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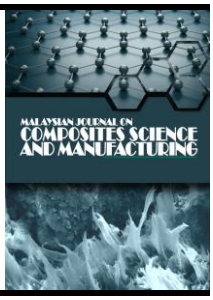

Rare Earth Elements Adsorption Using Electrospun Nanofiber of Blended Nylon 6-6 and Choline Ionic Liquid from Aqueous Solution

Junaid Afridi[1,*], M. Dzul Hakim Wirzal[1,2], Nur Syakinah Abd Halim[1], A.S. Abdul Manaf[1], S. Mohd Hizam[1], M. Ijaz Khalil[3]

[1] Chemical Engineering Department, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia
[2] Centre of Research in Ionic Liquid (CORIL), Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia
[3] University of Chester, Parkgate Rd, Chester CH1 4BJ, United Kingdom

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ABSTRACT

Rare earth elements are among the critical components that are essential to many sectors, especially the production of advanced products. These rare earth elements are now heavily dependent upon by large worldwide enterprises. There have been accounts of separating rare earth elements using diverse adsorbents, including functional polymer compounds, resins, biomaterials, and inorganic nanoparticles. Nevertheless, these materials often encounter constraints related to low adsorption capacity or the risk of causing secondary pollution. This study applied the electrospinning method for making and characterizing nanofibers and enhanced the adsorption of rare earth elements from aqueous solution with nylon 6,6 polymer and choline oleate mix. When compared to pure nylon 6,6 nanofibers, the electrospun nanofibers showed altered morphological characteristics, pore size, and diameter. The effective integration of choline oleate was validated by FTIR spectra, which showed that the functional groups in pure and blended nanofibers were comparable. Adsorption tests revealed that the mixed nanofiber exhibited a higher capacity for adsorbing rare earth elements compared to the pure nanofiber, reaching 295.66 mg/g for the mixed nanofiber and 16.17 mg/g after 24 hours. This improvement was ascribed to the blending-induced addition of functional groups, which promoted stable chelate connections between surface groups and REE ions. The study underscores the potential of choline oleate-blended nylon 6,6 nanofibers as effective adsorbents for REEs, emphasizing the importance of surface modification for improved adsorption performance.

1. Introduction

The International Union of Pure and Applied Chemistry (IUPAC) refers to lanthanides, scandium, and yttrium as rare earth elements [1]. Because of these essential elements' unique qualities, demand for them is predicted to grow exponentially in the next decades [2,3]. Modern products and

* *Corresponding author.*
E-mail address: junaid_22009546@utp.edu.my

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technologies that use these materials include ceramics, high-performance magnets, spacecraft, military aircraft, TVs, optical goods, catalysis, and metalworking [4,5]. The extraction and isolation of rare earth elements (REEs) are becoming more essential because of their rising demand across various industries, given their indispensable role in sustaining contemporary lifestyles [6, 7].

Although rare earth elements' comparable sized sustained triplet ions have almost equal chemical and physical features, separating them is more challenging and costly [8]. There are numerous sophisticated approaches and procedures available for the separation of REEs; however, many of them prove ineffective because they produce significant volumes of radioactive and dangerous waste [9]. According to reports, the NH_3 concentration of the nearly 22 million tons of wastewater produced yearly by the rare earth industry ranges from 2500 to 5500 mg per liter, exceeding China's national emission standard by a hundredfold [10,11]. Addressing this environmental issue requires an annual investment of over 1.6 billion yuan (US$250 million) [12]. The difficulty is in creating viable "clean" processes and strategies that save expenses, energy, and trash while improving the final product's purity [13].

Various techniques have been employed to retrieve REEs, including adsorption [14-16], ion exchange [17], solvent extraction [18], coprecipitation [19], and hydrometallurgy [20]. It is especially important to emphasize that one of the most reliable and affordable methods of treating wastewater is adsorption [21]. Its great efficiency, affordability, and ease of use are the reasons behind this [22, 23]. There have been reports of separating heavy metals and rare earth elements using a wide variety of adsorbents up to this point, these consist of functional polymer compounds, resin, biomaterials, and inorganic nanoparticles [24-26]. However, these materials frequently face limitations in terms of low adsorption capacity or the potential for secondary pollution [27].

The remarkable characteristics of nanofibers, including their strong stability in structure, cost-effectiveness, good porosity, large area of surface /volume proportions, thin layering, minimal base weight, and manageable thickness of the electrospun, make them extremely promising materials [28]. Functionalizing nanofibers with appropriate ligands can be achieved in a feasible and economical manner [29]. For applications involving the separation of REEs, these functionalized nanofibers provide a large surface area support that is efficient [30]. Using electrostatic forces, electrospinning is a feasible method for synthesizing nanofibers with diameters between 45 and 520 nm [31]. Numerous synthetic or natural polymers, as well as mixtures or hybrids of the two polymer types, can be used to make these nanofibers [32]. Nylon 6,6 is considered a flexible synthetic polymer support due to its capacity for covalently binding a large number of ligands [33]. Numerous studies on nylon 6,6 have been conducted as a result of its high mechanical qualities, cost-effectiveness, easy electrospinning, and outstanding physical and reactive properties [34]. Nylon 6,6 nanofiber, while versatile, may lack reactive functional groups [33]. Polymeric nanofibers are surface modified by chemical or physical treatments in modern methods intended to increase the adsorption capacity of nanofibers for metal ions [34].

Conversely, researchers have conducted extensive studies on ionic liquids (IL) as liquid extractants in separation processes due to their low vapor pressure and the ability to be regenerated using metal stripping agents [35]. However, poor biodegradability is a common problem for ionic liquids, which can have negative effects on the environment [36]. Furthermore, the pronounced toxicity exhibited by certain ionic compounds has prompted researchers to either minimize the utilization of ionic liquids or explore alternative, more environmentally friendly substitutes [37]. This research makes use of bio-based ionic liquids (IL), which integrate sustainable and green chemistry into the process. Renewable, biodegradable, and non-hazardous materials, such as sugars, amino acids, and amino alcohols, are used to improve environmental friendliness [38].

Among other macromolecules, amino acids have been selected for the making of ionic liquids. In addition to being abundant and inexpensive, amino acids include a range of functional entities in their side chains, which makes it simple to add chirality and a wide range of characteristics to the ionic liquid [39]. Furthermore, it has been shown that several surface functional entities, encompassing hydroxyl, carboxyl, and amino moieties, can proficiently capture metals through processes like ion exchange, surface binding, electron contribution, and electrostatic allure [40]. Thus far, no studies have been conducted on the making of electrospun nanofibers including amino-based ionic liquid (IL) for the separation of REEs. This work investigated the use of an ionic liquid based on amino acids in the fabrication of nanofibers intended to separate REEs from aqueous solutions.

2. Experimental

2.1 Materials

The study utilized various substances, including choline hydroxide solution (containing 47% weight of choline hydroxide in water, sourced from Sigma Aldrich), oleate (purity of 99%, from Sigma Aldrich), formic acid (with a concentration range of 97–100%, obtained from MERCK), glacial acetic acid (with a purity of 99.75%, procured from VWR Chemicals), nylon 6-6 pellets (purchased from Sigma Aldrich), and rare earth elements (III) nitrate nonahydrate (with a purity of 98%, acquired from Sigma Aldrich).

2.2 Synthesis of Choline Oleate

In Figure 1, the entire process of synthesis of choline oleate is shown. The synthesis procedure involved adding 7.8851 g of ($C_{18}H_{33}O_2$) oleate to 26.334 g of ($C_5H_{15}NO_2$) choline hydroxide solution. The resulting solution was stirred for 2 days at room temperature and then washed with ($C_4H_8O_2$) ethyl acetate to eliminate excess amino acids. Subsequently, the solution underwent rotary evaporation at 65°C for 60 minutes. [41]. To acquire the solutions, the resultant solution was further dried for 48 hours at 65°C in a vacuum furnace. After that, the choline-oleate solution was kept in an argon-filled dry box until it was needed for use or analysis.

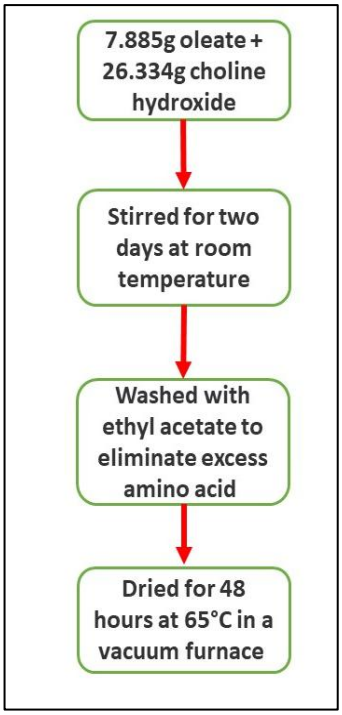

Fig. 1. Flowchart of Choline oleate synthesis

2.3 Preparing Choline Oleate and Nylon 6-6 Solution

Formic and acetic acid were used as solvents, and 1wt% pure choline oleate was added. The resulting solution was stirred for three hours in order to achieve homogeneity. Next, 2.8 g of nylon 6-6 pellets were gradually mixed into the mixture. After being stirred for a full 14 hours or until it became homogeneous at 65°C, the blended solution was ready for use. [42,43].

2.4 Synthesis of Polymer Nanofiber by Electrospinning

Electrospinning technology was utilized to fabricate polymer nanofibers. The needle was filled with a mixed solution that contained nylon 6-6 polymer and choline oleate. A consistently distributed electric field was created by applying an intense voltage of 26 kV, which charged the solution surface at the needle's tip. A 15-centimeter gap was kept between the collection and the syringe tip. The polymer flow rate was set at 0.4 mL/hr, while the rotation speed was maintained at 600 RPM. Before it reached the collector, the electric-charged stream of blended solution produced by the excessive voltage became solid, creating a network of tiny fibers.

2.5 Characterization

The characteristics of the nanofiber were examined, including its surface shape, a cross-section structure, porosity, functional groups. The characterization methods used were FESEM for surface shape, the dry-wet method for porosity evaluation, and FTIR for examining functional categories.

2.5.1 FTIR

FTIR was used to identify the chemically functional groups in the material and offer details on the bonds between compounds and molecular arrangement. For this study, the Perkin Elmer version was utilized.

2.5.2 FESEM

FESEM is a commonly used tool for analyzing the structure by visualizing the inner composition of nanofibers. In this work, the Zeiss Supra 55 VP type of FESEM was utilized. Using carbon tape, the nanofiber was attached to a metal exterior substrate and covered in a coating of gold. Afterward, the high-energy electron beam was scanned in a raster pattern across the surface of the nanofiber for detailed examination [44]. Imaging, qualitative study, and mapping the elements of the nanofiber may be accomplished using this approach.

2.5.3 Dry Wet Method

The dry-wet approach was utilized to assess the porosity of the nanofibers and calculate their weight and volume [45]. Before the nanofibers are measured for thickness (T) and weighed for their initial weight (W_1), they will first be cut into 2 centimeter × 2 centimeter (width by length) pieces. After 10 minutes of soaking in distilled water, the weight of the wet nanofiber (W_2) will be measured. Next, before calculating membrane porosity, the volume of the nanofiber (V_m) and the volume of water in the nanofiber (V_w) will be determined using Eq. (1) and (2), respectively. We will use Eq. (3) to compute the nanofiber porosity.

$$V_m = W \times L \times T \tag{1}$$

where, V_m = Nanofiber Volume (m^3), w = width of nanofiber (m), l = Length of nanofiber (m), t = Thickness of nanofiber (m).

$$V_w = \frac{W_2 - W_1}{\rho} \tag{2}$$

Vw = Water Volume(m^3),
W_1 = Dry nanofiber initial weight(kg),
W_2 = Wet nanofiber final weight (kg),
ρ = Water Density (kg/m^3).

$$P = \frac{V_w}{V_m} \times 100 \tag{3}$$

P = Nanofiber porosity (%)

2.6 Analysis of Adsorption

The ability of nanofiber to adsorb REEs in a solution was tested through experiments [46]. 0.728 grams of $REE(NO_3)_3{\cdot}9H_2O$ and one liter of purified water were used for making a 100 ppm REEs solution. The pH of this solution was inherently neutral (approximately pH 7). Six nanofiber portions,

each measuring two centimeters in area, were made. After that, these nanofibers were put into six flasks with a hundred milliliters of the REEs mixture in each. The first nanofiber was taken out after thirty minutes had passed, and ten milliliters of the fluid was retained. The aforementioned procedure was carried out once more after 1, 1.5, 2, 3, and 24 hours. To guarantee the nanofiber was fully submerged in the REEs solution, the flasks were shaken continuously during the experiment. Room temperature was used for the trials in order to replicate actual working circumstances. Eq. (4) was used to determine the total amount of REEs absorbed on the nanofiber at adsorption equilibrium denoted as Qe.

$$Qe = \frac{(c_0 - c_1) \times V}{m} \tag{4}$$

Qe is the adsorption capacity at equilibrium (mmol/g),
C_1 and C_o are the final and initial concentration of REE ions in a solution (mmol per Liter),
V is the volume solution (L),
m is the polymer nanofibers mass (g).

3. Results and Discussion

3.1 Study of Choline Oleate ^{1}HNMR

Proton NMR uses nuclear resonance with hydrogen-1 nuclei found in a substance's molecules in NMR spectroscopy to ascertain the molecular structure of the material. The choline oleate's 1 H NMR spectra are displayed in Figure 2. The chemical changes seen in the choline oleate nuclear magnetic resonance (NMR) spectrum are in good agreement with values found in previously published research [47]. Particularly, three methyl groups and nine hydrogen atoms are linked to a singlet peak at 3.20 ppm. Furthermore, a multiplet between 3.50 and 3.52 ppm corresponds to two hydrogen atoms connected to a methylene group next to an ethoxy group. Between 3.95 and 4.10 ppm, another multiplet was found, which is indicative of two hydrogen atoms inside a methylene group.

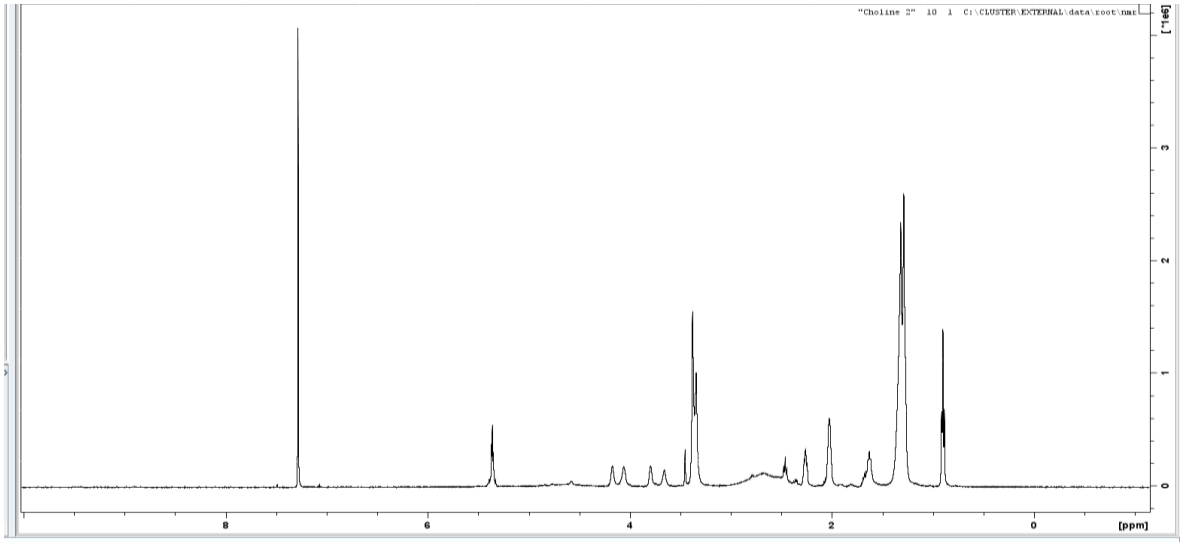

Fig. 2. Choline oleate's ^{1}H nuclear magnetic resonance spectrum

3.2 Characterization of Nanofibers

Figure 3 illustrates FESEM images of both nylon 6-6 nanofibers pure and nanofibers blended with 1 wt% choline oleate at a magnification of 20,000x. As seen in Figure 3, slight alterations in the structure or appearance of both the pure nanofiber and the blended nanofiber were observed. The diameter of the blended nanofiber was observed to be smaller than that of the pure nanofiber. Notably, no bead formation was observed on either nanofiber, indicating the miscibility of the ionic liquid in the blend. The polymer solution's concentration was the variable in this instance.

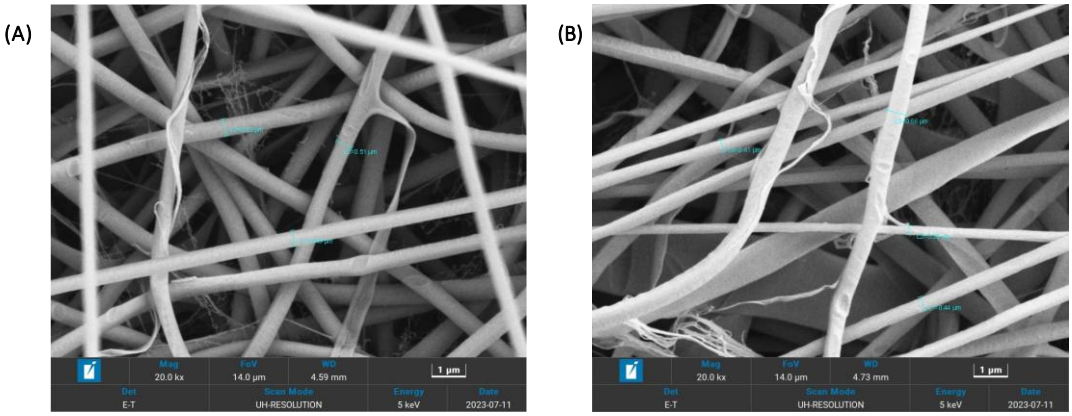

Fig. 3. FE-SEM image for (A) Pure nylon 6-6 nanofiber and (B) Blended with 1 wt% choline oleate at 20000x

The concentration of the polymer is important because it affects the viscosity of the solution, which is connected to the creation of beads on the nanofiber during the electrospinning process [48]. At low concentrations of the polymer solution, the tension between the surface and the electric field that is generated may cause polymer chains to break down, resulting in the development of beads on the nanofibers [49]. When the solution's viscosity is higher than the surface tension, smooth fibers are more likely to develop.

The characteristics of pure nanofiber and blended nanofiber with choline oleate are shown in Table 1. The table shows that choline oleate added to the polymer solution clearly affects the diameter of the nanofibers as well as their pore size. It is evident that mixing choline oleate has increased the pore size of the blended nanofiber since its pore size is substantially greater than that of the pure nanofiber. The increased pore size of the blended nanofiber is correlated with its simultaneous reduced diameter compared to the pure nanofiber. The nanofiber's pore size has increased as a result of this diameter decrease.

Table 1
Nanofiber properties

Nanofiber Type	Pore Size (μm^2)	Porosity (%)	Fiber Diameter (μm)
Pure Nanofiber	0.300 ± 0.02	87.98	0.530 ± 0.02
Blended Nanofiber	0.753 ± 0.03	77.60	0.512 ± 0.03

Ionic liquids (ILs) in polymer mixtures have been demonstrated in earlier research to have an impact on the morphologies of electrospun nanofibers [50]. This is explained by the fact that during electrospinning, IL ions are concentrated on the surface of polymer droplets near the needle's end [50]. Sung *et al.,* showed that the IL's surface is mostly coated in cations when it is kept at a low

temperature. The ionic liquid mixture's surface begins to fill with anions as the concentration of IL rises, changing the fiber diameter [51].

Figure 4 display the Fourier-Transform Infrared (FTIR) spectra for pure nanofiber and blended nanofiber. Upon inspection of these figures, it is evident that the blended nanofiber with choline oleate exhibits nearly identical functional peaks as the pure polymer nanofiber. In the FTIR spectra of the blended nanofiber, a noticeable N-H stretching peak appears at 3299.60 cm^{-1}, while for the pure nylon 6,6 nanofiber, it is at 3290.63 cm^{-1}. The CH^2 stretching peaks for both blended and pure nanofibers are observed at 3082 cm^{-1}. Additionally, the blended nanofiber displays a peak at 1633.35 cm^{-1}, and the pure nanofiber exhibits a peak at 1633.92 cm^{-1}, both representing the amide I band.

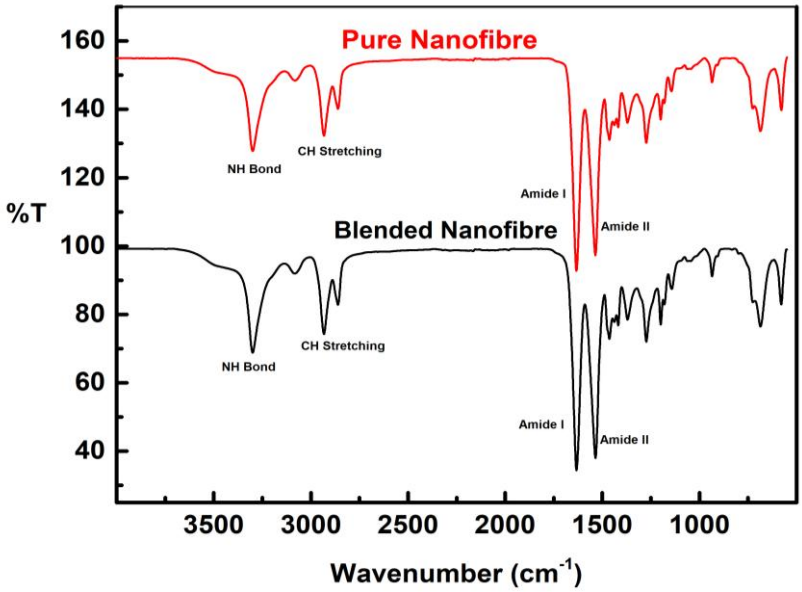

Fig. 4. Pure nanofiber and blended nanofiber FTIR spectra

3.3 Adsorption Analysis

Figure 5 illustrates the rare earth elements (REEs) absorption capacity of blended nanofiber compared to pure nanofiber. The adsorption equilibrium for blended nanofiber and pure nanofiber after 24 hours was recorded at 295.66 mg/g and 15.12 mg/g, respectively. There is a significant difference of nearly 92% between the two nanofibers, with the blended nanofiber exhibiting a superior adsorption capacity over the pure nanofiber.

Blending choline oleate and polymer together introduces several functional groups to the nanofiber surface, which accounts for the enhanced adsorption capability of the blended nanofiber. The surface functionality of the nanofiber is altered as a result of this procedure. Since element ions and carboxylate and amine groups have strong chelate connections, the blended nanofiber has a higher adsorption capability [52]. This result is consistent with other research, including that published by Song *et al.,* [53] which found a significant attraction between the positively charged steel surface and the negatively charged carboxylic acid group in the amino acid during friction. The interaction resulted in the nanofiber surface containing more metal-binding sites, which made it easier to remove REEs from the solution. In order to improve understanding of the bonding dynamics between the ionic liquid and metal ions, Foong *et al.,* [54] used statistical thermodynamic simulations to examine the sigma profile and sigma potential of the amino anion and cation. Furthermore, it was anticipated that oleate amino acid would react with metal ions in a dimeric state [55].

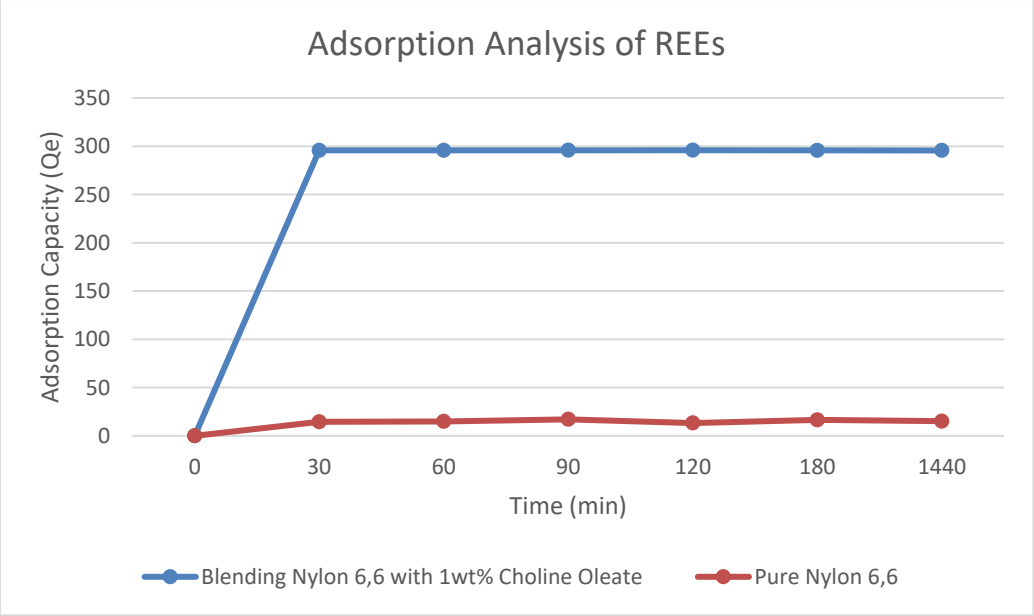

Fig. 5. Rare earth elements adsorption capacity

4. Conclusion

In this research, a nylon 6,6 nanofiber mixed with choline oleate was successfully fabricated. According to the study, adding choline oleate caused the nanofiber's diameter to decrease, which in turn caused the nanofiber's pore size to increase. The increased pore size of the blended nanofibers plays a crucial role in the adsorption of rare earth elements (REEs) by enhancing the accessibility of active sites on the nanofiber surface. This structural modification allows for greater diffusion of REE ions into the nanofiber matrix, facilitating their interaction with carboxylate and amine groups. The FTIR spectra indicated that the functional groups of the blended nanofibers were similar to those of pure nylon 6,6, confirming the successful incorporation of choline oleate.

When compared to pure nanofiber, adsorption studies showed a significant increase in the blended nanofiber's capacity to adsorb REEs. The blending procedure included a number of functional groups that resulted in stable chelate connections between REE ions and carboxylate and amine groups, which was the cause of this increase. As a result, the suggested blended nylon 6-6 with AAIL offered a fresh opportunity to create adsorption materials based on nanofibers for the very effective separation of REEs.

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