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# **Explorative Research Course: Recovering Rare Earth Elements from Electronic Waste Using Deep Eutectic Solvents**

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### **Abstract**

This study aims to demonstrate how a course design approach based on explorative research involving systems thinking can be implemented by recovering Rare Earth Elements (REEs) using Deep Eutectic Solvents (DES). The method used in this research is Design-Based Research (DBR). The instruments used were questions regarding the measurement of leaching samples from results/characterization, short questions about concept maps, and student response questionnaires. Data from measurements of leaching samples was measured using a Fourier Transform Infrared Spectrometer (FTIR), data about concept maps was measured by the number of component and process concepts in the context of electronic waste recycling that students were able to identify, and student response data was measured using a Likert scale. Based on the research results, recovery of REEs can be done using DES. It can be shown by a shift in the peak vibration of 497.65 cm<sup>-1</sup> from the sample before leaching to a vibration of 449.43 cm<sup>-1</sup> after leaching. In addition, this study yields new insights into the perceptions of future pre-service chemistry teachers regarding the possibility of new types of DES in the context of chemistry learning. According to pre-service chemistry teachers, recovering REEs from electronic waste and applying DES are interesting as a new context for laboratory learning. Context-based design of research activities can enhance system thinking and interest in chemistry. The results of study showed increased student's systems thinking abilities, as shown by the component and process concepts that emerged from the pre-test by 652 concepts while the post-test increased by 1208 concepts.

Keywords: deep eutectic solvents, electronic waste, explorative research course, rare earth elements, systems thinking

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### 1. Introduction

Educators must give students relevant learning experiences in order to meet the complex difficulties that face society today (Busta & Russo, 2020). One of the challenges facing the world today is related to environmental issues. Environmental issues are significant because they concern the sustainability of human life on Earth (Dale &

Newman, 2005). In the living environment, environmental pollution is a severe issue. It is connected to the notable rise in electronic trash over the past few decades (Chakraborty et al., 2022). Electronic waste results from discarded electronic products. Indonesia's ewaste production will increase from around 2.0 million to 3.2 million tonnes in 2040. It represents an economic value of US\$2.2 billion to US\$14 billion of valuable metals in e-waste.

In 2021, Java Island will contribute up to 56% of the total e-waste generation in this country. Thus giving rise to piles of electronic waste which have an impact on human health (Mairizal et al., 2021).

Metal makes up 60% of electronic trash, followed by plastic (15%) and a combination of plastic and metal (5%) (Ari, 2016; Widmer et al., 2005). Toxic metals, transition metals, and rare earth metals are the three categories of metal waste. Metal released into the environment damages sediment, water, and soil habitats. It is known that electronic waste contains valuable metals. One of them is rare earth metals, which have extensive benefits in their applications (Kisworo et al., 2021).

One of the most critical components in a tube TV is the Cathode Ray Tube (CRT). CRT is a monitor screen with fluorescent powder combined with rare earth metals, emitting light and color. Rare earth metals in the form of europium and yttrium are found in phosphorus powder. It is based on research that has been carried out. The recovery of REEs from electronic waste from fluorescent lamps obtained the elements Eu and Y. REEs has excellent potential to make a material with luminescent properties and as a sustainable material (Pateli et al., 2020). Nevertheless, research on recovering REEs from CRT TV has yet to be reported. It is a challenge for preservice chemistry teachers to promote systems thinking to solve the context of environmental problems related to electronic waste with content in a sustainable manner from a chemistry learning perspective (Kisworo et al., 2023).

The problem of electronic waste is a controversial social problem related to science that can be integrated into chemistry learning. Because it is related to green chemistry, it is challenging for chemistry education to demonstrate the ability to use molecular science to solve problems sustainably. The molecular basis of sustainability has a central role in designing environmentally friendly materials that do not negatively impact human health and the environment (Anastas

& Eghbali, 2010; Mahaffy et al., 2019). Therefore, chemistry learning that utilizes the molecular level is believed to transform hazardous materials in the environment into materials that can be reused through a sustainable green chemistry process (Anastas & Zimmerman, 2016).

Recovering the metal from the mixture can usually be done by extraction. Thus far, strong acids, strong bases, alkalis, and organic compounds have been employed as extraction solvents. These solvents possess high melting temperatures, rapid evaporation, and high boilina points and are combustible. potentially harming the environment. On the other hand, the principle of sustainable development encourages all chemical activities based on green chemistry. So, all this time, some solvents have contributed to environmental damage. Based on green chemistry, all types of compounds are expected to be designed to fulfill green chemistry aspects, including making solvents, which are often used in the extraction process. One of the solvents that has currently been researched and developed is DES. DES becomes a potential solvent because of its superior physicochemical properties, including low melting point and non-volatile non-flammable and properties. physicochemical properties make DES become a green chemistry-based solvent (Huang et al., 2019; Kareem et al., 2010). DESs are mixtures of hydrogen bond donors and acceptors with points ranging from ambient meltina temperature, as shown in Figure 1 (Vanda et DES physicochemical 2018). have properties similar to ionic liquids, such as low volatility (Hernani et al., 2016; Mudzakir et al., 2017; Pernaa et al., 2022). DES have proven helpful in the selective dissolution of metal oxides and in recovering metals from industrial process residues and metal ores.

Researching the leaching process of REEs recovery from CRT electronic waste through DES is a promising avenue for pre-service chemistry teachers. Students can solve contextual problems related to electronic waste by connecting content related to

sustainable molecular chemistry. Sustainable molecular chemistry can be represented by reusing REEs and using DES as environmentally friendly green solvents. Interconnected thinking is required to bridge this framework; in this instance, students need a system thinking framework.

Figure 1. Structure of Levulinic Acid and Choline Chloride

Teachers employ a research experience-based learning method to help students acquire the fundamental cognitive skills required for future creativity and decision-making. This competency is systems thinking (Kisworo et al., 2021; Mahaffy et al., 2018; Mahaffy et al., 2019). Students can develop competencies in the context of the scientific process, making lecture-based research experiences as the main goal in searching for scientific answers. Research has shown that learning based on research experience can improve student performance, providing basic and advanced research experience in solving science-related contextual problems. Research experience in chemistry learning cannot be separated from laboratory activities.

Research-based student worksheets necessary to support student activities in the laboratory. This worksheet is a component that has a vital role in the lecture process. The availability of student worksheets can help students obtain information about learning However, designing material. worksheets needs to be adapted to student needs (Werby & Cegelski, 2019). Students are given freedom and authentic experience of all the information they obtain through research experiences. The research is to link the material studied with the facts they obtain contextually through data collection, concepts from theoretical studies, and experimental work procedures.

It is hoped that this research can help overcome problems related to electronic waste, which is part of environmental issues, by strengthening students' systems thinking skills. Systems thinking skills are essential because they can connect components and processes between systems, context, and content and predict sustainability aspects. This can be done through lecture practice research experiences based on laboratory activities.

### 2. Research Method

In this section, the research method which is design-based research and the research participants will be explained.

### 2.1. Design Based Research (DBR)

This study was designed to inspire pre-service chemistry teachers through an activity based on the latest chemistry research. It shows examples of how materials can be developed using research-based approach. Development was conducted using a designresearch based (DBR) approach, methodology widely used in environmental design research-based learning (Anderson & Shattuck, 2012; Edelson, 2002). The project was carried out cooperatively by pedagogical professionals and content specialists to emphasize a holistic approach (Aksela, 2019).

We modified this DBR approach by adapting learning activities based on selected contexts that support the relevance of the research topic. Figure 2 shows the three-part activity design including the initial assignment, laboratory practicum stage, and final assignment (Pernaa et al., 2022).

# 2.2. The Participants

This research involved two groups of students (a total of 50 students), consisting of 22 second-year students and 28 third-year preservice chemistry teacher enrolled in the 2022/2023 academic year. Both groups participated in this research because they had received basic chemistry lectures. This research was conducted in the coordination chemistry course at one of the private universities in West Java province, Indonesia.

176

This course is mandatory for all undergraduate students majoring in chemistry education. Students use scientific practices, collaborate, ask broadly relevant and new questions, and can iterate throughout the course. Students work in small groups (five to six people) to design and conduct research in the laboratory during lectures.

### 2.3. Materials and Tools

### 2.3.1. Collect electronic waste

Electronic waste was collected in the form of TV tubes of various sizes. Next, the component parts are taken through a mechanical process (in the recycling process).

### 2.3.2. Samples and their analysis

The collected CRT sample (2 g) was transferred into a metal-free glass vial. It was then pelleted before being characterized with the FTIR instrument.

# 2.3.3. Laboratory research materials and tools

This research prioritizes extraction tools in closed containers. Some of the tools needed in this research are a Schlenk tube (a closed glass container with a tap), a hot plate stirrer, a centrifuge, 0.22  $\mu$ m Phet syringe filters, and an FTIR spectrometer.

### 2.3.4. DES Preparation

The solvent used in this study was eutectic solvents based on ionic liquids that were suited for metals and minerals leaching due to their low volatility and eco-friendly properties, often known as green chemistry. At this stage, students synthesized DES as extractants for CRT leaching. The DES was comprised of choline chloride ( $C_5H_4NOCl/ChCl$ ) and levulinic acid ( $C_5H_8O_3/Lev$ . A). Due to a hydrogen bond donor (HBD) in levulinic acid and a hydrogen bond acceptor (HBA) in choline chloride, these two chemicals can form DES.

### 2.3.5. Leaching process on CRT

The DES synthesis was based on the mole fractions comparison of the two compounds.

Explorative Research Course: Recovering Rare Earth Elements from Electronic Waste Using Deep Eutectic Solvents

The most effective mole fraction comparison was  $\chi$ ChCl: $\chi$ Lev.A = 0.3:0.7) (Patelli, et al., 2020), the the mixture was heated up to 80 °C accompanied by stirring at 500 rpm for 48 hours. After that, the mixture was centrifuged at 3600 rpm for 10 minutes and filtered using a 0.22  $\mu$ m syringe.

### 2.4. Data Collection and Analysis

This research instrument consists of research-based student worksheets and questionnaires. Each of these instruments has been validated by three experts in their field. The three experts differ in their expertise, including experts in the content, pedagogic, and evaluation fields. The response from the validators was to consider revising the instrument before data collection.

After students carried out the leaching activity, students then carried out further characterization analysis using an FTIR spectrometer instrument to identify the presence of functional groups in rare earth metals. FTIR analysis was conducted at the instrument chemistry laboratory at a state university in Bandung, Indonesia.

Meanwhile, data in the form of questionnaires was analyzed using a percentage comparison of the scores obtained by students with the maximum score. This questionnaire data analysis was conducted to determine student responses to implementing of the research-based student worksheet. A Concept map analysis was carried out to describe students' system thinking profiles in linking chemical content, context, and sustainability aspects.

### 3. Results and Discussion

Green solvents were introduced in the initial task to recover rare earth elements from CRT components found in electronic waste. Students can learn through research-based student worksheets or sample articles facilitated by researchers.

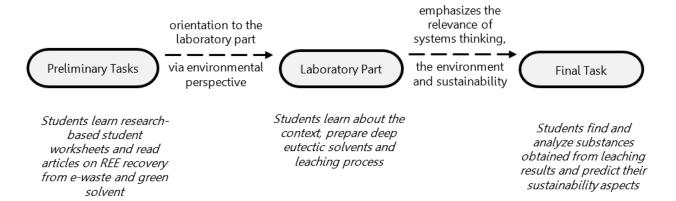


Figure 2. Structure of The Conducted Design Based Research

This worksheet emphasizes strengthening students' systems thinking skills in connecting the social environmental context in the form of electronic waste, environmentally friendly recycling processes, and the sustainable nature of chemistry.

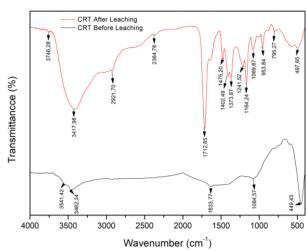
The object of research carried out by students is electronic waste in the form of tube TVs with CRT technology. The CRT on a tube TV produces colored light on the screen because it is coated with fluorescent powder containing rare earth metals. The worksheet guides students in recycling TV tube waste, from dismantling the components to getting a CRT, as shown in Figure 3.



Figure 3. Process of Taking a CRT from a used TV tube

The worksheet directs students to analyze rare earth metal content through instrumentation testing using an FTIR spectrometer. In the chemistry lab, students identified CRT samples from used TV waste using FTIR. Figure 4 shows

the results of CRT sample measurements using an FTIR spectrometer in the form of spectrum data before and after leaching, which students must analyze further.



**Figure 4. FTIR Spectrum of CRT Samples** 

Students can examine multiple peaks in the CRT's FTIR spectrum, as shown in Figure 4. The worksheet provides a table of FTIR measurement results so that the data can be presented and interpreted. Students could read a peak of 449.43 cm<sup>-1</sup>, and they identified the presence of rare earth metal group (Martín-Ramos et al., 2013). Based on this identification, it can be concluded that CRT from tube TV waste contains rare earth metals. Students will also extract metal as an objective.

Next, students construct a solvent based on green chemistry for the leaching procedure in

178

the laboratory portion, described in the worksheet's second section. The worksheet directs students to think systematically and predictively to obtain solvents that are based on green chemistry or are environmentally friendly. Students study the discourse, answer questions, and review assigned articles from the worksheet. From this assignment, some students were able to master scientific thinkina that the influence of the physicochemical properties of a compound on environmentally friendly conditions significant. Apart from that, students can gain knowledge about the formation environmentally friendly extractants. solvents that were successfully synthesized by the students were DES. DES were the solvents that the students could synthesize effectively. This solvent is inexpensive to synthesize, has moderate volatility, and is biodegradable and recyclable. One benefit of DES is its shallow vapor pressure (volatility), which makes it a solvent substitute viable and more environmentally friendly (Marcus, 2019).

Students synthesize DES in the laboratory by reacting choline chloride and levulinic acid. The reaction principle applied in this reaction process is heating at a temperature of 50 °C and rotation of 500 rpm (Figure 5a). The process is stopped when a clear liquid has formed, as shown in Figure 5b (Pateli et al., 2020).





Figure 5. Synthesize of DES (a) Heating and Stirrer and (b) DES is Formed

DES is a valuable solvent for extracting metals from metal ores and industrial waste. DES can recover valuable metals from industrial product waste, including electronic items.

Students experiment with a rare earth metal leaching experiment of CRT in the third section of this worksheet. The principle used is almost the same as DES synthesis: heating and stirring at 500 rpm. The difference is that at this stage, the heating temperature is 100°C using a sand bath for 48 hours. In laboratory work at this section, students use DES, as shown in Figure 6.



Figure 6. CRT Leaching Process in DES Extractant

After leaching, centrifugation continues by setting a rotation of 3600 rpm for 10 minutes. The final process was filtered using a Phet syringe filter measuring 0.22  $\mu$ m.

In the final task, students find and analyze substances obtained from the leaching results. Students can analyze the substances they obtain based on FTIR spectrometer measurements of CRT after leaching as shown in Figure 4.

Figure 4 of CRT after leaching shows a peak in 497.65 cm<sup>-1</sup>. The students can conclude that this material exhibits rare earth metal groups. A peak of 3417.98 cm<sup>-1</sup> indicates the vibration of the O-H group. The origin of this O-H group is suggested to be the levulinic acid solvent. A peak of 1712.85 cm<sup>-1</sup> indicates the vibration of the C=N group. It is indicated that the solvent choline chloride is the source of this C=N group.

Figure 4 shows that the DES extractant can extract rare earth metals from CRT electronic waste. Because of its negative charge, DES can attract positively charged metal ions, and rare earth metals easily form bonds. These connections can form rare earth metal coordination complexes. However, this study mainly focuses on recovering rare earth metals and does not address the coordination of complex compounds created.

# 3.1. Analysis of Systems Thinking Skills Based on Concept Maps

Systems thinking skills can be measured through visualization in concept maps as a starting point for students in connecting interrelated components and processes. Concept maps are used as an evaluation tool to measure systems thinking skills with the Systems Thinking Hierarchy (STH) model (Assaraf & Orion, 2010; Tripto et al., 2013). Student concept map data was taken twice before and after the research. The aim is to see the profile of students' systems thinking abilities.

The ability to identify components and processes is one of the systems thinking skills in the STH model. Data from the pre-test concept maps made by students obtained 652 concepts divided into 539 concepts of components and 113 concepts of processes. Meanwhile, the data obtained from the post-test included 1208 concepts, 898 concepts of components, and 310 concepts of processes. A comparison of the number of components and processes in the concept map created by students can be seen in Figure 7.

The data on concept maps shows that students tend to make concept maps in the form of components rather than processes (Figure 8). It is because the topic of deep eutectic solvents and rare earth metals has never been taught before, resulting in less comprehensive student understanding. In this condition, students only recognize chemical components and their definitions.

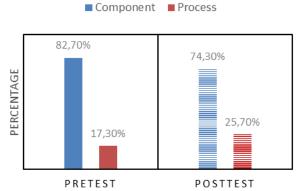


Figure 7. Comparison of The Number of Component and Process Concepts Created by Pretest and Posttest Students

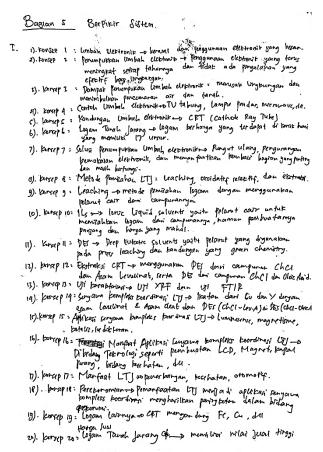


Figure 8. Component and Process Concept

Students ignore the visible processes, even though the processes involved in recovering rare earth metals from electronic waste are not only chemical processes but also involve processes in other fields of science, for example, environmental, social, and economic. Lack of identification of the processes in the

system causes weak dynamic thinking and cyclical thinking skills. So, systems thinking skills help find meaningful relationships between system components. One of the concept maps created by students is shown in Figure 9.

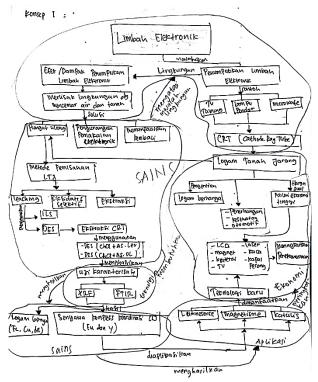


Figure 9. Concept Maps

# 3.2. Student Responses Regarding Research Experience-Based Course

Research-based student worksheets are implemented for twelve class sessions, each lasting 150 minutes. Students have carried out all the activities presented in this worksheet. Student achievement of core competencies and effectiveness of worksheets through distributing questionnaires to students.

The results of the Likert scale on a questionnaire related to chemistry lectures are shown in Figure 10. Fifty pre-service chemistry teachers participated in filling out this questionnaire. Based on the responses to a Likert scale questionnaire designed to help students learn chemistry, students believe chemistry fosters curiosity (76% strongly agree and 24% agree) and are interested in studying (88% strongly agree and 12% agree). The case

study of rare earth elements recovering from electronic waste using eutectic-based ionic liquids provides evidence. Students think that the practicum activities provided by the lecturer make students understand the material better (78% strongly agree and 22% agree). Students can master the chemistry subject matter taught (20% strongly agree, 62% agree, 14% disagree, and 4% strongly disagree). Students do not understand the chemistry material taught (12% agree, 52% 36% strongly disagree). disagree, and According to students, the chemical material studied has no benefit (8% agree, 24% disagree, 68% strongly disagree) and the chemical material has use value (46% strongly agree, 44% agree, and 10% disagree). Seeing the students' positive responses to statements 1, 2, 4, 5, 6, 7, and 8 indicates that the responses generated by students towards the research experience lecture on the case of recovering rare earth metals from electronic waste were very positive.

Statements 9, 10, 11, and 12 clarify this for the learning resources category. Students think that the learning resources (research-based worksheets) student used to enthusiasm for learning (70% strongly agree and 30% agree) and are interesting to learn (44% strongly agree, 52% agree, and 4% disagree), provide the required information (72% strongly agree and 28% agree). Apart from that, the arrangement of chemical material presented in learning resources is usually coherent or systematic (58% strongly agree and 42% agree). Based on statements 9, 10, 11, and 12, the learning resources provided during lectures are presented very well.

The learning media category contains 4 statements: numbers 13, 14, 15, and 16. Students think that the learning media used makes students active in the learning process (64% strongly agree, 32% agree, and 4% disagree). The learning media makes students understand the chemistry concepts being taught (20% strongly agree, 68% agree, and 12% disagree). The arrangement of chemical material in learning media is coherent or systematic (24% strongly agree, 58% agree,

and 18% disagree). The learning media lecturers use is equipped with learning videos that support the lesson material (72% strongly

agree and 28% agree). These results indicate that students welcomed the use of these learning media.

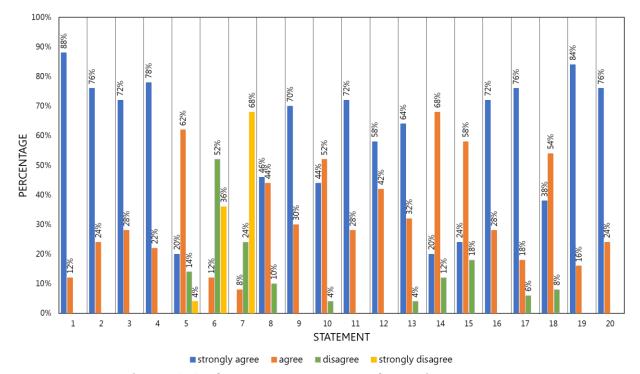


Figure 10. Student Responses to Research Experience Lectures

Statements 17 and 18 are examples of the systems thinking category. This statement was developed to see whether the current research-based student worksheet lectures are supporting the development of students' systems thinking skills. Students consider that their chemistry learning has trained them to develop systems thinking skills (76% strongly agree, 18% agree, and 6% disagree). The chemistry questions tested so far have contained systems thinking skills strongly agree, 54% agree, and 8% strongly agree). The responses given by students show that current chemistry learning has facilitated the development of systems thinking skills for students.

The final category is about sustainability aspects. This category was created to see whether so far studying chemistry has facilitated students' connecting chemistry learning with aspects of sustainability. The chemistry material provided makes students care about the environment (84% strongly

agree and 16% agree). Students consider that aspects of sustainable development have been accommodated in current chemistry lectures (76% strongly agree and 24% agree). All responses from students indicated positive perceptions regarding sustainable development aspects in chemistry learning.

After students complete the assignment, which consists of answering worksheet questions, their writing is examined to ensure it complies with core competencies and the relevant evaluation rubric. In general, most students could communicate their science, achieve competency in basic analysis of text and data, and collaborate to exchange new ideas.

It is also challenging for students to achieve systems thinking, a core competency. Students demonstrate systems thinking skills, for example, by integrating environmental problems related to electronic waste linked to chemical and social content and sustainability.

In the worksheet, several components challenge students; for example, students identify the content of valuable chemical elements in electronic waste, synthesize environmentally friendly solvents, and recover valuable elements such as rare earth metals as sustainable materials. Most students are used to laboratory activities and challenged to complete them. At the time of observation, the initial condition of the students was that they found it difficult to read the data from the FTIR spectrometer analysis on the initial CRT sample. However, students can actively study related articles to learn techniques for analyzing FTIR results. In addition, students also need help finding ways to analyze or present data to test research questions at the outset. This is because students must identify the type of graph in the form of a spectrum that must be explained completely to answer the research question. Students remain focused on scientific reasoning, predictions, and data. Lecturers guide students in analyzing data images and instruct them on how to analyze further.

The example above highlights how researchbased student worksheets challenge students to independently engage in creative and logical systems and analytical thinking to discover unknown results and interpretations for themselves. In overcoming all these challenges, lecturers consistently find that using laboratory methods is very effective because it encourages students to take responsibility for their learning strengthens systems thinking skills through problems independently. Students can solve problems contextually through the data they obtain. Lecturers consistently observe student activities, showing that students enthusiastic and eager to accept the challenge of exploring their data in new ways.

### 4. Conclusion

This research shows DES as an extractant that can recover REE from electronic waste in the form of TVs with CRT technology. It is proven by the results of the FTIR spectrum showing a wavelength of 449.43 cm<sup>-1</sup>, which identified the presence of the REE functional group in the coordination complex compound. This research also shows the importance of students' systems thinking skills, which are demonstrated in identifying components contained in electronic waste in the form of potential metals and metals that are harmful to the environment. Students can identify the potential content of CRT containing REE in electronic waste, identify the relationship between REE and sustainable minerals, and manage the REE recovery process with leaching separation method. as а Understanding the nature of the solvent used in the leaching process, generalizing the DES solvent as an extractant for leaching REE based on green chemistry principles. Understanding the physicochemical properties of REEs that can be reused in applications in the industrial world, thinking about predictions that DES solvent is a green solvent that can be used as leaching agent in recovering environmentally friendly metals, as well as REEs that are recovered as critical minerals that have guite wide applications sustainably. This research experience lecture is guided by a research-based student worksheet emphasizing students' systems thinking skills. From all aspects of the assessment that responded students to, the research experience course showed positive results on the learning process, learning resources, learning media, systems thinking skills, and made pre-service chemistry teachers aware of the environment and how to overcome environmental problems by considering sustainability aspects.

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