Reaktor

p-ISSN 0852 – 0798
e-ISSN 2407 – 5973

Website: http://ejournal.undip.ac.id/index.php/reaktor/

Reaktor, Vol. 23 No. 3, December Year 2023, pp. 77-91

Adsorption using Selective Adsorbents as An Effective Method for Rare Earth Elements Recovery– a Review

Nurul Jamilah[1,2)], Adam Badra Cahaya [1,*)], and Asep Riswoko[2)]

[1)] Department of Physics, Faculty of Mathematics and Natural Sciences, University of Indonesia
Kampus UI Depok 16424
[2)] Research Center for Polymer Technology, National Research and Innovation Agency (BRIN)
460th Building, South Tangerang, Banten 15314

[*)] Corresponding author: adam@sci.ui.ac.id

(Received: 09 August 2023; Published: 31 January 2024)

Abstract

Rare Earth Elements (REEs) are strategically important for the industry, especially in the manufacture of advanced-technology products and components, such as electric batteries for energy conversion and storage, defense and security industry, electric vehicles, specific components on smartphones, laptops, liquid crystal display, and others. Generally, REEs are processed by liquid-liquid extraction (LLE). In addition to high chemicals and operational costs, LLE process also generates hazardous waste that potentially harms the environment. Currently, innovative separation/recovery techniques are continuously developed for a more effective and environmentally friendly recovery of REEs. The adsorption method employing an appropriate adsorbent is one of the most efficient methods for recovering REEs, even at their low concentration. This method offers several advantages, including high release effectiveness, ease installation and operation, low maintenance costs, and reduced chemical consumption. This study reviews the mechanism, characterization, and several adsorbents from natural to synthetic materials, especially nanocomposite-based adsorbents for the recovery of REEs. In addition, the discussion of important parameters that affect adsorbent and adsorption process are also elaborated. It is concluded that the results several methodological breakthroughs have shown that they still require further research.

Keywords: rare earth elements; solid phase extraction; adsorption; adsorbent; nanocomposite

How to Cite This Article: Jamilah, N., Cahaya, A.B, and Riswoko, A. (2023), Adsorption using Selective Adsorbents as An Effective Method for Rare Earth Elements Recovery–a Review, Reaktor, 23 (3), 77 - 91, https://doi.org/10.14710/reaktor. 23. 3. 77 - 91

INTRODUCTION

With modern technologies continuously grow for more significant advancements, the demand for strategic minerals is now increasing than ever. Indeed, the utilization of strategically vital raw materials is the current trend in the development of renewable energy and environmentally friendly enterprises, specifically rare earth elements (REEs). Recently, the REEs are used in energy storage (electric batteries), energy conversion (solar cells, wind turbines, etc.), defense industry, electric vehicles, and other electronics industry (Jha, 2014). REEs are also important component in the manufacture of various modern devices, such as smartphones, digital camera, computer hard disk, fluorescent, and light-emitting-diode (LED) light, flat-screen television, computer monitor, electronic display, and hybrid automobile (Balaram, 2019; Humphries, 2010).

REEs are the lanthanide group concluding of scandium (Sc), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) dan yttrium (Y), which are divided into light REEs (LREEs, La-Eu) and heavy REEs (HREEs, and Gd -Lu and Y) (Voncken, 2016). In fats, all REEs have many similar chemical and physical properties because of their similar electron structure within their molecules (Voncken, 2016), and are often found together in a geological deposit. These properties are usually having an oxidation number of 3^+ in crystalline compounds and bonding with non-metals; the coordination number is usually greater than 6 and decreases to the right of the lanthanide series; and bonding with highly electronegative elements such as oxygen or fluorine. Another important property of REEs is the phenomenon of lanthanide contraction in the oxidation number 3^+. This phenomenon is a significant and progressive reduction in atomic and ionic radii that occurs in the lanthanide series as the atomic number increases (Voncken, 2016). When compared to other precious metals, REEs are not particularly rare, but their low concentration (about part per billion) and wide distribution make them difficult to separate, isolate and collect (Kim et al., 2016; J. Liu et al., 2021). Therefore, an appropriate method for separating and recovering of REEs from the geological deposit is highly required.

Generally, there are steps to extract high-purity REEs: extraction, concentration, purification, separation, and refining (Royen & Fortkamp, 2016). In general, these steps utilize liquid-liquid extraction (LLE), which employs metallurgical methods (pyrometallurgy or hydrometallurgy) on a large scale (Kaya, 2016). Although LLE is more widely used in industrial scale application, its efficiency has always been questioned due to its inability to extract polar compounds and impurities, high emulsion forming tendency, the loss of extractants into the liquid phase, long operational time, low product purity, and the requirement of toxic or flammable chemicals removal (Hidayah & Abidin, 2017). Taking into consideration of those shortcomings, an innovative and effective separation method for the extraction of REEs from secondary minerals is needed. One of them being a selective adsorption method using nanocomposite-based adsorbents in solid phase extraction (SPE). The SPE provides several advantages than the LLE, such as the availability of large surface area and better contact between the extractant and the REEs in the aqueous phase. These two main advantages can increase extraction efficiency, selectivity, and product quality, thereby reducing the consumption of chemicals in the separation and extraction of REEs. In addition, this method also has high desorption/desorption efficiency, is easy to install and operate, and requires little maintenance when compared to other methods. The adsorption kinetics and capacity of the process will determine the recovery efficiency the REEs (Cardoso et al., 2019).

This paper aims to review the technology used for the recovery of REEs using adsorbents and the latest developments in adsorbents synthesis, especially adsorbents based on nanocomposites. The first part of this paper discusses the adsorption mechanism and characterization of adsorbents. The second part of this paper, several developments of selective adsorbents are discussed, and finally the progress of REEs recovery technologies using nanocomposite-based adsorbents are also elaborated.

MECHANISM AND CHARACTERIZATION OF ADSORBENT IN RARE EARTH ELEMENTS RECOVERY TECHNOLOGY

Adsorbents are adsorbing substances or phase used in the adsorption system. Adsorption is the process by which a liquid or gas solute builds up on the surface of a solid or liquid to form an atomic or molecular film (El-Naas & Alhaija, 2013). Its process exploits the ability of certain substances to concentrate specific substances from fluid on their surfaces. Substances that are adsorbed on the adsorbent surface are called adsorbate substrates or solutes. The reverse of adsorption process is defined as desorption (Alaqarbeh, 2021; Anantharaman & Begum, 2011).

As previously explained, the REE recovery process uses a solid-liquid adsorption system. The adsorbent can exist in the form of a solid material, while the adsorbate is in the form of a liquid containing REE ions. Therefore, the mechanism of the adsorption process follows the interface layer model (Alaqarbeh, 2021). The interfacial layer describes the equilibrium of the adsorbent and adsorbate phases. The adsorbate is bound to the surface of the adsorbent in the first area, and the surface layer of the adsorbent is in the second area. The mechanism of the interfacial layer can be explained by two principles or types of adsorptions, namely physical adsorption (physisorption) and chemical (chemisorption) (Alaqarbeh, 2021; Ho, 2022). The surface interaction of the adsorbate and adsorbent can be illustrated in Figure 1 (Nandiyanto, 2020).

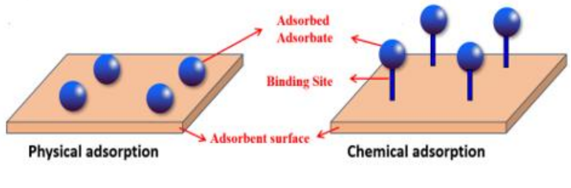

Figure 1. Illustration Showing Interaction between The Adsorbent Surface and The Adsorbate, Physical Adsorption and Chemical Adsorption. Adapted from (Nandiyanto, 2020).

Figure 2. Layer of Adsorption in Interfacial Region, Monolayer, and Multilayer. Adapted from (Nandiyanto, 2020).

In physical adsorption, the solute molecules are adsorbed on the solid surface due to physical interaction forces. The chemical structures of the substrate and adsorbent do not change because of the weak van der Waals forces that bind them together and cause reversible interactions (Anantharaman & Begum, 2011). If an equilibrium is reached, there is no transfer or sharing of electrons, and the associated electrons remain with their respective interacting species as they originally exist. This adsorption is only noticeable at temperatures below the adsorbate's boiling point and non-specific about the adsorbent. These result in a greater dependency on the characteristics of the adsorbate than those of the solid adsorbent, which is consistent with the theory that physisorption may be causing the formation of multilayers (Figure 2) (Anantharaman & Begum, 2011; Ho, 2022).

Meanwhile, in chemical adsorption, the adsorption process is irreversible and results in a chemical interaction between adsorbent and substrate stronger than physisorption. Both the adsorbent and substrate experience an electron density rearrangement that results in the formation of a chemical bond that can either be ionic or covalent (Alaqarbeh, 2021; Anantharaman & Begum, 2011). This adsorption can occur at high temperatures and is typically characterized by a high degree of heat of adsorption, greater than 20 to 150 Kcal/mole. Due to the high initial heat that causes a significant quantity of adsorption, a monolayer-like structure of chemical adsorption is formed, followed by a multilayer structure that is held together by physical forces (Figure 2) (Anantharaman & Begum, 2011; Ho, 2022). Adsorption occurs when a substance enters adsorbent pores according to the following possible mechanism (Widayatno et al., 2017).

1. Mass Transfer of adsorbent from solution to the outer surface of the grain adsorbent;
2. Diffusion of adsorbate in adsorbent pores;
3. The adsorbate mass transfer from solution in the pore to the pore surface adsorbent.

Adsorption usually involves the removal of solutes from the solution and their concentration at a surface until the equilibrium between the amount of solute in the solution and that at the surface is reached under constant temperature. It also suggests the idea of obtaining adsorption capacity throughout the process. Their expression is termed adsorption isotherm, which describe how the adsorbent interacts with and contacts the adsorbate or the amounts of adsorbed ions by the adsorbent and their interactions (El-Naas & Alhaija, 2013). The following equation (Equation 1) can be used to estimate the adsorption capacity at equilibrium (q_e,mmol/g) (Ashour et al., 2017; Ho, 2022)

$$q_e = \frac{V(C_0 - C_e)}{M}, \tag{1}$$

where V, M, C_0, and C_e, represent the volume (L), mass of adsorbent (g), initial adsorbate concentration (mmol/L), and equilibrium adsorbate concentration (mmol/L), respectively.

In order to represent various adsorption isotherm types, numerous theoretical and empirical models have been proposed, such as Langmuir, Freundlich, Sips, and the Brunauer-Emmett-Teller (BET) models. The difference of isotherm model forms relies on the type of adsorbent and the fluid's surface intermolecular interactions. The system can then be described, and the adsorption behavior can be predicted for use in practical process design, using the model that best fits the experimental data (El-Naas & Alhaija, 2013).

The Langmuir model is based on several presumptions (El-Naas & Alhaija, 2013):

1. Molecules are adsorbed at a fixed number of well-defined localized sites.
2. Adsorption is only possible with one layer of solute molecules.
3. All molecules have the same enthalpy of adsorption.
4. No interactions exist between molecules adsorbing on nearby sites.

The profile of Langmuir model (El-Naas & Alhaija, 2013) is governed by the following equation (equation 2) and illustrated in Figure 3.

$$q_e = \frac{q_m b C_e}{1 + bC_e}, \tag{2}$$

where q_e (mg/g) is the equilibrium amount of solute adsorbed in mg per gram of solid, C_e (mg/l) is the equilibrium concentration of solute in solution, and q_m (mg/g) and b (l/mg) are temperature-dependent parameters indicating the maximum adsorption

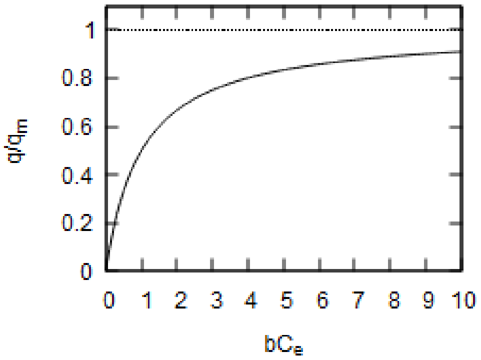

Figure 3. Model of Langmuir isotherm

capacity for the solid phase loading and the energy constant associated with the heat of adsorption, respectively.

In contrast to the Langmuir isotherm model, the Freundlich isotherm model does not have a thermodynamic basis and does not provide sufficient physical interpretation of the adsorption data (El-Naas & Alhaija, 2013).

$$q_e = a_f C_e^{1/n}, \tag{3}$$

where a_f is the Freundlich isotherm constant, and n is the heterogeneity factor in the Freundlich model (Ashour et al., 2017; El-Naas & Alhaija, 2013).
The Sips isotherm is an expression of both the Langmuir and Freundlich isotherms. It approaches the Freundlich isotherm at low sorbent concentrations, whereas at large concentrations, it approaches the Langmuir isotherm.

$$q_e = \frac{K_{LF} C_e^{nLF}}{1 + (a_{LF} C_e)^{nLF}}, \tag{4}$$

where, K_{LF} (l/g), n_{LF} and a_{LF} (l/mg) are constants.
The three models above can be used to represent the heterogeneous surface adsorption process and the monolayer/single layer adsorption capacity (El-Naas & Alhaija, 2013; Ho, 2022). Multi-layer adsorption is described by the Brunauer-Emmett-Teller (BET) which is presumptions (El-Naas & Alhaija, 2013):

1. Adsorbed molecules are immobile on the surface.
2. For all molecule in a certain layer, the enthalpy of adsorption is constant.
3. Every molecule in layers after the first has an equal adsorption energy.
4. No layer has to be finished before the next one begins.

The profile of BET model (El-Naas & Alhaija, 2013) is governed by the following equation (equation 5) and illustrated in Figure 4.

$$q = \frac{q_m K_B C}{(C_s - C)[1 + (K_B - 1)(C/C_s)]}, \tag{5}$$

where K_B is a constant related to adsorption energy and C_s is the solute concentration at saturation of all layers.

In adsorption process, the time reach equilibrium can be also predicted from the adsorption kinetics. Additionally, the adsorption kinetics demonstrates a strong reliance on the adsorbent material's physical and chemical properties, which also have an impact on the adsorption mechanism, which can be either film or pore diffusion or a combination of the two depending on the hydrodynamics of the system.

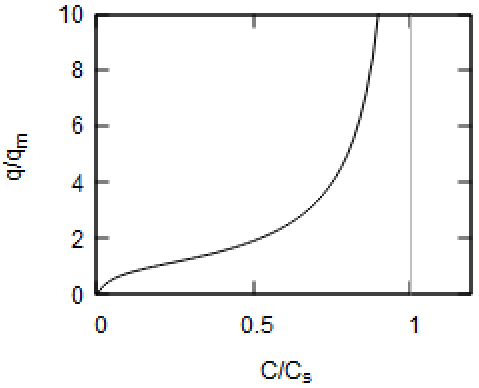

Figure 4. Model of Brunauer-Emmett-Teller (BET)

This kinetics can be analyzed using the nonlinear forms of the pseudo-first-order (equation 6) and pseudo-second-order (equation 7) models. The Lagergren pseudo-first order model is most frequently to describe the adsorption of solute from a liquid solution. Meanwhile, in the pseudo-second-order, the removal of the adsorbate from a solution is caused by physicochemical interactions between the two phases, and the rate-limiting step is the surface adsorption that involves chemisorption (El-Naas & Alhaija, 2013)

$$q_t = q_e(1 - e^{-k_1 t}), \tag{6}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}, \tag{7}$$

where k_1 (1/min) is the rate constant for first-order adsorption, k_2 (g/mg·min) is the rate constant for second-order adsorption, q_e (mg /g) is the adsorption capacity at equilibrium, and q_t (mg/g) is the adsorption capacity at any time t.
Meanwhile, the determination of adsorption efficiency can be measured through the following equation (8) (Nandiyanto, 2020).

$$\eta = 1 - C_e/C_o \tag{7}$$

where C_o is the initial concentration of adsorbate (mg/L). C_e is the concentration of adsorbate equilibrium (mg/L).

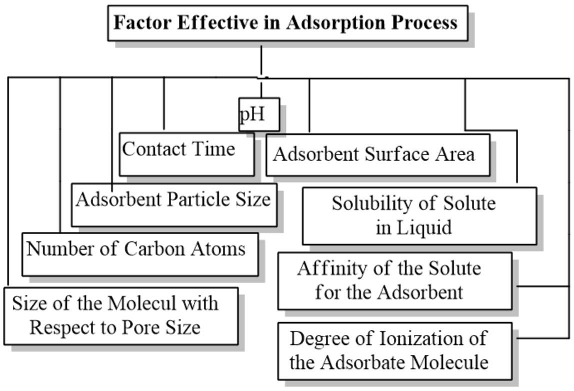

Figure 5. Important factors effecting the Adsorption Process (El-Naas & Alhaija, 2013)

This adsorption mechanism is greatly influenced by several factors, such as the characteristics of the adsorbate, operation conditions, and especially the physical and chemical characteristics of the adsorbent material (Pellenz et al., 2023) with the most important factors are illustrated in Figure 5 (El-Naas & Alhaija, 2013).

The characteristics of the adsorbate are related to the type of material to be adsorbed in the adsorption system, whether it is an electrolyte or not. Adsorption will proceed more rapidly and result in a greater adsorption if the adsorbate is an electrolyte solvent. This is due to the ionization of the electrolyte solution. Since there are ions in solution with opposing charges, the strength of the van der Waals attraction increases with the amount of adsorption (Widayatno et al., 2017).

Operating parameters affect adsorption process, which include pH and stirring if given. Ion-exchange materials' surface charge at any pH and subsequently their adsorption capacity can be affected by the acid strength (pK_a). For example, if the main components of an adsorbent are alcohol groups with a pK_a of approximately 10–18, then at pH 2–6, which is lower than the pK_a, the surface of the adsorbent will be acidic (neutral surface charge), and it cannot be an efficient adsorbent (Adom, 2020). Meanwhile, adsorption is also affected by stirring in the mixing process and the more quickly adsorbate molecules will collide with one another, so accelerating the adsorption process (Widayatno et al., 2017).

In physical characteristics, the most critical factor of an adsorbent is the pores microstructure that results in a high surface area; a highly porous solid may be carbonaceous or inorganic in nature, manufactured or naturally occurring, and under certain conditions may even have real molecular sieving properties. The adsorbent's surface area increases as its size decreases, increasing the probability of substances adhering to its surface and increasing the amount of adsorption. Additionally, the adsorbent must possess good mechanical characteristics, such as strength and resistance to attrition. Adsorbents must be chosen with high surface area and porosity as well as quick adsorption equilibrium kinetics to remove contaminants. Furthermore, the mechanical and adsorptive capabilities of the adsorbent must be restored effectively (Anantharaman & Begum, 2011; El-Naas & Alhaija, 2013; Pellenz et al., 2023). In this characteristic, adsorbent materials should be evaluated based on their structure, topography, morphology, magnetic properties, and size. X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), surface area and porosimetry analysis, vibrating sample magnetometry (VSM), and dynamic light scattering (DLS) are a few other methods that can be used to conduct these studies (Pellenz et al., 2023).

In the chemical characteristics of the adsorbent, several factors affect the adsorption mechanisms such as solubility to adsorbents, co-adsorption, and stirring process if given. If solubility is high, then the adsorption process will be hampered because dissolve solute/adsorbate opposite to the attractive force of the adsorbent on the adsorbate. Additionally, an adsorbent that has adsorbed a substance will have more adsorption energy for certain adsorbates than the initial adsorption energy. Furthermore, if mixing is done, the more quickly the stirring, the more the adsorbate molecules and adsorbents will clash, which will quicken the adsorption process (Widayatno et al., 2017). In this characteristic, adsorbent materials should be evaluated based on the surface of the material and are directly related to the adsorption mechanisms, such as hydrogen bonding, complexation, coordination/chelation, electrostatic, hydrophobic, and stacking interactions. Ultraviolet–visible spectroscopy (UV–vis), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray energy dispersive spectroscopy (EDX), and Zeta potential are a few other methods that can be used to conduct these studies (Pellenz et al., 2023).

In addition, other factors must be considered, one of which is the characteristics of the adsorbate. The characteristics of the adsorbate are related to the type of material to be adsorbed in the adsorption system, whether it is an electrolyte or not. Adsorption will take place faster and produce greater adsorption if the adsorbate is an electrolyte solvent. This is because the electrolyte solution is ionized so that in the solution there are ions with opposite charges which causes the Van der Waals attraction to increase so that the adsorption capacity increases (Adom, 2020).

For industrial purposes, there are various adsorbents divided based on the type of chemical interaction and the source of the adsorbent. Based on the type of chemical interaction, adsorbents used commercially can grouped into two, namely polar and non-polar adsorbent. Polar adsorbents are also called hydrophilic, included silica gel, activated alumina, and zeolite. It has great adsorption power to carboxylic acids, alcohols, alumina, ketones, and aldehydes. Meanwhile, non-polar adsorbents are also called hydrophobic, included nanomaterial adsorbent, adsorbent polymers and activated carbon. It has adsorption power which is great against amen and alkaline compounds (Widayatno et al., 2017).

DEVELOPMENT OF SELECTIVE ADSORBENT

Based on the adsorbent source, the type of adsorbent varies from natural to synthetic materials, which can be in raw materials, results of physical and/or chemical modifications, frameworks, and composite materials. There is material of adsorbent commonly applied, included zeolites, siliceous materials, clay materials (kaolinite, bentonite), activated carbon, chitosan, polymer adsorbent, nanocomposite, and other (Pellenz et al., 2023).

Mineral-Based Adsorbent

Mineral adsorbent is type of adsorbent which sourced from natural, such as clay materials, zeolite, and other materials. The most used types of mineral adsorbents are zeolite, silica, and clay material (El-Naas and Alhaija, 2016).

Zeolite is a microporous selective adsorbent that can be produced synthetically and naturally with a natural surface area of 99,096 m^2 /g (Asadollahzadeh et al., 2021; Sumari et al., 2018). Zeolite minerals are aluminosilicate crystals containing alkaline cations and alkaline earth which are characterized by the ability to reversibly hydrate/dehydrate and exchange some of the constituent cations with a homogeneous solution (aqueous), both without major changes in structure (Pabalan & Bertetti, 2001). The framework of the zeolite structure is formed from a tetrahedral TO_4 network (T is aluminum (AlO_4) or silicon (SiO_4) atoms) which are bonded to one another through the sharing of the four oxygen atoms in the corners (Vasconcelos et al., 2023). Due to their ion exchange, adsorption and molecular sieve properties, as well as their geographically widespread abundance, zeolite minerals have been widely used in various applications, one of which is zeolite mineral based adsorbents in rare earths recovery (Pabalan & Bertetti, 2001).

Ion exchange (IX) in REE recovery is the separation of REE ions from solution using inorganic solid oxides or organic ion exchange resins (in this case zeolite) which contain a negative charge. Usually, ion exchangers have the important property of stoichiometrically and reversibly exchange the ions they contain (A) for other ions that come from the solution (B). Therefore, it can be represented by the reversible reaction shown in Equation 9, the metal ion concentration is defined as overbar A˜ and B˜ (El Ouardi et al., 2023):

$$|Z_A|B^{Z_B}(aq) + |Z_B|R - A^{\sim Z_A}\,(s) \leftrightarrow |Z_B|A^{Z_A}(aq) + |Z_A|R - B^{\sim Z_B}\,(s) \qquad (8)$$

where z is the ionic charge, and R is the functional group in the resin.

One of the zeolite minerals in the recovery of REEs is the adsorption of Ce^{3+} by zeolite synthesized from kaolinite after the REE leaching process (Figure 6) (Ji and Zhang, 2022). In this method, REE recovery is carried out on kaolinite which was previously thermally activated at a temperature of 600 °C to become meta kaolinite which is then used for the leaching process at a fixed pH. At pH 0.00 at 25 °C, more than 90% of REEs were leached from meta kaolinite samples. The leaching residue then undergoes base activation for zeolite synthesis. Pure zeolite A with a relative crystallinity of 100% was successfully synthesized at a temperature of 80 ◦C for 6 hours using 3 M NaOH as an alkali activator. While the synthesis conditions become increasingly harsh, the metastable zeolite A gradually transforms into the more stable sodalite. Sodalite with high purity can absorb Ce^{3+} with an adsorption capacity of 53 mg/g at pH 6.0. The adsorption process parameters used were ion concentration of 3,000 mg/L, adsorbent weight of 2 g/L, and stirring at a speed of 400 rpm at a temperature of 25 °C.

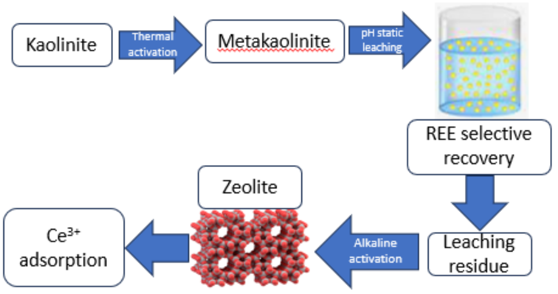

Figure 6. A Zeolite-Synthesized Kaolinite Illustration of the REE Recovery Process (Ji and Zhang, 2022)

Another research result is clinoptilolite transcarpathian zeolite which can adsorb Nd^{3+} and Gd^{3+} ions with different adsorption mechanisms (Asadollahzadeh et al., 2021; Vasylechko et al., 2018). This variation of the mechanism is effective for the separation of neodymium and gadolinium with maximum adsorption capacities for Nd^{3+} and Gd^{3+} ions under optimum conditions of 1.81 and 6.5 mg/g, respectively. In this case, Nd^{3+} is adsorbed by ion exchange mechanism while Gd^{3+} can be adsorbed by hydrolysis of Gd^{3+} which dissolves on the surface of the zeolite. The adsorption and desorption processes were both carried out at a temperature of 20 °C (Vasylechko et al., 2018).

Parameters of experiment to achieve optimal conditions for Nd^{3+} adsorption are flowrate of Nd^{3+} solution with a concentration of 1.0 µg/ml through absorbent 5 ml/min, zeolite grain diameter of 0.20–0.31 mm with a weight of 0.6 g/L and pH 6.5. The best Nd desorption process is using a 7 M HNO_3 solution with a desorption yield of around 98% Nd concentrated in zeolite (Vasylechko et al., 2018). Parameters of experiment to achieve optimal conditions for Gd^{3+} adsorption are pre-treatment of zeolite which is calcined at a temperature of 250 °C; flow rate of Gd^{3+} solution with a concentration of 1.0 µg/ml through absorbent 5 ml/minute; zeolite grain diameter of 0.20–0.31 mm with a weight of 0.6 g/L; pH 9.5. An effective Gd desorption process is a 1 M KCl solution, acidified to a pH of 2.6, with a desorption yield of about 100% Gd from the zeolite matrix (Vasylechko et al., 2018).

Silica is widely used as an adsorbent in REE recovery because of its high surface area, mechanical strength, thermal stability, and easy manufacturing processes. Moreover, it can be easily functionalized for specific adsorption (Asadollahzadeh et al., 2021). Silica in gel is widely used in various applications. Silica gel is made by agglomerating colloidal silicic acid which can produce porous and nanocrystalline granules in several sizes with a surface area range of 250 - 900 m^2/gram (El-Naas & Alhaija, 2013).

Recent research on silica as an adsorbent is carbon nanotubes (CNTs) reinforced silica composite with a maximum adsorption capacity for La, Sc and Y ions under optimum conditions, respectively 103; 32.9; and 68.8 mg/g. In this case, both types of CNTs, Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) are functionalized with nano-silica using silanization process, with (3-amino-propyl) triethoxy silane (APTES) as coupling agent. In addition, the coordination ligand, 1-(2-pyridylazo)-2-naphthol (PAN), is grafted onto the CNT-silica nanocomposite to increase selectivity through two different grafting routes/stages, namely the one-pot synthesis process. and step-by-step telescopic (Figure 7). The adsorption test parameters are using ion concentration of 2 – 5 mg/L, adsorbent weight of 1 g/L, pH 4, and contact time at 1440 minutes which is carried out at 25 °C (Asadollahzadeh et al., 2021; Ramasamy et al., 2019).

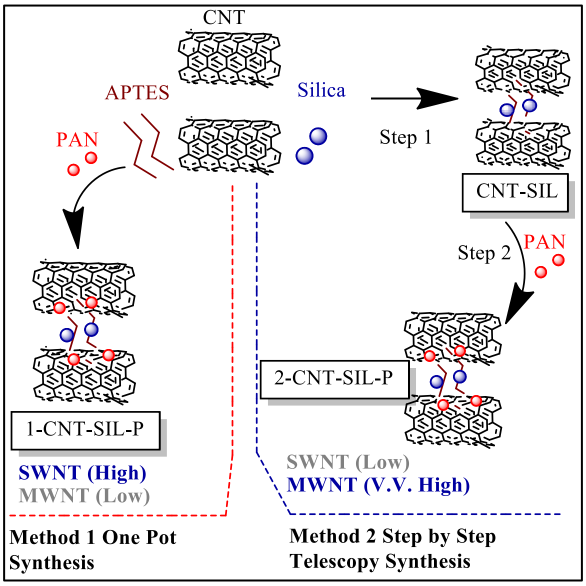

Figure 7. A schematic representation of the REE recovery process utilizing carbon nanotubes (CNTs) in reinforced silica (Ramasamy et al., 2019)

Clay material is a material taken from natural deposits with a surface area ranging from 150-250 m^2/g after acid treatment (El-Naas & Alhaija, 2013). One type of clay material used as an adsorbent for REE recovery is kaolinite (KLN) (Asadollahzadeh et al., 2021). One of the developments in this kaolinite material is grafting polyelectrolyte brushes on the kaolinite surface (PAA-KLN). PAA-KLN is kaolinite (KLN) grafted with PAA (polyacrylic acid) brushes containing many carboxyl groups to improve the adsorption performance of the kaolinite surface through the following steps: modification of the KLN surface by Al^{3+} catalyst, and high grafting efficiency. induced by BP (Benzophenone) encapsulated m-KLN particles and UV irradiation. Due to the good hydrophilic PAA chain in solution, PAA-KLN showed excellent adsorption performance for Ce^{3+}, which was able to reach equilibrium quickly within 40 minutes with a high adsorption capacity of 189.63 mg/g. The saturated adsorbent can be reused according to the desired performance of about 91% after six successive adsorption-desorption cycles using 0.2 M dilute hydrochloric acid. Other adsorption test parameters are an ion concentration of 100 mg/L, an adsorbent weight of 0.5 g/L, and a pH of 5.6 which was carried out at 25 °C (Asadollahzadeh et al., 2021; Zhou et al., 2018).

Biomaterial-Based Adsorbent

The biomaterial-based adsorbent is a type of adsorbent from biological materials, which the most commonly used are activated carbon, and chitosan (Ho, 2022; N'diaye et al., 2022; Opeolu et al., 2010). Activated Carbon/Charcoal is the oldest known adsorbent and is often synthesized from carbonaceous materials (agricultural waste, different parts of the plants, biomass, wood, lignite, coconut shells, coal, and other materials) with a high carbon content and a low inorganic concentration using various activation processes. Physical activation and chemical activation are both activation process (El-Naas & Alhaija, 2013; Ho, 2022).

In physical activation, it uses gases to create activated carbons from the precursor. Typically, activation is followed by carbonization of the precursor. The precursor is pyrolyzed in the first stage, known as carbonization, at temperatures between 600 and 900 °C in an inert environment (nitrogen, argon), producing char, which is typically nonporous. The process of activation involves exposing the material to oxidizing atmospheres (carbon dioxide, oxygen, or steam), typically at temperatures between 600 and 1200 °C. This removes the more disorganized carbon and creates a highly developed porous structure with a large surface area. Meanwhile, in chemical activation, chemicals like H_3PO_4, KOH, or NaOH are impregnated, and then the material is heated between 450 and 900 °C while being circulated with a gas (often nitrogen). It's thought that during chemical activation, the carbonization and activation processes happen simultaneously. Because it takes less time and heat to activate the material, chemical activation is typically chosen to physical activation (El-Naas & Alhaija, 2013). Generally, activated carbon which are product formed by either of the methods, has a large surface area ranging from 500 to 2000 m^2/g and an extremely porous structure (El-Naas & Alhaija, 2013). In other literature, surface area ranging typically from 800 to 1400 m^2/g and the presence of small pores of various sizes ranging typically from between 2 and 500 Å (Sorrels et al., 2018). This difference in characteristics is due to the type of material used. In general, coconut activated carbon is better at greater humidity levels than coal-based activated carbon (Sorrels et al., 2018).

Adsorption on activated carbon has been shown to typically not be selective because it happens due to Van der Waals forces (physisorption) (El-Naas

& Alhaija, 2013). Therefore, pure activated carbon is not suitable for REE recovery, so its surface is functionalized with the formation of oxygen functional groups to increase REE adsorption efficiency (Asadollahzadeh et al., 2021). One method of modifying the functionalization of activated carbon with oxygen functional groups for REE recovery is modification of activated carbon with Potassium Permanganate ($KMnO_4$) (Kano et al., 2017) and ethylenediaminetetraacetic acid (EDTA) (Babu et al., 2018).

Modification of activated carbon with Potassium Permanganate succeeded in absorbing several REE ions, namely Y, Yb, Sc, Lu, La, and Eu with an adsorption capacity of 89.5; 84.6; 121; 75.9; 71; and 97.2 mg/g, respectively. In addition, this method can be desorbed using 10% HNO_3 with a recovery of about 70% after 3 successive adsorption-desorption cycles. Other test parameters are ion concentration of 100 µg/L, adsorbent weight of 0.25 g/L, pH 3 and contact time of 480 minutes which was carried out at a temperature of 25 °C (Kano et al., 2017).

The modified activated carbon functionalized with EDTA (EDTA-AC) was able to absorb Nd^{3+} with an adsorption capacity of 71.42 mg/g. The EDTA-AC synthesis process was carried out by reacting oxidized activated carbon with N-[(3-trimethoxysilyl) propyl] ethylenediamine tri-acetic acid (TMS-EDTA) (Figure 8). The optimum conditions for the adsorption process are as follows: pH 5 (addition of 0.1 M NaOH), ion concentration of 0.15 mg/L, adsorbent weight of 2 g/L, and contact time of 240 minutes, carried out at a temperature of 20 °C with a stirring speed of 250 rpm. The desorption process uses 1M HCl after five successive adsorption-desorption cycles with a regeneration efficiency of about 90% (Babu et al., 2018).

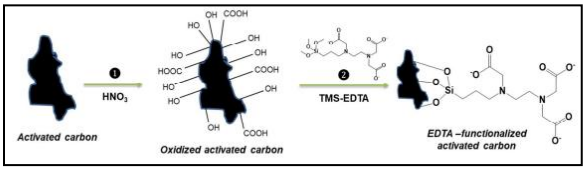

Figure 8. EDTA-AC synthesis with TMS-EDTA adapted from (Babu et al., 2018)

In this case, Nd^{3+} reacts with the organic EDTA- ligand to produce the Nd-EDTA complex. The reaction that occurs is as follows (Ouardi et al., 2023).

$$REE^{3+} + \gamma L^{n-}\ s \rightleftarrows REEL\gamma^{\ (3-\ \gamma n)} \tag{9}$$

Where L^{n-} is an inorganic or organic ligand and γ is the coordination number.

Chitosan (CS) or (β-(1 →4)-N-acetyl-d-glucosamine), is a biocompatible, biodegradable, and nontoxic polysaccharide achieved from the deacetylation of chitin, the major component of the exoskeleton of crustaceans such as shrimps, lobsters as well as from terrestrial organisms such as silkworms, honeybees, and mushrooms (Boakye et al., 2022). In contrast to other polysaccharides, chitosan contains nitrogen, and its carbon-2 amino group replaces the hydroxyl group of cellulose. According to reports, flake chitosan has a lower surface area (less than 10 m^2/g), is non-porous, and is non-adsorbent. As a result, adjustments that are both physical and chemical are needed to increase the surface area and improve the adsorption capacity. However, due to its many benefits, including chemical stability, affordability, good reactivity (due to hydroxyl and amino groups), and selectivity, chitosan has been employed to remove contaminants (Ho, 2022). One of the chitosan modifications to increase the adsorption capacity of rare earth ions is a chitosan sponge modified with diglycolic acid (Bai et al., 2018) and an ion-imprinted macro-porous chitosan membrane (II-MAC) (E. Liu et al., 2017).

Modification of chitosan with diglycolic acid successfully adsorbed Y and Eu ions with adsorption capacities of 40.7 and 79 mg/g, respectively. The parameters of the process are ion concentration of 20 mg/L, adsorbent weight of 6 g/L, pH 0.5 - 7, and contact time of 720 minutes which was carried out at a temperature of 25 °C (Bai et al., 2018).

Another modification of chitosan is II-MAC. In this case, ion-printed membrane materials (II-MAC) with interconnected 3D macro-porous structures were prepared using the immersion-precipitation-evaporation method to selectively adsorb Dy^{3+} (SPE method). With this modification, it can absorb Dy ions with a maximum adsorption capacity of 23.3 mg/g, optimum at pH 7.0; temperature of 25 °C, and adsorption equilibrium was reached within 150 minutes. In addition, the parameters of the adsorption process used were an ion concentration of 50 mg/L with an adsorbent weight of 1 g/L, while the desorption process used 1M HCl after one successive adsorption-desorption cycle with a regeneration efficiency of around 92%(E. Liu et al., 2017).

Polymeric-Based Adsorbent

Polymeric-based adsorbent or polymeric adsorbent is synthetic spherical polymers with defined pores and high surface areas that are mostly used in aqueous applications to remove organic compounds effectively and selectively. In addition, these adsorbents have an ideal skeleton strength, and their fundamental physical and chemical characteristics, such as internal surface area and pore size distribution, may be changed by altering the polymerization conditions. There are two methods of polymerization to synthesize polymer adsorbents: suspension polymerization and post-crosslinking of polymers (Pan et al., 2009).

In recent developments, impregnation technology has been successfully applied to increase the adsorption capacity of polymer adsorbents and ion exchange processes as a result of the influence of surface functional groups (Asadollahzadeh et al., 2021). One of these technologies in the recovery of REEs is the application of La-ion imprinted polymer as an adsorbent in the extraction of Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, and Gd^{3+} (Yusoff et al., 2017).

In this method, La-ion imprinted polymers (L-IIPs) are synthesized using the appropriate REE ions and a complexing agent as a Schiff base ligand with the addition of ethylene glycol-dimethyl acrylate (EGDMA) as a cross-linking agent. 4-vinylpyridine as functional monomer, and 2,2-azobisisobutyronitrile (AIBN) as initiator. After polymerization, a desorption process was carried out using a solution of 10 mL, 2 mol/L HCl for 2 hours of stirring (Figure 9). The results show that this method is efficient with very good selectivity for REE ions over other ions with the same radius and charge. The maximum adsorption capacity is estimated at 125.3; 126.5; 127.6; 128.2; and 129.1 mg/g for Pr, Nd, Sm, Eu, and Gd, respectively. The test parameters used were ion concentration of 50 mg/L, adsorbent weight of 0.5 g/L, pH 6 and contact time of 90 minutes (Yusoff et al., 2017).

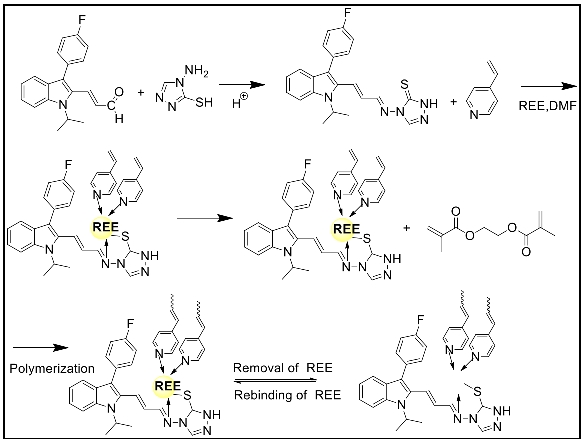

Figure 9. L-IIPs Synthesis Process (Yusoff et al., 2017)

Nanocomposite-Based Adsorbent

In recent technological developments, the properties of adsorbent materials can be significantly improved by several methods, including the addition of nanoparticles, namely the formation of nanocomposites. Adsorbent materials can be conjugated or blended with other materials to form composites. They can be conjugated with nanomaterials to form nanocomposite, such as Carbon-based Nanomaterial. Some Carbon-based nanomaterials that are the most commonly for the removal of hazardous metal ions and recovery of rare earth elements are graphene oxide (GO) and carbon nanotube (CNT).

Graphene is a planar two-dimensional material made of firmly bonded carbon atoms in a hexagonal honeycomb lattice with a molecular bond length of 0.142 nm thickness of each layer is about 0.33 nm. The most widely used and common resource for producing graphene is graphite (Figure 10 (a)) (Aqel et al., 2012; Badiei et al., 2021). The distinguishing qualities of graphene, such as its high surface area, excellent mechanical strength, high electrical and thermal conductivity, and high optical transmittance, are well explained by the chemical structure and shape of its layers. There are countless options for graphene's functionalization because of its chemical shape (Badiei et al., 2021). The most popular and recent techniques for producing or extracting graphene are chemical exfoliation, chemical vapor deposition (CVD), thermal CVD, microwave synthesis, and colloidal suspension from graphite oxide. However, there are downsides to every strategy. Therefore, the desired product's preferred size and purity are taken into consideration when choosing the preparation technique (Badiei et al., 2021; Cardoso et al., 2019).

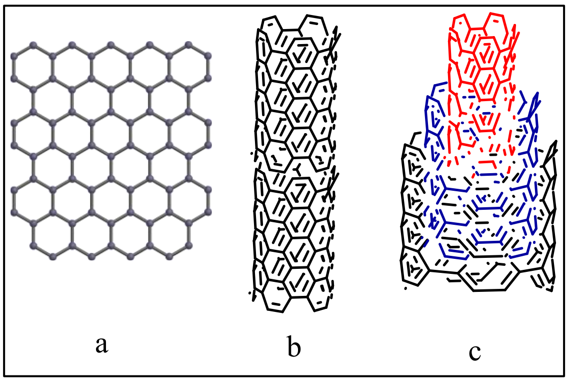

Figure 10. Type of CNTs and Other Carbon Structures. (a) Graphite Flat Sheet; (b). SWCNT; (c). MWCNT. (Aqel et al., 2012)

The oxidized derivative of graphene known as Graphene Oxide (GO) is produced through chemical or thermal reduction procedures with polar functional groups that contain oxygen, such as hydroxyl (-OH), epoxide (C-O-C), and carboxyl (-COOH) groups (Figure 11). It is a two-dimensional (2D) carbonaceous layered substance made of a carbon sheet with a variety of intriguing chemical, mechanical, and electrochemical characteristics. The hydroxyl and epoxide functional groups already present confer the hydrophobic character and aid in π-π interactions. The GO surface's carboxylate and hydroxyl groups can form hydrogen bonds and Van der Waals interactions to increase its adsorption capacity.

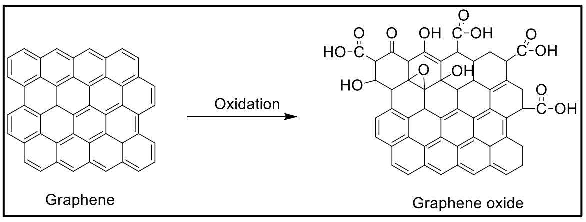

Figure 11. Structure of Graphene and Graphene Oxide (GO) (Badiei et al., 2021)

The whole sheet is strongly hydrophilic because of polar oxygen-containing groups and therefore is soluble in several solvents particularly in water, while insoluble in organic solvents such as toluene and chloroform (Badiei et al., 2021).

The potential of graphene oxide (GO) and graphene (G) for a variety of applications has been demonstrated during the past several years. G-based nanomaterials exhibit special physicochemical characteristics. Theoretical specific surface area of G-based nanomaterials is 2630 m^2 /g, and they exhibit highly intriguing qualities like as strong thermal conductivity (5000 W/mK) at room temperature, superior mechanical capabilities, and high electron mobility at room temperature (250,000 cm2/Vs) (Ashour et al., 2017).

Carbon nanotubes (CNTs) are a type of carbon having a diameter of a nano meter and a length of a micro meter (with a length to diameter ratio greater than 1000), which are distinctive nanostructures with exceptional electrical and mechanical capabilities because of their close resemblance to graphene or to their one-dimensional appearance. The cylindrical graphitic sheet (also known as graphene) that makes up the structure of CNT is rolled up into a seamless cylinder with a diameter of about a nano meter, where some CNT ends are open, while the others are sealed with complete fullerene caps (Aqel et al., 2012; Cardoso et al., 2019)

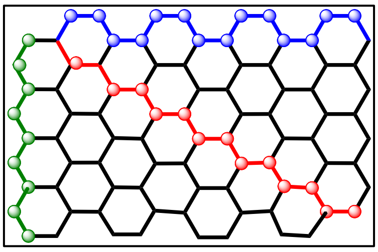

Figure 12. SWCNT classification: Chiral (Red), Zigzag (Green), and Armchair (Blue) (Cardoso et al., 2019)

From a structural perspective, there are two basic categories of carbon nanotubes, Single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). Single-walled carbon nanotubes (SWCNTs) are a single sheet of graphene which rolled across itself to create a cylindrical tube. Meanwhile, multi-walled carbon nanotubes (MWCNTs) are a multiple layer of graphene which rolled across themselves to create a cylindrical tube or a group of concentric SWCNTs with different diameters. The type of CNTs and other carbon structures can be seen in Figure 10 (Aqel et al., 2012). The hexagonal network of graphene in the SWCNT structure depends on how near they are to one another. These nanotubes can be found in three different shapes, known as armchair, zigzag, and chiral (Figure 12). The zigzag and chiral types of carbon nanotubes can either be conductors or semiconductors, but all carbon nanotubes of the armchair type are conductors (Cardoso et al., 2019).

The primary synthesis methods of CNTs can be categorized into the following: (1) high temperatures methods, such as electric arc discharge and laser ablation; and (2) moderate temperatures methods, such as chemical vapor deposition with catalyst assistance. The methods of carbon nanotube synthesis have been continuously improved to produce pure nanotubes in sufficient quantities (Cardoso et al., 2019).

Some researchers discovered that carbon nanotubes were more desirable than activated carbon and clay due to their great selectivity and advantageous Physicochemical stability. In addition, carbon nanotubes has unique properties, i.e. excellent electrical characteristics, a sizable specific surface area, good superior thermal conductivity (2000–6000 W/m.K), a high elastic modulus (1000–3000 GPa), and a high tensile strength (50–100 GPa) (Ho, 2022).

RECOVERY TECHNOLOGY OF RARE EARTH ELEMENTS USING NANOCOMPOSITE-BASED ADSORBENT

Based on the previous explanation, the basic principle of the adsorption process in REEs recovery is a method in which the adsorbate containing REE ions collects on the surface of the adsorbent and forms a molecule or a thin layer film. Adsorption can produce very selective separation and high concentration factor values. Easily controlled parameters make it possible to easily adapt this method to changing conditions. The functional groups on the surface of the adsorbent are used to selectively adsorb RE ions for the extraction and separation of REEs (Asadollahzadeh et al., 2021). Graphene oxide (GO) and carbon nanotubes are materials with carbon nanostructures. The structure of the surface is very complex and depends on the raw materials, production methods and pre-treatment processes. LTJ adsorption was mainly controlled by electrostatic forces, which are connected to the various surface functional groups (O donors), and primarily regulate the sorption of REEs. Additionally, the oxidation of the carbon surfaces results in a surface that is more hydrophilic and contains more functional groups that include oxygen, such as hydroxyl (-OH), carbonyl (-C=O), and carboxyl (-COOH) groups, which can improve the ion exchangeability of the carbon material and also increase the possibility of further modification and functionalization of the graphite surface (Cardoso et al., 2019; Pyrzynska et al., 2016).

The efficiency of the entire process depends on variables such as adsorption capacity or kinetics that may affect the recovery of REEs. However, the following factors must be considered in the adsorption process to recover REEs (Cardoso et al., 2019):

- The pH of the batch will have an impact on the metal ions and the sorbent; the surface charge of the sorbents depends on how acidic the electrolyte is around them. Because REE adsorption is mostly caused by electrostatic forces, the surface charge of the sorbents must be negative.

- Temperature, as insufficient temperatures might reduce the sorption process' effectiveness.
- Dose of sorbent, as the recovery rate should theoretically increase with dose
- REE initial concentration because, for a given dose of sorbent, higher concentration values result in lower rates of sorption;
- Stirring rate, which regulates the rate of mass transfer and particle dispersion.

In addition to the above, another factor that must be considered is the material used as a sorbent. The following is a recovery process that uses nanocomposite-based adsorbents, including GO and CNTs, materials that are generally used.

Graphene-Based Composite

The graphene oxide has good adsorption capabilities because of its O-based surface functional group, but in more complicated aqueous conditions it loses effectiveness because REEs have a high affinity for O donors (Cardoso et al., 2019). Schematic of the chemical reaction of the adsorption process of REE ions on GO adsorbent occurs due to the deprotonation of the GO surface (Figure 13). Therefore, several functionalization methods of graphene have been carried out to obtain new properties for material efficiency, such as GO nanosheet, magnet GO and others.

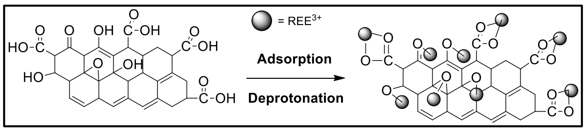

Figure 13. Schematic of the adsorption process of REE Ions on GO Surfaces (Ashour et al., 2017)

One of GO's developments in REE recovery is GO nanosheet which synthesized and used as a coagulant for REEs. The GO nanosheet adsorption capabilities of La^{3+}, Nd^{3+}, Gd^{3+}, and Y^{3+} which parameters experiment is (Ashour et al., 2017):

- All metal ions solutions were subjected to a range of pH values between 3 and 8, and either nitric acid or sodium hydroxide were used to change the pH values.
- To evaluate the adsorption kinetics at pH = 6,
- The contact time was adjusted from 1 to 120 min. The time to reach equilibrium is 30 minutes.
- The temperature range used to explore the thermodynamics of adsorption was 278 K to 318 K. The temperature at which equilibrium is reached is 298 K
- From 5 mg/L to 50 mg/L starting concentrations were used to study the adsorption isotherms.
- Desorption process using HNO_3 solution (0.1 – 1.0 M). The percentage of recovery is around 99% achieved at a concentration of 0.1 M HNO_3.

The adsorption capacities of La^{3+}, Nd^{3+}, Gd^{3+}, Y^{3+} is estimated at 85.67; 188.6; 225.5; and 135.7 mg/g, respectively (Ashour et al., 2017).

The next development of this material is the modification of GO into GO@MgSi (graphene oxide@$Mg_3Si_4O_9(OH)_{10}$) coated silicate nanocomposite which has been successfully preconcentrated Eu^{3+}. This nanocomposite has a hierarchical structure with ultrathin MgSi lamellae spread over the surface of the GO sheet. The high adsorption capacity for Eu^{3+} is around 344.82 mg/g. The test parameters used were ion concentration of 25 - 50 mg/L, adsorbent weight of 1.2 g/L, pH 2-10.5 and contact time of 300 minutes which was carried out at a temperature of 25 °C. The desorption process used 1M HCl solution with a recovery of about 60% after 4 successive adsorption-desorption cycles (Wang et al., 2018).

Carbon Nanotubes (CNTs)

As previously explained, CNTs explicitly include a variety of unique physicochemical characteristics, making it an attractive research target in various fields, one of which is as an adsorbent in REE recovery. Because of this, researchers are continuously developing practical applications and characterization of the CNT manufacturing process. The improved CNT properties were successfully manifested through surface functionalization. Functionalization can be covalent (chemical functionalization) or non-covalent (physical functionalization) which affects the surface characteristics, directly affecting the ability of the carbon nanotubes to sorb (Figure 14) (Cardoso et al., 2019).

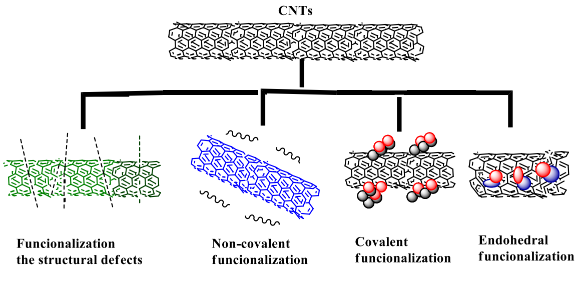

Figure 14. Types of Functionalization Techniques for Carbon Nanotubes (Cardoso et al., 2019)

The pH value of the CNT is an important in the uptake of rare earths ions because the surface charge depends on the acidity of the surrounding electrolyte. At $pH>pH_{PZC}$ (Point of Zero Charge), metal ions which are positively charged can be absorbed by oxidized negatively charged CNTs. T hus, the uptake of metal ions generally increases with increasing pH. The optimum pH value is in the range of 1.5 – 3. Therefore, low pH acidic solutions such as HNO_3 and HCl are used for the desorption and recovery of REEs in CNTs (Pyrzynska et al., 2016).

In other research, the effect of pH on adsorption capacity can be seen in the modification of CNT-COOH carried out at pH 2 and 4. CNT-COOH was able to adsorb REE ions of 37.9 mg/g and 42.5 mg/g at pH 2 and 4, respectively. These values are higher than GO (36.5 mg/g and 39.7 mg/g at pH 2 and 4, respectively) and Activated Carbon (2.1 mg/g and 2.2 mg/g at pH 2 and 4, respectively). The adsorption process used ion concentration of 300 mg/L, adsorbent weight of 5 g/L, and a contact time of 4 hours which was carried out at room temperature. The desorption process used 2M HNO_3 solution with an average recovery of 101.3 ± 3.0% for pH 2 and 105.5 ± 0.8% for pH 4 (Kilian et al., 2017).

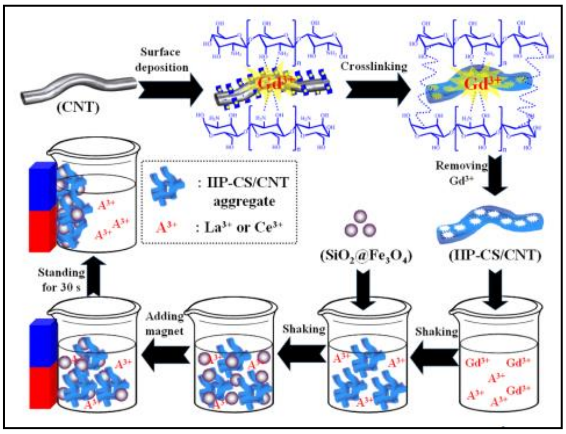

Figure 15. IIP-CS/CNT Preparation and Its Application in Ion Gd^{3+} Selective Adsorption Processes. Adapted from (Li et al., 2015)

In addition to the research above, CNT managed to obtain a maximum adsorption capacity of 121.51 mg/g with adsorption equilibrium achieved within 120 minutes of magnetically retrievable imprinted chitosan/carbon nanotube nanocomposite (mIIP-CS/CNT). In this method, the newest magnetic imprinting nanotechnology can selectively capture Gd^{3+} ions from the REE mixture solution. The development method was carried out by adding Gd^{3+}-imprinted chitosan/CNT nanocomposite (IIP-CS/CNT) and silica-coated magnetite nanoparticles ($SiO_2@Fe_3O_4$) in an adsorbate solution containing REEs. IIP CS/CNT was prepared in advance using the surface deposition−crosslinking method which clearly showed the formation of a coating structure. Interestingly, monomers close to IIP-CS/CNT were netted as a single entity, as the network contains multiple interstitial spaces. When IIP-CS/CNT and $SiO_2@Fe_3O_4$ are dispersed in a mixed REE solution, the magnetic sub microsphere $SiO_2@Fe_3O_4$ will be trapped or attached to the IIP-CS/CNT network leading to magnetization of IIP-CS/CNT. Meanwhile, Gd^{3+} ions can be captured spontaneously. selectively by IIP-CS/CNT magnetization (Figure 15). The adsorption process parameters used an ion concentration of 10,000 µg/L, an adsorbent weight of 2 g/L, and pH 7, which was carried out at a temperature of 43 °C. The desorption process used 1M HCl solution with a constant adsorption capacity of 88 – 86 mg/g after 5 consecutive adsorption-desorption cycles (Li et al., 2015).

CONCLUSION

Rare Earth Elements (REEs) are crucial raw materials for high-tech devices and components in advanced technology. A variety of separation/preconcentration procedures have been implemented as a response of the rising demand for REEs from secondary sources in aqueous solution or wastewater, one of them is adsorption. Adsorption provides several advantages, including high removal efficiency, ease of installation and operation, and low maintenance costs. This process requires adsorbents made of a variety of materials, such as mineral-based adsorbent, polymeric-based adsorbent, biomaterial-based adsorbent, and nanocomposite-based adsorbent. However, the efficiency of the entire REEs recovery process depends on the physical and chemical characteristics of the adsorbent. The physical characteristics of the adsorbent relate to the surface area of the adsorbent, while the chemical characteristics of the adsorbent relate to the ability of the surface of the adsorbent material to the adsorption mechanism that occurs. The choice of adsorbent must have a high surface area and porosity as well as fast adsorption equilibrium kinetics to remove contaminants. Furthermore, the mechanical ability and adsorption of the adsorbent must be reversed (desorption) effectively.

Nanocomposite-based adsorbents are materials that have great potential in the recovery of rare earths. This is based on the several advantages possessed by nanocomposite-based adsorbents, especially GO and CNT, among the raw materials in the form of carbon which are abundant in nature, easy to modify and function, have a large surface area with quite large porosity, are very appropriate for application in adsorption systems and has effective desorption ability. In addition, CNT is more desirable than activated carbon and clay due to its high selectivity, favorable physicochemical stability, excellent electrical characteristics, good thermal conductivity (2000–6000 W/m.K), high elastic modulus (1000–3000 GPa), and high tensile strength (50–100 GPa). The resulting adsorption capacity comparison results between oxidized activated carbon (AC-COOH), GO, and oxidized CNT (CNT-COOH) at pH 2 and 4 show that CNT-COOH > GO > AC-COOH.

So far, many developments has been made to produce the right adsorbent materials that can increase adsorption. Despite the significant of the recent progresses, the purification and recovery of REEs remains a challenging activity and requires continuous researches to improve.

REFERENCES

Adom, S. (2020). *Effects of pH on adsorption of copper(II) onto ground peanut hulls*. Western Carolina University.

Alaqarbeh, M. (2021). Adsorption Phenomena: Definition, Mechanisms, and Adsorption Types: Short Review. *RHAZES: Green and Applied Chemistry*, *13*(0), 43–51. https://doi.org/10.48419/IMIST.PRSM/RHAZES-V13.28283

Anantharaman, N., & Begum, K. M. M. Sheriffa. (2011). *Mass transfer : theory and practice*. PHI Learning.

Aqel, A., El-Nour, K. M. M. A., Ammar, R. A. A., & Al-Warthan, A. (2012). Carbon nanotubes, science and technology part (I) structure, synthesis and characterisation. *Arabian Journal of Chemistry*, *5*(1), 1–23. https://doi.org/10.1016/J.ARABJC.2010.08.022

Asadollahzadeh, M., Torkaman, R., & Torab-Mostaedi, M. (2021). Extraction and Separation of Rare Earth Elements by Adsorption Approaches: Current Status and Future Trends. *Separation & Purification Reviews*, 1–28. https://doi.org/10.1080/15422119.2020.1792930

Ashour, R. M., Abdelhamid, H. N., Abdel-Magied, A. F., Abdel-Khalek, A. A., Ali, M. M., Uheida, A., Muhammed, M., Zou, X., & Dutta, J. (2017). Rare Earth Ions Adsorption onto Graphene Oxide Nanosheets. *Solvent Extraction and Ion Exchange*, *35*(2), 91–103. https://doi.org/10.1080/07366299.2017.1287509

Babu, C. M., Binnemans, K., & Roosen, J. (2018). Ethylenediaminetriacetic Acid-Functionalized Activated Carbon for the Adsorption of Rare Earths from Aqueous Solutions. *Industrial and Engineering Chemistry Research*, *57*(5), 1487–1497. https://doi.org/10.1021/ACS.IECR.7B04274/SUPPL_FILE/IE7B04274_SI_001.PDF

Badiei, M., Asim, N., Mohammad, M., Alghoul, M., Samsudin, N. A., Akhtaruzzaman, M., Amin, N., & Sopian, K. (2021). New graphene nanocomposites-based adsorbents. *Handbook of Nanomaterials for Wastewater Treatment: Fundamentals and Scale up Issues*, 367–416. https://doi.org/10.1016/B978-0-12-821496-1.00006-4

Bai, R., Yang, F., Zhang, Y., Zhao, Z., Liao, Q., Chen, P., Zhao, P., Guo, W., & Cai, C. (2018). Preparation of elastic diglycolamic-acid modified chitosan sponges and their application to recycling of rare-earth from waste phosphor powder. *Carbohydrate Polymers*, *190*, 255–261. https://doi.org/10.1016/J.CARBPOL.2018.02.059

Balaram, V. (2019). Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geoscience Frontiers*, *10*(4), 1285–1303. https://doi.org/10.1016/J.GSF.2018.12.005

Boakye, P., Ohemeng-Boahen, G., Darkwah, L., Sokama-Neuyam, Y. A., Appiah-Effah, E., Oduro-Kwarteng, S., Asamoah Osei, B., Asilevi, P. J., & Woo, S. H. (2022). Waste Biomass and Biomaterials Adsorbents for Wastewater Treatment. *Https://Www.Intechopen.Com/Journals/7/Articles/22, 2022*, 1–25. https://doi.org/10.5772/GEET.05

Cardoso, C. E. D., Almeida, J. C., Lopes, C. B., Trindade, T., Vale, C., & Pereira, E. (2019). Recovery of Rare Earth Elements by Carbon-Based Nanomaterials—A Review. *Nanomaterials 2019, Vol. 9, Page 814*, *9*(6), 814. https://doi.org/10.3390/NANO9060814

N'diaye, A. D., Kankou, M. S., Hammouti, B., Nandiyanto, A. B. D., & Al Husaeni, D. F. (2022). A review of biomaterial as an adsorbent: From the bibliometric literature review, the definition of dyes and adsorbent, the adsorption phenomena and isotherm models, factors affecting the adsorption process, to the use of typha species waste as adsorbent. *Communications in Science and Technology*, *7*(2), 140–153. https://doi.org/10.21924/CST.7.2.2022.977

El Ouardi, Y., Virolainen, S., Massima Mouele, E. S., Laatikainen, M., Repo, E., & Laatikainen, K. (2023). The recent progress of ion exchange for the separation of rare earths from secondary resources – A review. *Hydrometallurgy*, *218*, 106047. https://doi.org/10.1016/J.HYDROMET.2023.106047

El-Naas, M. H., & Alhaija, M. A. (2013). Modelling of adsorption processes. *Mathematical Modelling*, 579–600.

Hidayah, N. N., & Abidin, S. Z. (2017). The evolution of mineral processing in extraction of rare earth elements using solid-liquid extraction over liquid-liquid extraction: A review. *Minerals Engineering*, *112*, 103–113. https://doi.org/10.1016/J.MINENG.2017.07.014

Ho, S. (2022). Low-Cost Adsorbents for the Removal of Phenol/Phenolics, Pesticides, and Dyes from Wastewater Systems: A Review. *Water 2022, Vol. 14, Page 3203*, *14*(20), 3203. https://doi.org/10.3390/W14203203

Humphries, M. (2010). *Rare Earth Elements: The Global Supply Chain*. https://digital.library.unt.edu/ark:/67531/metadc31365/m1/1/high_res_d/R41347_2010Sep30.pdf

Jha, A. R. (2014). Rare earth materials: Properties and applications. *Rare Earth Materials: Properties and Applications*, 1–332. https://doi.org/10.1201/B17045/RARE-EARTH-MATERIALS-JHA

Kano, N., Pang, M., Deng, Y., & Imaizumi, H. (2017). Adsorption of Rare Earth Elements (REEs) onto Activated Carbon Modified with Potassium Permanganate (KMnO4). *Journal of Applied Solution Chemistry and Modeling*, *6*(2), 51–61. https://doi.org/10.6000/1929-5030.2017.06.02.1

Kaya, M. (2016). Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes. *Waste Management*, *57*, 64–90. https://doi.org/10.1016/J.WASMAN.2016.08.004

Kilian, K., Pyrzyńska, K., & Pęgier, M. (2017). Comparative Study of Sc(III) Sorption onto Carbon-based Materials. *Solvent Extraction and Ion Exchange*, *35*(6), 450–459. https://doi.org/10.1080/07366299.2017.1354580

Kim, D., Powell, L., Delmau, L. H., Peterson, E. S., Herchenroeder, J., & Bhave, R. R. (2016). A supported liquid membrane system for the selective recovery of rare earth elements from neodymium-based permanent magnets. *Separation Science and Technology*, *51*(10), 1716–1726. https://doi.org/10.1080/01496395.2016.1171782

Li, K., Gao, Q., Yadavalli, G., Shen, X., Lei, H., Han, B., Xia, K., & Zhou, C. (2015). Selective Adsorption of Gd3+ on a Magnetically Retrievable Imprinted Chitosan/Carbon Nanotube Composite with High Capacity. *ACS Applied Materials and Interfaces*, *7*(38), 21047–21055. https://doi.org/10.1021/ACSAMI.5B07560/SUPPL_FILE/AM5B07560_SI_001.PDF

Liu, E., Xu, X., Zheng, X., Zhang, F., Liu, E., & Li, C. (2017). An ion imprinted macroporous chitosan membrane for efficiently selective adsorption of dysprosium. *Separation and Purification Technology*, *189*, 288–295. https://doi.org/10.1016/J.SEPPUR.2017.06.079

Liu, J., Martin, P. F., & Peter McGrail, B. (2021). Rare-earth element extraction from geothermal brine using magnetic core-shell nanoparticles-techno-economic analysis. *Geothermics*, *89*, 101938. https://doi.org/10.1016/J.GEOTHERMICS.2020.101938

Nandiyanto, A. B. D. (2020). Isotherm Adsorption of Carbon Microparticles Prepared from Pumpkin (Cucurbita maxima) Seeds Using Two-Parameter Monolayer Adsorption Models and Equations. *Moroccan Journal of Chemistry*, *8*(3), 8-3 (2020) 745-761. https://doi.org/10.48317/IMIST.PRSM/MORJCHEM-V8I3.21636

Opeolu, B. O., Bamgbose, O., Arowolo, T. A., & Adetunji, M. T. (2010). Utilization of biomaterials as adsorbents for heavy metals removal from aqueous matrices. *Scientific Research and Essays*, *5*(14), 1780–1787. https://doi.org/10.5897/SRE.9000983

Pabalan, R. T., & Bertetti, F. P. (2001). Cation-Exchange Properties of Natural Zeolites. *Reviews in Mineralogy and Geochemistry*, *45*(1), 453–518. https://doi.org/10.2138/RMG.2001.45.14

Pan, B., Pan, B., Zhang, W., Lv, L., Zhang, Q., & Zheng, S. (2009). Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters. *Chemical Engineering Journal*, *151*(1–3), 19–29. https://doi.org/10.1016/J.CEJ.2009.02.036

Pellenz, L., de Oliveira, C. R. S., da Silva Júnior, A. H., da Silva, L. J. S., da Silva, L., Ulson de Souza, A. A., de Souza, S. M. de A. G. U., Borba, F. H., & da Silva, A. (2023). A comprehensive guide for characterization of adsorbent materials. *Separation and Purification Technology*, *305*, 122435. https://doi.org/10.1016/J.SEPPUR.2022.122435

Pyrzynska, K., Kubiak, A., & Wysocka, I. (2016). Application of solid phase extraction procedures for rare earth elements determination in environmental samples. *Talanta*, *154*, 15–22. https://doi.org/10.1016/J.TALANTA.2016.03.022

Ramasamy, D. L., Puhakka, V., Doshi, B., Iftekhar, S., & Sillanpää, M. (2019). Fabrication of carbon nanotubes reinforced silica composites with improved rare earth elements adsorption performance. *Chemical Engineering Journal*, *365*, 291–304. https://doi.org/10.1016/J.CEJ.2019.02.057

Royen, H., & Fortkamp, U. (2016). *Rare Earth Elements - Purification, Separation and Recycling*. https://urn.kb.se/resolve?urn=urn:nbn:se:ivl:diva-311

Sorrels, J. L., Baynham, A., Randall, D. D., & Schaffner, K. S. (2018). Carbon adsorbers. *US Environmental Protection Agency*, 1–47.

Sumari, Fajaroh, F., Santoso, A., & Wardani, R. K. (2018). Performance of Activated Natural Zeolite/Cu as a catalyst on Degradation of Glycerol into Ethanol

Assisted by Ultrasonic. *Journal of Physics: Conference Series*, *1093*(1), 012036. https://doi.org/10.1088/1742-6596/1093/1/012036

Vasconcelos, A. A., Len, T., de Oliveira, A. de N., Costa, A. A. F. da, Souza, A. R. da S., Costa, C. E. F. da, Luque, R., Rocha Filho, G. N. da, Noronha, R. C. R., & Nascimento, L. A. S. do. (2023). Zeolites: A Theoretical and Practical Approach with Uses in (Bio)Chemical Processes. *Applied Sciences 2023, Vol. 13, Page 1897*, *13*(3), 1897. https://doi.org/10.3390/APP13031897

Vasylechko, V., Stechynska, E., Stashkiv, O., Gryshchouk, G., & Patsay, I. (2018). Sorption of Neodymium and Gadolinium on Transcarpathian Clinoptilolite. *Acta Physica Polonica A*, *133*(4), 794–797.

Voncken, J. H. L. (2016). *Physical and Chemical Properties of the Rare Earths*. 53–72. https://doi.org/10.1007/978-3-319-26809-5_3

Wang, Y., Chi, B., Xiao, C., Chen, D., Wang, Y., & Liu, M. (2018). Graphene oxide@Mg3Si4O9(OH)10: A hierarchical layered silicate nanocomposite with superior adsorption capacity for enriching Eu(III). *Chemical Engineering Journal*, *338*, 628–635. https://doi.org/10.1016/J.CEJ.2017.12.144

Widayatno, T., Yuliawati, T., & Susilo, A. A. (2017). ADSORPSI LOGAM BERAT (Pb) DARI LIMBAH CAIR DENGAN ADSORBEN ARANG BAMBU AKTIF. *Jurnal Teknologi Bahan Alam*, *1*(1), 17–23. https://journals.ums.ac.id/index.php/jtba/article/view/JTBA-0004

Yusoff, M. M., Mostapa, N. R. N., Sarkar, M. S., Biswas, T. K., Rahman, M. L., Arshad, S. E., Sarjadi, M. S., & Kulkarni, A. D. (2017). Synthesis of ion imprinted polymers for selective recognition and separation of rare earth metals. *Journal of Rare Earths*, *35*(2), 177–186. https://doi.org/10.1016/S1002-0721(17)60897-4

Zhou, Q., Fu, Y., Zhang, X., Luo, T., & Luo, W. (2018). Light induced growth of polyelectrolyte brushes on kaolinite surface with superior performance for capturing valuable rare-earth Ce3+ from wastewater. *Materials Science and Engineering: B*, *227*, 89–99. https://doi.org/10.1016/J.MSEB.2017.10.013