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Extraction of Rare Earth Elements from Coal Ash by Chemical Leaching using Deep Eutectic Solvents

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Abstract: The supply of rare earth elements is less, and its demand is high and there is a need for a secondary source to fulfill this demand. This research adopted coal ash as an alternative resource of rare earth elements. mineral acids, ionic liquids, and organic acids were used for the extraction of rare earth elements (REEs) from Coal Ash (CA) which were corrosive, expensive, hazardous, and not friendly to the environment. Our approach was to find innovative reagents that were green to the environment and extract REEs from CA as a replacement for mineral acids, ionic liquids, and organic acids. The researchers synthesized a novel Deep Eutectic Solvent (Choline chloride & Humic acid) for the extraction of REEs. The study conducted experiments on the coal of Sindh Engro Thar Coal Mining Company (SECMC), Pakistan. Based on literature and ASTM standard D-2013 coal was crushed and ground to a size of -250 microns. The leaching experiments were designed with two different parameters (1-2 hours) time and temperature (60-90 Celsius) at a constant 500 revolutions per minute (rpm). After leaching, the filtrate was centrifuged at 4000 rpm for 10 minutes. Both the feed and leachate were analyzed using various techniques, X-Ray fluorescence (XRF), X-Ray Diffraction (XRD), Inductively coupled plasma mass spectrometry (ICP-MS), Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electronic Microscope (SEM). In feed characterization, the XRF results showed that Calcium had the highest percentage which was 35.676%. Calcium sulfate, Diborane, and Magnesium oxide mineral phases were detected by XRD. ICPMS analysis showed the CA sample contained a total of 351.41 PPM of REEs. The concentration of heavy rare earth elements (HREEs) was 119.5 PPM, while the light rare earth elements (LREEs) were 231.91 PPM. Moreover, Lutetium had a PPM value of 96.56 and was the most prevalent REE. In FTIR spectroscopy $C\equiv C$, C=O, C-H bond, C-O-C, N-O bond, and SiO functional groups were found. In SEM analysis, luminous and non-luminous features could be seen in the matrix which indicates the presence of minerals by raw CA sample while both luminous and non-luminous features were disseminated in CA dipped with DES sample. The leaching efficiency of the DES was increased by increasing the temperature and time. The highest leaching efficiency we achieved was at 90 degrees Celsius for 2 hours which was 90%, While, at 60 degrees Celsius for 1 hour the DES was at its lower peak and the efficiency was 62%. Our results showed that the DES was effective in extracting REEs from CA.

Keywords: Novel DES, Hydrometallurgy, ICP-MS, REEs In Thar Coal Ash, Leaching of REEs

1. Introduction:

Rare earth elements (REEs) are a group of 17 metallic elements with unique physical and chemical properties. Despite their name, REEs are relatively abundant in the Earth's crust, but are dispersed in low concentrations and are often difficult to extract. Rare earth elements (REEs) are classified into two classes i.e., light rare earth elements (LREE) and heavy rare earth elements (HREE). The light rare earth elements (LREE) from La to europium (Eu). Heavy rare earth elements (HREE) containing Gd to Lu plus Y.

REEs are widely used in various industries such as electronics, green energy, and defense due to their unique properties such as high magnetism, luminescence, and catalytic activity. The HREE are regarded as more essential resources because of their extensive applications in photo-electro-magnetism, such as laser media, radiation sources, scintillation crystals, and magnetic materials, etc., which play an irreplaceable role in advanced technology and national defense [13-12]. REEs comprises a gigantic demand in the areas of phosphors, catalyst, batteries, coal ash (CA), metal alloys, and in defense as well [17]. These elements have become increasingly important in recent years due to the growing demand for technology and the transition to a low-carbon economy. However, the production and supply of REEs are often subject to geopolitical tensions and environmental concerns, making the development of sustainable REE extraction and recycling methods critical for the future.

From 1993-2011, China was the most REE-producing country across all over the world, by the time they started exporting REEs for benefits. According to the United States geological survey (USGS), there were 120 million tons of REEs in 2019 of which China contains 45% of it [21]. Other countries with significant REE reserves include the United States, Australia, Russia, Brazil, India, and Malaysia. However, the extraction and processing of REEs can be environmentally challenging, and many of these countries have faced criticism for their handling of REE mining and production. In addition, the production and supply of REEs can be subject to geopolitical tensions and trade disputes, highlighting the need for diversification of REE sources and the development of sustainable extraction and recycling methods. Overall, while REEs are not evenly distributed throughout the world, there are significant reserves outside of China that could potentially be developed to meet growing global demand.

REEs extraction was a complex area of research, and numerous approaches have been investigated and studied extensively i.e., the ionic liquid (IL) betainium bis (trifluoromethyl sulfonyl) imide ([Hbet][Tf2N]) for preferential extraction of REE’s from different CFAs. Efficient extraction relies on [Hbet][Tf2N]’s thermomorphic behavior with water: upon heating, water and the IL form a single liquid phase, and REEs are leached from CFA via a proton-exchange mechanism [18]. The recovery of rare element from CA are 79% and 89% using NaOH and Na_2CO_3 roasting, respectively, compared to 20% REE recovery in baseline acid leaching [17], extraction of REE’s from microsphere flower carbon (MFC). The extraction of REEs using ionic liquids, organic acids, and mineral acids presents a number of challenges. Firstly, the separation efficiency can be low due to the presence of impurities in the ore, leading to poor yields and low purity of the final product. Secondly, the use of organic acids and mineral acids can result in hazardous waste streams and environmental pollution, which can have detrimental effects on the surrounding ecosystems. Thirdly, the process can be costly due to the high cost of these reagents and the energy-intensive processes involved. Fourthly, the use of strong mineral acids and organic acids can pose safety hazards to workers due to their corrosive and toxic properties. [18]

DES can be used in hydrometallurgy to dissolve metal ions, especially those that are challenging to leach with conventional solvents. Moreover, DES can be used to concentrate metals for subsequent processing, separate distinct metals from one another, and selectively recover metal ions from solutions. DES has a number of benefits over conventional solvents, including lower toxicity, lower volatility, and higher stability throughout a larger range of pressures and temperatures. Hydrometallurgy frequently uses choline chloride, urea, glycerol, and ethylene glycol as Main components. To maximize the performance of the DES for a particular application, its unique composition might be modified. DES has the potential to increase the sustainability and effectiveness of hydrometallurgical processes overall. Based on the above analysis it is imminent to prepare DESs which have not been used till now for the dissolution of REEs [1,6,16-17].

The potential of DESs for processing metal oxides can be seen in their ability to give a high solvation potential even for hardly soluble metal oxides under relatively moderate conditions. Extensive studies have been conducted on how easily metal oxides including rare earth oxides, dissolve in different DESs [1]. The possibility of dissolution and separation of REEs from several sources including coal and coal ash, has been investigated by leaching with DEEs [17]. REEs can be effectively dissolved and separated using DESs with the right amount of acidity and low viscosity.

The research aimed to find green reagents for the extraction of REEs from coal ash, as an alternative to mineral acids, organic acids, and ionic liquids. We synthesized a novel green deep eutectic solvent (DES) i.e., combination of organic acid (Humic Acid) and a salt (Choline Chloride) for the extraction of REEs from coal ash. The DES was more efficient, less time taker, biodegradable and friendly to environment. In hydrometallurgical operations, particularly for the extraction and separation of metals from ores, concentrates, and other materials, DES has been utilized as a solvent more and more frequently. We found that the DES was effective in leaching REEs from coal ash, with a maximum extraction efficiency of 87.8% achieved at 89°C, using a DES composition of 1:1 (humic acid: choline chloride), and a reaction time of 120 minutes.

2. Materials and Methods:

The CA sample used in the test work was collected from a Sindh Engro Thar Coal Mining Company (SECMC), Pakistan. Choline chloride (ChCl) (CAS No. 67–48-1), Humic acid (HA) was all of high purity (>98%). Sieves (Ogawa Seiki Co. Ltd), hot plate (Benate, Australia, Model-MS400) and furnace (Lindberg Muffle) were also used. For the characterization analysis, the ashed samples were sent for X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Radiation (FTIR) and Induced Coupled Plasma – Mass Spectrometry (ICP-MS) (figure-3). For XRD (Model, JDX-3532, JEOL Japan), sample was sent to (Centralized Resource Laboratory, University of Peshawar), Pakistan. FTIR analysis were carried out utilizing FTIR Cary-600 instrument present at Department of Chemistry, University of Engineering and Technology. For ICP-MS (NexIONTM 350X), the sample was sent to National Centre of Excellence in Geology, University of Peshawar, Pakistan.

3. Synthesis of DES:

The DES system consisting of HA and ChCl was synthesized by mixing the ChCl and HA in 1:1 M ratio [7] i.e., Hydrogen Bond Donor (HBD) and Hydrogen Bond Acceptor (HBA) [20].This combination was stirred at 500 revolution per minute from 89 degree Celsius temperature on a hot plate (Benate, Australia, Model-MS400) using magnetic stirrer, of 5ml size (purchased from AST), for a duration of 2 hours[13] (figure 1).

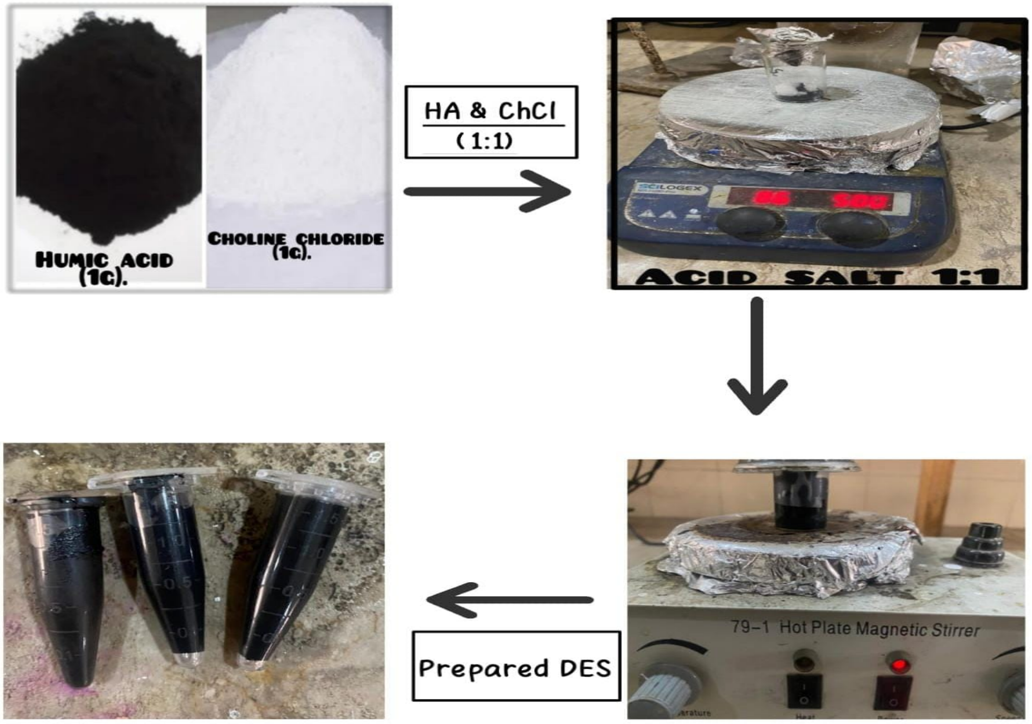

Figure 1 : Flowsheet of the DES preparation process

4. Methodology:

Leaching was performed by mixing coal ash and prepared DES with a solid to liquid ratio of 1:5. Coal ash was taken in a cylindrical flask and then 5 ml prepared DES was added into it. For each experiment, the leaching temperature was set at 55° Celsius to 90° Celsius [7] and leaching time of 1-2 hours [19-20] were set as per the experimental design (Table 2 and figure 2). The stirring speed of magnetic plate was set to 500 revolution per minute. After the dissolution of REEs in DES, the concentrate was further separated by centrifugation (Centurion Scientific-C2 Series) at 4000 revolutions per minute for approximately 10 minutes [22]. The samples obtained after 6 experiments were ready to be sent for chemical analysis tests. The experiments had two variables: time and temperature demonstrated by leaching flowsheet explained in figure 3. These were primarily focused on to determining the best leaching efficiency of extracting REEs from CA. We designed and performed 6 experiments varying in temperature and time (Table-2) [7]. The complete methodology of this project has been discussed by a flowsheet following as shown figure 3.

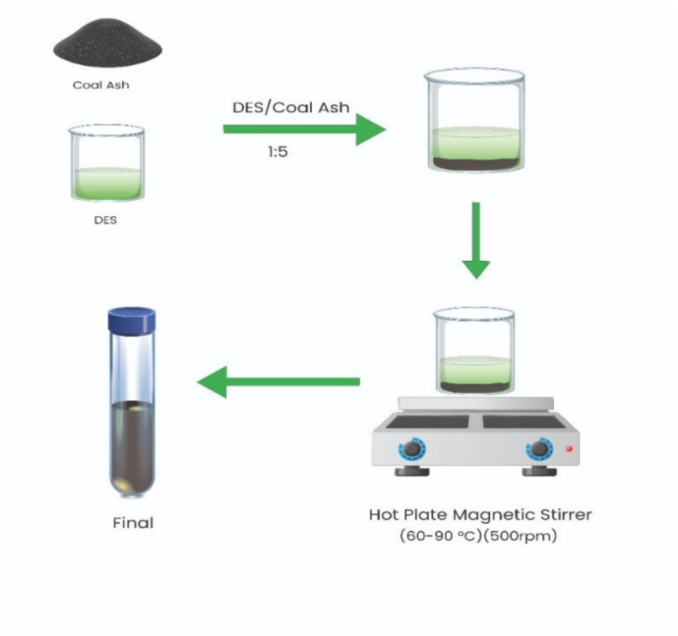

Figure 2: Leaching Process, For the leaching process, firstly we took 1:5 of Liquid/solid, mixing of prepared DES and Coal Ash.

Table1: Experimental design comprised of total 6 experiments.

Experiment No	Salt	Acid Type	Leaching Time/Hour	Temperature Celsius	Revolution Perminute	Solid To Liquid Ratio
1	Choline Chloride	Humic Acid	1	55	500	1:5
2	Choline Chloride	Humic Acid	1	60	500	1:5
3	Choline Chloride	Humic Acid	1	90	500	1:5
4	Choline Chloride	Humic Acid	2	55	500	1:5
5	Choline Chloride	Humic Acid	2	60	500	1:5
6	Choline Chloride	Humic Acid	2	90	500	1:5

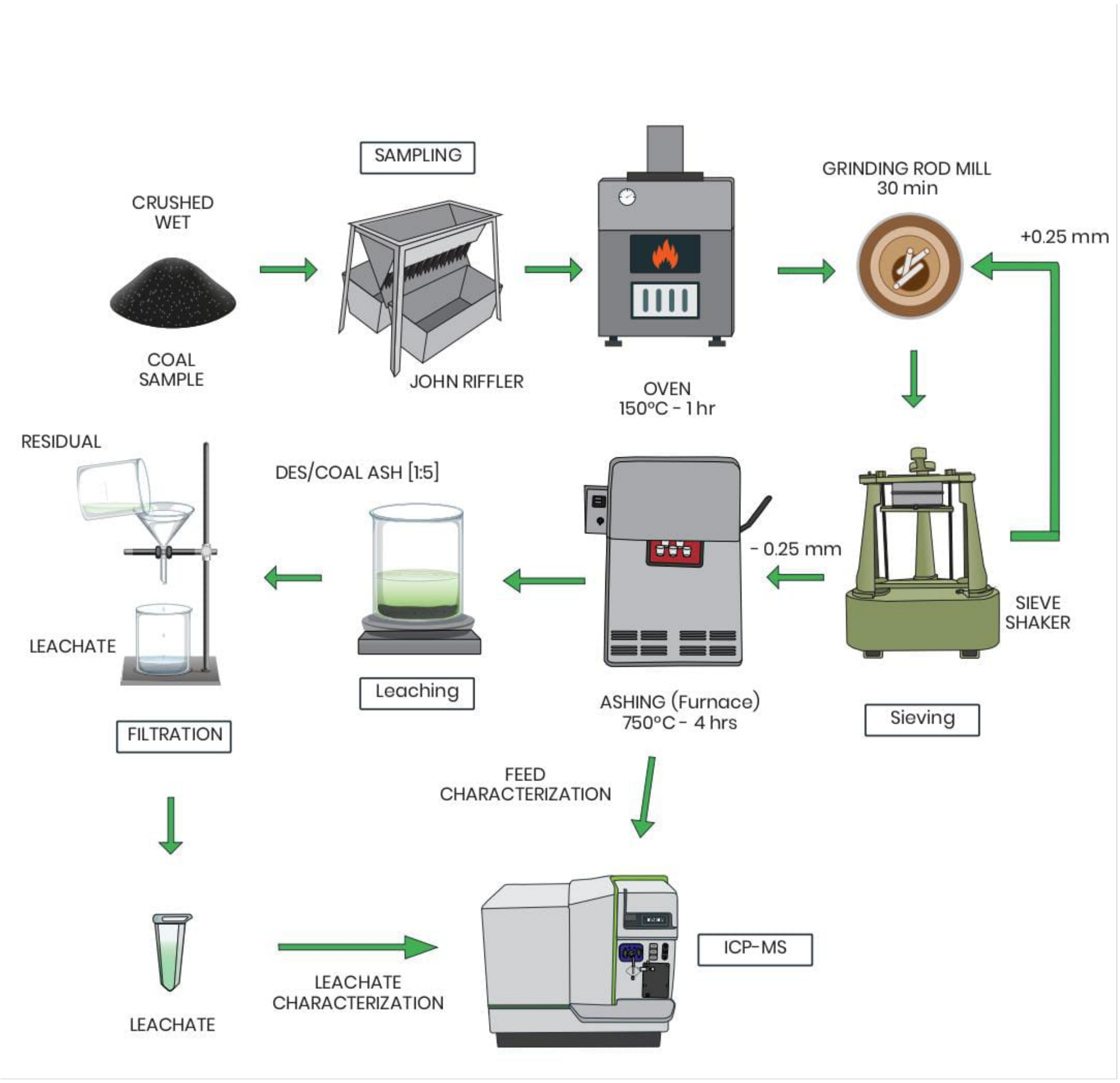

Figure 3: Methodology for REEs extraction

5. Results and Discussion:

The aim of this research was to discover innovative, environmentally friendly reagents for the extraction of rare earth elements (REEs) from coal ash, serving as sustainable alternatives to traditional extractants such as mineral acids, organic acids, and ionic liquids. These conventional methods, while effective, often pose environmental hazards due to their toxicity and waste generation and also, they were costly. The focus was on identifying green reagents that not only minimize ecological impact but also maintain or enhance the efficiency of REE extraction, providing a cleaner and more sustainable solution to recovering these valuable resources from coal ash. This section discusses the findings from leaching experiments and characterization analysis.

In feed characterization analysis the main results were the XRF, XRD, ICPMS, FTIR, and SEM. The composition of various elements found in feed sample by XRF, were namely Calcium (Ca), Iron (Fe), Sulfur (S), Aluminum (Al), and Titanium (Ti). Among these elements, Calcium was the most abundant, comprising 35.676% of the total composition, followed by Iron at 23.804% and Sulfur at 20.844%. Aluminum and Titanium made 9.832% and 7.143%, respectively. The X-ray diffraction analysis of the coal ash sample revealed a crystalline structure, with identifiable mineral phases including Calcium Sulphate, Diborane and Magnesium Oxide (Figure 4). The CA was also analyzed with XRD, and the main components were calcium sulfate, hematite. [2].

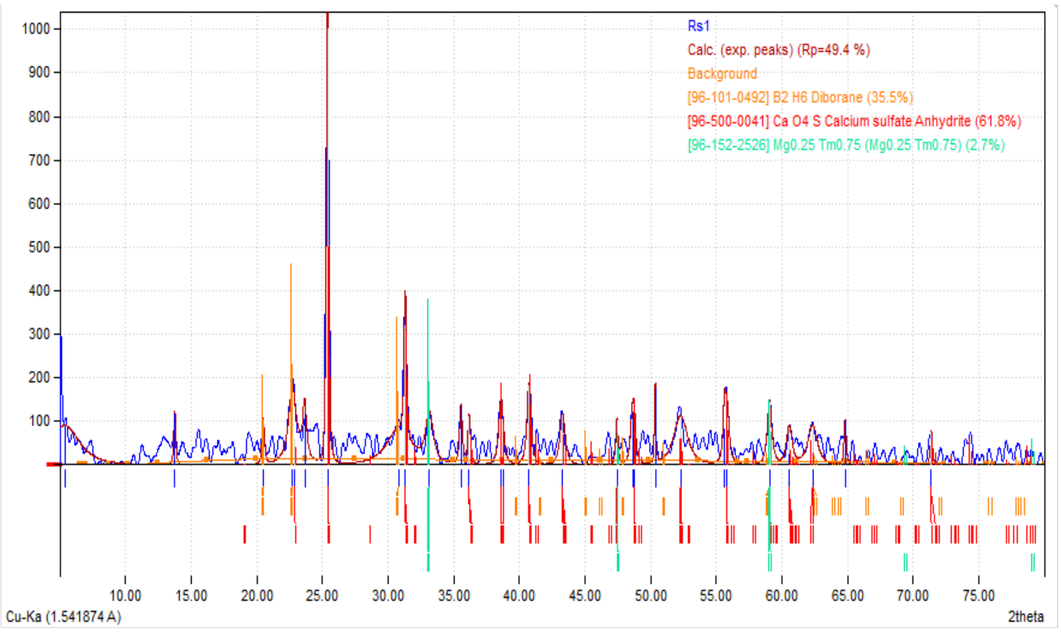

Figure 4: The above figure depicts the phase minerology present in the coal-ash.

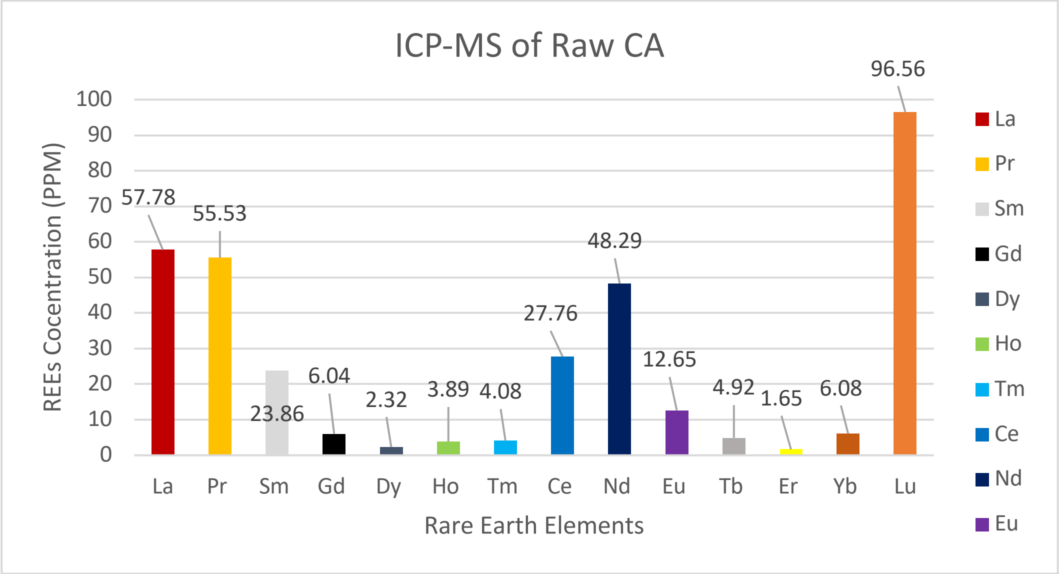

Figure 5: ICP-MS Results of Coal Ash.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS):

From ICP-MS results, it was observed that the concentration of REEs in the coal ash sample was 351.41 PPM. In the coal ash sample, HREEs had a concentration of 119.5 PPM, and LREEs had a concentration value of 231.91 PPM. It was also noticed that Lutetium was the most abundant REE with a value of 96.56 PPM, which made up 27.47% of the whole REEs. The concentration of 17 REEs is shown in figure 5.

***Fourier Transform Infrared (FTIR) Spectroscopy*:**

The FTIR spectrum of coal ash as shown in figure 6 indicated the broad peak around 2117 cm^-1 corresponded to the stretching vibration of C≡ C bonds. While at 1751 cm^-1 C=O was detected. At 1423 cm-1 C-H bond was analyzed, and C-O-C. The peak at 1423 cm^-1 correspond to C-H stretching vibrations in aliphatic hydrocarbons or aromatic CH groups. We analyzed that OH bond with medium-sharp peak at 3690 cm^-1, OH bond with broader peak at 3242 cm^-1, C=O=O at 2340 cm^-1, C≡ C at 2117 cm^-1, N-O at 1565 cm^-1, and CH bond at 1371 cm^-1 as shown in figure 7 depicts the results of coal ash dipped with DES. The Peak at 1595 cm-1 is assigned to N-O (Nitro Compound), which is also due to the Humic Acid. The major difference in the surface characteristics of coal ash sample mixed with DESs is that the mineral part is almost vanished and is mostly dominated by C-H functional group compound which is due to the organic salt i.e., Choline Chloride [15].

The FTIR spectra of functionalized cellulose showed various bands at different wavelengths indicating the presence of OH bonds, NH2 thiourea group, NH thiourea group, cellulose glucopyranose cycle C-H bonds, CN bond, C=S bond, and C-O and O-C-O cellulosic bonds. These bands were at similar wavelengths as those observed in pure cellulose and pure thiourea, but with varying intensities [2]. The spectra were normalized to the intensity of the 3800-400 cm1 band. Several bands in the region of 3500 cm1 to 1620 cm1 were assigned to O-H in planar water, while others were attributed to Si-O and Al-O stretching and bending vibrations. IR bands caused by aluminosilicates can be divided into three parts, with different polarization effects of cations and polymerization levels affecting their strength. Additionally, a weak peak attributed to Fe-O is observed around 560 cm1 in some samples. And figure 8 Illustrates the comparison between the Figure 7a and 7b, this clearly showed that there is not much difference between them but an additional functional group that was N-O, this was due to the Humic Acid because Humic acid contains functional group of N-O.

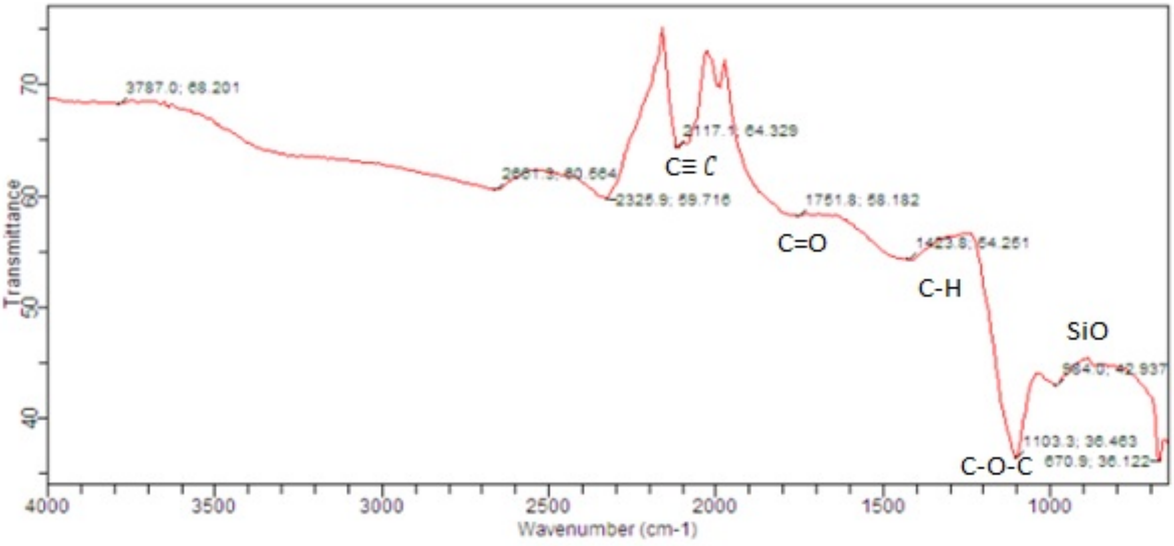

Figure 6: it illustrates FTIR spectra of feed coal ash.

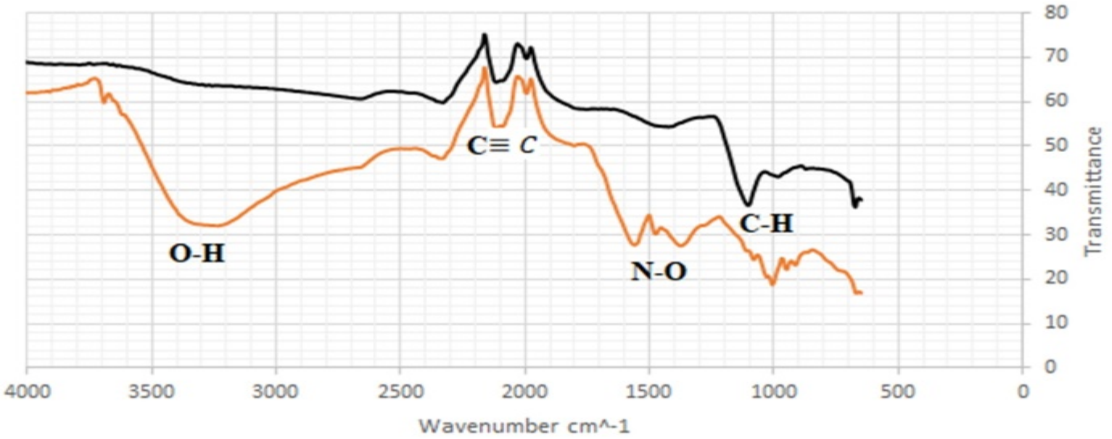

Figure 7: It depicts the results of coal ash dipped with DES

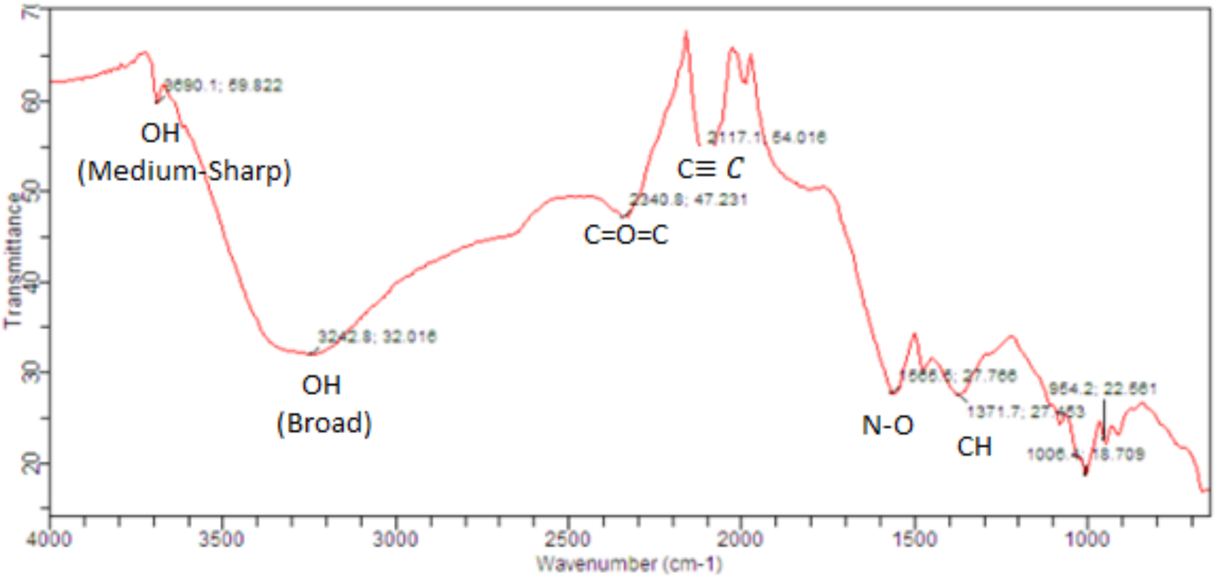

Figure 8: It illustrates the comparison between the Figure 6 and 7.

Scanning Electron Microscope (SEM):

CA feed sample and CA dipped with DES both were analyzed by incorporating SEM-EDX as shown in figure 9 and 10. Meanwhile, figure 11 represents the elements found in raw coal of Thar.

It was observed that the coal ash sample (figure 9) was a bulk microstructure containing dissipated network of shining crystallites showing the presence of mineral. The luminous and non-luminous features could be seen in the matrix which indicate the presence of minerals. Many fissures, cleats, cracks were also observed. These might had resulted from the heating of silica or its assemblage due to the thermal shock during ash preparation of coal.

The SEM analysis of leached out coal ash sample was also carried to observe the any difference in the topography, morphology or any other difference in physical features. It can be seen in (figure 10) that due to leaching the luminous particles that were disseminated throughout the bulk surface are collected at one point.

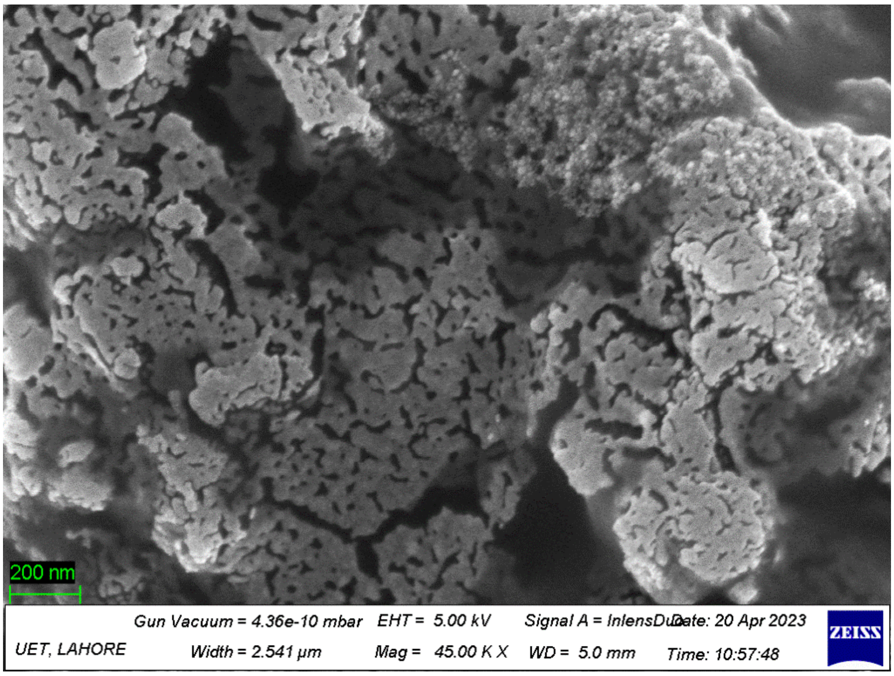

Figure 9: SEM micrograph of virgin coal ash sample.

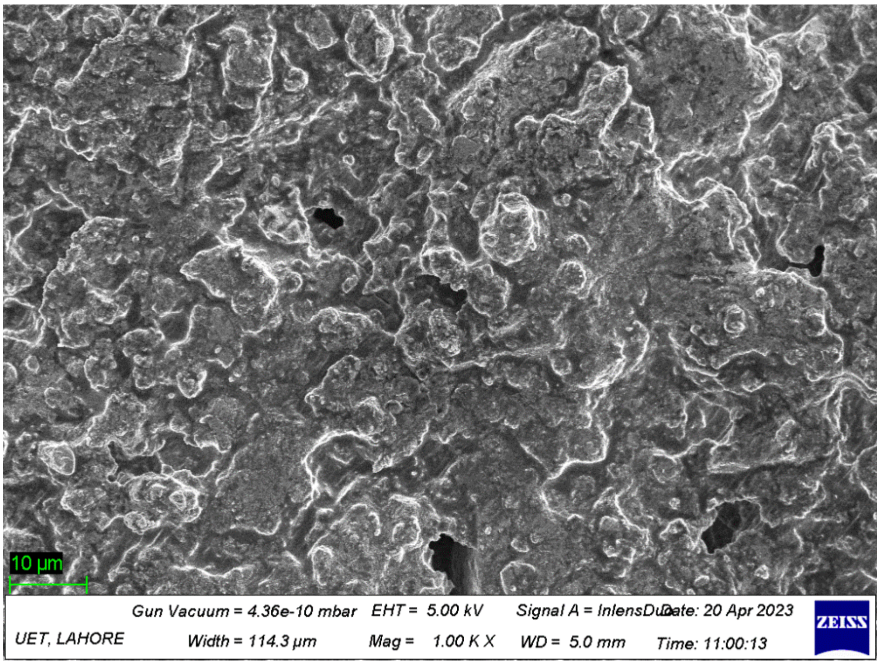

Figure 10: SEM micrograph of virgin coal ash sample

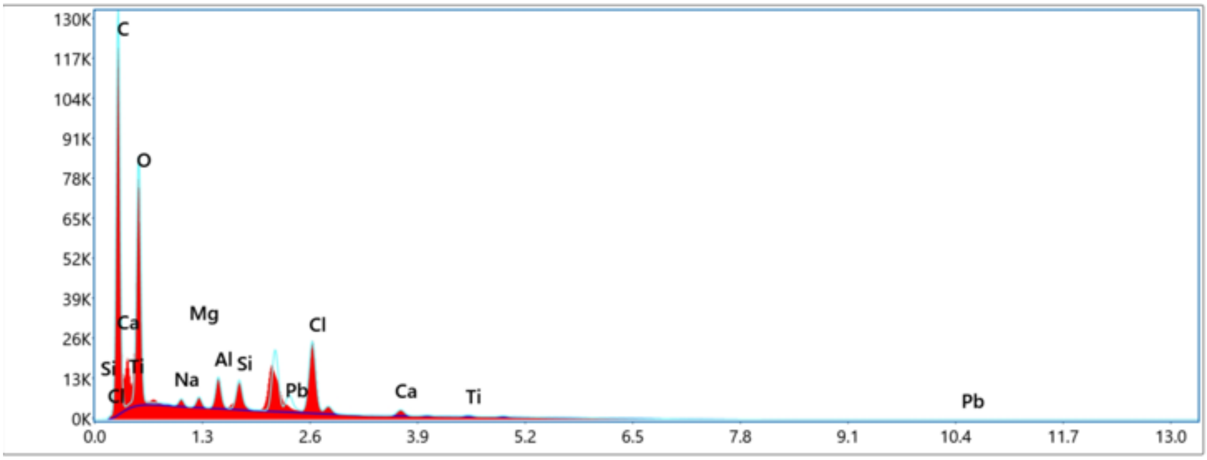

Figure 11: Shows the elements found in raw Coal Ash sample.

The non-luminous dark surface is increased because the shiny particles are collected at one point due to the weathering by leaching. The size reduction of the luminous region confirms the demineralization had taken place.

The Mossbauer spectra indicated the presence of iron-bearing minerals, including pyrite, ankerite, illite, and jarosite. Quartz, clay, and carbonates, which are non-iron-bearing minerals, were also observed in the SEM analyses by Banerjee R, et al [3]. Mollah MYA et al had proved that leaching did not have a significant impact on the morphology of ash particles as SEM micrographs that they were resistant to acidic and buffer leaching solutions[14]. The particles did not undergo any deformation or aggregation due to leaching, but the surfaces appeared smoother as the surface deposits were dissolved into the leaching solution. Leaching did not alter the morphology of ash particles, except for the smoothing of their surfaces due to the dissolution of surface deposit. While, it was observed from our results that leached out coal ash sample was also carried to observe the any difference in the topography, morphology or any other difference in physical features.

Leaching Efficiency:

For the given DES, prepared at 90^{0}C and time of 2 hours, maximum leaching efficiency was obtained that was 90% and while the temperature decreased to 55^{0}C and time reduced to 1 hour, the efficiency was lowest and it was 61%. In fact, the optimum temperature obtained for Leaching of coal ash sample with the DES of Choline Chloride and Humic Acid was 90^{0}C, as maximum efficiencies were obtained at this temperature (Table 2) (Figure 12).

REEs are extracted by scientists by using DESs. [11] used DES combination of HBA, guanidine hydrochloride (GUC), and HBD L-lactic acid (LAC). This DES Showed 95% recovery with highest efficiency as compared to others. [5] used Urea, Malonic acid, and Citric acid with choline chloride. While Malonic acid & Choline Chloride, and mixture of urea + Malonic acid with Choline Chloride indicated higher efficiency to dissolve REEs. It was observed by Ebrahimi E et al that the p-Toluene sulfonic acid (PTSA) & p-Toluene sulfonic acid (PTSA), and Choline chloride (ChCl) & p-Toluene sulfonic acid (PTSA) showed the highest efficiency to dissolve REEs. The recovery of rare element from CA are 79% and 89% using NaOH and Na_2CO_3 roasting, respectively, compared to 20% REE recovery in baseline acid leaching [17]. The leaching efficiency of sulfuric acid for dissolving REEs in coal ash was 80% [10]. Our approach was to maximize of our recovery as compared to sulfuric acid. We found that the DES was effective in leaching REEs from coal ash, with a maximum extraction efficiency of 90% achieved at 89°C, using a DES composition of 1:1 (humic acid: choline chloride), and a reaction time of 120 minutes.

The leaching efficiencies of 6 experiments performed for this research were calculated by using the following equation. Different set of parameters were opted among which the time and temperature were the variable parameters, and RPM and Concentration Ratio were the constant variables i.e. 500 and 1:5 respectively.

The percentage recovery of each rare earth elements from ICPMS results was calculated by:

$$\%\ \boldsymbol{of\ rare\ earth\ elements\ Recovered} = \frac{\left\{\boldsymbol{ICPMS\ value}\ \left(\frac{\boldsymbol{mg}}{\boldsymbol{l}}\right) * \boldsymbol{V(l)}\right\}}{\boldsymbol{MO\ (mg) * EG}}$$

ICPMS value = result of Inductive Coupled Plasma Mass Spectrometry of each. element

V solution = Final Volume of solution in Liter

MO = Mass of ore.

EG = Element grade in ore in wt.%

Table 2: Shows the efficiency of the leaching experiments performed with the DES

EXPERIMENTS	**DES**	**CONSTANT PARAMETERS**	**DIFFERENTIAL PARAMETERS**	**Leaching Efficiency (%)**
		RPM, Concentration Ratio	***Temperature (^{0}C), Time (hrs.)***	
1	*ChCl & HA*	*500, 1:5*	*55,1*	*61*
2			*60,1*	*65*
3			*90,1*	*72*
4			*55,2*	*79*
5			*60,2*	*84*
6			***90,2***	***90***

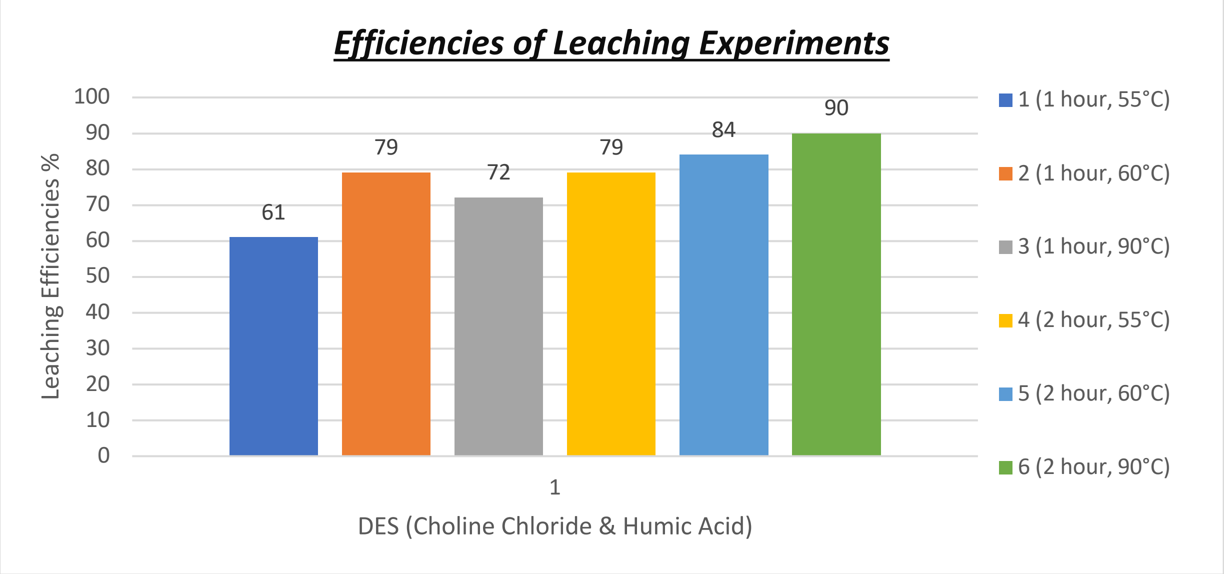

Figure 12: The graph illustrates the leaching efficiency of DES (choline chloride & Humic acid) at temperature varying from 60-90 degrees Celsius and time 1-2 hours.

Effect of time duration on leaching efficiency:

The leaching efficiency was observed to increase with time. The change in efficiency followed a linear relationship as the time increased from 1 hour to 2 hours at 55^0C, 60^0C and 90^0C separately in figure (13,14and 15).

The influence of reaction time on the leachability of REE was studied in the range of 1 to 6 hour at constant temperature of 80 °C and L/S weight ratio of 10. The leaching efficiency for 1 hour was 52% and it was 63% at 2 hours but in our experiments the leaching efficiency was almost 61% at 1 hours and 79% at 2 hours [7]. While, by increasing time from 1 hour to 2 hour our results were 79% to 84%. Similarly, Duration of leaching of REE from coal ash the carboxylic acid concentration was kept at 5% and the leaching temperature was 90 °C for this study. The results for variation in leaching efficiency with 30, 60, 120, 240 and 360 min of leaching duration for different carboxylic acids are 20%, 30%, 35%, 37% and 40% respectively [3]. So, we can compare to this study our approach had also proved that by increasing the time leaching efficiency would also be increased.

Effect of temperature on leaching efficiency:

Same as with the increase in time, the leaching efficiency also increased with temperature. It was interestingly observed that the maximum leaching efficiency (69.54 %) obtained when the running temperature of leaching process was at 90^0C (figure 16 and 17). The effect of reaction temperature on the leachability of REE from CFA using ChCl: pTSA(1:1) and ChCl:LA(1:2), respectively. The reaction temperature was varied from 40 °C to 100 °C at fixed contact time of 6 h and liquid to solid (L/S) weight ratio at 10%.

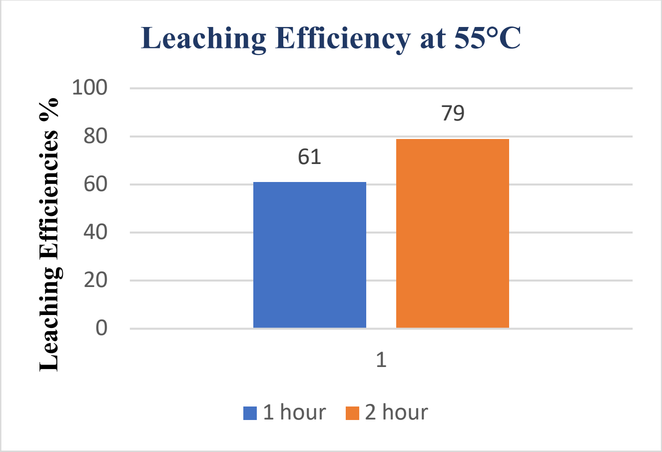

Figure 13:Leaching efficiency at 55 ^{0}C for 1 and 2 hours.

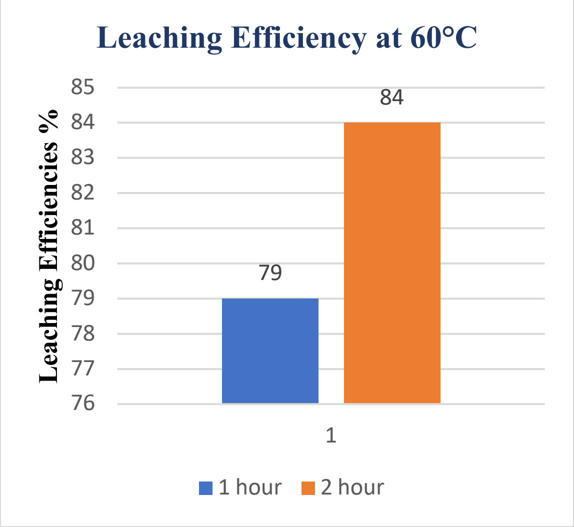

Figure 14: Leaching efficiency at 60 0C for 1 and 2 hours.

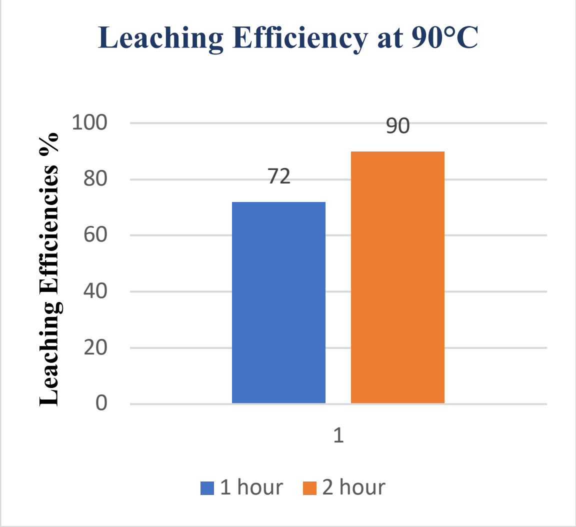

Figure 15: Leaching efficiency at 90 0C for 1 and 2 hours.

The leachability of REE increased with the rise in the reaction temperature for both systems. The leachability of LREE was relatively higher than that of HREE at all the temperatures investigated. The leaching efficiency at 55°C was 65%, at 60°C was 70% and at 90°C it was almost 89% but in our case the leaching efficiency at 55°C was 45%, at 60°C was 60% and at 90° it was 69.54 %.[7] In one of the research studies, recovery rates of REEs from coal ash obtained from U.S. coal power plant by Hydrochloric acid, Sulfuric Acid and Nitric acid, it was found that Sulfuric acid had the lowest leaching efficiency of 12% for REEs without any chemical roasting. One of the reasons of lower recovery of REEs was that they were associated with aluminosilicate glassy phase which hinder their solubility in leaching with acids[17]. Similarly, direct leaching of REEs from ash was carried with diluted sulfuric acid and the dissolution percentage remained only 8-45% at 30 to 80°C and for 120 minutes [9] And these results shown that their leaching efficiencies were also increased by increasing time and temperature.

The effect of temperature on leaching efficiency of REEs from CA was investigated thoroughly. Increase of temperature is understood to ameliorate the dissolution of rare earth elements, thus improving the leaching characteristics. A series of leaching tests were performed at different temperatures (60, 70, 80 & 90 °C) in which the acid concentration was kept at 5% and the leaching duration was 1 h. The results obtained for leaching efficiencies were 20%, 25%, 30% and 35% respectively [3].

It was observed that the leaching efficiencies of the DESs increased slightly when the leaching duration was changed from 1 hour to 2 hours. However, it was also noted that the increase in efficiency was not significant when the leaching duration was increased for only 1 hour. This suggests that leaching for an extended duration may enhance the efficiency of DESs.

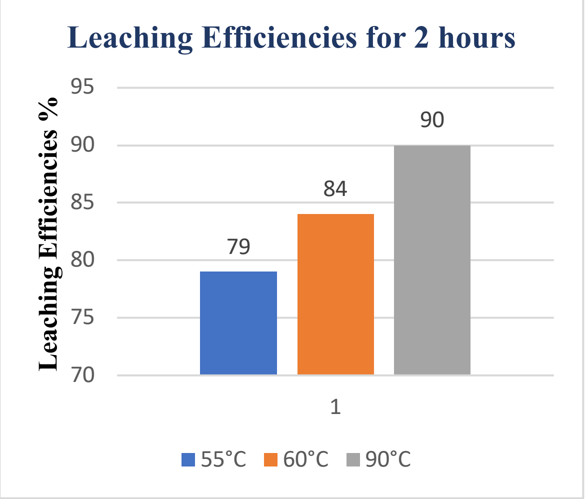

Figure 16: It illustrates graphically the effect of increase in temperature on leaching efficiency for 2 hours.

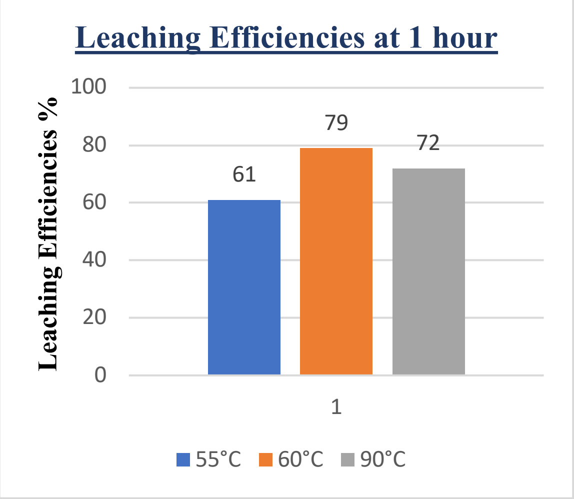

Figure 17: It illustrates graphically the effect of increase in temperature on leaching efficiency for 1 hour.

6. Conclusions

The objective of this research was to develop innovative and eco-friendly reagents for extracting Rare Earth Elements (REEs) from coal ash, aiming to replace conventional extractants such as mineral acids, organic acids, and ionic liquids which are corrosive, hazardous and costly. Traditional methods, while effective, often have harmful environmental effects due to their toxicity and waste production. We conducted experiments on the coal of Sindh Engro Thar Coal Mining Company (SECMC), Pakistan. Based on literature and ASTM standard D-2013 coal crushed and grinded up to a size of -250 microns. The leaching experiments were designed with two different parameters (1-2 hours) and temperature (60-90 Celsius) at constant 500 rpm. After centrifugation at 4000 rpm for 10 minutes, we separated the REEs. Both the feed and leachate were analyzed using various techniques such as, XRF, XRD, ICP-MS, FTIR, and SEM.

And here are the main results found and analyzed from ICP-MS and FTIR spectroscopy. It was noted from ICPMS analysis the sample of coal ash contained a total of 351.54 PPM of REEs. The concentration of HREEs in the coal ash sample was 119.5 PPM, while the concentration of LREEs was 231.91 PPM. It is also noticed that Lutetium was the most abundant REE having value 96.56 PPM and Lanthanum, and Praseodymium contained second highest REE concentration that was 57.78, and 55.53 PPM respectively. In the FTIR spectra of feed CA we found C≡ C at 2117 cm^-1, C=O at 1751 cm^-1, C-H bond at 1423 cm^-1, C-O-C at 1103 cm^-1, and SiO at 984 cm^-1 while in the results of CA dipped with DES, we analyzed that OH bond with medium-sharp peak at 3690 cm^-1, OH bond with broader peak at 3242 cm^-1, C=O=O at 2340 cm^-1, C≡ C at 2117 cm^-1, N-O at 1565 cm^-1, and CH bond at 1371 cm^-1.

The leaching efficiency of the DES was increased by increasing the temperature and time. The highest leaching efficiency we achieved was at 90 degrees Celsius for 2 hours which was 90%, While, at 60 degrees Celsius for 1 hour the DES was at its lower peak and the efficiency was 61%.

The results of this research study have both regional and global positive impact. With the utilization of results the sustainable goals of United Nations (UN) were adopted through this research and valuable contribution were made to the concept of circular economy in Pakistan and it will benefit the SECMC to collaborate with foreign multinational companies and it will enhance their work and revenue. In addition to all, the motto of Environmental Protection Agency (EPA) regarding the green environment was promoted. As a consequence of REEs separation from coal ash with DESs, the supply chain of REEs worldwide shall be filled. Moreover, the production of DESs is vital for researchers in chemistry and polymer synthesis.

In view of the results of this research study, it is recommended that the mechanism of the reaction between DESs and REEs during leaching must be assessed. The use of simulation software for the formation of DESs and leaching needs to be implied because it will provide with optimized conditions and possible results, thus will make the whole process time saving with less cost expenditure. Organic acids such as Mesaconic Acid, Glyceric Acid, and Acetoacetic Acid have not been used yet and they have the capability to form DES. Apart from REEs, transition elements are also suggested for the extraction from coal waste. It is the replacement of mineral acids, ionic liquids, and organic acids from the industry as well.

7. Author’s Contribution:

Conceptualizations, testing and experimental work; Ahsan Mehmood, Muhammad Sharif, Adil Hussain . Writing and review; Muhammad Suleman, Dr. Muhammad Badar Hayat

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استخلاص العناصر الأرضية النادرة من رماد الفحم عن طريق الترشيح الكيميائي باستخدام المذيبات الأيوتيكتية العميقة

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المستخلص: يعد توافر العناصر الأرضية النادرة محدودًا مع تزايد الطلب عليها، مما يستدعي الحاجة إلى مصادر ثانوية لتلبية هذا الطلب. اعتمد هذا البحث على رماد الفحم كمصدر بديل للعناصر الأرضية النادرة. تم استخدام الأحماض المعدنية، والسوائل الأيونية، والأحماض العضوية لاستخلاص العناصر الأرضية النادرة (REEs) من رماد الفحم (CA)، والتي كانت مواد تآكلية، مكلفة، خطرة، وغير صديقة للبيئة. هدف هذا البحث إلى إيجاد كواشف مبتكرة تكون صديقة للبيئة لاستخلاص العناصر الأرضية النادرة من رماد الفحم كبديل للأحماض المعدنية، السوائل الأيونية، والأحماض العضوية. قام الباحثون بتصنيع مذيب أيوتيكي عميق جديد (Choline chloride) وحمض الهيوميك لاستخلاص العناصر الأرضية النادرة. أجريت الدراسة على فحم شركة سند إنجرو لتعدين الفحم في ثار (SECMC)، باكستان. تم سحق وطحن الفحم إلى حجم - 250 ميكرون بناءً على الأدبيات والمعيار ASTM D-2013. تم تصميم تجارب الترشيح مع أخذ عاملين مختلفين في الاعتبار: الزمن (1-2 ساعة) ودرجة الحرارة (60-90 درجة مئوية) بسرعة دوران ثابتة قدرها 500 دورة في الدقيقة. بعد الترشيح، تم استخدام الطرد المركزى بسرعة 4000 دورة في الدقيقة لمدة 10 دقائق للحصول على المحلول. تم تحليل كلاً من العينة الأولية والمحلول باستخدام تقنيات متعددة: الأشعة السينية الوميضية (XRF)، حيود الأشعة السينية (XRD)، التحليل الطيفي الكتلي بالبلازما المحفزة (ICP-MS)، مطياف الأشعة تحت الحمراء التحويلي (FTIR)، والمجهر الإلكتروني الماسح (SEM).

في توصيف العينة الأولية، أظهرت نتائج XRF أن الكالسيوم كان العنصر الأعلى بنسبة 35.676%. تم الكشف عن أطوار معدنية مثل كبريتات الكالسيوم، الديبوران، وأكسيد المغنيسيوم بواسطة XRD. أظهر تحليل ICP-MS أن عينة رماد الفحم احتوت على إجمالي 351.41 جزء في المليون من العناصر الأرضية النادرة. بلغت نسبة العناصر الأرضية النادرة الثقيلة (HREEs) 119.5 جزء في المليون، بينما كانت العناصر الأرضية النادرة الخفيفة (LREEs) 231.91 جزء في المليون. علاوة على ذلك، كان اللوتيتيوم هو العنصر الأكثر وفرة بقيمة 96.56 جزء في المليون. في FTIR تم اكتشاف روابط كيميائية مثل C≡C، C=O، C-H، C-O-C، N-O، ومجموعات وظيفية SiO. في تحليل SEM، كانت هناك ملامح مضيئة وغير مضيئة في المصفوفة، مما يشير إلى وجود معادن في العينة الخام من رماد الفحم، بينما تم توزيع كل من الملامح المضيئة وغير المضيئة في العينة بالمذيب الأيوتيكي العميق (DES). ازدادت كفاءة الترشيح للمذيب الأيوتيكي العميق بزيادة درجة الحرارة والزمن. أعلى كفاءة ترشيح تم تحقيقها كانت عند 90 درجة مئوية لمدة ساعتين وبلغت 90%، بينما عند 60 درجة مئوية لمدة ساعة كانت الكفاءة عند أدنى مستوى وبلغت 62%. أظهرت نتائج هذا البحث أن المذيب الأيوتيكي العميق كان فعالًا في استخلاص العناصر الأرضية النادرة من رماد الفحم.

الكلمات المفتاحية. العناصر الأرضية النادرة، رماد الفحم، الترشيح الكيميائي، التعدين المائي، مطياف كتلة البلازما