore sizes (3, 5, 12, and 22 nm) (Kaneko et al., 2018) and using amino, carboxylic, and diglycolic anhydride functionalized mesoporous silica with a sheet and spherical morphologies as well as non-porous stöber silica (Kaneko et al., 2019). Zhang and their colleagues (Zhang, Avdibegović, et al., 2017) used titanium(IV) alkylphosphate grafted MCM41 for adsorption in the binary equimolar solutions of Sc-La and Nd-Dy. Ravi et al. (2018) functionalized KIT-6 and KCC-1 with EDTA and employed them for Nd(III) adsorption from single-element solution (Ravi, Zhang, et al., 2018). The same team, in a different study, used benzene-1,3,5-triamido-tetraphosphonic acid (BTATPA) modified SBA-15 for adsorption of Nd(III), Y(III), La(III), and Ce(III) from single element solution and reported K<sub>d</sub> (ml/g) values of ~10<sup>4</sup>, ~10<sup>4</sup>, ~1.5\*10<sup>5</sup>, and ~1.04\*10<sup>5</sup> respectively (Ravi, Lee, et al., 2018). In other studies, SBA-15 functionalized with phosphorus acid achieved a maximum Gd(II) adsorption capacity of 204.4 mg/g (Gao et al., 2017), and sulfhydryl MCM-41 (SH-MCM-41) showed maximum adsorption capacities of 560.56, 467.60, and 540.68 mg/g for La(III), Gd(III), and Yb(III), respectively (Li et al., 2019).

Mesoporous silica foam (MSF) and fibrous nano-silica KCC-1 were grafted with poly(amidoamine) dendrimers (PAMAM) using 3-aminopropyltriethoxysilane (APTES) and glutaraldehyde (GTA) as a crosslinking spacer (Lee et al., 2019). The adsorption capacity of MSF based adsorbent PAMAM@GTA-NH<sub>2</sub>-MSF was higher than KCC-1 based adsorbent PAMAM@GTA-NH<sub>2</sub>-KCC-1 with values of 86, 104, 110, and 132 mg/g for La(III), Ce(III), Nd(III), and Gd(III) respectively for MSF based adsorbent. Both adsorbents showed selectivity for Gd(III) from a solution containing Na(I), Ca(II), Mg(II), Al(III), and Fe(III) with the recovery of 75.8% with PAMAM@GTA-NH<sub>2</sub>-MSF and 67.2% with PAMAM@GTA-NH<sub>2</sub>-KCC-1. The recovery of Gd(III) increased to 86% with further functionalization of PAMAM@GTA-NH<sub>2</sub>-MSF with N-(phosphonomethyl) iminodiacetic (PMIDA) (Lee et al., 2019). N-methyl-N-phenyl-1,10-phenanthroline-2-carboxamide (MePhPTA) functionalized mesoporous silica adsorbed Eu(III) and Sm(III) with maximum adsorption capacities of 125.63 and 124.38 mg/g, respectively at pH 4 (Awual et al., 2013). Ordered mesoporous silica functionalized with 4-tert-Octyl-4-((phenyl)diazenyl)phenol (TOPP) reached maximum Yb(III) adsorption of 139.19 mg/g at pH 5 and was selective against Na(I), K(I), Ca(II), Mg(II), Zn(II), and Al(III) (Rahman et al., 2020). Hollow mesoporous silica nanosphere (HMSNs) functionalized with amino-phosphonic acid had an adsorption capacity of 387.3 mg/g for Gd(III) at pH 5 (Yin et al., 2020).

## Carbon-based supports

Carbon-based adsorbents and supports have various forms, such as mesoporous carbon, activated carbon, graphene oxide, and carbon nanotubes. Carbon-based support can be an alternative to silica supports to overcome the low stability of silica-based support in acidic conditions (Hu et al., 2018). However, the surface functionalization of carbon-based supports can be more challenging than silica-based supports (Hu et al., 2018).

#### Ordered mesoporous carbons

Ordered mesoporous carbons (OMCs) can work as better solid support under acidic conditions because of higher chemical resistance than mesoporous silica while possessing comparable porosity and surface area (Hu et al., 2018). However, the synthesis and functionalization of OMCs are more challenging than OMS. Ordered mesoporous carbon synthesis can be done by hard or soft template methods.

In the hard template method, an ordered mesoporous solid (mostly ordered mesoporous silica) is used as a mold, and its pores are impregnated with a selected carbon precursor (e.g., Sucrose), which is then polymerized and carbonized (Eftekhari & Fan, 2017). In the end, the template is dissolved and removed using strong acid (e.g., HF) or base (e.g., NaOH) (Chuenchom et al., 2012). The porosity and structure of OMC can be tuned by selecting an appropriate hard template.

On the other hand, in the soft template method, OMC is directly synthesized by self-assembling a block of copolymer surfactant and a carbon precursor. In this method, the template is removed by a thermal process. The pH, temperature, and gel composition can be varied to control the porosity and morphology of the mesoporous carbon (Ma et al., 2013). In comparison with the hard template method, OMCs synthesized through soft templates have a continuous framework with thick pore walls, hence have more stability against thermal and oxidation treatment during functionalization (Eftekhari & Fan, 2017).

In adsorption studies involving OMCs, Parsons-Moss et al. (2014) investigated Eu(III) adsorption using a carbon-silica nanocomposite (C-CS) type OMC functionalized with -COOH and reported adsorption capacity ( $q_m$ ) of 138 mg/g at pH 4.0. Perreault et al. (2017) functionalized CMK-8, a 3D cubic ordered mesoporous carbon, with different DGA-based ligands. Among these CMK-8 based adsorbents, the K<sub>d</sub> value for different Ln(III) in the presence of Al(III) and Fe(III) were highest for diglycolylester grafted CMK-8 (CMK-8-DGO) followed by oxidized CMK-8 (CMK-8-O) and chloropropyl diglycolylamide grafted CMK-8 (CMK-8-PGA) (legend 6-8, Figure 2). Bertelsen et al. (2019) modified two OMC materials, MC-*l*-MSN, and CMK-3 type OMC, with bis-(2-ethylhexyl) phosphoric acid (HDEHP) and investigated batch adsorption of Eu(III) as well as column separation of Nd(III) and Eu(III) using HDEHP-OMC-*l*-MSN. The HDEHP-OMC showed q<sub>m</sub> of 0.35 mmol (or 53.2 mg) Eu(III)/g. Mesoporous carbon was functionalized with a single stranded oligo consisting of 100 thymine units, and it achieved adsorption of 9.57, 38.27, and 52.15 mg/g, for Lu(III), Dy(III), and La(III), respectively. The adsorbed amounts of REEs increased with an increase in the metallic radius from Lu to La (Gismondi et al., 2022; Unsworth et al., 2020).

#### Activated carbon /Graphene oxide /Carbon nanotube

Activated carbon. Activated carbon (AC) is an environmentally friendly and low-cost adsorbent with a high surface area but has little affinity for REE(III) in native form; thus, functionalization with ligands that have affinity for REEs is required for its application in REEs adsorption (Asadollahzadeh et al., 2020). The ligands used for AC functionalization are Schiff's base derived from 3 diethylenetriamine and 3,4-dihydroxybenzaldehyde (AC-DETADHBA) (Marwani et al., 2017), Carboxylic acid (Kilian et al., 2017; Marwani et al., 2017), and EDTA (Babu et al., 2018). The EDTA functionalization of AC (AC-EDTA) increased adsorption capacity to 71.4 Nd(III) mg/g from 19.1 Nd(III) mg/g at pH 5 (Babu et al., 2018). The adsorbent AC-EDTA showed higher selectivity towards HREEs. Carboxyl functionalized AC (AC-COOH) showed an adsorption capacity of 89.50 mg/g for La(III) at pH 6.0, whereas AC-DETADHBA showed a higher adsorption capacity of 144.80 mg/g for La(III) at the same pH (Marwani et al., 2017). In a different study, AC-COOH showed very low adsorption of 2.1 mg/g for Sc(III) at pH 2.0 (Kilian et al., 2017), suggesting that the pH plays a vital role in AC-COOH adsorbents, likely due to the weakly acidic nature of -COOH group.

**Graphene oxide.** Graphene oxide (GO) contains hydroxyl, epoxide, carbonyl, and carboxyl groups, essential sites for functionalization with ligands. Moreover, due to the presence of these groups, GO can adsorb REEs without functionalization. A colloidal graphene oxide suspension had Gd(III) adsorption capacity of 286.86 mg/g at pH 5.9 (Chen et al., 2014). Graphene oxide nanosheets (GONS) obtained maximum adsorption of 175.44 mg/g for Eu(III) at pH 6 (Sun et al., 2012). The maximum Eu(III) adsorption decreased slightly to 167.16 mg/g at pH 2 (Sun et al., 2012). In another study with GO nanosheet, the maximum adsorption capacities were in the order of Gd(III)>Nd(III)>Y(III)>La(III) with values 225.5, 188.6, 135.7, and 85.7 mg/g at pH 6, respectively (Ashour et al., 2017). Unmodified Graphene oxide showed an adsorption capacity of 39.7 mg/g for Sc(III) at pH 4, which was better than -COOH functionalized AC and chelating resin Chelex 100 (contains iminodiacetic acid) but lower than -COOH modified MWCNT (Kilian et al., 2017). Higher adsorption of 89.7 mg/g and 70.2 mg/g for Eu(III) using GO and magnetic GO (by modifying with Fe<sub>3</sub>O<sub>4</sub>) was achieved at pH 7 (Li et al., 2015).

GO was used to produce amine-functionalized mesoporous graphene (AMG) followed by functionalization

with carbamoyl phosphine oxide moiety (CMPO, triethylphosphonoacetate) and it reached an adsorption capacity of 26.9 mg/g for La(III) (Kim et al., 2019).  $Fe_3O_4$  and  $MnO_2$  modified GO nanocomposites, Fe<sub>3</sub>O<sub>4</sub>/MnO<sub>2</sub>/rGO (FMG), provided high maximum adsorption capacities of 1016 and 981 mg/g for La(III) and Ce(III), respectively, at pH 7 (Liu et al., 2020) and is among the adsorbents with the highest capacity for REE(III) (Table 1). Another adsorbent, polyaniline functionalized GO, achieved 250.74 mg/g Eu(III) adsorption (Sun et al., 2013). Polyurethane sponge was used as a support polymer for titanium phosphate with graphene oxide (GO@TiP-Sponge) and showed a maximum capacity of 576.17 mg/g for Dy(III) (Peng et al., 2020). In comparison, GO@TiP had a maximum Dy(III) adsorption capacity of 316.75 mg/g (Peng et al., 2020). GO- tris(4-aminophenyl)amine composite had a Langmuir adsorption capacity of 46.35 mg/g for Yb(III) at pH 6 (Zhao et al., 2021). Another GO-based adsorbent, graphene oxide/poly (N-isopropyl acrylamide-maleic acid) [GO/P(NIPAM-MA)] cryogel, adsorb La(III) with equilibrium adsorption capacity of 33.1 mg/g at pH 5 with separation factors of 2.86, 7.57, 8.00, 6.69, and 1.45 for La over Cu, Co, Ni. Nd, and Yb, respectively (Yang et al., 2020). GO functionalized with 3-[2-(2-aminoethylamino) ethylamino] propyl-trimethoxysilane (GO-APTS) showed adsorption capacities of 110.0, 93.4, 103.2, 83.7, 97.2, 48.3. and 92.8 mg/g for Ho(III), Er(III), Eu(III), Lu(III), Tm(III), Y(III), and Yb(III), respectively (Bao et al., 2022). The adsorbent was selective for Ho(III) over alkali or alkaline-earth metal ions with SFs of above 600. A further modified adsorbent combining GO-ATPS with  $Fe_3O_4$  resulted in lower capacities of 72.1, 67.1, 65.2, 65.0, 73.2, 36.3, and 68.7 mg/g for Ho(III), Er(III), Eu(III), Lu(III), Tm(III), Y(III), and Yb(III), respectively, due to lower APTS fraction in the composite (Bao et al., 2022).

**Carbon nanotubes.** Carbon nanotubes (CNTs) are tubes of graphite sheets and can be divided into two types: Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) with a set of concentric nanotubes. The examples of CNTs based adsorbent studied for REEs separation include oxidized MWCNTs (Alguacil et al., 2020; Behdani et al., 2013; Fan et al., 2009; Koochaki-Mohammadpour et al., 2014; K. Li et al., 2015), CNT modified with -COOH (Kilian et al., 2017), MWCNT modified with tannic acid (Tong et al., 2011), and MWCNT/Fe<sub>3</sub>O<sub>4</sub> composites (Chen et al., 2009; Fan et al., 2009). The CNT modified with -COOH showed higher adsorption (37.9 mg/g) for Sc(III) than AC-COOH (2.1 mg/g) at pH 2.0 (Kilian et al., 2017). The adsorption of Sc(III) onto CNT-COOH increased to 42.5 mg/g at pH of 4.0. Oxidized MWCNTs showed good adsorption (80-100%) for target REE(III) in the presence of competitive ions, and the adsorption increases with pH since at higher pH, the surface is negatively charged, leading to higher sorption of positively charged REE(III) cations (Cardoso et al., 2019). A CNTs/GO hybrid hydrosols had Gd(III) adsorption capacity of 534.76 mg/g at pH 5.9 (Lanyu Guo et al., 2018). CNT modified with furfuryl amine and further functionalized with poly(acrylic acid) reached a maximum equilibrium Eu(III) adsorption capacity of 130.8 mg/g as opposed to 46.67 mg/g for pristine CNT at pH 7 (Linru Guo et al., 2020).

## Other supports/adsorbents

#### Magnetic nanomaterials

Researchers have explored adsorbents obtained after coating  $Fe_3O_4$  nanoparticles with  $SiO_2$  or  $TiO_2$  shell and then the functionalization of the surface of the coated layer. The advantage of magnetic nano-adsorbent is the convenient collection/separation of adsorbents by using magnets after adsorption, avoiding the issue involved with the isolation of nanoparticles, which tends to form stable sols in batch reactors. The coating with  $SiO_2$  or  $TiO_2$  provides higher surface -OH density, which results in higher surface ligand density and easier functionalization. The coating also protects the  $Fe_3O_4$  nanoparticle from oxidation.

Polido Legaria et al. (2017) used EDTA, DTPA, and triethylenetetraminehexaacetic acid (TTHA) functionalized SiO<sub>2</sub> nano-adsorbents, both magnetic and nonmagnetic, and reported uptake up to 300 mg REE(III)/g. REE uptake order was Dy(III) > Nd(III) > La(III) for EDTA-functionalized, Nd(III) > La(III) > Dy(III)for DTPA-functionalized, and La(III) > Nd(III) > Dy(III) for TTHA-functionalized adsorbent. Kostenko et al. (2019) synthesized Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (MNPs) with and without a coating of silica and functionalized them with aminomethylenephosphonic (MNPs/SiO<sub>2</sub>-AMPA and MNPs/AMPA). The adsorption capacities for Eu(III) were 69 and 77 mg/g for MNPs/SiO<sub>2</sub>-AMPA and MNPs/AMPA at pH 7.0, respectively. Magnetic Fe<sub>2</sub>O<sub>3</sub> coated with silica and functionalized with APTMS, ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-NH<sub>4</sub>OH@SiO<sub>2</sub>(APTMS)) achieved maximum Dy(III) adsorption of 23.3 mg at pH 7 (Kegl et al., 2019). Magnetic nanoparticle functionalized with poly(aminoethylene N-methyl 1-formic acid, 1-phosphonic acid) (PAEMFP) reached 25 mg/g Nd(III) adsorption capacity at PH 6 (Miraoui et al., 2016). Other research involving coated magnetic nano-adsorbents for REEs adsorption include silica-coated magnetic particle grafted with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl (P507) using 3-chloropropyltryethosysilane as silane-coupling agent (Wu et al., 2013) and magnetic Fe<sub>3</sub>O<sub>4</sub> coated with SiO<sub>2</sub> and TiO<sub>2</sub> and modified with N-[(3-trimethoxysilyl) propyl] EDTA (TMS-EDTA) (Dupont et al., 2014).

Some studies have directly functionalized the magnetic nano-particles (Chen et al., 2012; Gaete et al., 2021; Ngomsik et al., 2012; Yang et al., 2012). Citric acid-functionalized maghemite nanoparticles had  $q_m$  of 74.4 mg/g and 71 mg/g for Eu(III) and La(III), respectively (Ngomsik et al., 2012), Magnetic nano-particles Fe<sub>3</sub>O<sub>4</sub> with humic acid coating (Fe<sub>3</sub>O<sub>4</sub>@ HA MNPs) synthesized through chemical coprecipitation was able to remove 99% of Eu(III) at pH 8.5 (Yang et al., 2012). In another study, bentonite was used as a support to prepare di (2-thylhexly) phosphoric acid-immobilized magnetic GMZ bentonite and was used to adsorb Eu(III) (capacity of 48.02 mg/g at pH 3.05) (Chen et al., 2012). Another adsorbent, phosphoric acid-functionalized magnetite nanoparticle (PA-MNP), showed a capacity of 18.4, 17.6, and 23.9 mg/g for La(III), Pr(III), and Sm(III), respectively at pH 4 (Gaete et al., 2021).

#### Metal-organic frameworks

Metal-organic frameworks (MOFs) have ordered crystalline porous structures composed of a threedimensional network of metal or metal oxide clusters held together by multidentate organic ligands (i.e., linker), e.g., aromatic polycarboxylates. MOFs have received considerable attention as support for grafting various REEs selective ligands. The desirability of MOFs as support lies in their high surface area, high porosity, adjustable pore size, and tunable surface functionality (Baumann et al., 2019).

The MOF, HKUST-1, showed an adsorption capacity of 353 mg/g for Ce(III) at pH 6 (Zhao et al., 2019). MOF ZIF-8 showed higher adsorption capacity (385 mg/g) for La(III) than another MOF ZIF-90 ( $q_m = 168$  mg/g for La(III)) that had a different linker (Jiang et al., 2016). MOF Zeolitic imidazolate frameworks-8 nanoparticle (ZIF-8 NP) has adsorption capacities of 28.8 mg/g, 281.1 mg/g, and 430.4 mg/g for La(III), Sm(III), and Dy(III), respectively at pH 7 (Abdel-Magied et al., 2019). MOF ZIF-8 functionalized with -COOH showed an adsorption capacity of 175 mg/g for Nd(III), significantly higher than unfunctionalized ZIF-8 (57 mg Nd(III)/g)) (Ahmed et al., 2021). Another MOFsUiO-66-(COOH)<sub>2</sub> functionalized with poly-acrylonitrile had maximum adsorption capacities of 214.1 mg/g and 191.9 mg/g for Tb(III) and Eu(III), respectively at pH 6 (Hua et al., 2019). Similar MOF UiO-66 dual functionalized with -COOH and -NH<sub>2</sub>obtained equilibrium adsorption capacity of 79 mg/g for Gd(III), significantly higher than pristine UiO-66 with 16 mg Gd(III)/g (Ahmed, Lee, et al., 2019). A MOF, ZnGA, synthesized by the reaction of zinc acetate and glutaric and then functionalized with polymer-based on p-chlorocresol and piperazine had Y(III) adsorption capacity of 377.02 mg/g at pH 6 (Mahmoud et al., 2019).

In several different studies, MIL-101 was functionalized with different functional groups and used for REEs adsorption (de Decker et al., 2016; Kavun et al., 2021; Y.-R. Lee et al., 2018; Lou et al., 2019; Ryu et al., 2021). Among MIL-101 functionalized with -NH<sub>2</sub>, ethylenediamine (ED), diethylenetriamine (DETA), and N-(phosphonomethyl)iminodiacetic acid (PMIDA), the REE adsorption capacity increased in the order of MIL-101 < MIL-101-NH<sub>2</sub> < MIL-101-ED < MIL-101-DETA < MIL-101-PMIDA with the highest being 90.0 mg Gd(III)/g onto MIL-101-PMIDA at pH 4.5 (Lee et al., 2018). Acrylic acid-functionalized MIL-101 had adsorption capacities of 90.21, 104.59, 58.29, and 74.94 mg/g for Sc(III), Nd(III), Gd(III), and Er(III), respectively, at pH 5.5, and was selective for Sc(III) in the presence of other REEs and competitive cations (Lou et al., 2019). In a different study involving MIL-101 functionalization with tributyl phosphate (TBP), HDEHP, and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), the adsorption capacity increased in the order of MIL-101-TBP < MIL-101-Cyanex 272 < MIL-HDEHP with a maximum adsorption capacity

of 57.47 mg/g at pH 5.5 for HDEHP functionalized adsorbent (Kavun et al., 2021). The MIL-101-HDEHP showed selectivity factors of 22.8 and 7.7 for Er(III) over Nd(III) and Gd(III) in Er(III)-Nd(III)-Gd(III) mix solution with all three adsorbent showing high selectivity (>90%) for Er(III) over Co(II), Ni(II), Cu(II), and Zn(II).

#### Metal-based supports

A metal-based support Mesoporous Zirconium Titanate (ZrTi-0.33) was functionalized with methylphosphonic acid (MeP), amino trismethylenephosphonic acid (ATMP), phosphono-imido-dicarboxylic acid (PIDC), 4-amino,1-hydroxy,1,1-bis-phosphonic acid butane (HABDP), and 1-hydroxylethylene-1,1-bis-phosphonic acid (HEDP) bis-phosphonic acids, 1,4-diphosphonic acid butane (BuDP) and 1,4-diphosphonic acid benzene(BenDP) and used for <sup>153</sup>Gd(III) adsorption (Griffith et al., 2010). ATMP based adsorbent achieved the highest  $K_d$  (>10000 in 10<sup>-3</sup> M and 10<sup>-5</sup> M HNO<sub>3</sub>).

Similar support, mesoporous TiO<sub>2</sub> particle, was functionalized with dimethylphosphato-ethyltriethoxysilane and reached Ce(III) adsorption capacity of 92.6 mg/g while completely separating Ce(III) from Sr(II) and Cs(I) (Moloney et al., 2014). Mg-Fe hydrotalcite modified with Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid) showed separation factor (SF) >6.3 for La(III)/Nd(III) (Gasser & Aly, 2013) and >3.6 for Ce(III)/Eu(III) (Gasser et al., 2017).

#### **Composite supports**

A composite support of nano-silica (12 nm particle size) and AC (0.8 mm pellets) was modified with 1-(2-Pyridylazo) 2-naphthol (PAN) (Ramasamy, Puhakka, Repo, Ben Hammouda, et al., 2018). The adsorbent obtained adsorption capacities of 103.5, 112.7, and 84.1 mg/g for La(III), Sc(III), and Y(III), respectively. Another composite support consisting of nano-silica grafted carbon nanotubes (both SWCNT and MWCNT) functionalized with 1-(2-pyridylazo)-2-naphthol (PAN) were selective for Sc(III) in mixed REE solution (Ramasamy et al., 2019). However, the adsorption capacities for Sc(III) were lower than La(III) and Y(III) in mono-element solution with adsorption capacities of 12.68, 80.68, and 48.34 mg/g for Sc(III), La(III), and Y(III), respectively, in the SWCNT and 103.2, 32.92, and 68.78 mg/g, respectively with the MWCNT (Ramasamy et al., 2020). MWCNT embedded with  $Fe_3O_4$  nanoparticles were functionalized with carbon disulfide and achieved 23.23 mg/g La(III) adsorption (Huang et al., 2021). A nano porous graphene and zinc-trimesic acid (Zn-BTC) MOF composite showed selectivity for Ce(III) with SFs 12,081.04, 20.05, and 328.80 for Ce(III) over Lu(III), La(III), and Pr (III), respectively (Wu et al., 2021). The SFs between adjacent lanthanide Nd/Pr, Sm/Eu, Gd/Tb, and Tb/Dy reached 9.80, 3.11, 2.20, and 1.68. The maximum capacity of the adsorbent was about 300 mg REEs/g. Another composite consisting of nano porous graphene oxide and zinc- terephthalic acid (Zn-BDC) MOF reached a maximum capacity of 344.48 mg REEs/g with high SFs for Sc, i.e., Sc/Tm [?] 529.57, Sc/Er [?] 461.91, and Sc/Y [?] 445.70 (Chen et al., 2022). It was also selective for Tm and Er with SFs for Tm/Eu [?] 4.55, Tm/Pr [?] 4.20, Tm/Nd [?] 3.96, and Er/Eu [?] 3.9. A composite obtained via the introduction of a MOF MIL-101 shell over a magnetite ( $Fe_3O_4$ ) core and functionalized with  $-SO_3$  and diethylenetriamine (DETA) extracted REEs from aqueous and brine solution with efficiency up to 99.99% (Elsaidi et al., 2018).

A silica/polymer (SiO<sub>2</sub>-P) composite support synthesized by immobilizing styrene-divinylbenzene copolymer (SDB) in porous silica (SiO<sub>2</sub>) was functionalized with 2,6-bis(5,6,7,8-tetrahydro-5,8,9,9-tetramethyl-5,8-methano-1,2,4-benzotriazin-3-yl)pyridine (Me<sub>2</sub>-CA-BTP) and was used for Ln(III) adsorption. Similar SiO<sub>2</sub>-P supports were functionalized with a mixed trialkyl phosphine oxide (TRPO) (where R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> are different alkyl groups) (Yu et al., 2018) and functionalized with HDEHP for REEs(III) adsorption (Zhang et al., 2019).

An organic-inorganic hybrid hydrogel, polyethylenimine–acrylamide/SiO<sub>2</sub>, showed selectivity factors of 105-450 for REEs over other metals (Wang et al., 2017). A porous carboxymethyl cellulose hydrogel containing polyacrylic acid had a monolayer adsorption capacity ( $q_m$ ) of 381.72 mg/g for La(III) at pH 5.58 and 320.47 mg/g for Ce(III) at pH 5.83 (Roosen et al., 2016; Zhu et al., 2016). Chitosan containing acrylic acid-co-styrene sulfonate/smectite clay hybrid granular hydrogel (CTS-g-(AA-co-SS)/ISC) had adsorption capacities of 232.97 mg/g for Gd(III) and 185.47 mg/g for Ce(III) at pH 5 (WANG et al., 2017). A magnetic MnFe<sub>2</sub>O<sub>4</sub>@SiO<sub>2</sub>-chitosan composite achieved one of the highest adsorption capacities of 1030 mg/g and 1020 mg/g for La(III) and Ce(III), respectively, (Table 1) (Liu et al., 2021).

Similar to chitosan containing hydrogel, many composite supports are based on composites of biological materials with inorganic materials or polymers (Iftekhar, Ramasamy, et al., 2018). REEs adsorption has been studied with silica-chitosan hybrid beads functionalized with EDTA, DTPA (Roosen et al., 2014), PAN, and acetylacetone (Ramasamy, Puhakka, Iftekhar, et al., 2018), Zn/Al Layered double hydroxide (LDH) intercalated cellulose (CL) (Iftekhar et al., 2017b), cellulose-silica nanocomposite (Iftekhar et al., 2017a), and Gum Arabic (GA)-polyacrylamide-silica nanocomposite (Iftekhar, Srivastava, et al., 2018). Among these adsorbents, silica-chitosan-PAN showed the highest adsorption capacities of 199.8, 198.8, and 123.4 mg/g for La(III), Sc(III), and Y(III), respectively, at pH 5. The LDH-CL adsorbent had q<sub>m</sub> values of 102.25, 92.51, and 96.25 mg/g for Y(III), La(III), and Ce(III), respectively at pH 7 (Iftekhar et al., 2017b). The cellulose-silica nanocomposite and the GA-polyacrylamide-silica nanocomposite reached q<sub>m</sub> of 29.48 mg/g and 7.90 mg/g for La(III), respectively and 23.76 mg/g and 11.05 mg/g for Sc(III), respectively at pH 6 (Iftekhar et al., 2017a; Iftekhar, Srivastava, et al., 2018). The EDTA and PDTA functionalized silica-chitosan had adsorption capacity (q<sub>m</sub>) of 0.27 mmol/g (or 38.9 mg/g) for Nd(III) at pH 6 (Roosen et al., 2014), and equilibrium capacity of 6.74 mg/g and 8.99 mg/g for Sc(III) at pH 2.

# Molecular/Ion-imprinted polymers

Molecular/ion-imprinted polymers (MIPs/IIPs) are sorbents with specific recognition sites for a desired molecule or ion (Chen et al., 2016; Ensing & De Boer, 1999; Fu et al., 2015; Wackerlig & Schirhagl, 2016). This is achieved by copolymerizing functional monomers and cross-linkers in the presence of the target molecule/ion that acts as a template molecule. Then the template ion/molecule is removed chemically, leaving behind a binding site-specific to the template (Chen et al., 2016; Fu et al., 2015).

The IIPs show high selectivity for the target REEs. Biju, Gladis, and Rao (2003) achieved high selectivity for Dy(III) over Y(III), Nd(III), Lu(III), and La(III) with selectivity factors (SFs) of around 66, 82, 175, and 116, respectively by using Dy(III) ion-imprinted polymer based on 5,7-dichloroquinoline-8-ol and 4vinyl pyridine. Similarly, Er(III) (Kala et al., 2004, 2005; Rao et al., 2006) and Nd(III) (Guo et al., 2009) ion-imprinted polymers based on 5,7-dichloroquinoline-8-ol and 4-vinyl pyridine were prepared and tested for selectivity over different lanthanides. In all of these investigations, the selectivity of the imprinted ion was significantly increased (Guo et al., 2009; Kala et al., 2004, 2005; Rao et al., 2006). Similarly, several IIPs (Pr(III)-IIP, Nd(III)-IIP, Sm(III)-IIP, Eu(III)-IIP, and Gd(III)-IIPs) were synthesized with maximum sorption capacities of 125.3, 126.5, 127.6, 128.2, and 129.1 mg/g for Pr(III), Nd(III), Sm(III), Eu(III), and Gd(III), respectively (Yusoff et al., 2017). A phosphonic-based La(III)-ion imprinted polymer showed an adsorption capacity of 62.8 mg/g for La(III) and a selectivity factor of 54.57 for La(III) over Cu(II) (Ni et al., 2021).

Dolak et al. (2015) used Nd(III)-IIP to selectively extract Nd(III) in the presence of Ce(III), La(III), and Eu(III). The selectivity coefficient for Nd(III) over Ce(III), La(III), Eu(III) were 234.3, 129.6, and 248.4, respectively; however, the maximum adsorption capacity was only 15.03 mg/g. In different investigations, Gd(III) ion-imprinted polymers bearing N,N"-bisacetamidostyrene diethylenetriaminetriacetic acid (DTPA-bisamide) (Garcia et al., 1998; Vigneau et al., 2001) and N-acetamidostyrene ethylenetriaminetriacetic acid (EDTA-amide) (Vigneau et al., 2001) exhibited at least 3-fold increase in selectivity than analogous non-imprinted polymers. The authors noted that DTPA (nine-coordinate chelating agent) based Gd(III)-IIP showed higher Gd/La selectivity (maximum value of ~8.3) for Gd(III) in a binary solution of Gd(III) and La(III) than EDTA (five-coordinate chelating agent) based Gd(III)-IIP (around 3.0). The same DTPA-based Gd(III)-IIP was used to separate Gd(III) and other lanthanides and actinides (Vigneau et al., 2002). Other studies on imprinted polymer include La(III)-IIP (Mustapa et al., 2016), Ce(III)-IIP (Keçili et al., 2018;

Mustapa et al., 2016), Y(III)-IIPs (Zulfikar et al., 2017), Nd(III)-IIP (Moussa et al., 2017), ionic imprinted mesoporous bilayer films (IIBFs) for Dy(III) and Nd(III) adsorption (Zheng et al., 2018), Gd (III)-imprinted membranes (GIMs) (Cui et al., 2019), and Gd(III)-imprinted divinylbenzene and methacrylic acid copolymer (Bunina et al., 2021). The IIPs show a stronger affinity for the imprinted REE cation compared to other REEs.

Surface ion-imprinted polymers are derivative of IIP technology and include the formation of IIP on a surface. A surface-IIP was prepared for L(III) using MCM-41 as support and APTES as the functional monomer (Qin et al., 2022). The surface-IIP showed an adsorption capacity of 272.2 mg/g. Other examples of surface-IIP are Ce(III)-imprinted polymer with attapulgite support (Pan et al., 2010), Ce(III)-imprinted polymer functionalized potassium tetratitanate whisker (Zhang et al., 2010), Ce(III)-IIP functionalized on SBA-15 (Meng et al., 2014), and Gd(III) imprinted magnetic ordered mesoporous carbon (OMC) (Patra et al., 2017).

The limitation in the application of IIP stems from the large number of inaccessible adsorption sites since these sites are embedded inside the polymer (Canfarotta et al., 2016; Dong et al., 2021; Huang et al., 2019). Considering that IIP preparations are usually a sophisticated and chemically expensive process, presence of inaccessible sites is a big hindrance for widespread industrial application. Additional challenges arise due to low mass transfer rates (Aravind & Mathew, 2018; Dong et al., 2021; H. Xu & Guo, 2012). These limitations can be improved with surface ion-imprinted polymers (Dong et al., 2021), but more research effort is required in this direction.

# **Elution solutions**

## Mineral acids

In the adsorption-based separation process, the use of mineral acids for desorption of adsorbed ions and regeneration of the adsorbent is commonplace. However, in the case of REEs chromatographic separation using strongly acidic cation-exchange resin, the use of mineral acids such as HCl,  $H_2SO_4$ ,  $HNO_3$ , and HBr as eluents results in very low separation among REEs (Korkisch et al., 1967; Nelson, 1965). However, these acids can be used to separate REEs from other monovalent and divalent ions using strongly acidic cation resin (Fritz & Garralda, 1963; Page et al., 2019; Strelow, 1960; Strelow et al., 1965). Between various strong mineral acids, the distribution coefficients ( $K_d$ ) for different REE ions with strongly acidic cation-exchange resin are higher for HCl (Strelow, 1960) than  $H_2SO_4$  and  $HNO_3$  (Strelow et al., 1965) (i.e., in 0.5 M HCl,  $K_d = 2480, 2460, 1460$  in 0.5 N  $H_2SO4$ ;  $K_d = 1860, 1800, 1380$  and in 0.5 N  $HNO_3$ ;  $K_d = 1870, 1840, 1020$  for La(III), Ce(III), and Y(III), respectively).

In the case of weakly acidic cation-exchange resins, strong mineral acids can be used for desorption. At very low pH, the excess of hydrogen ions results in the desorption of REE ions from the resin surface through ion-exchange. Thus, strong mineral acids are used for the regeneration of resin in many cases. For example, HCl was used with various carboxyl based weakly acidic cation-exchanger D152 (0.5 M HCl) (Xiong et al., 2008), D155 (0.25 M HCl+0.5 M NaCl) (Xiong, 2008), D113 (4 M HCl) (Xiong et al., 2009), and D151 (0.5 M HCl) (Yao, 2010). In the case of strongly basic anion-exchangers, the elution of the adsorbed anionic REE-ligand complex is carried out with HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>SCN, and CH<sub>3</sub>COOH solutions (Faris & Warton, 1962; Hubicki & Olszak, 1998, 2002; Koodynska & Hubicki, 2012).

Similarly, chelating resins can be regenerated using mineral acids. In a study with multiple chelating resins, Page et al. (2017) achieved high elution (>97%) for iminodiacetic (IDA) resins with 0.1-1 M HCl, the highest being 99.9% with 1 M HCl. For sulfonic/phosphonic (SP) and aminophosphonic (AP) resins, a higher strength of HCl (2-4 M) achieved 58-80% elution. In another study, 2 M HCl and 2 M HNO<sub>3</sub> were used for desorption of La(III), Ce(III), and Nd(III) ions from chelating resin Dowex M 4195; however, the highest desorption was only 43.9% for Ce(III) achieved with 2 M HNO<sub>3</sub> (Kołodyńska et al., 2019). Other examples of mineral acid as eluent for chelating resins are 2 M HCl for iminodiacetic acid resin (IDAAR) (Xiong et al., 2006); 1 M HCl, 6 M HCl, 1 M HNO<sub>3</sub>, and 6 M HNO<sub>3</sub> for Tulsion CH-90 resin (Dutta et al., 2008).

Mineral acid, HNO<sub>3</sub>, was used in the desorption step for REE adsorbed onto alumina and hematite (Kosmulski, 1997b; Marmier et al., 1997). The elution of REE from amorphous ZrP with 1 M mineral acids decreased in the order of  $H_2SO_4 > HNO_3 > HCl > H_3PO_4$ , with the highest being 85.1% and the lowest of 73.2% (Xu et al., 2018). In the case of inorganic TiP, 0.5 M HNO<sub>3</sub>+0.5 M H<sub>3</sub>PO<sub>4</sub>eluted 98.3% Sc(III) (Wenzhong Zhang, Koivula, et al., 2017). Other inorganic nanomaterials have been desorbed using 0.001 M HCl (Zhao et al., 2019), 0.3 M HCl (Marwani et al., 2018), 0.2 M HNO<sub>3</sub>(Ghobadi et al., 2017, 2018), and 0.05-0.8 M HNO<sub>3</sub> (Tu & Johnston, 2018). 0.2 M HNO<sub>3</sub> desorbed >80% REE from  $Co_{0.2}Mn_{0.8}Fe_2O_4$ and  $Co_{0.8}Mn_{0.2}Fe_2O_4$ (Ghobadi et al., 2017) and >90% REE from MnFe<sub>2</sub>O4 and MnFe<sub>2</sub>O<sub>4</sub>-GO (Ghobadi et al., 2018). With CuFe<sub>2</sub>O<sub>4</sub>nanoparticles, 100% REE desorption was obtained with 0.05-0.8 M HNO<sub>3</sub> (Tu & Johnston, 2018).

Mineral acid HCl is very frequently used as an eluent in solvent-impregnated resins. The examples of the use of different concentrations of HCl as eluent for SIRs include the use of 0.15 M HCl (Lee et al., 2010a, 2010b), 0.2 M HCl (Park et al., 2005), 0.5 M HCl (Yin et al., 2020), 1 M HCl (Kumar et al., 2011), and 2 M HCl (Aardaneh et al., 2008). Kumar et al. (2011) used HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, and reported 99.7%, 99.1%, 100%, and 74.6% elution at 1 M concentration. HCl with strength >0.1 M achieved almost complete desorption of La(III) from P227-impregnated XAD-7HP (Yang et al., 2020). Nitric acid solutions are also effective for elution from different SIRs (Helaly et al., 2012; Louis & Duyckaerts, 1984, 1985). İnan et al. (2018) used 0.01 M HNO<sub>3</sub> to desorb REEs from Cyanex impregnated Amberlite XAD-7. 0.1 M HNO<sub>3</sub> was used as a stripping agent for SIL obtained through ([A336] [CA-100]) impregnation into XAD-7 (Sun et al., 2009). Another SIL loaded with Sc(III) was stripped using 1 M HCl and 1 M HNO<sub>3</sub> with efficiencies >90% and 100% with 1 M H<sub>2</sub>SO<sub>4</sub> (Avdibegović et al., 2017).

Similarly, for surface-functionalized adsorbents and ion-imprinted polymers, mineral acids are mostly used for the desorption of REEs. The strength of the acid solution used for desorption has varied from 0.1 M HCl to 2.0 M HCl (e.g., 0.1 M HCl (Ahmed, Lee, et al., 2019; Kostenko et al., 2019; Y.-R. Lee et al., 2018; Ryu et al., 2021), 0.25 M HCl (Hua et al., 2019), 0.3 M HCl (Lou et al., 2019), 0.5 M HCl (Chen et al., 2014; Ravi, Lee, et al., 2018), 1.0 M HCl (Babu et al., 2018; Gasser et al., 2017; Moussa et al., 2017), 2 M HCl (Li et al., 2019; Qin et al., 2022; Yusoff et al., 2017), and 1.0-2.0 M HCl (Ogata et al., 2015a)). Other mineral acids such as HNO<sub>3</sub> with the strength of 0.01-6.55 M (Ashour et al., 2017; Shuangyou Bao et al., 2022; Bertelsen et al., 2019; Callura et al., 2018; Chen et al., 2014; Noack et al., 2014; Rahman et al., 2020; Ravi, Zhang, et al., 2018; Zhao et al., 2021) and  $H_2SO_4$  (e.g., 0.1 M - 1 M  $H_2SO_4$  (Ogata et al., 2015a), 0.1 M  $H_2SO_4$ (Gaete et al., 2021)) have been used as well. Mineral acids have usually provided desorption in the order of 90-100% for functionalized adsorbent and ion-imprinted polymers. The mechanism of desorption with mineral acid is the ion-exchange reaction between protons and the adsorbed ions (Ogata et al., 2015a).

### Organic acids and complexing ligands

Along with mineral acids, various organic acids and complexing ligand solutions have been used for the desorption of REEs from different adsorbents. In the case of strongly acidic cation-exchange resins, the organic acid and complexing ligands play a vital part as eluent since they can increase the chromatographic separation between REEs in the elution step due to their difference in affinity for different REEs (Boyd, 1978; B. Chen et al., 2017; Spedding et al., 1947, 1954; Strelow & Victor, 1990). The examples of organic acids used as eluents in REEs separation include acetic, malonic, phthalic, and other carboxyl acids, hydroxy acids, phosphonic, and amino phosphonic acids (Koodynska & Hubicki, 2012).

However, the best results for REEs desorption and separation from strong acidic cation-exchange resins were obtained using complexing ligand as eluent, primarily eluents based on polyamino-polycarboxylic acid such as ethylenediaminetetraacetic acid (EDTA) (Smith & Hoffman, 1956; Spedding et al., 1954a; Spedding & Powell, 1954); Diethylenetriaminepentaacetic acid (DTPA) (Chuveleva et al., 1974, 1995; Hale & Hammer, 1972; Kharitonov et al., 2009b; Kogan & Ratner, 1971), nitrilotriacetic (Kharitonov et al., 2009a; Martynenko

et al., 1968, 1972; Wheelwright, 1969), hydroxy-ethylethylenediaminetriacetic (Hagiwara, 1969; James et al., 1961; Strelow & Victor, 1990), cyclohexane-1,2-diaminetetraacetic (Gschneidner & Eyring, 1982), and iminodiacetic acids (Martynenko et al., 1972).

The advantage of using polyamino-polycarboxylic acid as eluent is that they form strong complexes with REE, reducing the consumption of ligand and resulting in concentrated elutes. Also, the stability constant of different REEs with these complexes differs more than their ion-exchange constants, which results in a higher degree of separation ( Chen et al., 2017; Ehrlich & Lisichkin, 2017; Koodynska & Hubicki, 2012). The most widely used polyamino polycarboxylic is ethylenediaminetetraacetic acid (EDTA). EDTA is readily available, inexpensive, and easy to regenerate. Additionally, due to the multidentate nature of EDTA, the REEs form 1:1 complexes with EDTA, which reduces metal zone tailing.

EDTA has been used as a stripping agent for SLEs and functionalized adsorbents (Gupta & Sengupta, 2017; Li et al., 2018; Liu et al., 2009; Zhao et al., 2016). EDTA and oxalic acid were used for desorption with amide functionalized multiwalled carbon nanotubes (Gupta & Sengupta, 2017). Other organic compounds used for desorption of REEs include acetonitrile (Abdel-Magied et al., 2019; Jiang et al., 2016; Zheng et al., 2015), methanol (Abdel-Magied et al., 2019), and ammonium oxalate (Florek et al., 2014, 2015; Giret et al., 2018; Hu et al., 2017, 2019; Juère et al., 2016; Perreault et al., 2017).

# Application to real samples

Examples of using solid-liquid separation at an industrial level are scarce. Diphonix was used to extract REE from the nitric acid solution from apatite processing on a pilot scale at Akron public corporation (Ehrlich & Lisichkin, 2017). However, there are lab studies in literature where various adsorbents have been used to separate REEs from various natural samples such as bauxite mud (Hu et al., 2019; Ochsenkühn-Petropulu et al., 1995; Roosen et al., 2016; ZHOU et al., 2008); Silicate & niobium mining deposits (Hu et al., 2017); apatite, orthite, and slag (Kostenko et al., 2019; Ogata et al., 2016); bastnäsite (Dolak et al., 2015), acidic mine drainage (Hermassi et al., 2021; Ramasamy et al., 2019; Ramasamy, Puhakka, Iftekhar, et al., 2018; Ramasamy, Puhakka, Repo, Ben Hammouda, et al., 2018); spiked seawater (Callura et al., 2018; Noack et al., 2016); spiked river/groundwater and sewage water (Marwani et al., 2009); REE mineral leachate (Giret et al., 2018); industrial wastewater (Li et al., 2013); leached solution of spent Ni-MH cells (Gasser & Aly, 2013; Kołodyńska et al., 2019), thin-film phosphors leached solution (Schaeffer et al., 2017), phosphoric acid plant effluent (Al-Thyabat & Zhang, 2015), zinc mine ore (Fonseka et al., 2021), and coal fly ash (Brown & Balkus, 2021; Hovey et al., 2021; Mondal et al., 2019).

These adsorbents showed varying degrees of success for REEs extraction (Figure 4). REEs extraction from red mud used ion-exchanger Dowex 50W-X8 in combination with the solvent extraction method (Ochsenkühn-Petropulu et al., 1995). The whole separation process resulted in an average 93% recovery of Sc(III). High La(III) and Nd(III) recovery (98%) from spent Ni-MH cells were achieved using layered double hydroxide (or hydrotalcite) functionalized with Cvanex-272 (Fe-Mg-LDH-Cvanex-272) (Gasser & Alv, 2013). In another study, 95% of REE were separated at pH 4.2 from the waste sulfate solutions of uranium leaching solution using carboxyl adsorbent CYBBER LX 280, after an initial step involving  $Fe(OH)_3$  precipitation (Lokshin et al., 2013). Bidentate phthaloyl diamide (PA) functionalized KIT-6 showed high selectivity for Lu(III) from a leached solution of silicate and niobium mining deposit samples (legend 6-11, Figure 4) (Hu et al., 2017). The adsorbent tetradentate phenylenedioxy diamide (PDDA) functionalized KIT-6 showed a higher affinity for HREEs in the case of KIT-6-1,2-PDDA (legend 14 Figure 4) and LREEs with KIT-6-1,3-PDDA (legend 15 Figure 4) while extracting REEs from red bauxite residue (Hu et al., 2019). Silica gel functionalized with phosphonoacetic acid (PAA), N, N-bis(phosphonomethyl) gylcine (BPG), diethylenetriaminepentaacetic acid (DTPA), and diethylenetriaminepentaacetic dianhydride (DTPADA) were able to adsorb REEs from spiked brine samples with high efficiency (legend 16-26, Figure 4) (Callura et al., 2018; Noack et al., 2016). Nd(III)-ion imprinted polymer extracted 100% Nd(III) from bastnäsite leachate solution (Dolak et al., 2015).

In fly ash leachate solution, bis(ethylhexyl)amido diethylenetriaminepentaacetic acid-functionalized silica showed selectivity for REEs over Fe and Al that were present in much higher concentrations than REEs (~700- to 90,000-fold excess) (Hovey et al., 2021). Eu(III) was selectively recovered (88% Eu(III) recovery, <10% recovery of competitive ions) from zinc mine ore leachate solution adjusted to pH 5.5 using PMIDA functionalized MOF (Cr-MIL-PMIDA) (Fonseka et al., 2021). The single-element Eu(III) adsorption at pH 5.5 was 90-91%; thus, the presence of a high concentration of competing ions did not affect the Eu(III) adsorption. The Langmuir maximum capacity ( $q_m$ ) for Eu(III) on Cr-MIL-PMIDA was 69.14 mg/g.

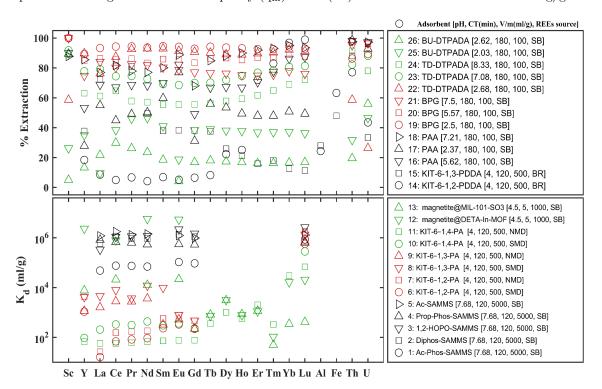


Figure 4: Distribution coefficient ( $K_d$ ) for various adsorbents in actual REE solution. The legends include adsorbents with the experimental condition (pH, contact time (CT), V/m ratio (volume of solution/mass of adsorbent and source of the REE solution)). Sources of REEs: SRW: spiked river water, SB: spiked brine, SMD: Silicate mining deposit, NMD: Niobium mining deposit, BR: Bauxite residue Source for data: Adsorbent 1-5 (Yantasee et al., 2009), 6-11 (Hu et al., 2017), 12-13 (Elsaidi et al., 2018), 14-15 (Hu et al., 2019), 16-26 (reported pH is equilibrium pH) (Callura et al., 2018).

#### Difficulties with adsorption data present in literature:

Adsorption studies often involve isotherms and report maximum adsorption capacity  $(q_m)$ . However, in many cases, the adsorption experiments only include a mono-element solution, making it difficult to predict the behavior of these adsorbents in a multielement solution or an actual field REEs solution (e.g., acid mine drainage, bauxite leachate). The presence of competitive ions can reduce the adsorption capacity of adsorbents for target ions by varying degrees. It is necessary for an adsorbent to retain its adsorption capacity in multielement solutions and be selective for the efficient separation of target elements. While many adsorption studies do include multi-element adsorptions, the type and concentration of competitive ions differ in different studies, making it difficult to compare the mechanism and performance of these adsorbents with each other. Even so, it should be a general practice to test the adsorbent in a multielement solution with competitive ions and actual field solutions.

# Summary and outlook

The adsorption-based REEs separation has been explored for a long time, and the technology has evolved. For separating REEs from other cations with a different charge, cation exchangers may be recommended. However, for the selective separation of specific REEs, ligand-functionalized adsorbents promoting complexation are more suitable.

There remain strikingly large gaps in two directions with adsorption-based REE separation: 1) lack of industrial-level applications and setups, and 2) lack of fundamental level modeling and understanding of surface ligand behavior with the REE. Although there have been many REE separation studies at laboratory scale, there is a lack of examples of conversion to industrial level applications.

The challenges in SPE with functionalized adsorbents are the selection of selective ligands and predicting the behavior of these ligands once they are grafted onto a specific solid surface. No quantitative relationship has been developed between free-solution thermodynamics data and surface complexation constants for the functionalized adsorbents. Future research can employ quantum chemistry calculations to select ligands and predict the behavior after grafting. Understanding and modeling the ligand grafted on the solid surface and recognizing the difference in metal-ligand interaction on the surface against the metal-ligand interaction in the free solution can help better develop functionalized adsorbents.

## Appendix A. Abbreviations

AC Activated carbon

AER Anion exchange resin

APTS 3-[2-(2-aminoethylamino) ethylamino] propyl-trimethoxysilane

APTES 3-aminopropyl triethoxysilane

APTMS 3-aminopropyl trimethoxysilane

ATMP Amino tris(methylene phosphonic acid)

ATS Aluminum silicotitanates

BHPA N-Benzoyl-N-phenylhydroxylamine

BPG Bis(phosphonomethyl) glycine

CER Cation exchange resin

CN Coordination number

CNT Carbon nanotube

COK Centre for Research Chemistry and Catalysis

Cyanex 272 Bis(2,4,4-trimethylpentyl)-phosphinic acid

DETA Diethylenetriamine

DGA Diglycolamide

DMF N,N-dimethylformamide

DOODA 3,6-dioxaoctanediamidopropyl

DTPA Diethylenetriaminepentaacetic acid

DTPADA Diethylenetriaminepentaacetic dianhydride

EDTA Ethylenediaminetetraacetic acid

GO Graphene oxide

GONS Graphene oxide nanosheet

HDEHP Bis(2-ethylhexyl) hydrogen phosphate

HREE Heavy rare earth element

IER Ion exchange resin

IIP Ion-imprinted polymer

KIT Korean Advance Institute of Science and Technology

LREE Light rare earth element

MCM Mobil Composition of Matter

MIP Molecular imprinted polymer

MOF Metal-organic framework

MSF Mesoporous silica foam

MWCNT Multi-walled carbon nanotube

OMC Ordered mesoporous carbon

OMS Ordered mesoporous silica

PA Phthaloyl diamide

PAA Phosphonoacetic acid

PAN 1-(2-pyridylazo)-2-naphthol

PC88A 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester

PDDA Phenylenedioxy diamide

PES Polyethersulfone

PMIDA N-(phosphonomethyl)iminodiacetic acid

PVA Polyvinyl alcohol

**REE** Rare earth element

SBA Santa Barbara Amorphous

SIL Supported ionic liquid

SIR Solvent impregnated resin

SLE Supported liquid extraction

SLLE Supported liquid-liquid extraction

SPE Solid-phase extraction

SWCNT Single-walled carbon nanotube

TEHDGA N,N,N'N' tetrakis-2-ethylhexyldiglycolamide

TMO Transition metal oxide

TODGA N,N,N',N'-Tetraoctyl diglycolamide

TTHA Triethylenetetraminehexaacetic acid

ZrP Zirconium organophosphonates

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