A New Paradigm for Anionic Water Pollutant Adsorption: High-Entropy LDHs

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ENEV038T

Motivation

- Nuclear fission energy: 10% of the entire energy generated, 30% for Korea
- Radioactive anions released

Isotope	Half-Life
Cs-137	~ 30 years
Sr-90	~ 28.8 years
I-129	**~ 15.7 million years**
I-131	~ 8 days
Tritium	~ 12.3 years
Pu-239	~ 24,100 years

Table 1. 7 long-lived radioactive isotopes of nuclear fission

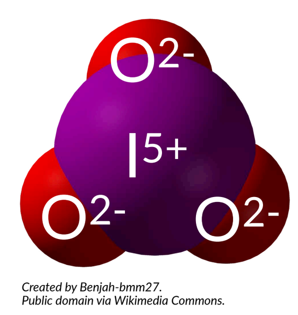

Figure 1. Iodate

▹ I-129 is present as IO_3^- in coolant.
▹ Iodine has outstanding half-life.
▹ Artificial adsorption is required.

Table 2. Previous methods and their problems

Previous Methods	Problems
Activated carbon	IO_3^- adsorption rate of 29.9% Need to acidify processing water to adsorb
Ag-zeolite	Extremely expensive IO_3^- adsorption rate of 3.6%

Layered Double Hydroxide, LDH

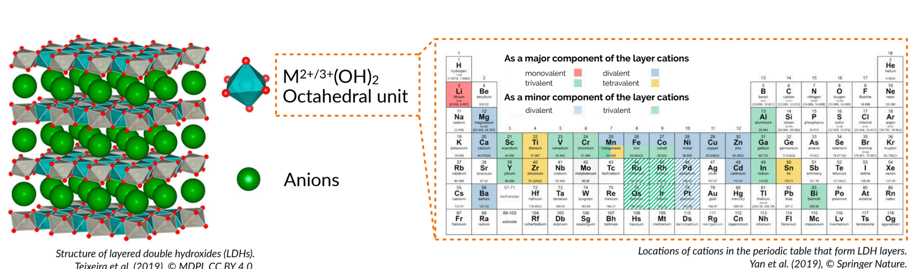

Figure 2. Layered Double Hydroxide, LDH

$$\left[\mathrm{M}^{2+}_{1-x}\mathrm{M}^{3+}_{x}(\mathrm{OH})_2\right]^{x+}(\mathrm{A}^{n-})_{x/n}\cdot m\mathrm{H_2O}$$

- Flexibly designable and cheap
- Anions can be captured through surface adsorption and anionic exchange
- Insufficient maximum adsorption rate of under 90%

Goal

Increase the IO_3^- adsorption rate!

Approach

High-Entropy LDH

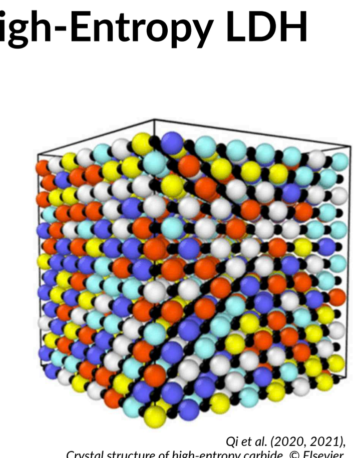

Figure 3. High-entropy material

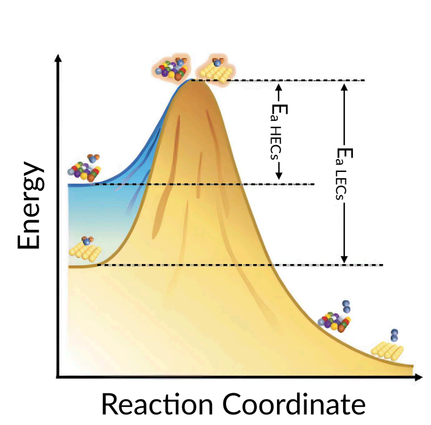

Figure 4. Reduction of activation energy

- 5+ elements mixed at 5-35 at.%
- Stable and multifunctional
- Reduces activation energy to adsorb
- Creates abundant active sites

▶ Experimental Process

1. Find optimal composition of high-entropy LDH via machine learning
2. Synthesize high-entropy LDH and measure its IO_3^- adsorption rate
3. Verify the validity of the approach

Experiment 1: Predicting LDH Compositions for Iodate Adsorption via ML

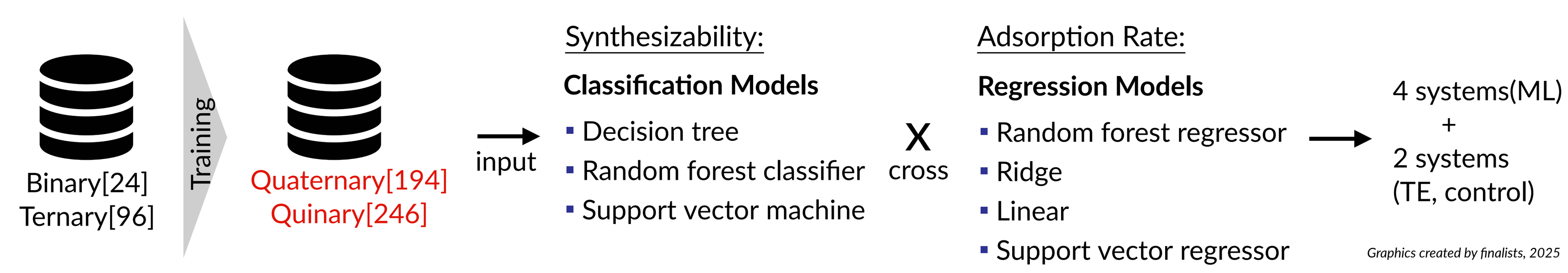

Figure 5. Machine learning process for LDH composition determination

Table 3. Selected LDH compositions

Sample No.	Composition	Selection Method
#4.1	$(NiCu)_3(CrAl)_1$	Machine learning
#4.2	$(Cu)_3(CrFeAl)_1$	Machine learning
#4.3	$(NiCu)_3(FeAl)_1$	Trial and Error
#5.1	$(CoNiCu)_3(CrAl)_1$	Machine learning
#5.2	$(NiCu)_3(CrFeAl)_1$	Machine learning
#5.3	$(NiZnCu)_3(FeAl)_1$	Trial and Error

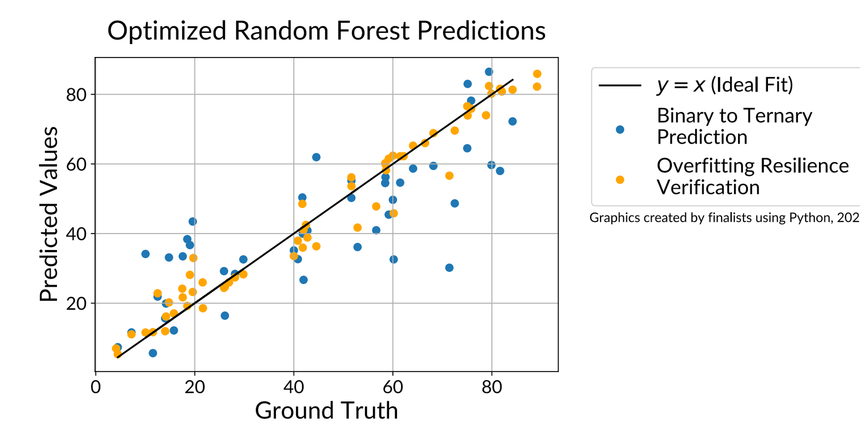

Figure 6. Machine learning's validity

- Blue dots: validity of machine learning
- Yellow dots: No signs of overfitting observed

Experiment 2: Synthesis and Verification of LDHs

1. LDH Synthesis (Co-precipitation)

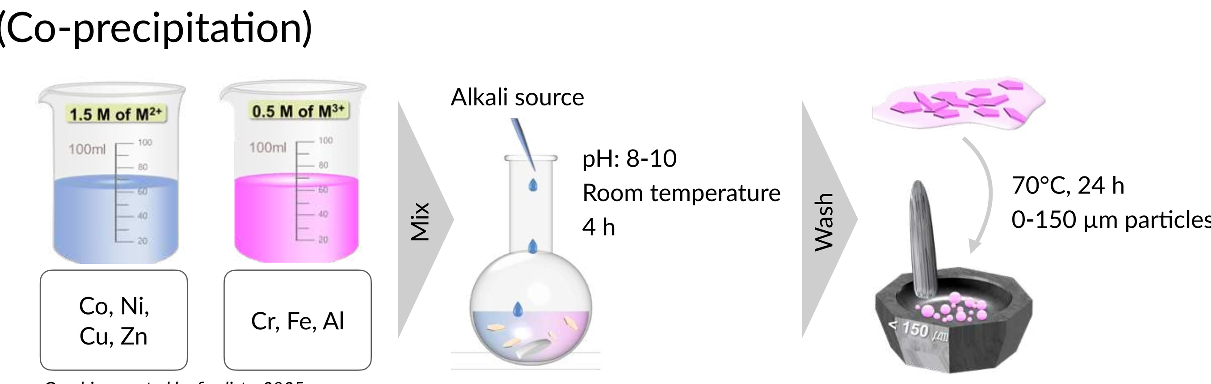

Figure 7. LDH synthesis using co-precipitation method

2. LDH Synthesis Verification

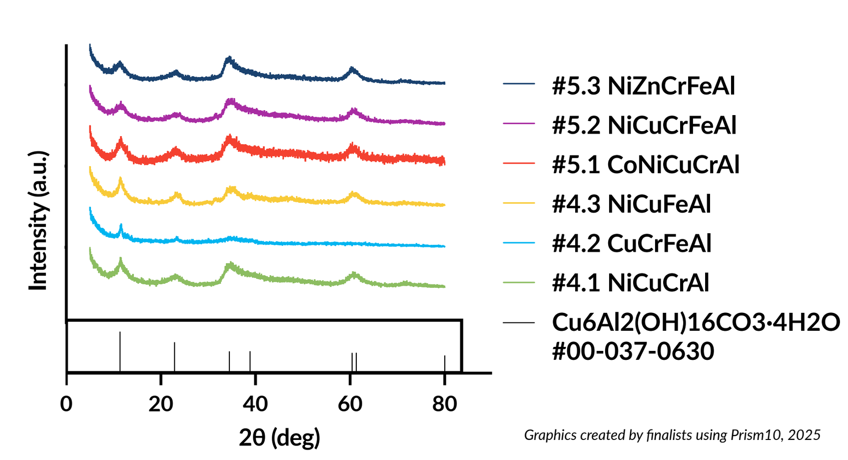

Figure 8. Comparison of powder XRD patterns

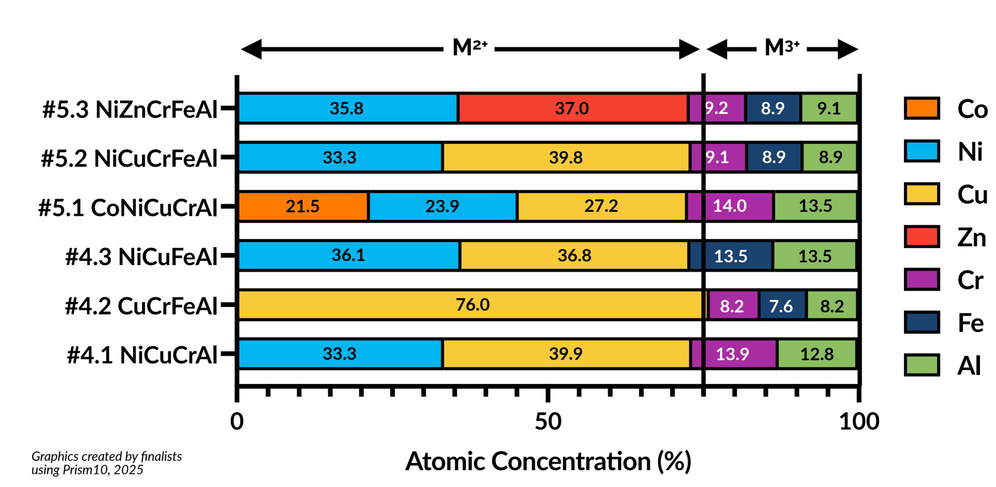

Figure 9. Ratio of elements in compositions

- Figure 8 illustrates the successful synthesis of LDH by comparing the peaks.
- Figure 9 shows that the synthesis was done with designed ratio: $\left[\mathrm{M}^{2+}\right]:\left[\mathrm{M}^{3+}\right]=3:1$ and equimolar within metals of same ionic charge.

Experiment 3: Iodate Adsorption Performance Measurement

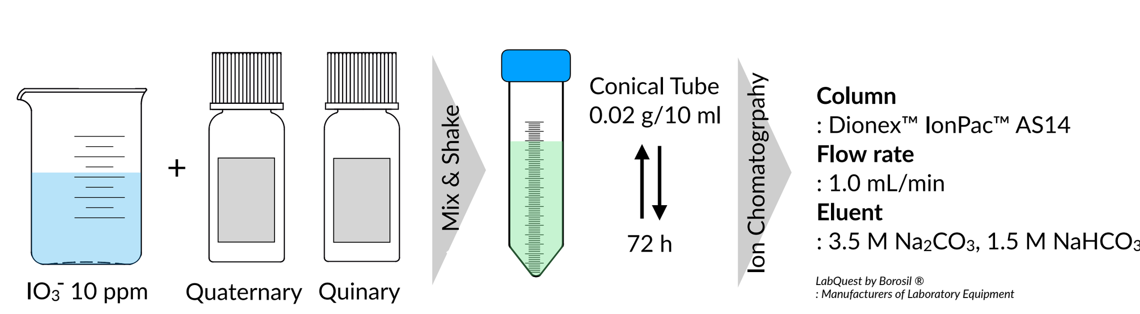

Figure 10. IO_3^- adsorption experiment process

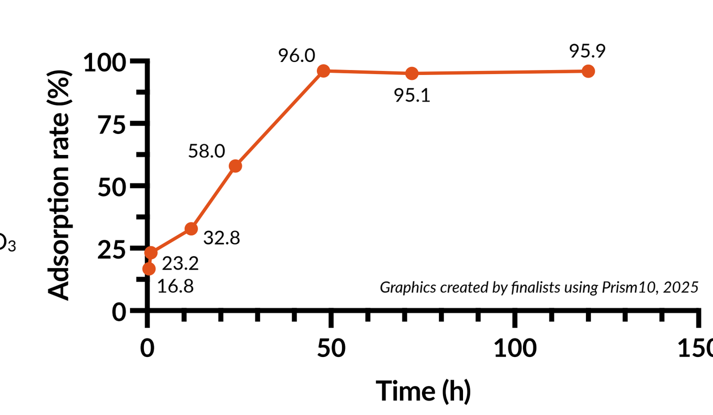

Figure 11. IO_3^- adsorption kinetics of #4.2 CuCrFeAl under a same condition

- Adsorption rate is convergent after adsorbing for 48 hours.
- 72 hours of adsorption is enough.

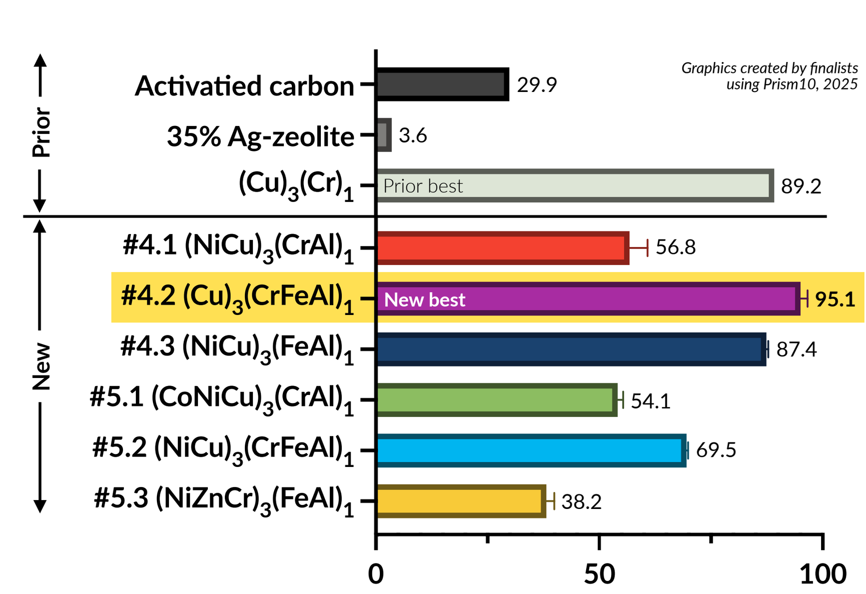

Figure 12. Comparison of IO_3^- adsorption rates with previous methods

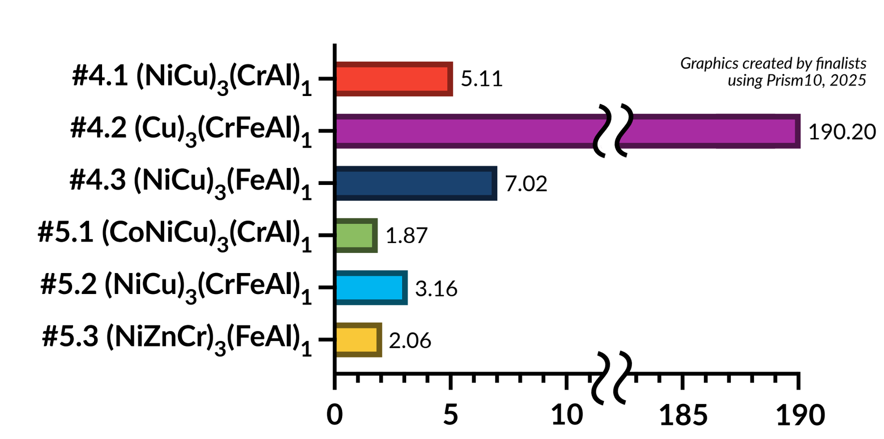

Figure 13. Specific surface area of LDH

Discussion

▶ Analysis of the results

- The specific surface area and adsorption rate show a similar trend. (Figure 13 and Figure 12)
  : Low crystalline materials have more surface defects, resulting in a higher surface area.
- Powder XRD indicates that sample #4.2 exhibits low crystallinity. (Figure 8)
  : Higher surface area leads to more adsorption.

$$\therefore \frac{1}{\text{Crystallinity}} \propto \frac{\text{Surface area}}{\text{Mass}} \propto \text{Adsorption rate}$$

▶ So, how can we maximize the adsorption rate?

- Expand the idea to high-entropy effect.
- Balance the composition.
- Find optimized number of elements.

The configurational entropy is:

$$\Delta S_{\text{quaternary}} = -R\sum_{i=1}^{n} x_i \ln x_i \geq 1.39R,$$

where R is the gas constant.

Even in quaternary LDHs, the entropy increase is sufficiently high to exhibit high-entropy effects.

$\therefore$ **Approach is proven valid.**

Applications

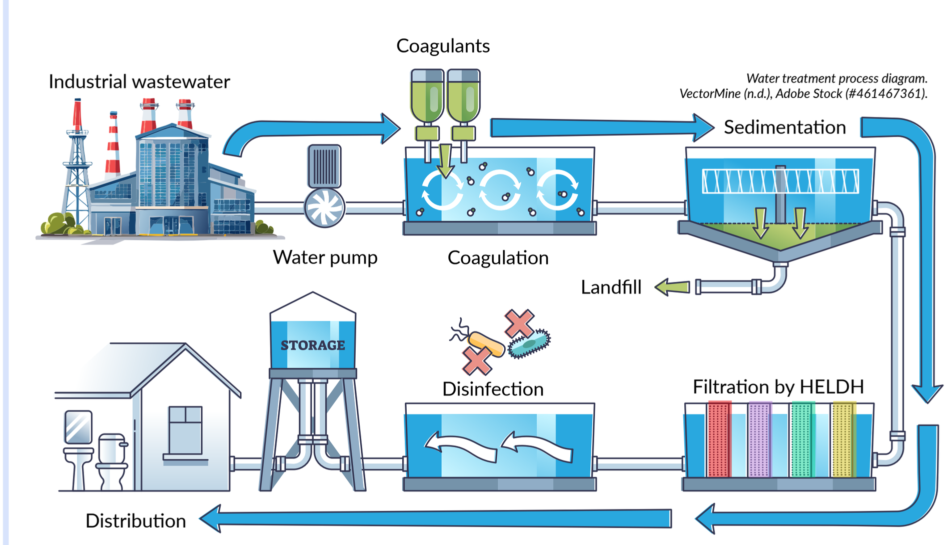

Figure 14. LDH filtration of industrial wastewater

- Textile, paper, chemical manufacturing industries release wastewater that contains IO_3^-.
- LDH fixation into filter helps adsorb flowing anionic pollutants.

Conclusion

- Expanding an idea to high-entropy LDH led to a remarkable improvement in performance.
- $(Cu)_3(CrFeAl)_1$ was discovered following this expansion, increasing the previous maximum from 89.2% to **95.1%**.
- It will pave the way to adsorb a broader range of anionic pollutants, ultimately contributing to environmental preservation.

References

[1] Deng, C. et al. (2024). High entropy materials for catalysis: A critical review of fundamental concepts and applications. Nano Energy, 120, 109153.

[2] Saju, D. et al. (2020). Layered Double Hydroxides: Fundamentals to Applications. Layered Double Hydroxide Polymer Nanocomposites, 1–76.

[3] Wei, J. et al. (2019). Machine Learning in Materials Science. Infomat, 1(3), 338–358.