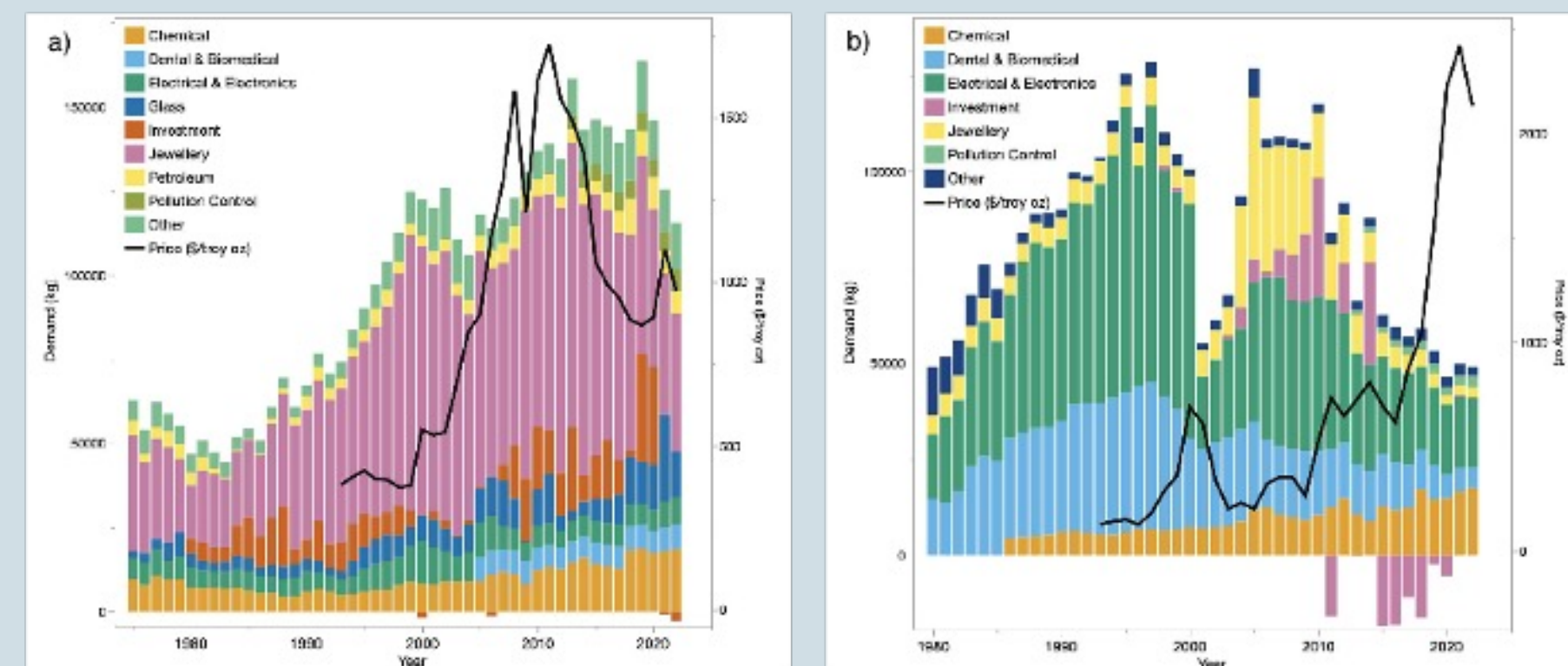


Pd/Pt separation by sulfur-modified adsorbents

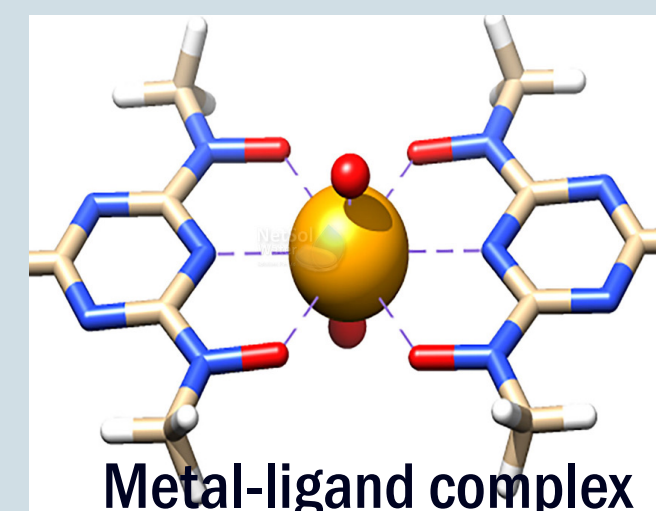
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INTRODUCTION

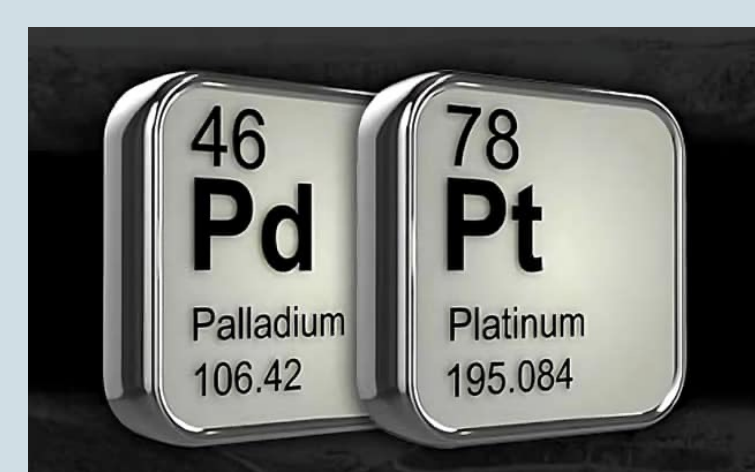


Palladium (Pd) and platinum (Pt) belongs to platinum group metals (PGMs). Many current technologies including catalysis, electronics and H₂ production depend on PGMs. But PGMs natural sources tend to deplete in 100-200 years[1]. Recovering PGMs from e-waste and other wastes are of outmost importance. Waste sources will become more dilute and with higher impurities in the future, so we need highly selective separation technologies to address the problem.



In waste streams, Pd and Pt are difficult to separate. The Pd/Pt separation factor lies in 10-18 [3], which is lower than average level. Therefore, there is a need for adsorbents capable of highly separating Pd/Pt. According to Hard and Soft Acid and Base (HSAB) theory, sulfur-ligands have the potential to address this need. Since soft ligands could better differentiate soft metals.

PROBLEMS

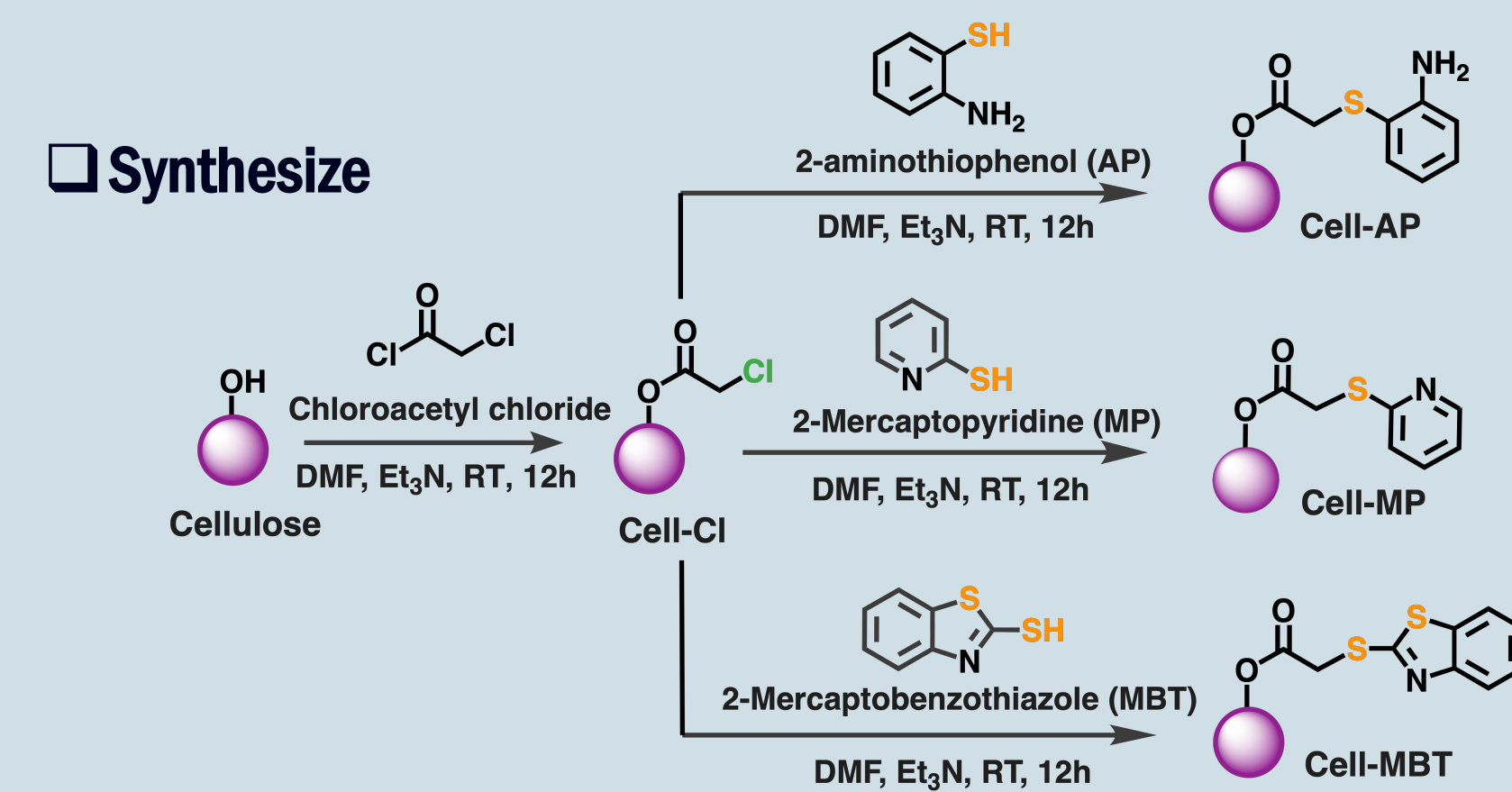


- PGMs tend to deplete within 100-200 years. PGMs-related industries will be influenced. How to recover PGMs?
- Pd and Pt are difficult to separate, affecting the purity of products. How to separate Pd and Pt?
- The mechanism of Pd/Pt separation is not clear. Why can some specific ligand separate Pd/Pt?

OBJECTIVES

- Synthesize sulfur-modified adsorbents.
 - Functionalize cellulose with sulfur-ligands AP, MP, and MBT.
 - Characterize the adsorbents using FTIR, SEM, XPS and BET techniques.
- Selective separation of Pd over Pt.
- Test the selectivity of Pd over Pt and 17 other metals. Conduct optimal pH, isotherm, kinetics, thermodynamic, and reusability studies.
- Understanding the mechanism of Pd/Pt selectivity.
 - Run DFT calculation to understand the reason why adsorbents have higher selectivity for Pd over Pt.

MATERIALS & METHODS



Adsorbents Cell-AP, Cell-MP, and Cell-MBT were synthesized by attaching ligands 2-aminothiophenol (AP), 2-mercaptopyridine (MP), 2-mercaptobenzothiazole (MBT) on cellulose surface.

Characterization

FTIR for the functional groups; SEM for microscopic structure; XPS for elemental composition; BET for the surface area and pore size; Zeta potential for the point of zero charge (pzc).

Adsorption experiments

$$q_e = \frac{(C_0 - C_e)}{m} * V \quad q_e = K_F C_e^{1/n}$$

Adsorption capacity Freundlich isotherm

$$K_d = \frac{C_0 - C_e}{C_e} * V/m \quad q_t = \frac{q_e^2 k_2 t}{(1 + q_e k_2 t)}$$

Partition coefficient Pseudo-second-order

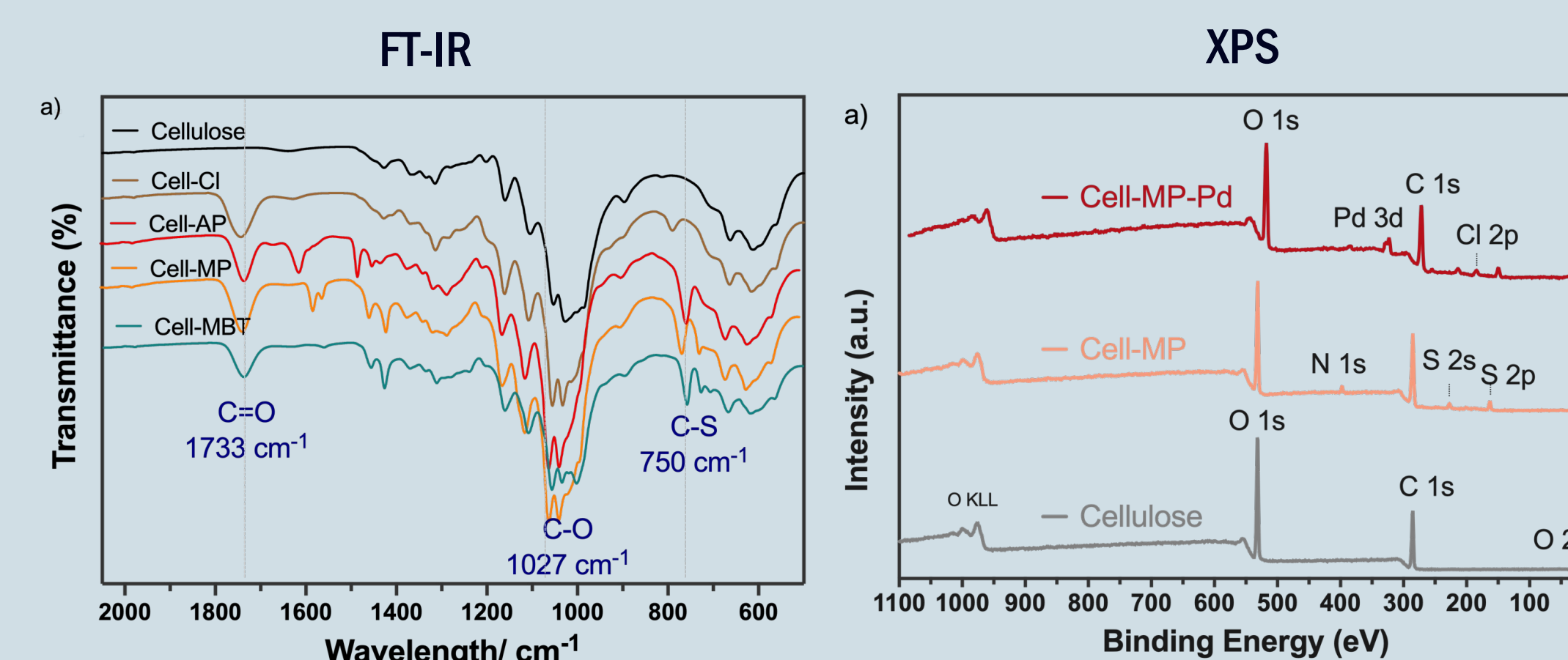
Isotherm, kinetic, thermodynamic and reusability were studied. Condition: 10 mg adsorbents in 10 ml solution, 25°C, 24 hours, mixed in 30 rpm, pH adjusted.

DFT calculations

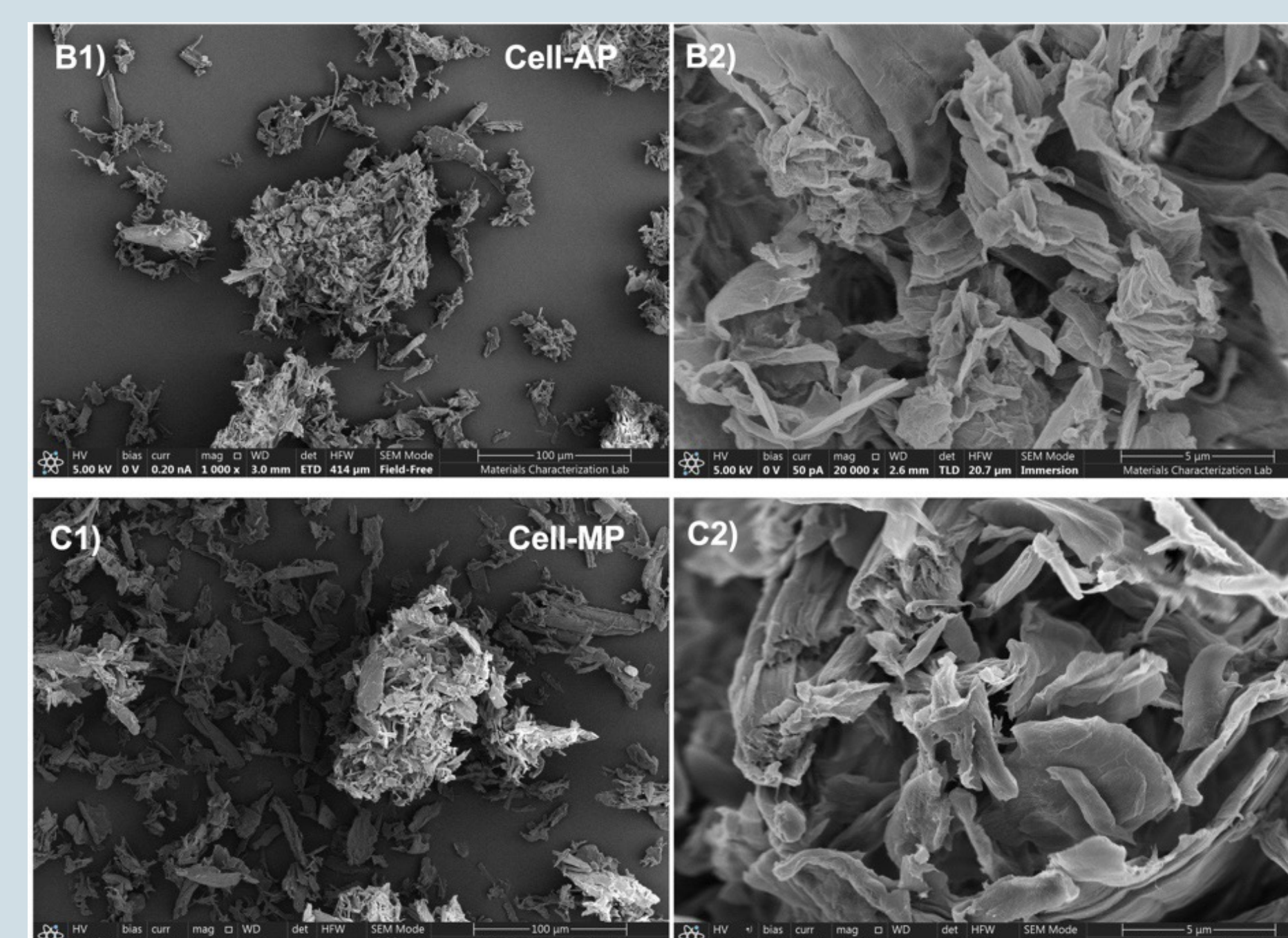
The structure of metal-ligand complexes were optimized by Gaussian 06. The binding energies and softness index were calculated.

RESULTS

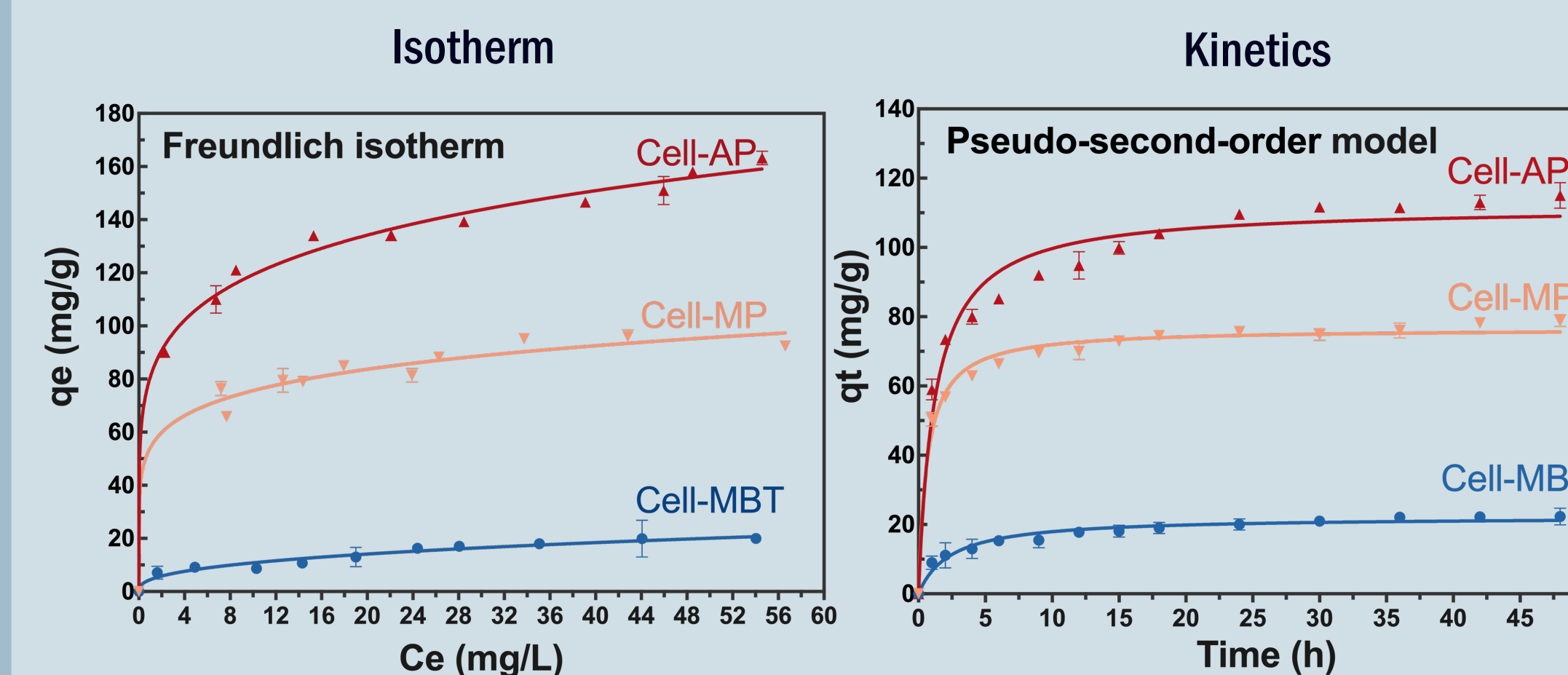
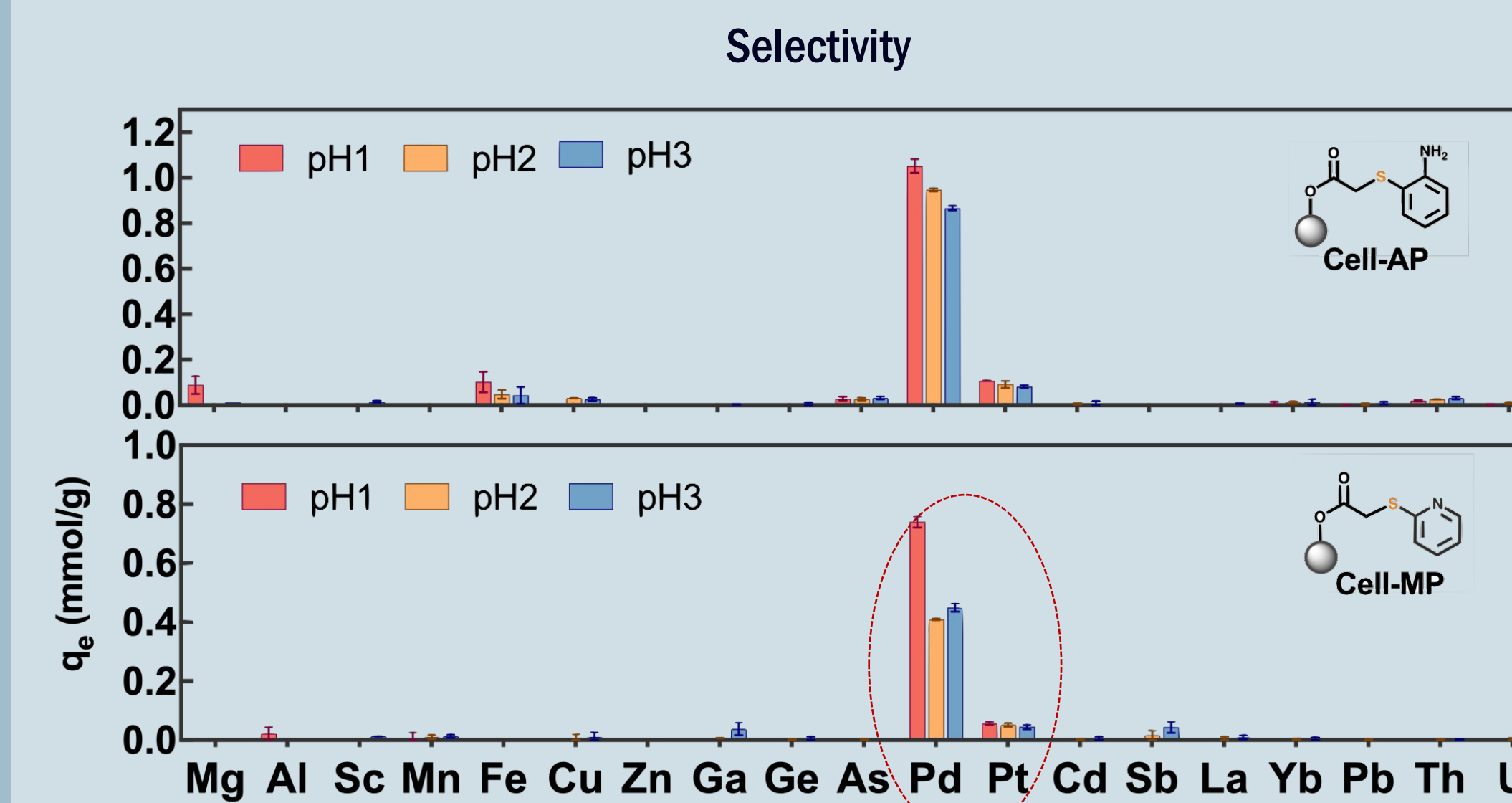
Characterization



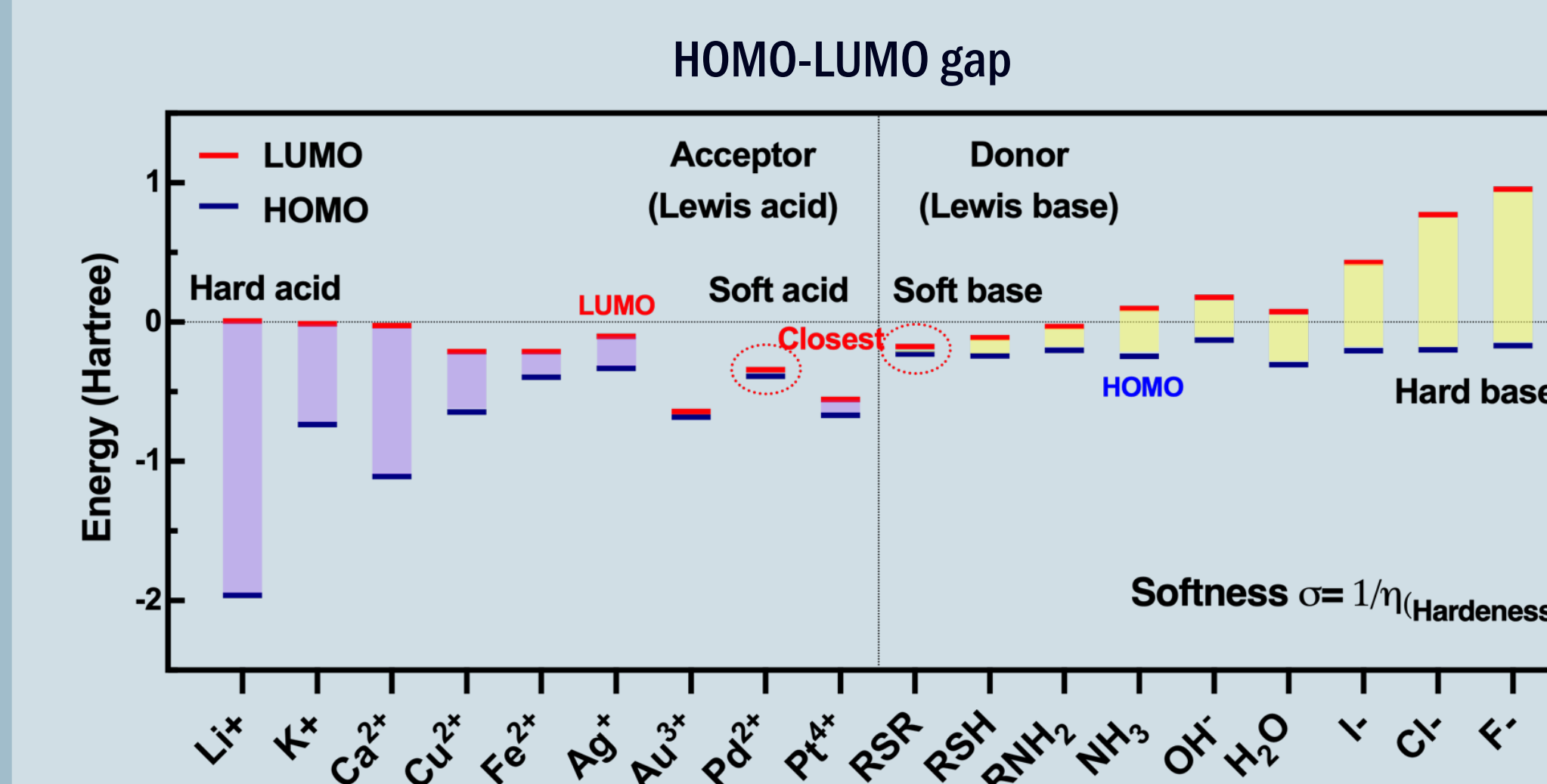
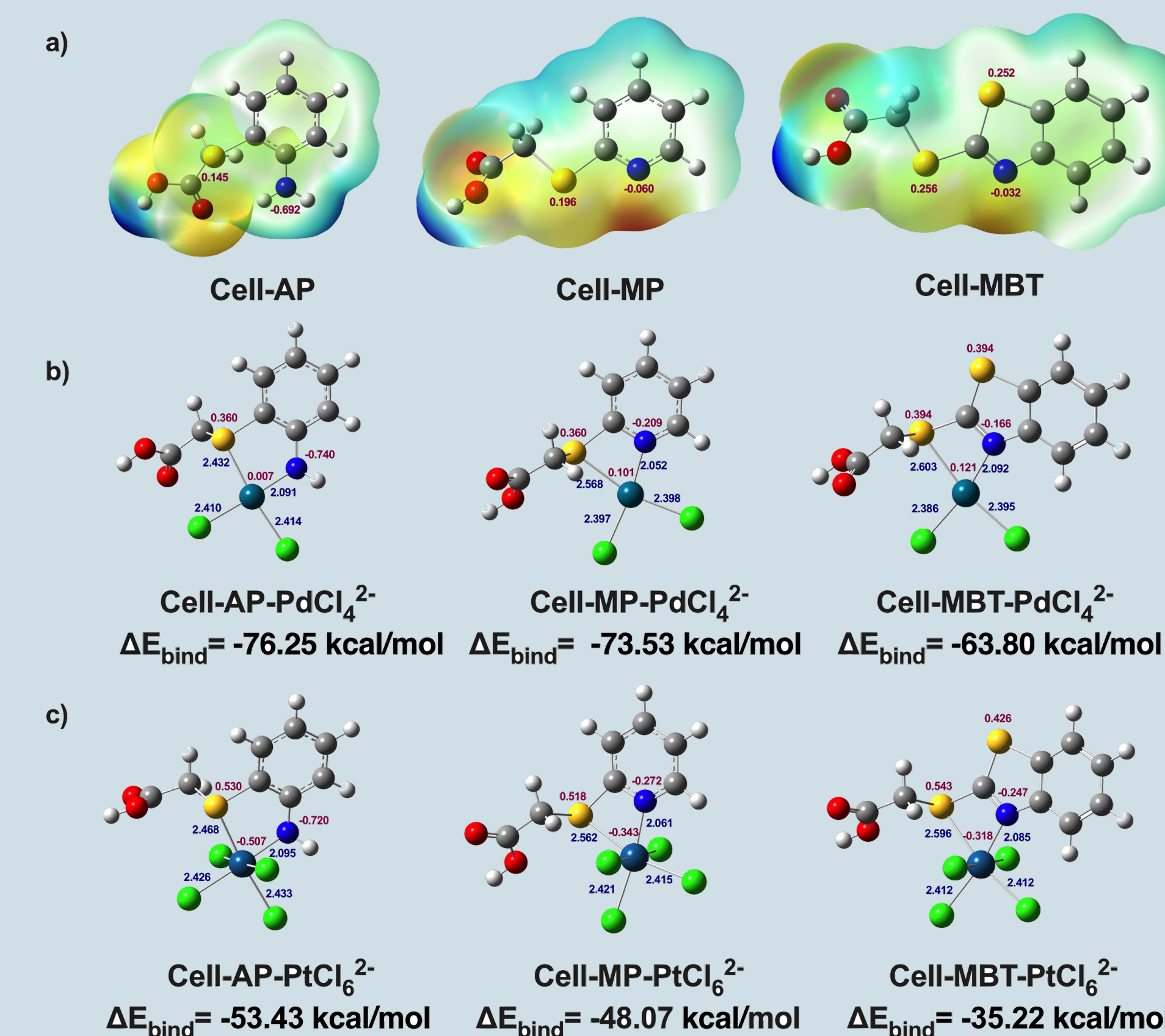
SEM



RESULTS



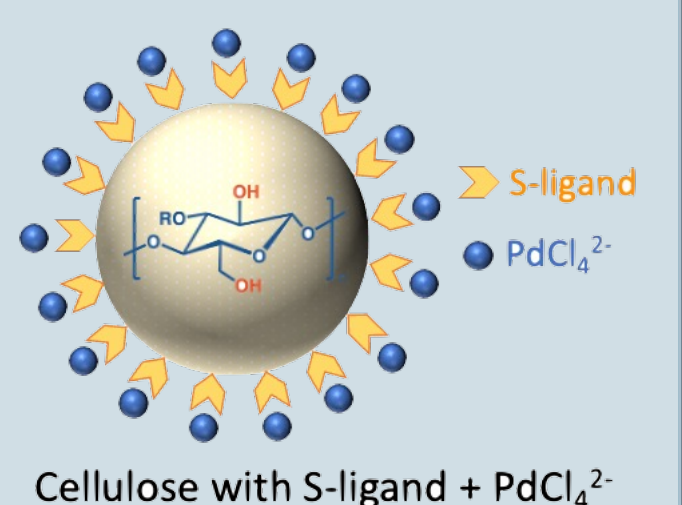
DFT calculation



CONCLUSIONS

- Characterization: FTIR confirmed C=O bond and C-S bond; XPS confirmed N and S element; SEM showed the rough microstructure.
- Selectivity: The maximum Pd/Pt separation factor reached to 64.50. The maximum adsorption capacity for Pd(II) reached 163.3 mg/g.
- Isotherm and Kinetic: showed that adsorption follows Freundlich isotherm and pseudo-second-order model.
- Desorption: The adsorption capacity remains 87% after 5 cycles.
- DFT calculation: The binding energy of ligands to PdCl₄²⁻ was higher than that to PtCl₆²⁻. The bond length and charge had the same trend.
- HOMO-LUMO gap: Pd²⁺ has higher softness index than Pt⁴⁺.

In conclusion, the sulfur-modified adsorbents achieved a high selectivity of Pd over Pt, with a higher separation factor (64.50) than most previous studies (10-18). The Pd/Pt selectivity was attributed to the higher binding energy of the sulfur ligand to Pd²⁺ than to Pt⁴⁺.



FUTURE WORK

- Functionalize sulfur-ligands on other solid supports.
 - Modify sulfur-ligands on solid supports that has stronger chemical and physical properties.
- Adopt the adsorbents in an electrochemical system.
 - Coat selective sulfur-adsorbents on electrode in an electrochemical system. Switch potential to control adsorption-desorption cycles.

REFERENCES

- L. MacDonald, D. Zhang, A. Karamalidis, Platinum group metals: Key solid phase adsorption technologies for separation from primary and secondary sources, Resources, Conservation and Recycling 205 (2024).
- D. Zhang, L. MacDonald, P. Raj, A.K. Karamalidis, Thiol-functionalized cellulose adsorbents for highly selective separation of palladium over platinum in acidic aqueous solutions, Chemical Engineering Journal 494 (2024).
- R.E.C. Torrejos, E.C. Escobar, J.W. Han, S.H. Min, H. Yook, K.J. Parohinog, S. Koo, H. Kim, G.M. Nisola, W.-J. Chung, Multidentate thia-crown ethers as hyper-crosslinked macroporous adsorbent resins for the efficient Pd/Pt recovery and separation from highly acidic spent automotive catalyst leachate, Chemical Engineering Journal 424 (2021).

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