Preliminary Study of Exploring the Multi-elements Layered Double Hydroxides for Iodate Decontamination by Machine Learning

Sujeong Lee [a], Juhwan Noh[c], Tien-Shee Chee[a], Ho Jin Ryu[a,b,]*
[a]Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST)
[b]Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology (KAIST)
[c]Chemical Data-driven Research Center, Korea Research Institute of Chemical Technology (KRICT)

[*]Corresponding author: hojinryu@kaist.ac.kr

***Keywords:** Machine Learning, Multi-elements, Layered Double Hydroxides, Iodate, Decontamination*

1. Introduction

Iodine is one of the fission products, especially, I-129, a long-lived radionuclide ($T_{1/2}$ = 1.6x10^7 yrs). This radionuclide is notable for its various physical states, including gas, liquid and solid, as well as in multiple oxidation states (-1, 0, +1, +5, +7) [1]. Its high mobility poses a significant risk, facilitating its spread to the environment and people [2]. Thus, the decontamination of iodine is a critical necessity to mitigate these risks.

Aqueous iodine is primarily sourced from the reprocessing of spent fuel and incidents of fuel failure [3]. Based on the environmental conditions such as pH level, and the presence of organic matter, the chemical species of aqueous iodine were mainly iodate (IO_3^-), about 70%, from the report of the Hanford site and Savannah River site [4]. Conventional silver-based adsorbents such as Ag-activated carbon and Ag-zeolite, have been used to capture iodine due to their chemical affinity for iodide (I^-) form. However, Ag lacks chemical affinity to iodate (IO_3^-) as explained by the hard and soft acids and bases (HSAB) theory. Thus, it recently highlighted a growing necessity for the development of new adsorbents specifically targeted at efficiently capturing iodate (IO_3^-) from contaminated environments.

Layered double hydroxides (LDHs) are attractive adsorbents due to compositional flexibility and different adsorption mechanisms towards anions. They have been studied to remove harmful anions from contaminated water [4]. Especially, few researchers have studied the performance of LDHs for iodate (IO_3^-) such as MgAl, MgFe, CoCr, CoAl, NiCr, and NiAl [4–6]. However, the effect of the metal elements within these reported LDHs on the iodate (IO_3^-) removal remains unclear. The lack of understanding of the mechanism presented challenges in exploring the optimal LDH composition among the vast number of potential metal combinations. The extensive constituents of layered double hydroxides have not been explored yet due to the limitations of interest, time, and cost.

Recently, there has been a new paradigm (4th paradigm) in materials discovery called the data-driven approach. This new paradigm harnesses the power of data, utilizing the tremendous amounts of experimental and simulation results accumulated over the past few decades rather than intuition or personal experience. Through the use of advanced data analysis tools such as machine learning, researchers can handle these large datasets efficiently to identify correlations and hidden rules that might not have been discovered before. Consequently, the new paradigm has accelerated the high-performance innovative materials discovery [7,8].

In this study, we explored the multi-elements LDHs for decontamination of iodate (IO_3^-) assisted by machine learning. This approach reduced the numerous potential experiments, while also saving time and resources. To the best of our knowledge, this study was the first instance of utilizing a data-driven strategy to investigate multi-elements adsorbents specifically for radionuclide removal.

2. Methods and Experiment

2.1 Synthesis of the multi-elements layered double hydroxides

The synthesis process followed the methods described in previous works [9].

2.2 Batch adsorption tests of the multi-elements layered double hydroxides for iodate (IO_3^-)

To evaluate the adsorption performance of synthesized multi-element LDHs, 0.02 g of the powder was immersed in 10 mL of a 10 ppm iodate (IO_3^-) solution in 15 mL of conical PP tubes. The PP tubes were then placed in a shaker and mixed at 180 rpm at 25 ℃ for 72 hours. Three samples were prepared under each condition to ensure reproducibility and reliability. The initial and final concentrations of iodate (IO_3^-) were measured by ion chromatography (IC).

2.3 Characterization

The crystal structure of synthesized all multi-elements LDHs was investigated by X-ray diffraction (XRD; SmartLab, Rigaku) with CuKα radiation at 45 kV and 200 mA. Data were collected in the range of 2θ=5 °-80° with a step of 0.01° and a scanning time of 10 s per step. Furthermore, the adsorption capacity of each LDH system was evaluated by ion chromatography (ICS-6000, Thermo Scientific).

2.4 Machine learning-assisted multi-elements design

The synthesizability of multi-element LDHs was evaluated based on the XRD and XRF results. The adsorption performance of synthesized multi-element LDHs was evaluated by eq. (1). The synthesizability and adsorption performance evaluated experimentally were used as a training set, including the elements of LDHs.

$$Adsorption\ Capacity\ (\%) = \frac{(C_i - C_f)}{C_i} \times 100\ (\%) \quad \textbf{(1)}$$

where, C_i (mg/L) is the initial solution concentration, C_f (mg/L) is the final solution concentration.

Then, the machine learning models were trained by these data to predict the unexplored constituents of multi-elements LDHs area. The next experiment point was determined based on machine learning predictions regarding specific constituents of multi-element LDHs. The feedback workflow between experiment and machine learning is illustrated in **Fig. 1**.

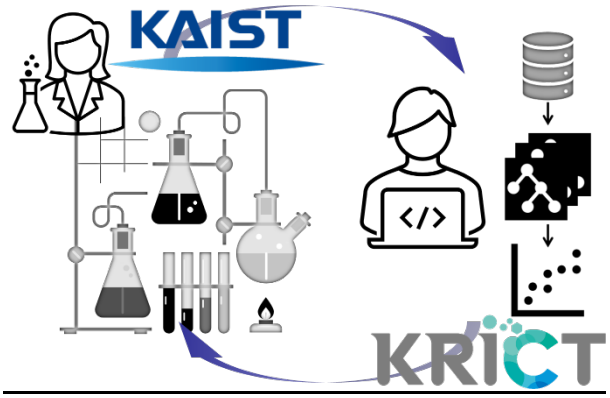

Fig. 1. Workflow of machine learning-assisted experiment

3. Results and Discussion

3.1. Constructing a database of synthesizability and adsorption capacity of multi-elements LDHs

The XRD patterns of multi-element LDHs were categorized into three distinct scenarios. One was fully synthesized as the hydrotalcite structure as shown in **Fig. 2(a)**. Another showed the mixture of the hydrotalcite phase and the secondary phases such as malachite, bismutite, rhodochrosite as shown in **Fig. 2(b)**. The other was full of secondary phases without having the hydrotalcite phase as shown in **Fig. 2(c)**. Thus, each multi-element LDH was assessed based on the relative ratio of LDH phase to all phases in the system, serving as a synthesizability index for training output set.

The adsorption performance of iodate (IO_3^-) of synthesized LDHs having a synthesizability index over 0.5 was evaluated as illustrated in **Fig. 3**. The adsorption capacity was varied between 3%-92% which was the role of the training output set. Especially, Ni-based, or Cu-based multi-elements LDHs showed a higher adsorption capacity than the reported performance of CoCr, CoAl and NiAl. Each constituent had its role for capturing iodate (IO_3^-), but advanced analysis such as XPS, Raman and TEM were required to reveal the interactions between iodate (IO_3^-) and each metal element in LDHs.

Based on these experimental results, determining the next exploring multi-elements LDHs was difficult because the mechanism of capturing iodate (IO_3^-) onto LDHs remains a topic of ongoing debate. Thus, we have tried to apply the data-driven approach to exploring the multi-elements LDHs.

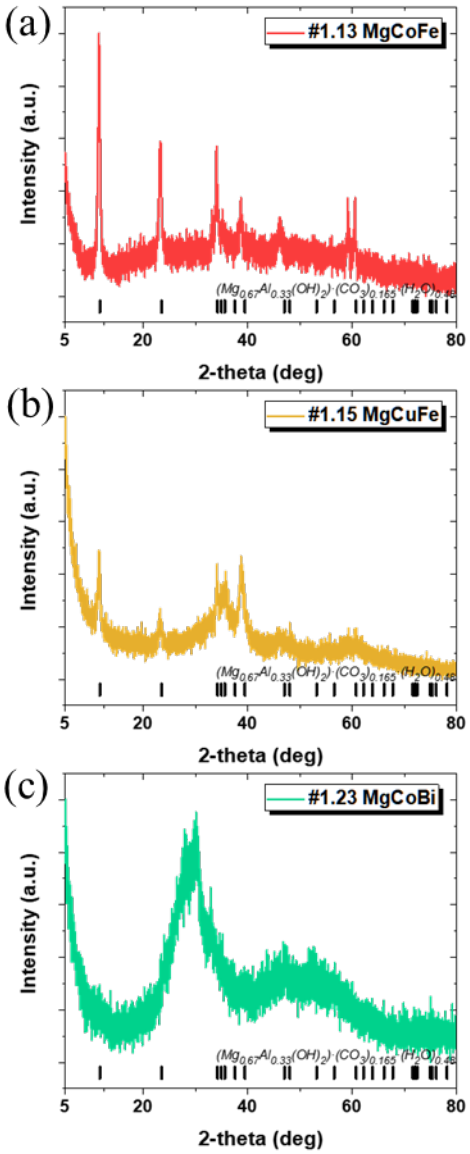

Fig. 2. XRD results of parts of multi-elements LDHs

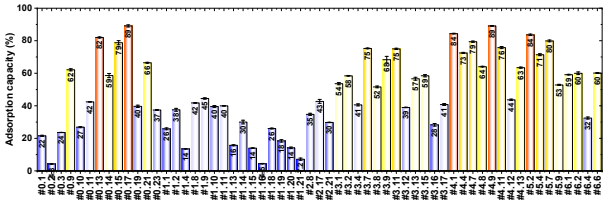

Fig. 3. Adsorption capacity of parts of multi-elements LDHs

3.2. Machine learning-assisted exploring the multi-elements LDHs

The machine learning, trained using the preliminary experimental database from *section 3.1,* predicted the unexplored constituents of multi-element LDHs as shown in **Fig. 4**. The preliminary experimental database of binary and ternary LDHs demonstrated linearity between the actual experiment values and those predicted by machine learning, indicating the feasibility of using machine learning to explore the multi-element LDHs. Specifically, the exploration of quaternary and quinary LDHs could be particularly effective, given the vast number of systems available for investigation. Consequently, machine learning could select a certain multi-elements LDHs system within the vast number of unexplored constituent areas.

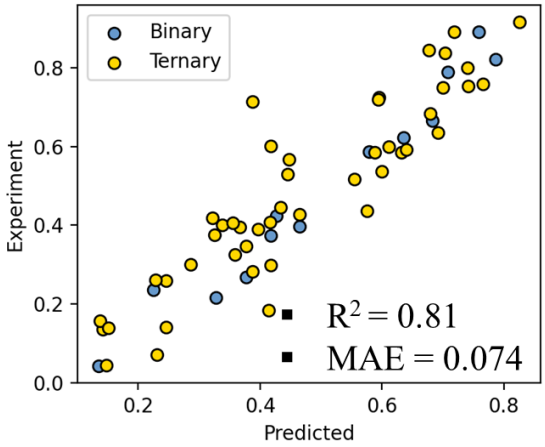

Fig. 4. Example of trained machine learning performance

4. Conclusions

This study marks a pioneering effort to leverage machine learning for the exploration of multi-element adsorbents for radionuclide removal. While the investigation is ongoing, preliminary results suggested significant advantages, including reduced time and cost. Once machine learning assists in identifying the optimal multi-element LDHs for iodate (IO_3^-) removal, subsequent research will focus on elucidating the binding mechanisms between metal combinations and iodate (IO_3^-). This top-down approach to materials discovery not only promises to explore new materials but also has the potential to be applied to a wider range of multi-element materials, including high entropy ceramics and alloys, thereby broadening the scope of future material innovations.

Acknowledgments

This study is supported by NRF-2021M2D2A1A02043946 and the KAI-NEET, KAIST.

REFERENCES

[1] S.E. Pepper, A. Baker, C.J. Maher, M.J. Carrott, J. Turner, B.C. Hanson, Iodine behaviour in spent nuclear fuel dissolution, Prog. Nucl. Energy. 169 (2024) 105062. https://doi.org/10.1016/J.PNUCENE.2024.105062.

[2] B. Grambow, Mobile fission and activation products in nuclear waste disposal, J. Contam. Hydrol. 102 (2008) 180–186. https://doi.org/10.1016/J.JCONHYD.2008.10.006.

[3] A. Tigeras, M. Bachet, H. Catalette, E. Simoni, PWR iodine speciation and behaviour under normal primary coolant conditions: An analysis of thermodynamic calculations, sensibility evaluations and NPP feedback, Prog. Nucl. Energy. 53 (2011) 504–515. https://doi.org/10.1016/J.PNUCENE.2011.02.002.

[4] T.G. Levitskaia, S. Chatterjee, B.W. Arey, E.L. Campbell, Y. Hong, L. Kovarik, J.M. Peterson, N.K. Pence, J. Romero, V. Shutthanandan, B. Schwenzer, T. Varga, RedOx-controlled sorption of iodine anions by hydrotalcite composites, RSC Adv. 6 (2016) 76042–76055. https://doi.org/10.1039/C6RA13092E.

[5] J. Kang, F. Cintron-Colon, H. Kim, J. Kim, T. Varga, Y. Du, O. Qafoku, W. Um, T.G. Levitskaia, Removal of iodine (I− and IO3−) from aqueous solutions using CoAl and NiAl layered double hydroxides, Chem. Eng. J. 430 (2022) 132788. https://doi.org/10.1016/J.CEJ.2021.132788.

[6] J. Kang, T.G. Levitskaia, S. Park, J. Kim, T. Varga, W. Um, Nanostructured MgFe and CoCr layered double hydroxides for removal and sequestration of iodine anions, Chem. Eng. J. 380 (2020) 122408. https://doi.org/10.1016/J.CEJ.2019.122408.

[7] L. Himanen, A. Geurts, A.S. Foster, P. Rinke, Data-Driven Materials Science: Status, Challenges, and Perspectives, Adv. Sci. 6 (2019) 1900808. https://doi.org/10.1002/ADVS.201900808.

[8] A. Mannodi-Kanakkithodi, M.K.Y. Chan, Computational Data-Driven Materials Discovery, Trends Chem. 3 (2021) 79–82. https://doi.org/10.1016/J.TRECHM.2020.12.007.

[9] S. Lee, T. Chee, H.J. Ryu, Q. Engineering, Binary and Ternary Layered Double Hydroxides for Iodine Decontamination, in: KNS, 2023: pp. 26–28.

[10] X. Yu, B. Wang, C. Wang, C. Zhuang, Y. Yao, Z. Li, C. Wu, J. Feng, Z. Zou, X. Yu, B. Wang, C. Wang, Y. Yao, Z. Li, C. Wu, J. Feng, Z. Zou, C. Zhuang, 2D High-Entropy Hydrotalcites, Small. 17 (2021) 2103412. https://doi.org/10.1002/SMLL.202103412.