Doctoral School of Chemical Engineering and Material Sciences

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UTILIZATION OF THE BAUXITE RESIDUE TO RECOVER SCANDIUM RARE EARTH ELEMENT

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INTRODUCTION

Red mud (RM) or Bauxite residue (BR) is a by-product that originates through the Bayer method of alumina (Al_2O_3) manufacture from the bauxite mineral ores. Yearly, almost two tonnes of BR is produced for each tonne of Al_2O_3 mined from the Bayer method. It's assessed that around 160 million tonnes of BR are manufactured each year, whereas almost four billion tonnes have already been stored around the world. The disposal and lasting storage of the waste volumes occupy a big land. In turn, and this causes higher costs and obligations for Al_2O_3 manufacturers. The high alkalinity of BR (i.e. pH=10–13) is a main environmental concern. Moreover, spills have led to major environmental incidents. In 2015, the collapse of a tailing dam in the state of Minas Gerais in Brazil was evidenced as well the serious ecological and socio-economic impact of storing solid waste residue at large scale. In October 2010, an extremely serious environmental catastrophe occurred in Ajka, Hungary. This disaster focused the attention of the governmental people and scientists on the possibility of the processing and reutilization of the BR and decreasing drastically the storage volume of wet red mud. BR comprises considerable concentrations of Rare Earth Elements (REEs), but their retrieval being a challenge. Among the REEs, scandium represents up to 95% of the economic value of the RM. As a consequence of its big quantities as well as the ease of mining and leaching, RM can be an important origin of scandium (Sc), which is a rare and costly metal because of its limited accessibility and the tasks linked to its retrieval and purification; the Sc_2O_3 (99.99%) present price is (3800 US$/kg). The biggest challenges to scandium beneficiation remain the low natural abundance of the element in mineral deposits as well as its association with other elements having very similar chemical properties as previously stated. Sc is initially utilized for making the alloys of Al–Sc that are characteristically include 2%wt.% Sc. Such alloys are considerably tougher than the traditional high-strength alloys, with an elevated strength, a high grain refinement, without welds' hot cracking, and outstanding resistance to corrosion resistance. Moreover, scandium was utilized in certain contemporary uses, like fuel cells, oil well tracer, electronic parts, analytical standards, and high-intensity metal halide lamps. And, the Sc participation in the Solid Oxide Fuel Cells (SOFC) formation is also too appealing owing to the vigorous O_2-ion conductivity of the Sc_2O_3-stabilized ZrO_2 materials.

Hydrometallurgy is a well-built method to extract the rare earth elements from the REE-carrying materials, like normal ores as well as the else secondary origins. It involves two main stages: leaching and separation. In the stage of leaching, rare earth elements are separate from the REE-carrying materials employing chemical substances in aqueous solution. After that, various detaching procedures are utilized for recovering the rare earth elements from the aqueous solution. REEs separation as well as retrieval from the aqueous solution found through hydrometallurgy being, in general, conducted via many traditional methods comprising co-precipitation, precipitation, adsorption, liquid membrane (LM), ion exchange (IX), liquid-liquid extraction (LLE), or solvent extraction (SX). The SX and the IX are the high broadly utilized methods for the REEs retrieval from the residues such as RM. The SX provides virtuous split-up parameters as well as the likelihood for treating big amounts of BR leachate solution. Nevertheless, it's related to many ecological topics owing to the big organic solvents volumes utilized, such as kerosene and hexane. The ionic liquids (IL) have been introduced as a greener substitution to the traditional solvents, like bis(2-

ethylhexyl) phosphoric acid (commercial names D2EHPA or P204) tributyl phosphate (TBP).

1. SIGNIFICANCE, SCOPE OF THE TOPICS, AND DEFINITIONS

This PhD dissertation aims to introduce a new, efficient, and sustainable approach/technique for Sc recovery from RM by applying liquid-liquid and solid-liquid extraction processes. Thus, the main objectives of the dissertation can be given as follows:

- Optimisation of several parameters of the acid leaching process, such as the type of acid leaching agents, contact time, temperature and solid (S: red mud) to liquid (L: leachate) ratio;
- Investigation the selectivity of different organophosphorus liquid extractants, such as bis-2-ethylhexyl phosphoric acid (D2EHPA), tributyl phosphate (TBP), and trioctylphosphine oxide (TOPO) for extraction of Sc from red mud leachate;
- Study the ability of ion exchange technique (50Wx8 resin) for advanced purification as complementary stage for solvent extraction process.
- Investigation the effect of various parameters, such as the concentration of extractants, temperature and pH of solution, aqueous to organic (A/O) volume phases ratio, and shaking-extraction time on Sc extraction efficiency from red mud leachate;
- Study of the extraction ability of liquid macrocyclic compounds towards Sc (III) by liquid–liquid extraction from model solution using response surface methodology (RSM) and the determination of the optimum conditions of extraction process; and
- Preparation, characterization and application of Fe_3O_4/SiO_2/OPCs (OPCs = D2EHPA, TOPO, TBP) solid

phases for the separation of Sc from red mud leachate by solid-liquid extraction process.

2. MATERIALS AND METHODS

2.1 Red Mud Acid Leaching

Different leaching methods were applied in the present study to optimize the leaching process, maximize the Sc, and minimize the major elements, such as Fe, Ti and Al content. Mechanical, microwave (MW)-assisted, high-pressure leaching (HPL), and Sulfation–Roasting–Leaching (SRL) digestions processes were used to transform the metals content of the RM into ionic form. Among these methods, the mechanical digestion process was chosen for its cost and efficiency compared with the other methods. The RM samples used in this study were obtained from the Ajka RM disposal facility in Hungary, and these samples were further dried at 105 °C for 24 h.

2.2 Iron Content Removal from Red Mud

The removal trivalent iron from the obtained leachate solutions was investigated by two proposed extractants by solvent extraction techniques. The red mud was leached by 7 mol/L of HCl acid solution before the solvent extraction. Two extractants tri-noctylamine (N235) of 10 vol% (or 20 vol.%, and 30 vol.%) in kerosene or pure diethyl ether were used. The extractants structure is shown in Fig. 1. Equal volumes (10 mL) of the organic phase (N235 or diethyl ether) and aqueous phase (red mud leachate solution) were mixed for 15 min in a separation funnel. In solvent extraction by diethyl ether, the extraction cycle was repeated two times for the same leachate sample to achieve better iron removal efficiency. The separated aqueous phase was investigated by ICP-OES instrument.

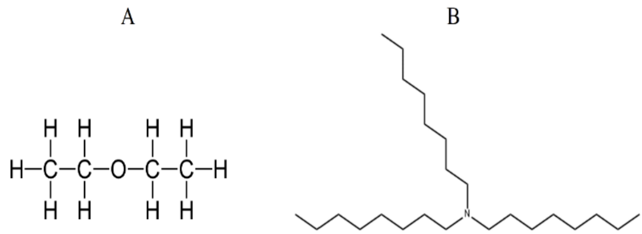

Fig. 1. Chemical structures of organic extractants for iron removal: (A) diethyl ether, (B) tri-noctylamine (N_{235})

2.3 Liquid-Liquid Extraction

2.3.1 Liquid-Liquid Extraction by Organophosphorus Compounds

Two main organophosphorus compounds as extractants were investigated involving D2EHPA and TBP. The third one (TOPO) was suggested for purification step. The following parameters have been chosen to be the key variables in D2EHPA and TBP systems: concentration of extractant, A/O phase ratio, concentration of stripping solution, pH value, extraction time and temperature. The chemical structures of D2EHPA, TBP and TOPO extractants are depicted in Fig.2.

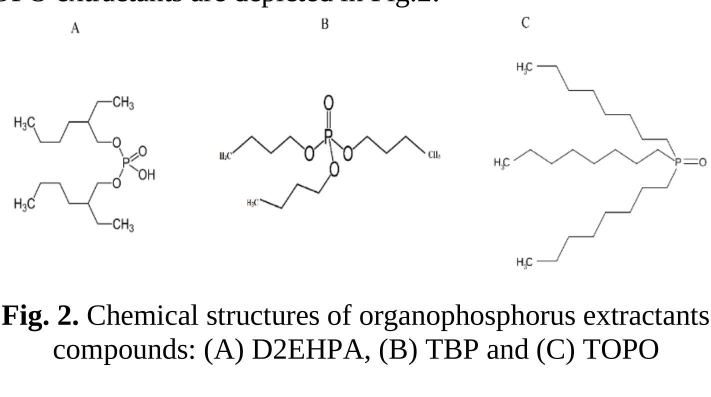

Fig. 2. Chemical structures of organophosphorus extractants compounds: (A) D2EHPA, (B) TBP and (C) TOPO

2.3.2 Liquid-Liquid Extraction by Macrocyclic Compounds

Extraction and stripping experiments were carried out for Sc model solution at 25°C with three types of macrocyclic compounds, DC18C6, K 2.2.2 and C 2.2 which their structures are illustrated in Fig.3.

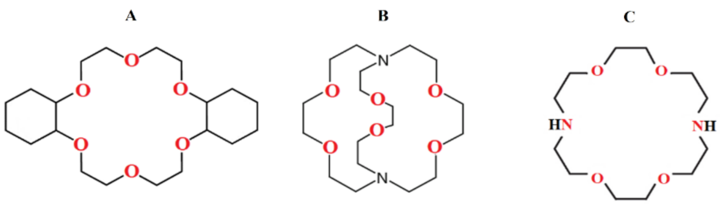

Fig.3. Chemical structures of macrocyclic extractants compounds: (A) DC18C6, (B) K 2.2.2 and (C) C 2.2

2.4 Preparation of Solid Phase for Solid-Liquid Extraction

2.4.1 Preparation of Iron Oxide Magnetic Nanoparticles

The co-precipitation technique was employed to produce iron oxide nanoparticles. To achieve that, 4.4 g of $FeCl_3 \cdot 6H_2O$ and 1.98 g of $FeCl_2 \cdot 4H_2O$ were dissolved successively in 60 mL of de-aerated water by nitrogen gas. However, the solution was purged with nitrogen for 30 min to avoid the oxidation of Fe(II) ions. The co-precipitation process was carried out at two pH values pH 10 and pH 11 in order to prepare the optimum morphology and the nanoscale dimensions of iron oxide nanoparticles. Under continuous stirring at 25 °C of the ferric and ferrous iron mixture, 140 mL of the 0.8 mol/L of NH_4OH were added to the solution, and the pH was adjusted with (0.1 mol/L) HCl. During the addition of NH_4OH solution, it was observed that there is a color variation and after 5 min, the color has been changed from brown to black totally. The produced iron oxide nanoparticles were collected by external magnetic field. This characteristic is very advantageous for particle separation from the sample solutions. The sample is abbreviated as Fe_3O_4.

2.4.2 Preparation of Fe_3O_4/SiO_2/OPCs by Sol-Gel Method

It was proposed to immobilize the OPCs molecules over a solid support to prepare efficient solid–phase extraction (SPE) system. The incorporation of OPCs molecules, such as D2EHPA, TBP and TOPO was carried out by the entrapment technique of sol–gel method. The first step was the hydrolysis of tetraethyl orthosilicate (TEOS) which used as precursor for synthesis of siloxanes groups. 3 mL of TEOS were mixed with 1 mL of water and 0.1 mL of 1 mol/L HCl at room temperature at vigorous stirring for an hour to complete the hydrolysis of TEOS. Then 1 mL of D2EHPA or TBP, or 350 mg of TOPO dissolved in 3mL tetrahydrofuran (THF) was then added separately to the solution. After 10 min of stirring, 10 wt% of Fe_3O_4 were added to the mixture and sonicated for 5 min, followed by stirring at 72 h at the room temperature in order to complete the condensation. Finally, the obtained product was washed with distilled water and dried at 75 °C for 12 h and ground into powder using mortar and pestle. The prepared samples are abbreviated in the text as Fe_3O_4/SiO_2/D2EHPA, Fe_3O_4/SiO_2/TBP and Fe_3O_4/SiO_2/TOPO.

2.3 Characterization methods

The physicochemical properties of the solid phase were examined using several characterization techniques to obtain information about the structural, chemical and surface properties of the prepared adsorbents such as Fourier transform infrared spectroscopy (FTIR), Brunauer–Emmett–Teller (BET) method, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX). the concentration of metal ions was measured by inductively coupled plasma - optical emission spectrometry (ICP-OES).

3. NEW SCIENTIFIC FINDINGS

One of the main goals of this PhD thesis was to develop new techniques for the recovery of scandium from the acidic leachates of red mud bauxite residue. The recovery of scandium from the acidic solutions was studied by different separation technologies: Solvent extraction (organophosphorus or macrocyclic liquids), ion exchange, and solid phase extraction (organophosphorus compounds modified solid support).

3.1 Recovery of Scandium from Real Red Mud Leachate by Solvent Extraction with Organophosphorus compounds

3.1.1. I set and optimize the experimental parameters for effective and selective dissolution of scandium from red mud. 80% of Sc (79 ppm) dissolution was achieved under the following conditions: 7 mol/L HCl at a S/L ratio of 1:30 for 5 h at 75 ℃ reflex system. This leachate was further purified by liquid-liquid extraction method in order to remove other dissolved elements such as Fe 14wt%, Al 7wt%, Ti 2.1wt%, La 155 ppm, Y 101 ppm. The iron content was mainly removed by diethyl ether and remaining metals ions with organophosphorus extractants [1,2,3].

3.1.2. I recommend the Protocol C (Fig. 4) of triple liquid-liquid extraction for the efficient recovery of scandium from the red mud leachate at industrial scale. At Protocol C the highest Sc recovery 81% (869 ppm) from 7 mol/L HCl leachate solution was achieved after triple extraction with

10 vol% TBP, A/O = 3:1 and 5 min extraction time. The iron (150ppm) and titanium (1.5 ppm) content was lower and Al, La and Y were not observed in final recovered solution [1,2,3].

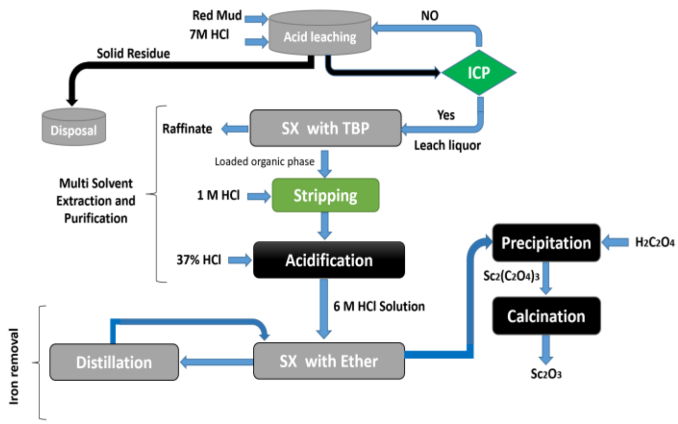

Fig. 4. Proposed flowsheet of Sc recovery from red mud leachate based on triple liquid-liquid extraction by TBP (Protocol C)

3.2 Recovery of Scandium from Model Solution by Solvent Extraction with Macrocyclic Compounds

The main aim of this part was to figure out how well DC18C6, K 2.2.2 and C 2.2 macrocyclic compounds work as novel extractants for Sc (III) by using a central composite rotatable design technique. The following points are determined:

3.2.1. The experimental results obtained were in very good correlation with the predicted STATISTZICA and WinQSB softtwares ones, demonstrating the model's validity and its application for Sc recovery from real leachate of 75 mg/L initial concertation. The results showed that 0.006 mol/L K 2.2.2 and C 2.2 in 1,2 dichloroethane have a greater Sc capturing affinity compared to DC18C6 under the same experimental conditions: A/O ratio1, pH of solution 4, 11 min contact time. Therefore extraction efficiency was higher 99 and 97 % for K 2.2.2 and C 2.2 respectively in comparison with DC18C6 (E 15%) macrocyclic extractant [4].

3.2.2. I concluded that the incorporation of scandium into the macrocyclic compounds was feasible. The change in Sc concentration was monitored by AAS technique. K 2.2.2 and C 2.2 compounds has unique features and capable of encapsulating metal ions in their cage-like cavities to form stable complexes. This could be of potential value in the separation and purification of Sc in REEs processing [4,5,6].

3.3 Recovery of Scandium from Real Red Mud Leachate by SPE with Organophosphorus Compounds

The knowledge gained in the field of REE extraction with organophosphorus compounds (OPCs) has been implemented to develop a new type of solid phases for solid-liquid techniques. The following points are determined:

3.3.1. The FTIR, BET and EDX-SEM results confirmed that OPCs (D2EHPA, TBP and TOPO) were successfully incorporated to Fe_3O_4/SiO_2 solid phase/support by entrapment sol–gel preparation technique with formation of particles between 20 to 500 nm in size. Moreover, the formation of the P=O, P-O- functional (active) group for Sc binding was confirmed by FTIR analysis [7].

3.3.2. Among of solid samples the highest 97% Sc removal efficiency from 79 ppm Sc containing red mud leachate was achieved over Fe_3O_4/SiO_2/TBP solid phase (adsorbent). I recommend this solid phase for testing in the recovery of scandium from the red mud at pilot-plant scale.

PUBLICATION LIST

Published articles related to thesis research.

1. **Salman, A. D**.; Juzsakova, T.; Jalhoom, M. G.; Abdullah, T. A.; Le, P.-C.; Viktor, S.; Domokos, E.; Nguyen, X. C.; La, D. D.; Nadda, A. K.; Nguyen, D. D., A selective hydrometallurgical method for scandium recovery from a real red mud leachate: A comparative study. Environmental Pollution, 2022, 308, 119596.**IF= 9.9.**

2. **Salman, A. D**.; Juzsakova, T.; Rédey, Á.; Le, P.-C.; Nguyen, X. C.; Domokos, E.; Abdullah, T. A.; Vagvolgyi, V.; Chang, S. W.; Nguyen, D. D., Enhancing the Recovery of Rare Earth Elements from Red Mud. Chemical Engineering & Technology 2021, 44 (10), 1768-1774. **IF= 1.7**

3. **Salman, A. D**.; Juzsakova, T.; Mohsen, S.; Abdullah, T. A.; Le, P.-C.; Sebestyen, V.; Sluser, B.; Cretescu, I., Scandium Recovery Methods from Mining, Metallurgical Extractive Industries, and Industrial Wastes. Materials 2022, 15 (7), 2376. **IF= 3.7.**

4. **Salman, A. D**.; Juzsakova, T.; Jalhoom, M.; Ibrahim, R.; Domokos, E.; Al-Mayyahi, M.; Abdullah, T.; Szabolcs, B.; Al-Nuzal, S., Studying the extraction of scandium (III) by

macrocyclic compounds from aqueous solution using optimization technique. International Journal of Environmental Science and Technology, 2022, 1-18. **IF= 3.5.**

5. **Salman, A. D.;** Juzsakova, T.; Jalhoom, M. G.; Le Phuoc, C.; Mohsen, S.; Adnan Abdullah, T.; Zsirka, B.; Cretescu, I.; Domokos, E.; Stan, C. D., Novel hybrid nanoparticles: synthesis, functionalization, characterization, and their application in the uptake of scandium (III) ions from aqueous media. Materials, 2020, 13 (24), 5727.**IF= 3.7.**

6. **Salman, A. D**.; Juzsakova, T.; Jalhoom, M. G.; Le, P.-C.; Abdullah, T. A.; Cretescu, I.; Domokos, E.; Nguyen, V.-H., Potential Application of Macrocyclic Compounds for Selective Recovery of Rare Earth Scandium Elements from Aqueous Media. Journal of Sustainable Metallurgy, 2022. **IF= 3.**

7. **Salman, A. D**.; Juzsakova, T.; Ákos, R.; Ibrahim, R. I.; Al-Mayyahi, M. A.; Mohsen, S.; Abdullah, T. A.; Domokos, E., Synthesis and surface modification of magnetic Fe_3O_4@ SiO_2 core-shell nanoparticles and its application in uptake of scandium (III) ions from aqueous media. Environmental Science and Pollution Research 2021, 28 (22), 28428-28443. **IF= 3.1.**

Conference oral presentation related to thesis research

1. **Salman, A.D**, Juzsakova T., Igor Cretescu, Brindusa Sluser, Le Phuoc Cuong,.:Process Development for Recovery of Rare Earth Elements from Red Mud, Conference on Air And Water - Components Of The Environment, Babeş-bolyai University, Cluj-Napoca, Romania, March 22-24, 2019**.**

2. **Salman, A.D,** Juzsakova1, T, Igor Cretescu, Le Phuoc Cuong,.:Recovery of the Rare Earth Elements of the Red Mud, Conference on Environmental Science, Sapientia Hungarian University of Transylvania, Cluj-Napoca, Romania, April 3-6, 2019**.**

3. **Salman,A.D,** Abdullah,T. A, Khader E. H., Juzsakova T..:Investigation of the Effect of Nano-Silica Admixture on Mechanical Properties of Oil Well Cement (OWC), Conference on Postgraduate Studies In Chemical Engineering, CEPC3-2019, University of Technology,Baghdad, Iraq , May 5-7, 2019**.**

4. **Salman, A.D**, Juzsakova T., Barbooti M, M.:Technological Development for Recovery of Rare Earth Elements from Red Mud, Conference on Postgraduate Studies In Chemical Engineering, CEPC3-2019, University of Technology, Baghdad, Iraq , May 5-7, 2019.

5. **Salman,A.D**, Juzsakova T., Abdullah,T. A,.: Development for Recovery of Rare Earth Elements from Red Mud, Conference on Environmental Management, Engineering, Planning and Economics, Held with the SECOTOX , Mykonos island, Greece, May 19-24, 2019.

6. **Salman A.D.,** Juzsakova T., Zoltán Bakonyi, Abdullah T. A., Igor Cretescu, Ákos Rédey,.: Recovery Of Rare Earth Elements From Red Mud, 10th International Conference On Environmental Engineering And Management, Department of Environmental Engineering and Management Faculty of Chemical Engineering and Environmental Protection, Technical University of Iaşi, Romania, September 18 – 21, 2019.

7. **Salman A.D**, Juzsakova T., Domokos Endre, Abdullah T. A.,.: Recovery of Rare Earth Elements from Red Mud, 25th International Conference on Chemistry, Cluj-Napoca, October 24–26, 2019.

8. **Salman A.D**., Juzsakova T., Abdullah T. A., Mohammad A. Al-Mayyahi, Raheek I. Ibrahim, Al-Lami Munaf,.: Recovery Of Rare Earth Elements From Red Mud , 15th International Conference on Waste Management, Ecology and Biological Sciences (WMEBS-19) ,Budapest Nov. 8-9, 2019.

9. **Salman A.D**., Juzsakova T., Endre Domokos, Abdullah T. A.,.: Recovery of Rare Earths From Red Mud By High-Pressure Acid Leaching, International Joint Conference on Environmental and Light Industry Technologies, Obuda University, Budapest, Hungary,21 − 22 November ,2019.

10. **Salman A.D**., Juzsakova T., Redey Akos,.: Novel Techniques for Recovery of Rare Earth Elements from Red Mud. Green Solutions Conference,University of Pannonia, Faculty of Engineering, Institute of Environmental Engineering,18 December, 2019.

11. **Salman, A. D.;** , Juzsakova T, Moayyed G. Jalhoom, Raheek. Ibrahim, Endre Domokos, Thamer Abdullah, Saja Mohsen, Balogh Szabolcs, Saadi M. D. Al-Nuzal. Studying the Extraction of Scandium with Macrocyclic Compounds from Aqueous Solution. 4th SEE SDEWES conference, Sarajevo, Bosnia 28th June – 2nd July 2020.

12. **Salman A.D**, Tatjána Juzsakova, Mohammad A. Al-Mayyahi, Moayyed G. Jalhoom, Thamer Adnan Abdullah, Saja Mohsen , Endre Domokos, Tamas Korim . Synthesis, Surface Modification and Characterization of Magnetic Fe_3O_4@SiO_2 Core-Shell Nanoparticles. 5th International Scientific Conference on Advanced Engineering Technologies Basrah, Iraq, 18-19 August (ISC-AET'2020).

13. **Salman A.D**, T. Juzsakova, Moayyed G. Jalhoom, T. A. Abdullah, Endre Domokos, Rédey Ákos., Recovery of Scandium (III) By Liquid-Liquid Extraction of Macrocyclic Compounds From Nitrate Solutions. Sustainable Environmental Protection & Waste Management Responsibility, November 19 – 20, 2020 RKK – Óbuda University, Budapest, Hungary.

14. **Salman A.D**, Juzsakova T, Moayyed G. JALHOOM, Thamer Adnan ABDULLAH, Phuoc-Cuong LE, Endre Domokos, Recovery Of Scandium From The Bauxite Residue By Solvent Extraction. 12th ICEEE–2021-2021, November 18-19, 2021 Óbuda University, Budapest, Hungary.

15. **Salman A.D**, Juzsakova T, M. G. Jalhoom, Phuoc-Cuong Le , Thamer Adnan Abdullah , M. A. Al-Mayyahi, , Endre Domokos. Synthesis and Surface Modification of Magnetic Fe_3O_4/SiO_2/OPCs Nanoparticles And Its Application In Uptake of Scandium (III) Ions From Acidic Media. Obuda.

Conference poster presentation related to thesis research

1. **Salman A.D**, Juzsakova,T., Bakonyi,Z., Domokos,E.: New Strategy for the Recovery of Rare Earth Elements (REEs) from Hungarian Red Mud, Conference on Global and Regional Environmental Protection, GLOREP 2018, Timisiora, Romania, November 15-17, 2018.

2. **Salman A.D**, Juzsakova,T., Bakonyi,Z., Pap,T., Domokos,E.: Experimental Investigation to Recovery of Rare Earth Elements (REEs) from Hungarian Red Mud Using Optimization Technique, 9th International Conference on Climatic Changes and Environmental(Bio) Engineering, Óbuda University, Budapest, November 22-24,2018.

SCIENTOMETRIC DATA

Number of publications which are base of the PhD thesis: 7
Total number of publications: 20
Impact factors are base of the PhD thesis: 31.1
Total impact factor: 68.7
Abstract in international conference proceeding related to PhD thesis: 18
h-index (Scopus): 8
Veszprem, February 09, 2023