陕西科技大学
SHAANXI UNIVERSITY OF SCIENCE & TECHNOLOGY

Construction of CS-SA(GTA) Polyelectrolyte Gel for Efficient Capture of Metallic Mineral ions from Tannery Effluent

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AICLST 2022

12 th Asia International Conference On Leather Science And Technology
18th -20th Oct., 2022 in Palmerston North, New Zealand

18th Oct., 2022

THE MAIN CONTENTS

1 Part

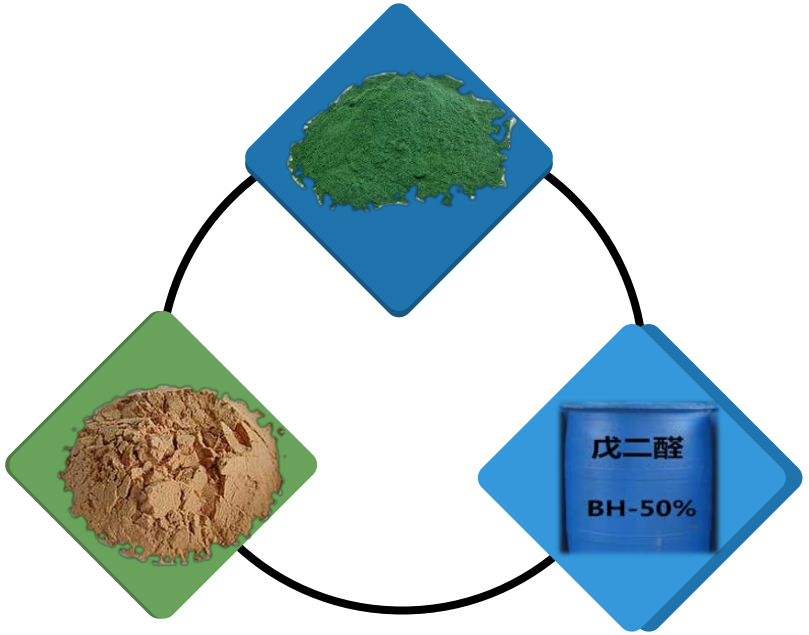
Background

1. Background

1.1 Leather tanning

Metallic Minerals

(Chrome tanning agent)



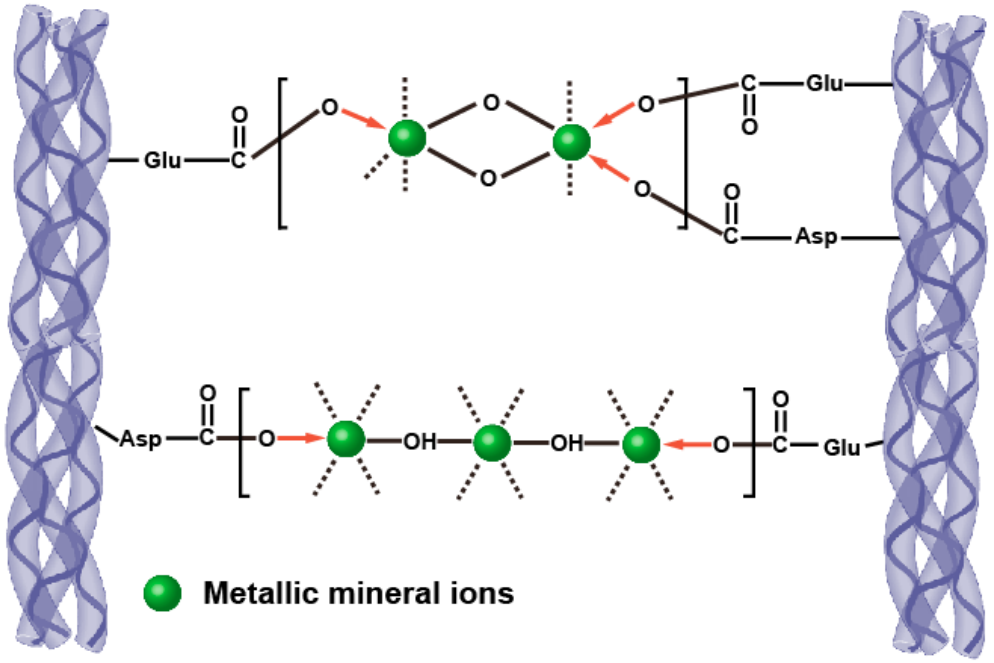
Vegetable tannins

Organic tanning agent

Metallic Minerals play an important role in leather tanning process.

1. Background

1.2 Metallic minerals containing effluents



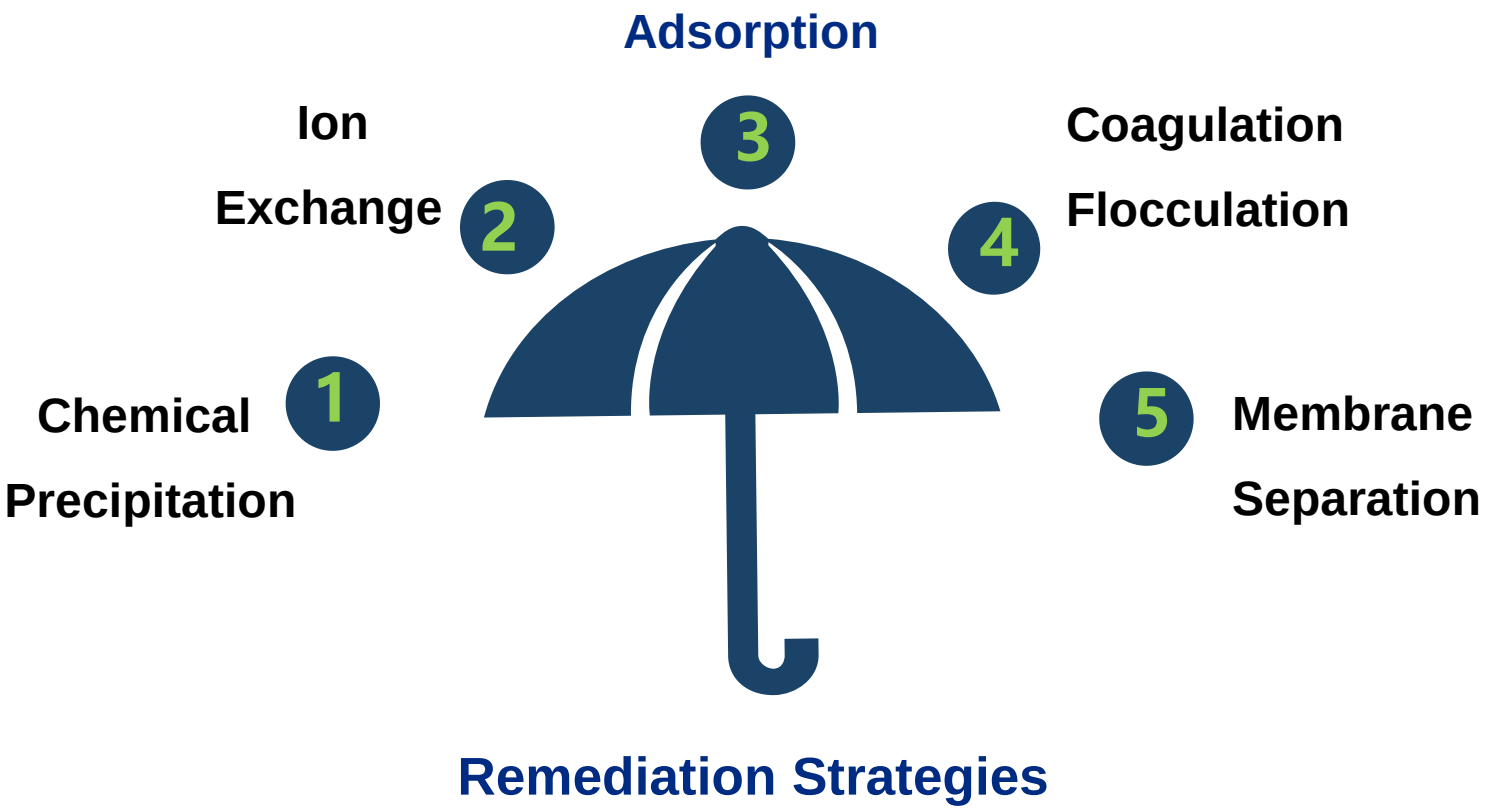
Limited functional ligands (carboxyl)

Large amounts of metallic minerals residue in the effluents

Remediation of metallic minerals containing effluents is urgent.

1. Background

1.3 Strategies for metallic minerals containing effluents remediation

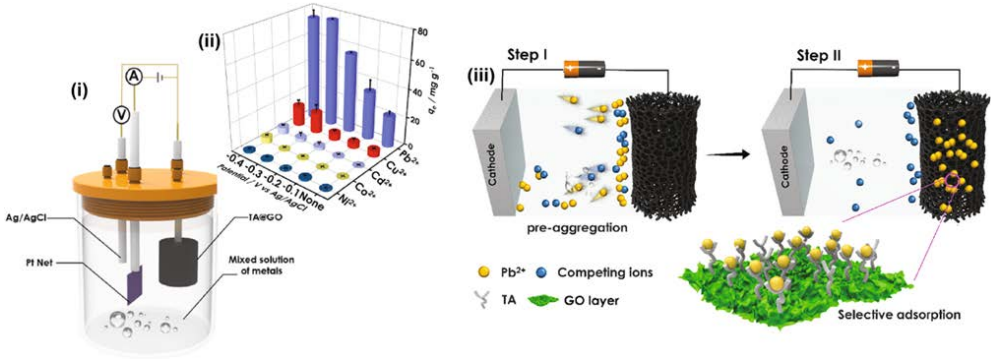


Adsorption technology is promising in recent years.

1. Background

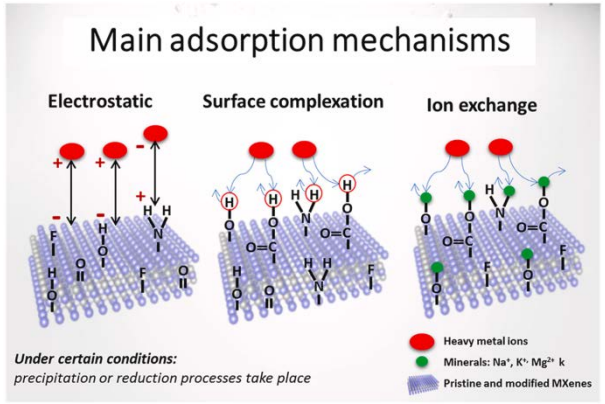
1.4 Intelligent adsorbents for metallic mineral ions remediation

Graphene



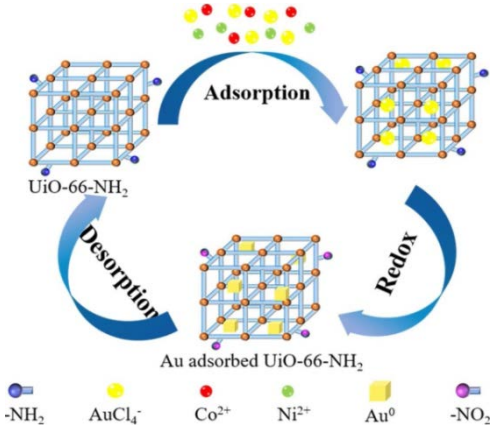
Chem. Eng. J. 2021, 416

Mxenes



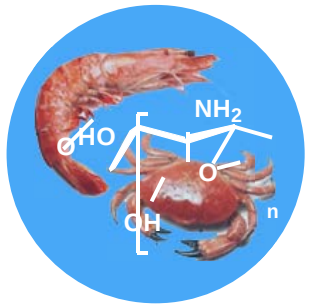
Chemosphere, 2022, 295, 133849

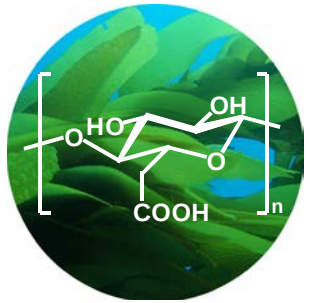
MOF



J. Hazardous Mater. 2020, 391, 122175

Chitosan (CS)





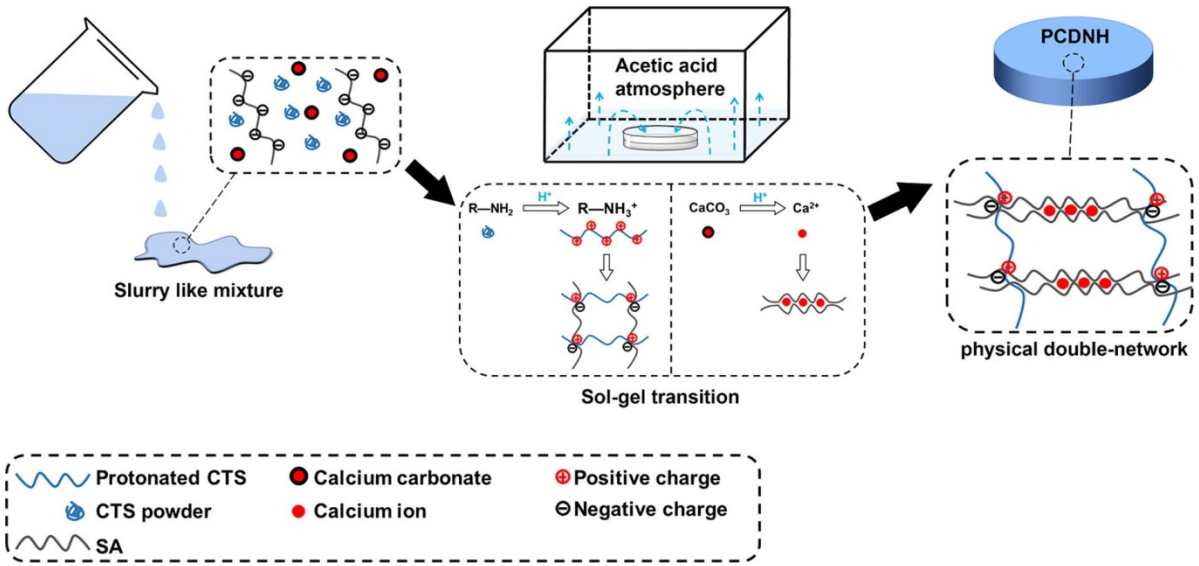
Sodium Alginate (SA)

CS and SA are fascinating in their universality and biodegradability.

1. Background

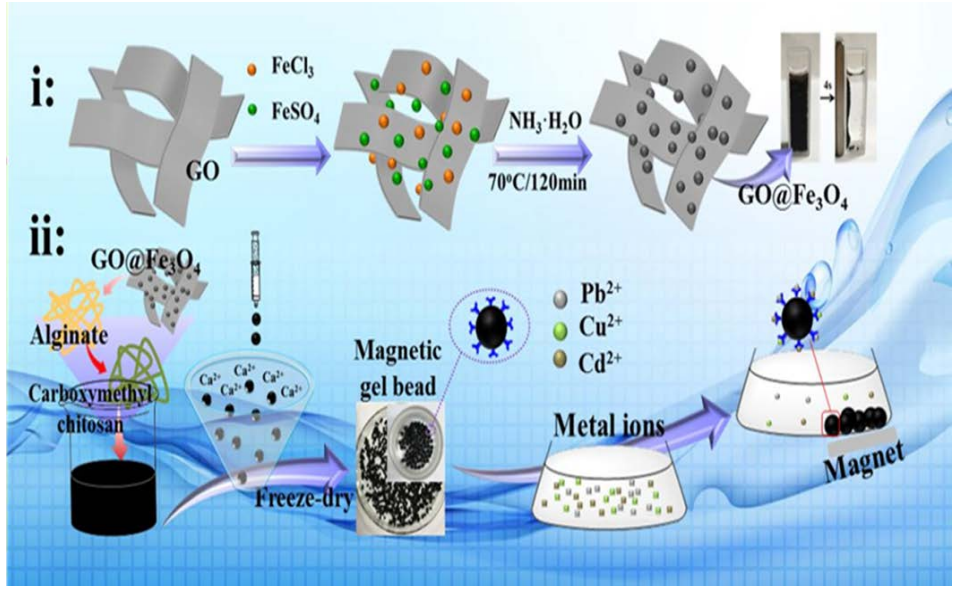
1.5 Research on CS-SA adsorbents

For Pb^{2+}, Cu^{2+} and Cd^{2+} adsorption



Chem. Eng. J., 2020, 393, 124728

For Pb^{2+}, Cu^{2+} and Cd^{2+} adsorption



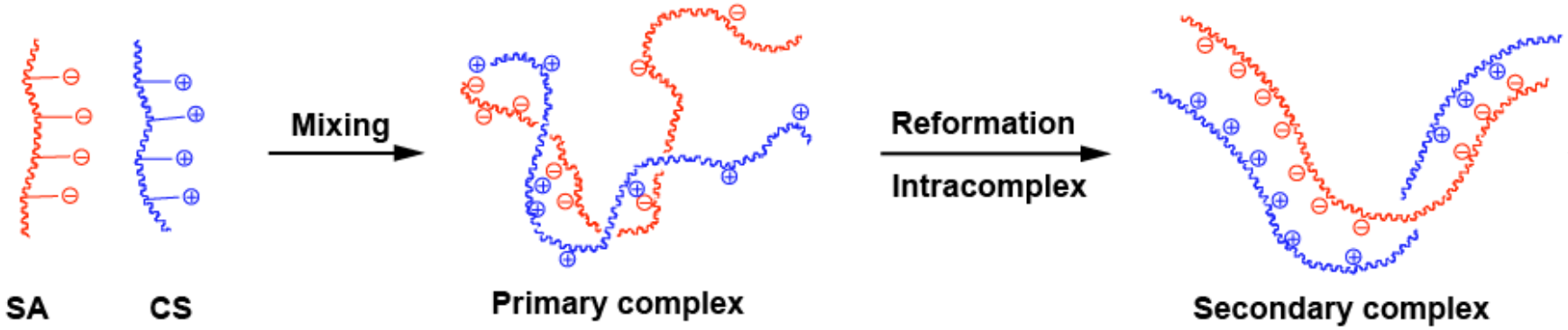
Carbohyd. Polym., 2019, 216, 119

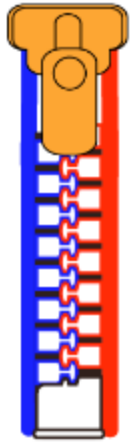
CS-SA adsorbents are widely used in metal ions remediation.

1. Background

1.6 Challenges of CS-SA polyelectrolyte adsorbents

Artif. Cells Nanomed Biotechnol, 2016, 44, 1615





Closed zipper

Low adsorption capacity { **1. Bearing a compact structure (Weak swelling behavior)**; **2. Functional ligands (carboxyl groups) being occupied or masked** } **Deficiencies**

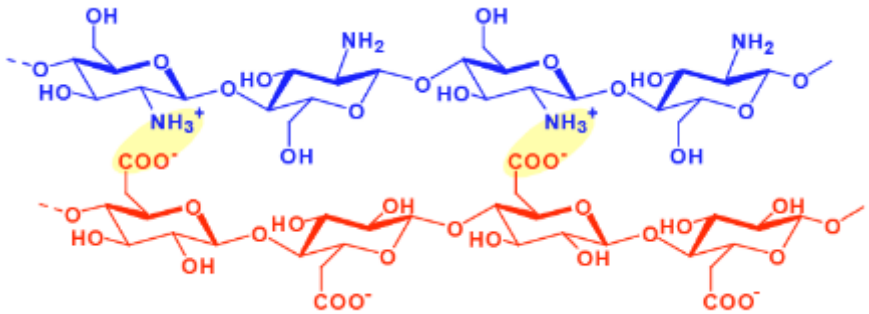
Traditional CS-SA adsorbents have limits in metal ions remediation.

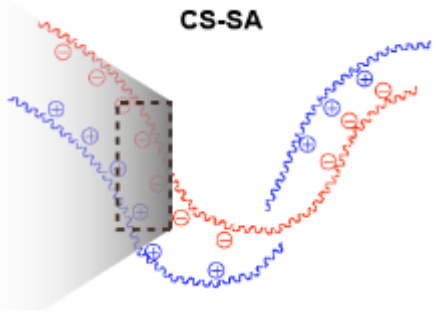
2 Part

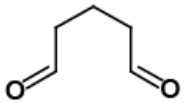
Design and Experiment

2. Design

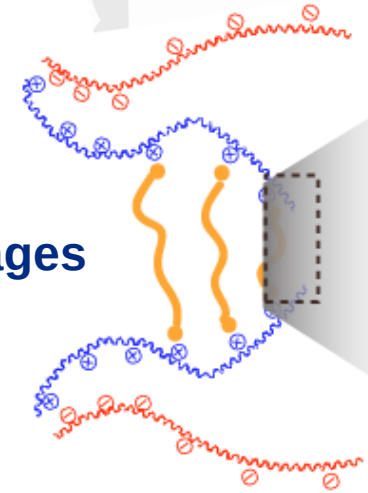
Electrostatic interaction





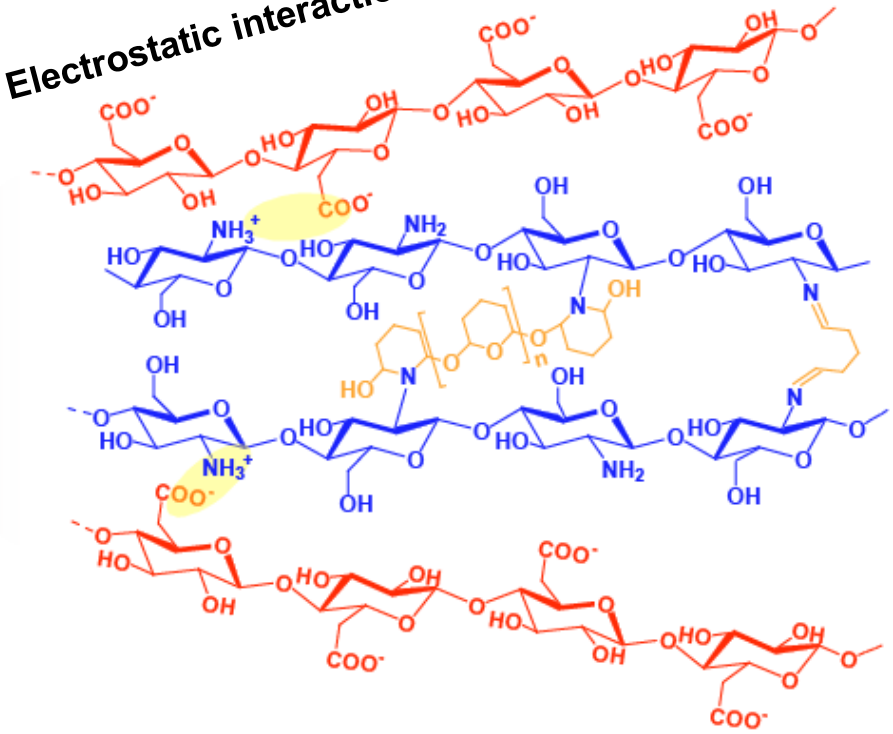


Unzipper (GTA)



CS-SA(GTA)

Electrostatic interaction



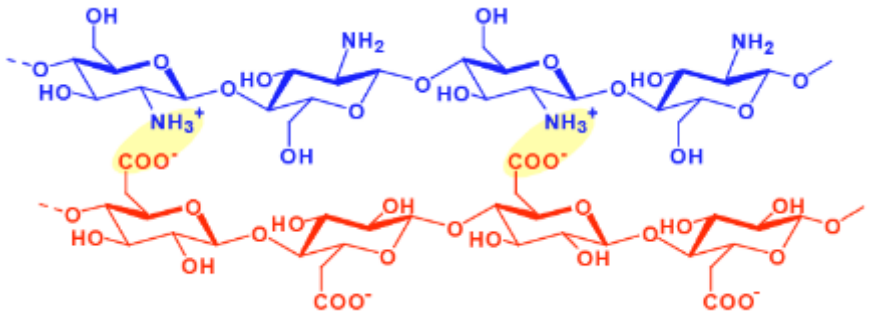
Schiff base reaction

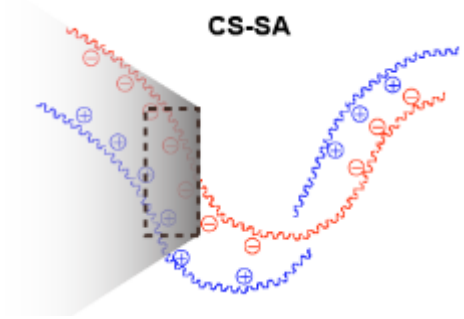
1. Bearing a loose structure
2. More carboxyl exposition

Advantages

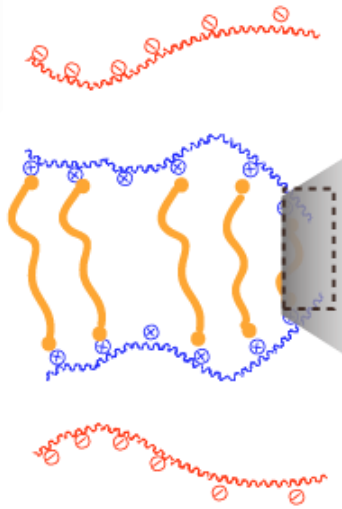
2. Design

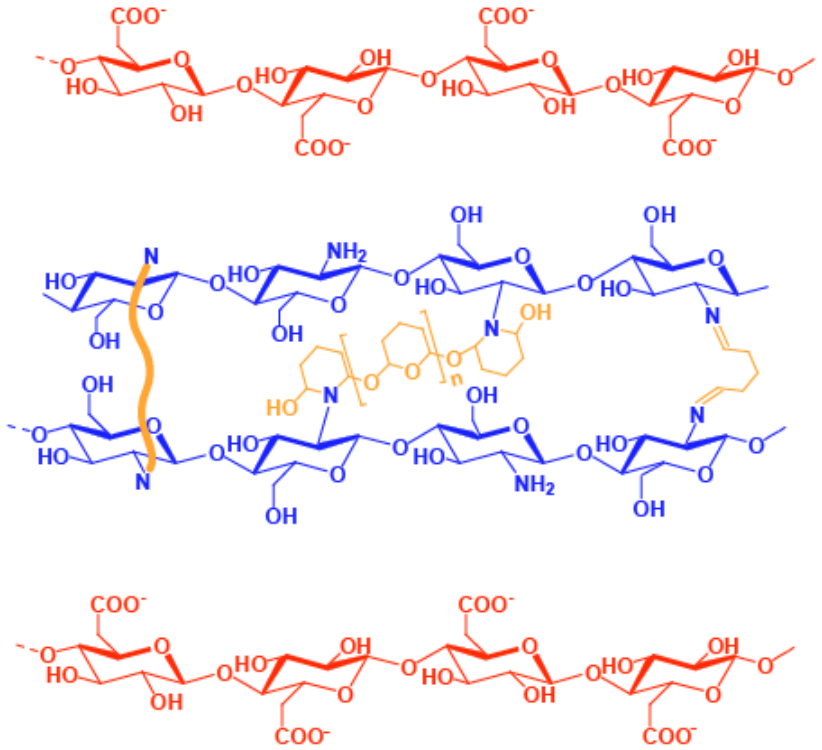
Electrostatic interaction





More GTA addition

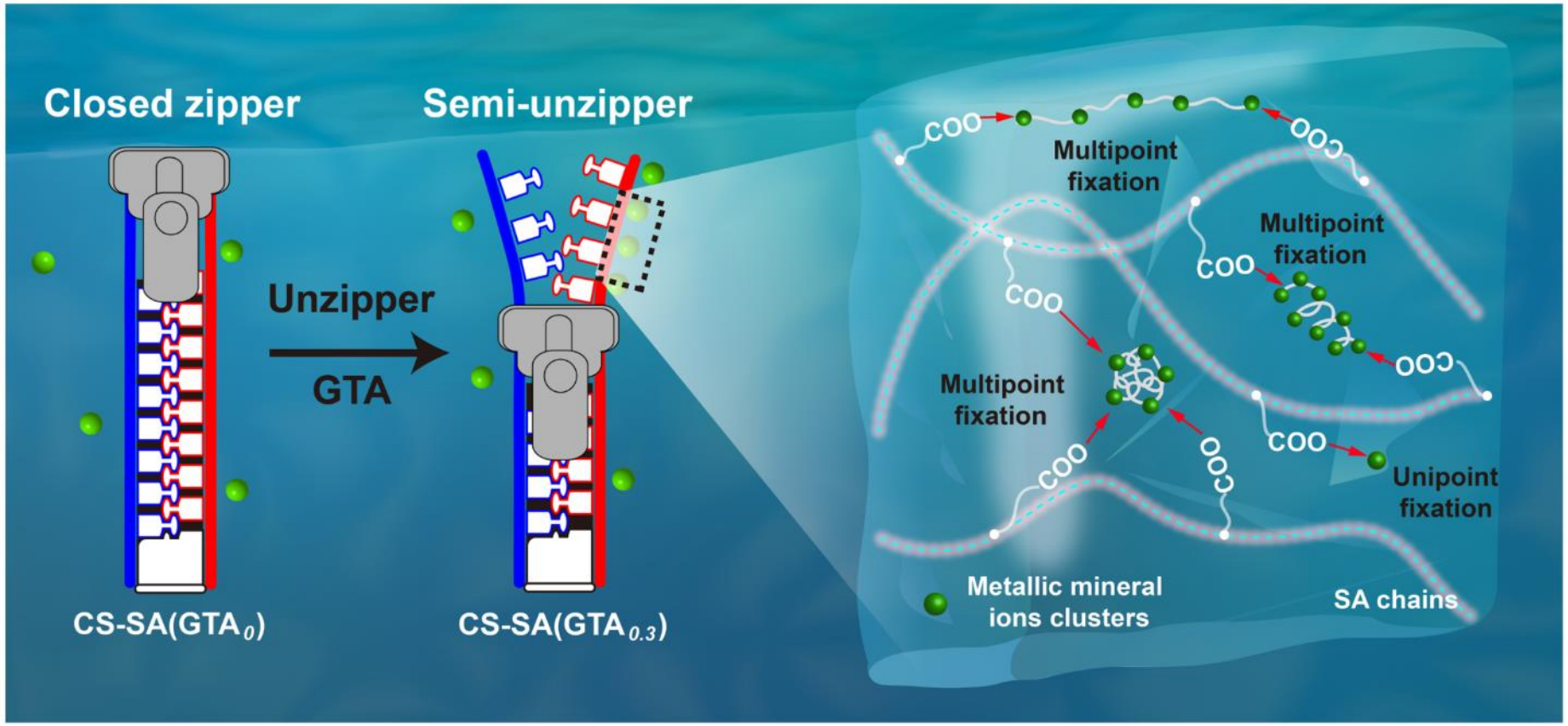




Collapse of the structure

(Structure compact and carboxyl marked)

2. Design



Chem. Eng. J., 2023, 452, 139532

Constructing semi-unzipping CS-SA(GTA) gel

for efficient capture of metallic mineral ions from tannery effluent

2. Experiment

CS-SA(GTA$_0$)

CS-SA(GTA$_{0.3}$)

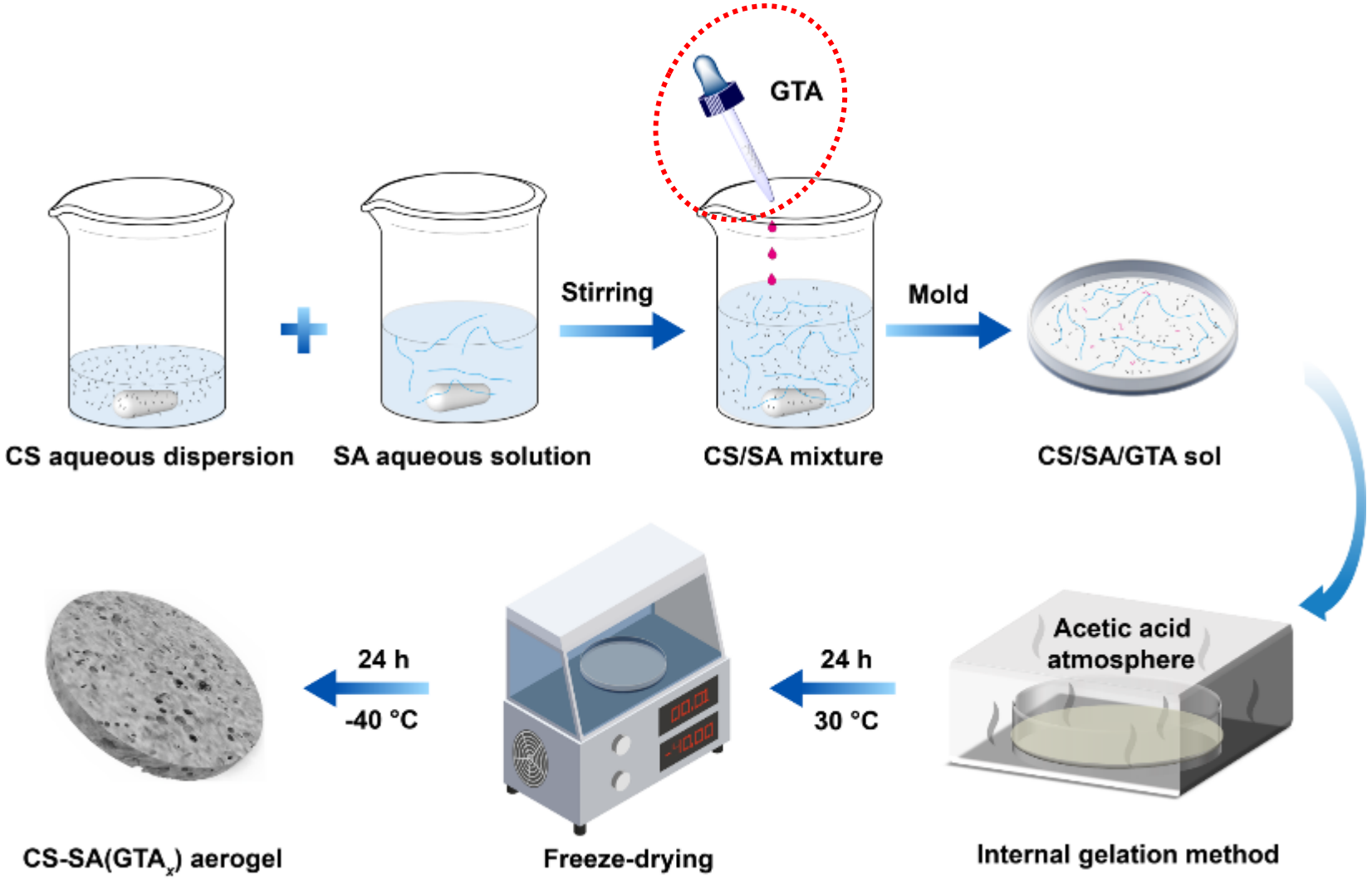


Fig. 1. The synthesis procedure of CS-SA(GTA$_x$) aerogel, the subscript value referring to the volume of added GTA.

3 Part

Results and Discussion

3. Results and Discussion

1. Semi-unzipping CS-SA(GTA) materials characterization

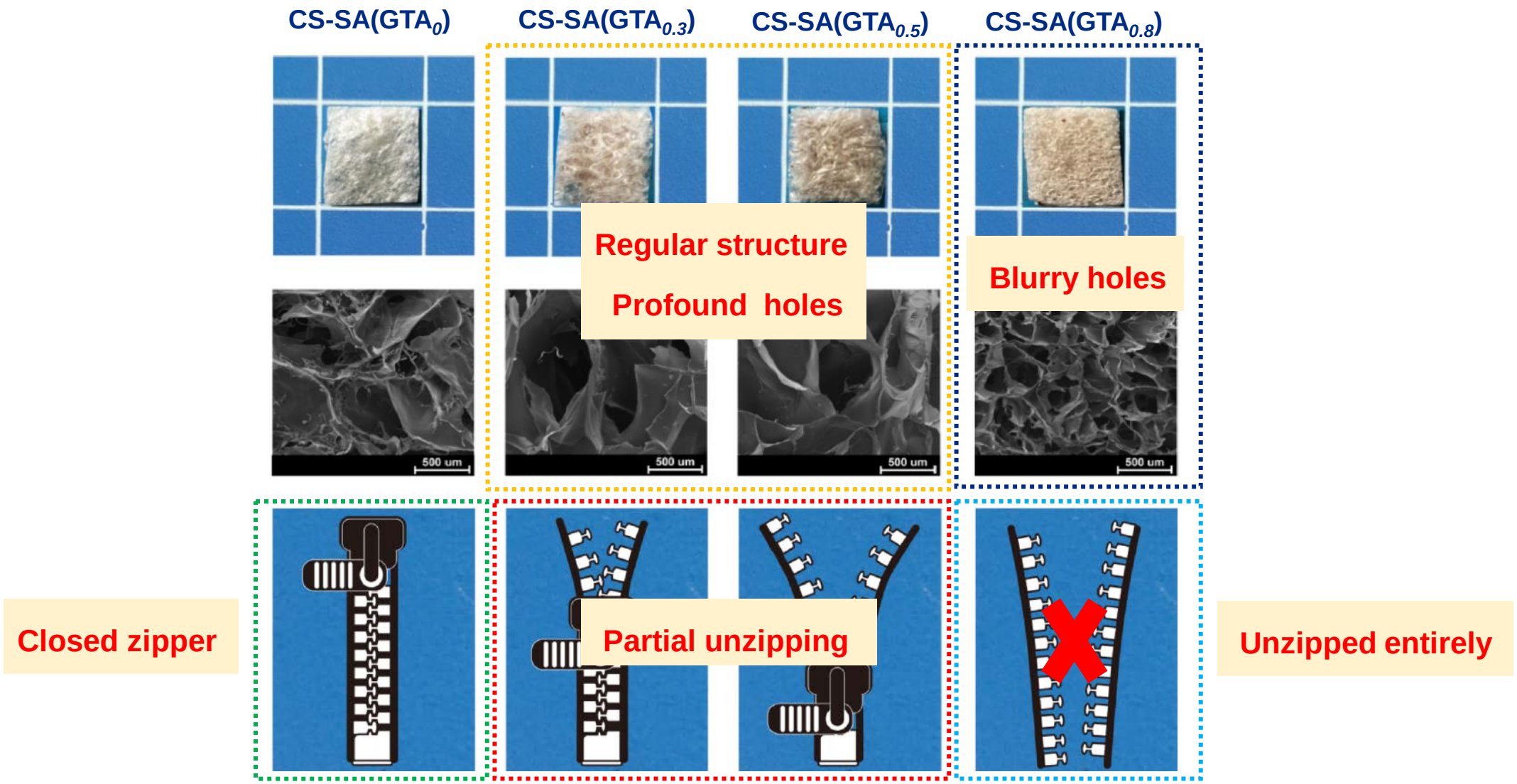
- **Structure (including macro-, micro-, crystal-, and chemical bonding- structure)**
- **Properties (involving thermal stability, rheological property, swelling behavior, and electronegativity)**
- **Semi-unzipping mechanism**

2. Capturing metallic mineral ions by CS-SA(GTA)

- **Simulated metallic mineral ions (Cr^{3+}, Fe^{3+}, Al^{3+}, and Zr^{4+}) adsorption**
- **Cr^{3+} containing tannery effluent adsorption**

3. Results and Discussion

3.1 Macro- and micro- structure of CS-SA(GTA)

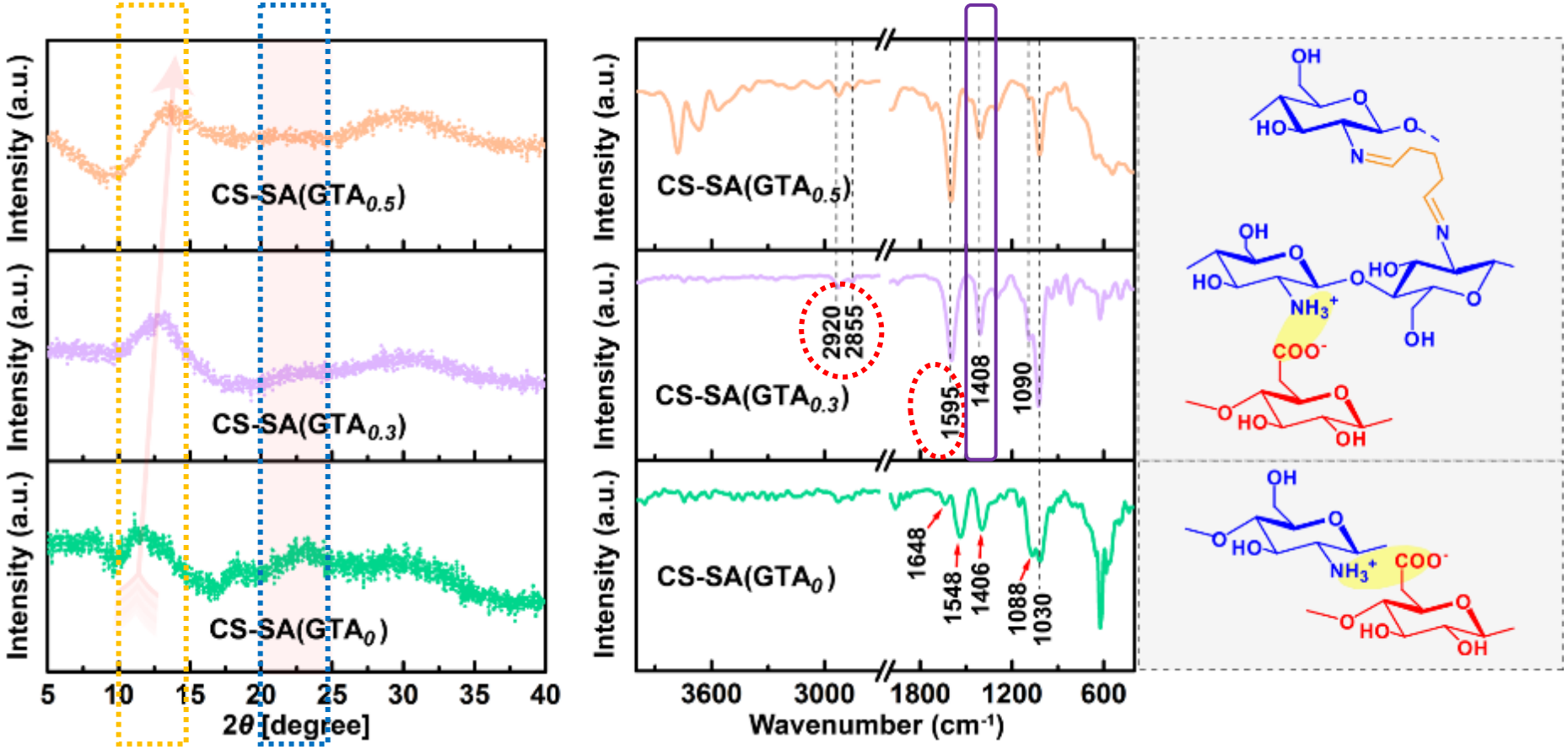


3. Results and Discussion

3.2 Crystal- and chemical bonding- structure of CS-SA(GTA)

Amorphous structure

Carboxyl content



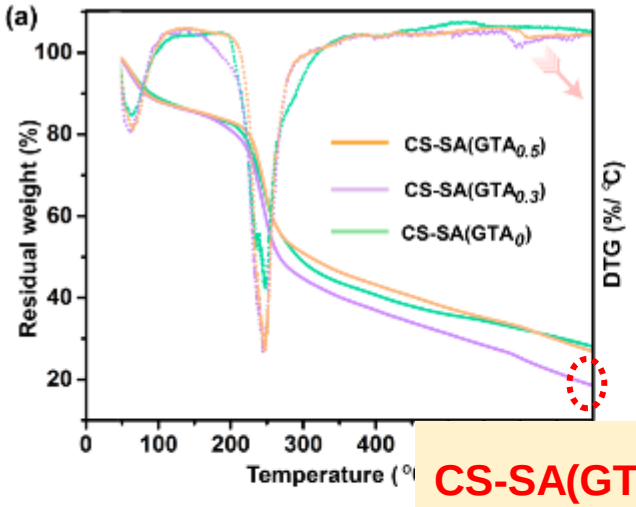
Schiff base reaction

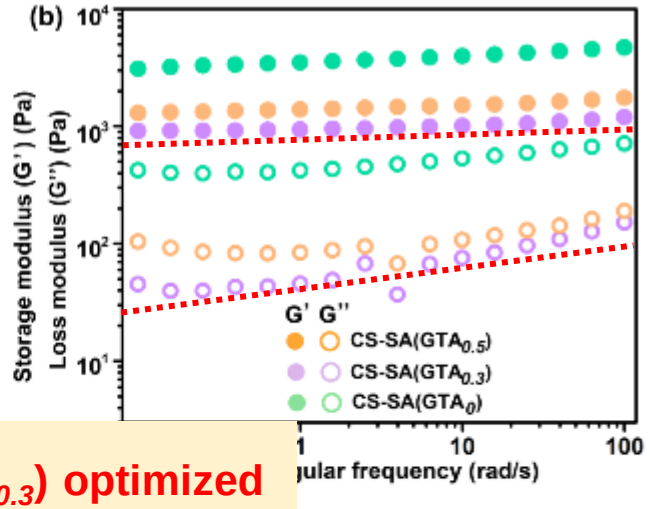
Schiff base reaction

3. Results and Discussion

3.3 Properties of CS-SA(GTA)

Thermal stability

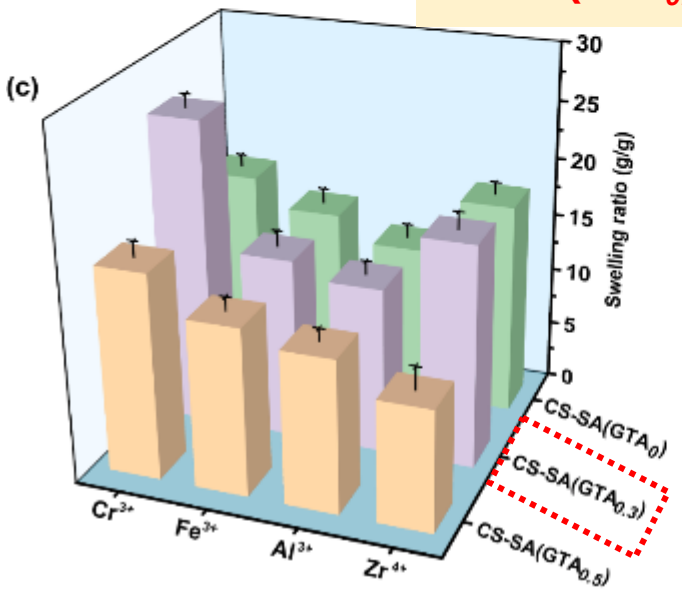


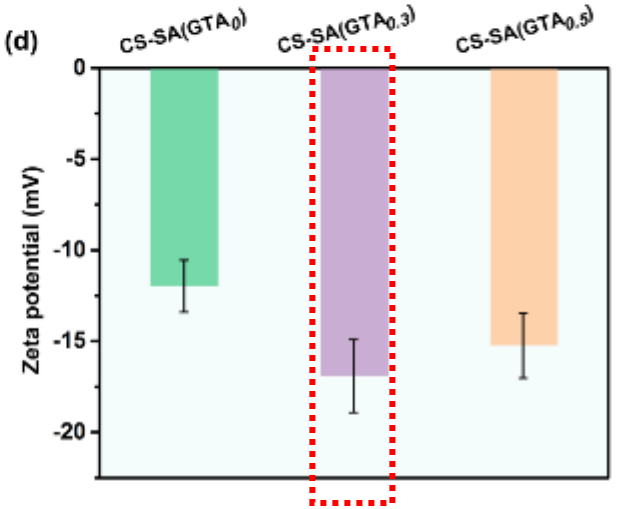


Rheological property

CS-SA(GTA$_{0.3}$) optimized

Swelling behavior

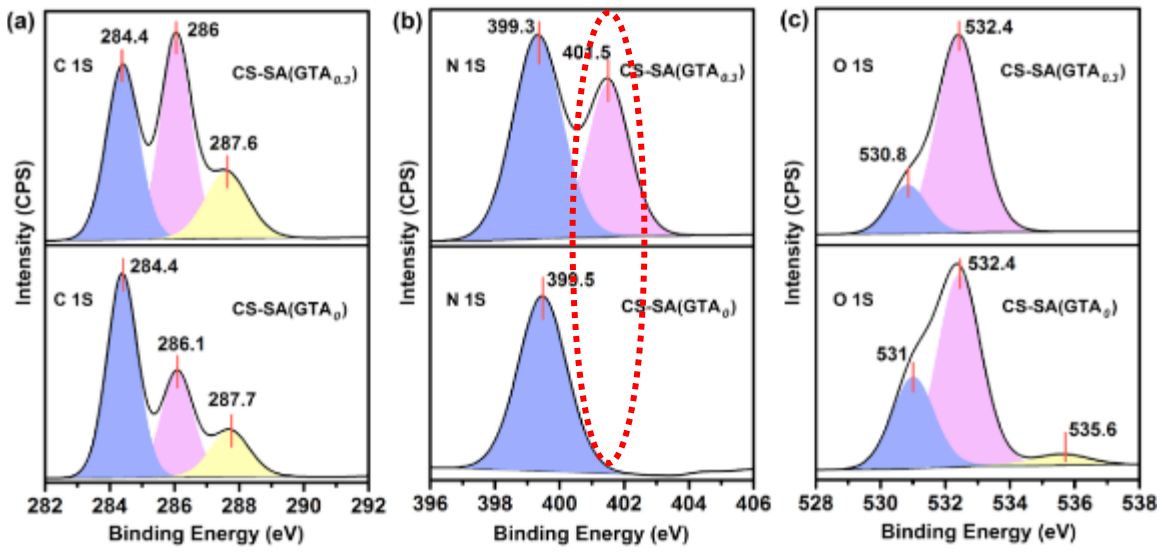




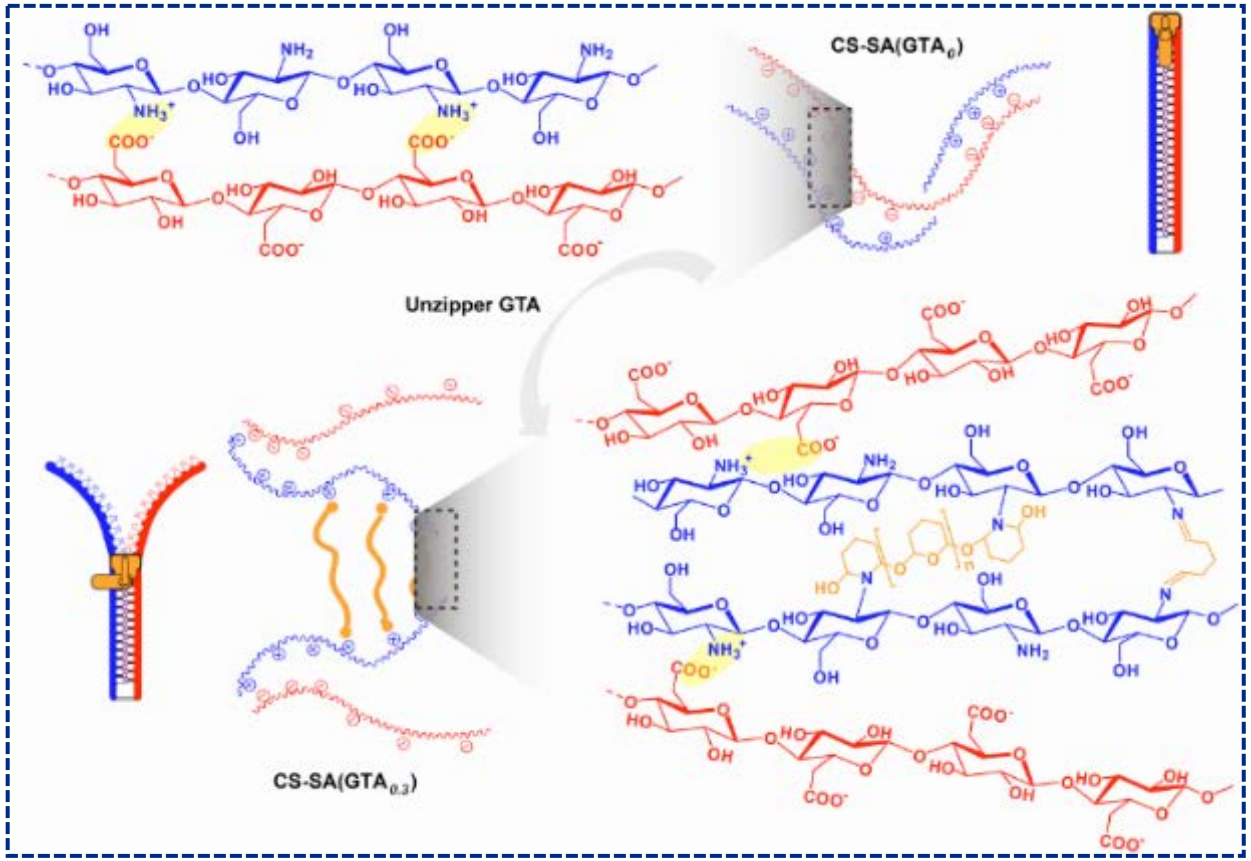
Electronegativity

3. Results and Discussion

3.4 Semi-unzipping mechanism

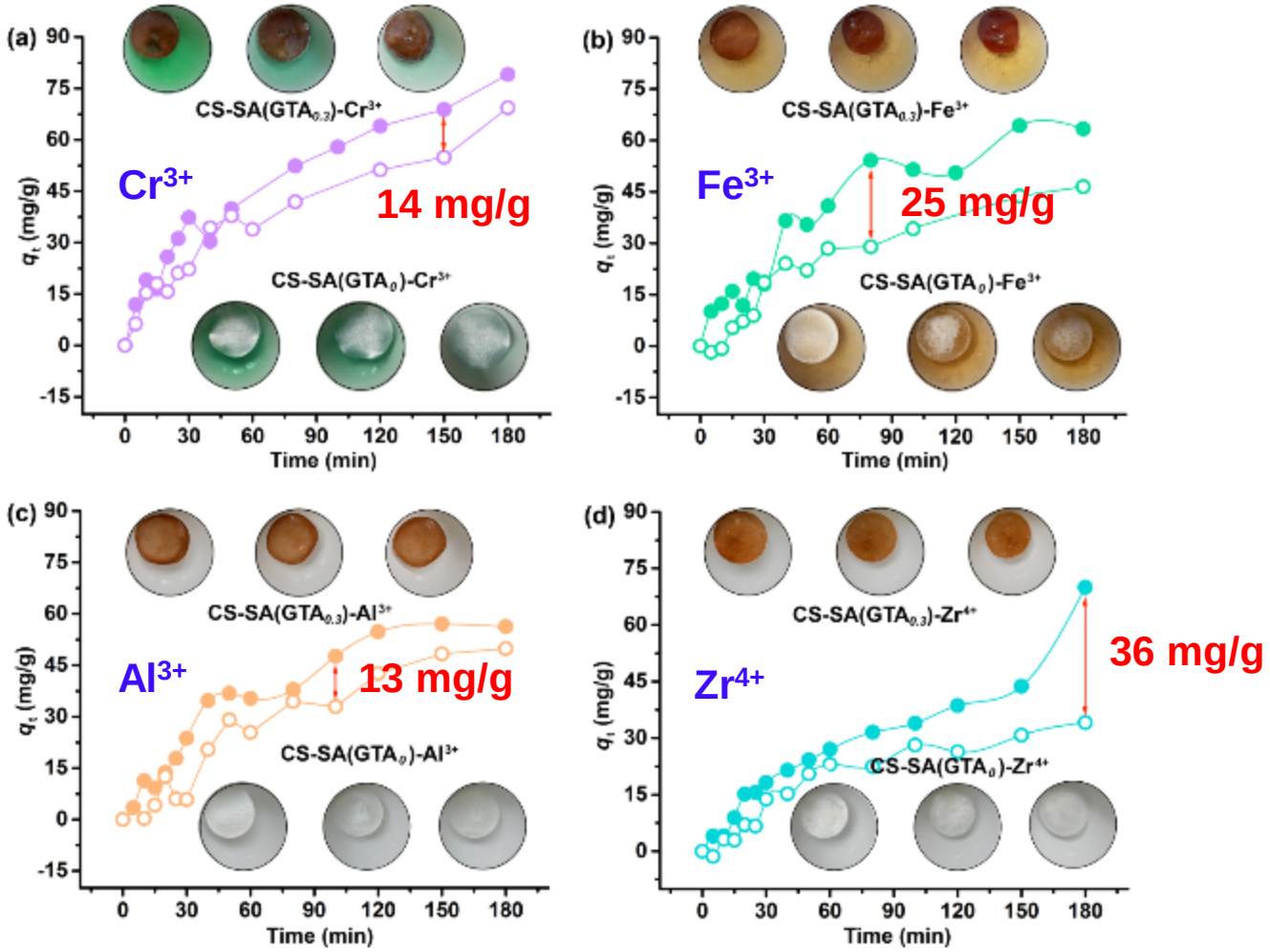


Semi-unzipping of CS-SA($GTA_{0.3}$)



3. Results and Discussion

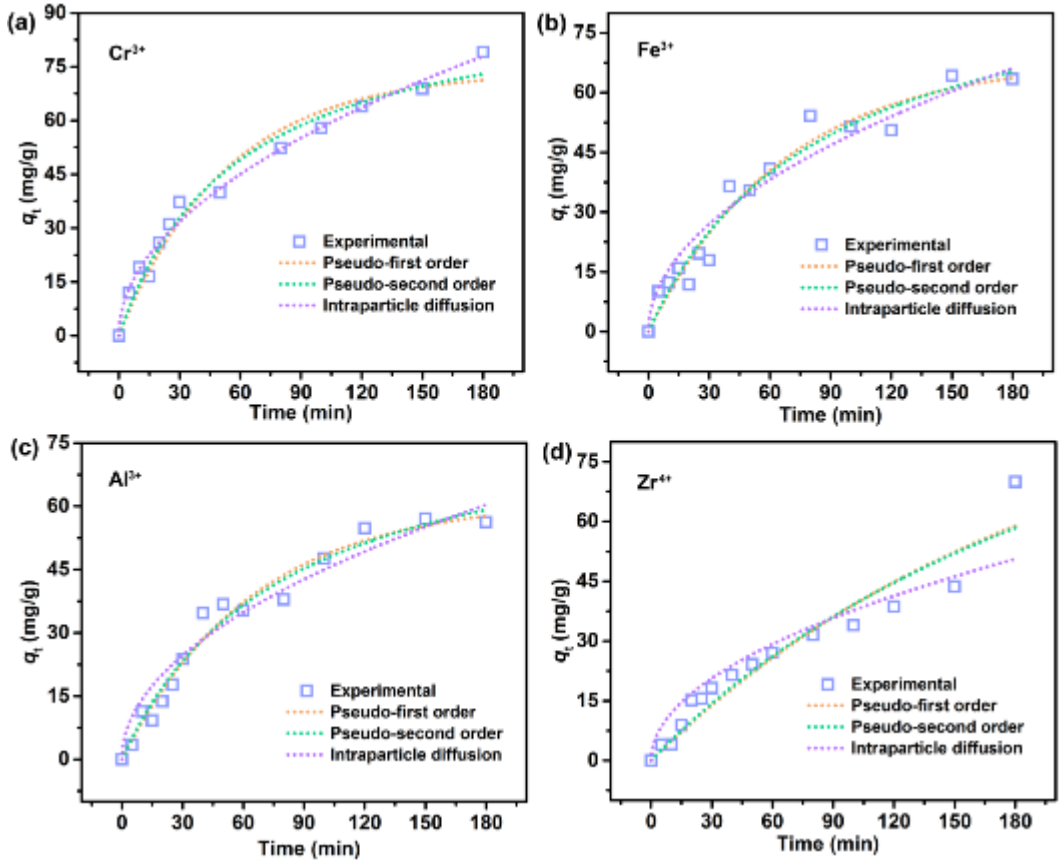
3.5 Cr^{3+}, Fe^{3+}, Al^{3+}, and Zr^{4+} capture ability by CS-SA($GTA_{0.3}$)



Higher capture ability of CS-SA($GTA_{0.3}$)

3. Results and Discussion

3.5 Cr^{3+}, Fe^{3+}, Al^{3+}, and Zr^{4+} capture ability by CS-SA($GTA_{0.3}$)

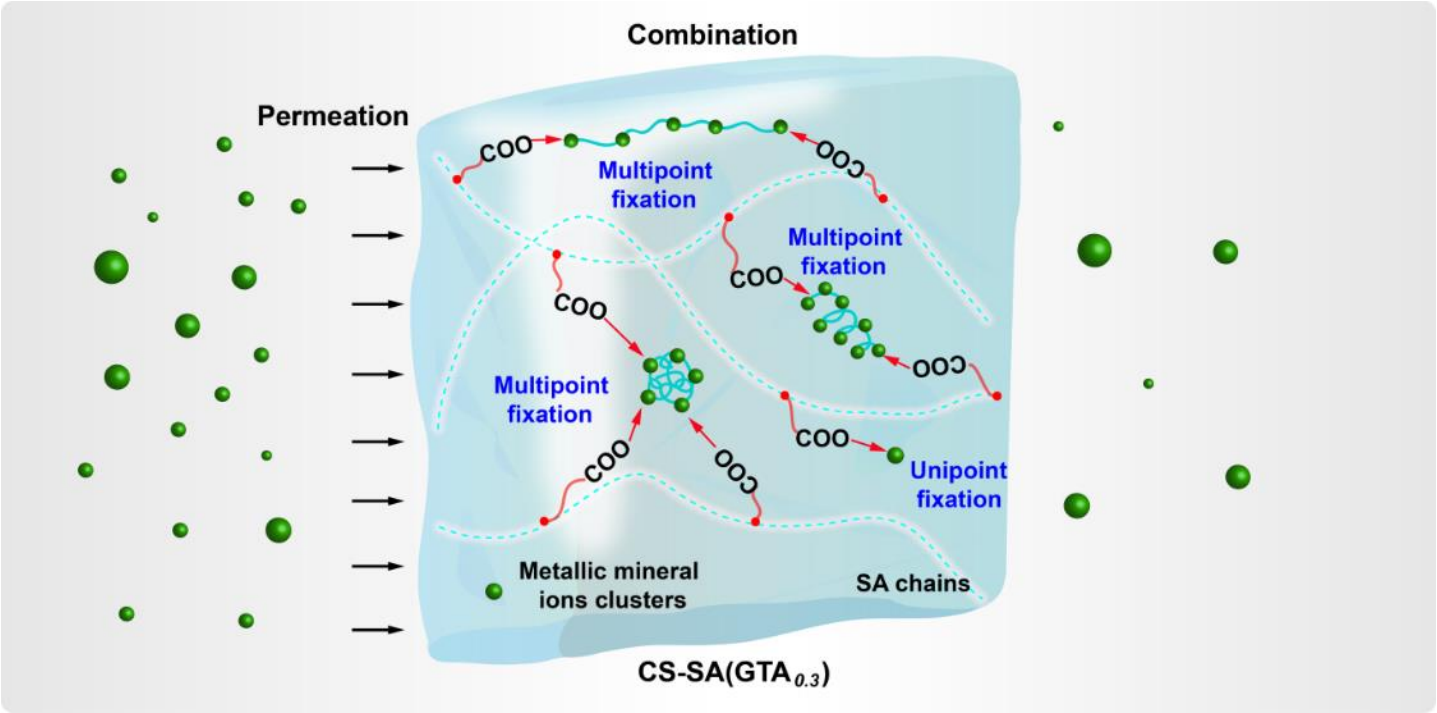


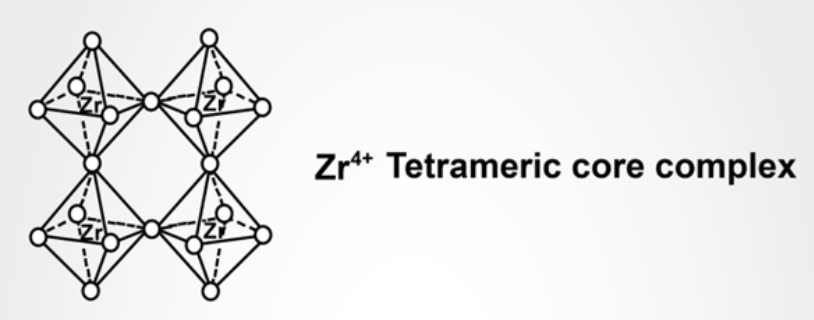
	Metallic mineral ions			
	Cr^{3+}	Fe^{3+}	Al^{3+}	Zr^{4+}
Pseudo-first order	**A single class of adsorption site**			
q_e (mg/g)	73.68	68.28	61.40	99.02
k_1 (min^{-1})	0.02	0.02	0.02	0.01
χ^2	23.40	19.36	10.39	27.23
R^2	0.96	0.96	0.97	0.92
Pseudo-second order	**Chemical adsorption**			
q_e (mg/g)	96.42	95.95	85.49	151.57
k_2 (g/mg·min)	1.5×10^4	1.0×10^4	7.8×10^3	1.2×10^4
χ^2	14.63	20.00	11.04	26.14
R^2	0.95	0.95	0.97	0.92
Intraparticle diffusion				
k_3 (mg/g·$min^{1/2}$)	5.81	4.93	4.50	3.77
χ^2	6.62	29.25	22.14	39.84
R^2	0.99	0.93	0.94	0.88

Carboxyl is the only adsorption site for these mineral ions by coordination bond

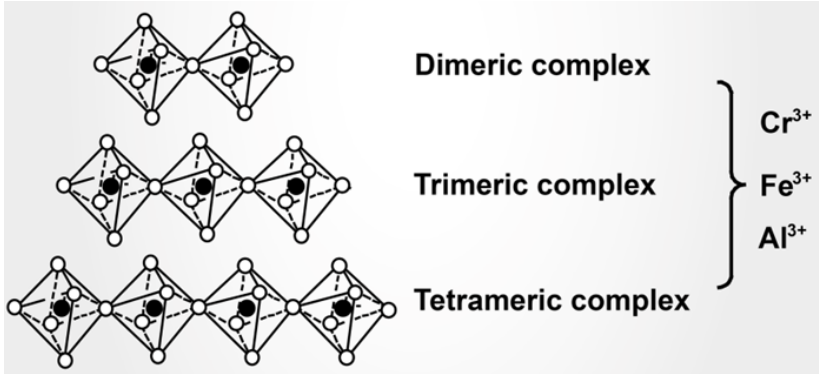
3. Results and Discussion

3.6 Cr^{3+}, Fe^{3+}, Al^{3+}, and Zr^{4+} capture mechanism





Architectural model

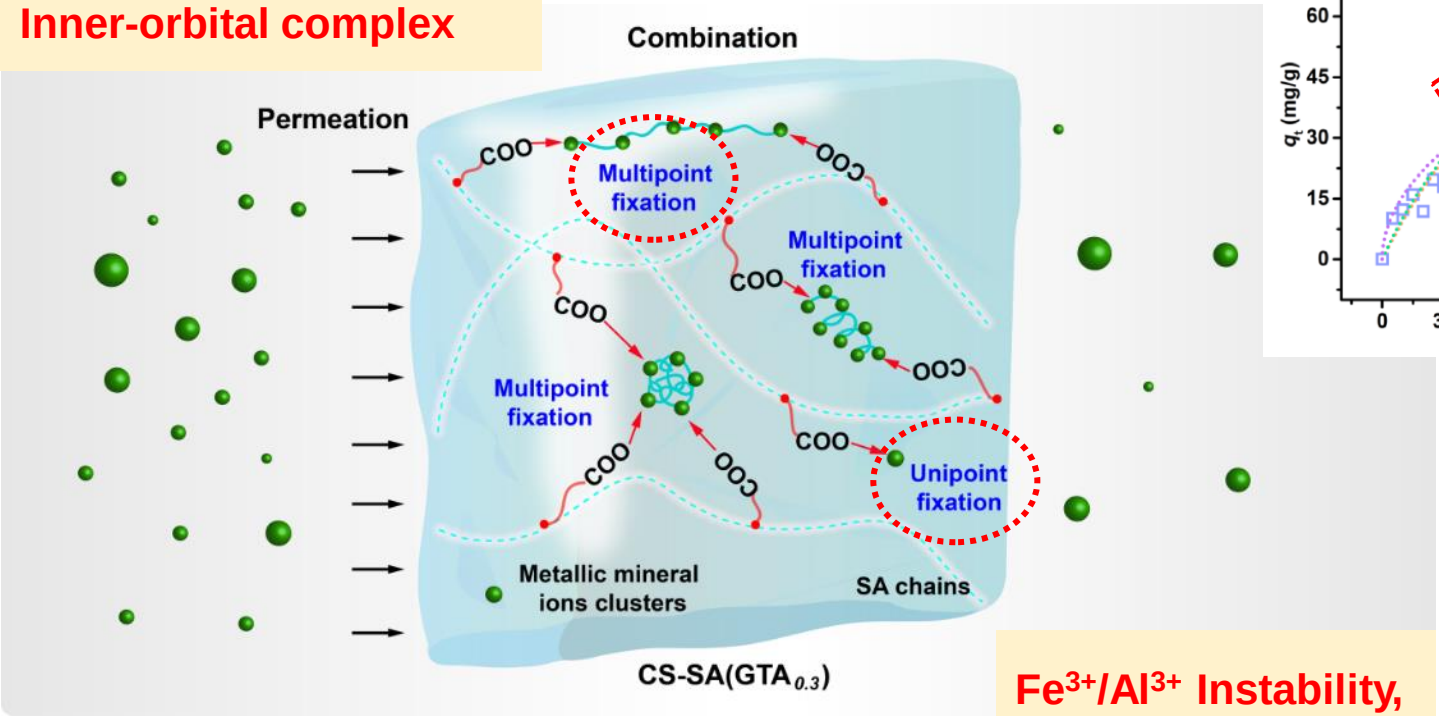


Linear structure

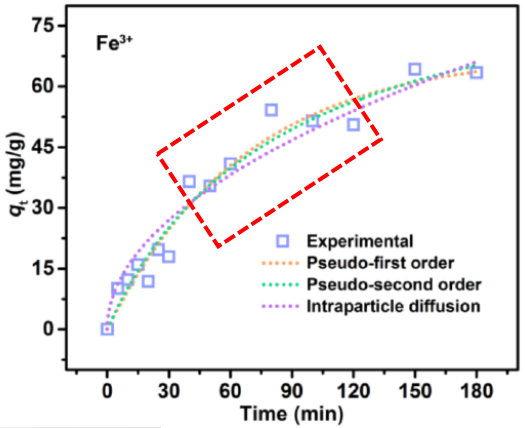
3. Results and Discussion

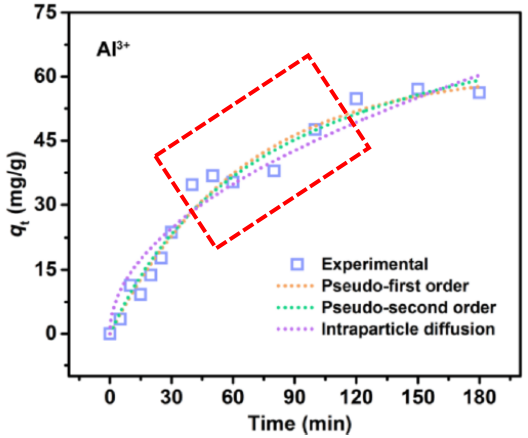
3.6 Cr^{3+}, Fe^{3+}, Al^{3+}, and Zr^{4+} capture mechanism

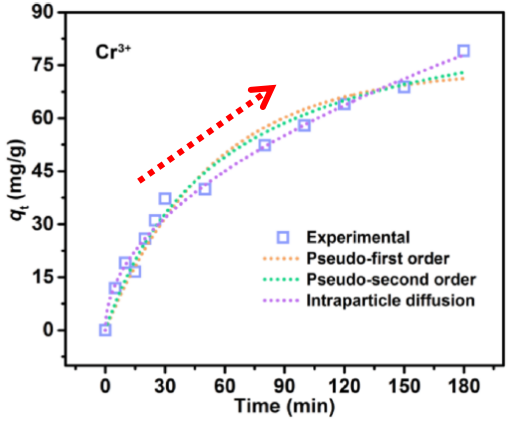
Cr^{3+} Stability, Covalent, Inner-orbital complex



Fe^{3+}/Al^{3+} Instability, Electrovalent

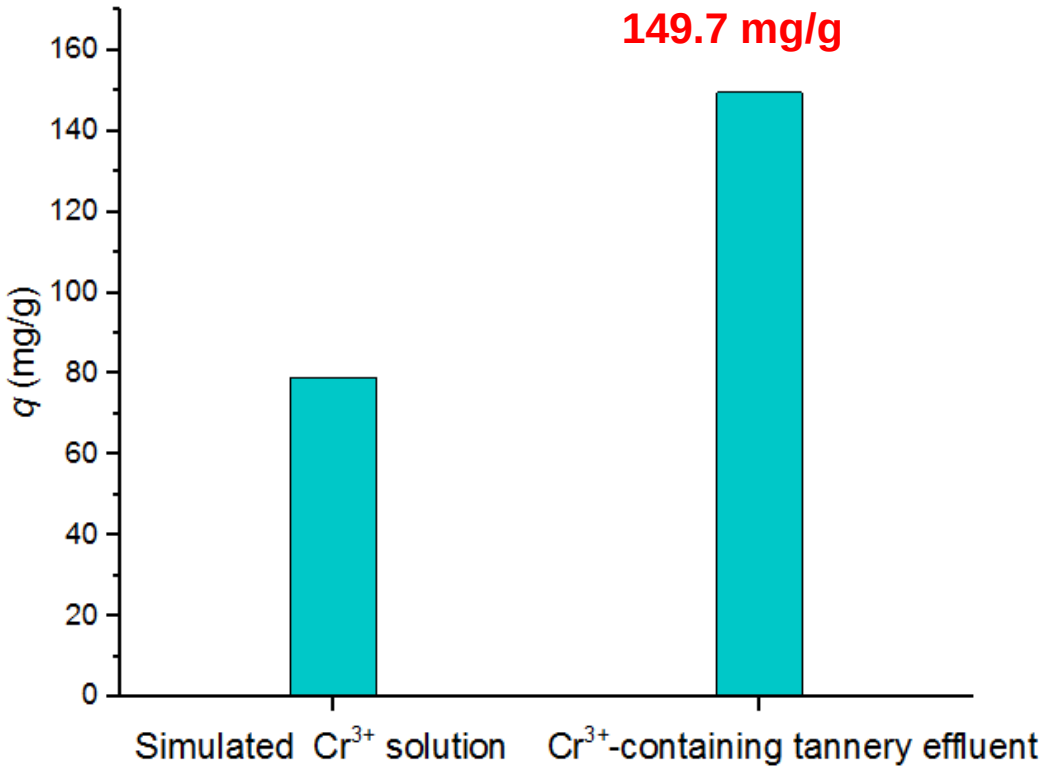






3. Results and Discussion

3.7 Cr^{3+} removal from tannery effluent by CS-SA($GTA_{0.3}$)



CS-SA($GTA_{0.3}$) is promising in mineral ions- containing tannery effluent remediation

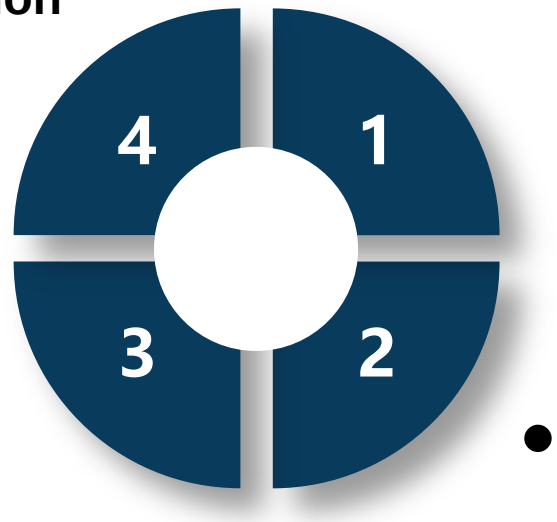
4 Part

Conclusion and Acknowledgement

4. Conclusion

- **Semi-unzipping of CS-SA($GTA_{0.3}$) was promised for practical application in leather effluent remediation.**

- **Semi-unzipping of CS-SA($GTA_{0.3}$) with loose, porous, and amorphous structure was successfully constructed.**

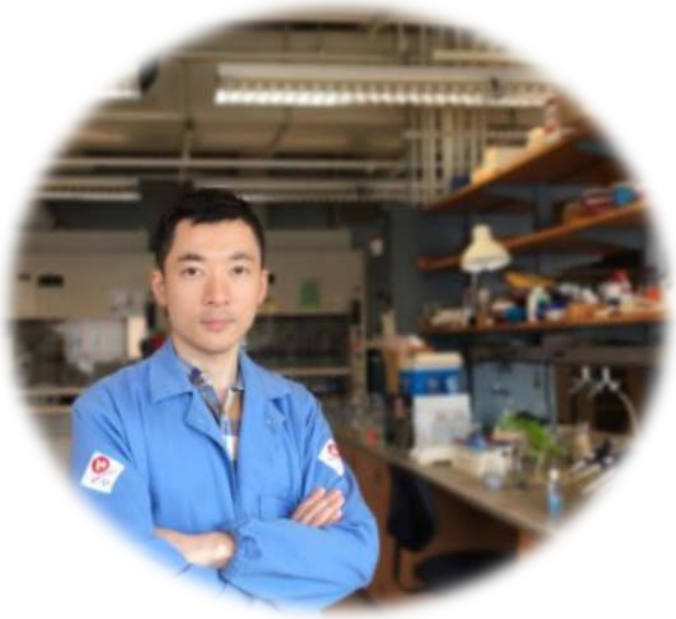


- **Semi-unzipping of CS-SA($GTA_{0.3}$) demonstrated efficient capture ability to Cr^{3+}, Fe^{3+}, Al^{3+}, and Zr^{4+}.**

- **Semi-unzipping of CS-SA($GTA_{0.3}$) showed a good swelling behavior and had more carboxyl groups exposition.**

4. Acknowledgement

- Natural Science Basic Research Program of Shaanxi;
- Opening Project of the Key Laboratory of Leather Chemistry and Engineering (Sichuan University), the Ministry of Education;
- Open Foundation of Shaanxi Collaborative Innovation Center of Industrial Auxiliary Chemistry and Technology.



Prof. Yi Chen
(Sichuan University)

My group

陕西科技大学
SHAANXI UNIVERSITY OF SCIENCE & TECHNOLOGY

Thanks for your listening!

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Shaanxi University of Science & Technology

AICLST 2022

12 th Asia International Conference On Leather Science And Technology
18th -20th Oct., 2022 in Palmerston North, New Zealand

18th Oct., 2022