EGU conference 2018

Investigating the potential of synthetic humic-like acid (SHLA) to remove metal ions from contaminated water

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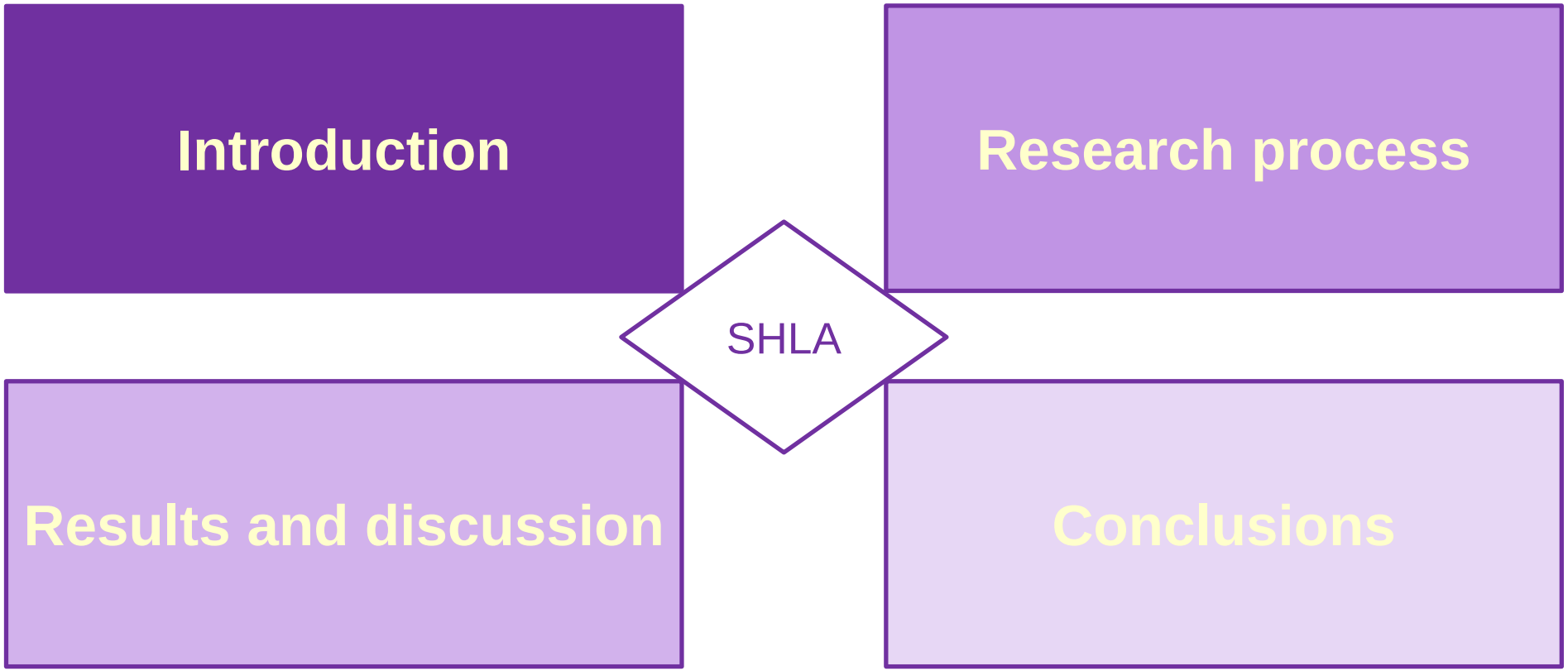

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Introduction

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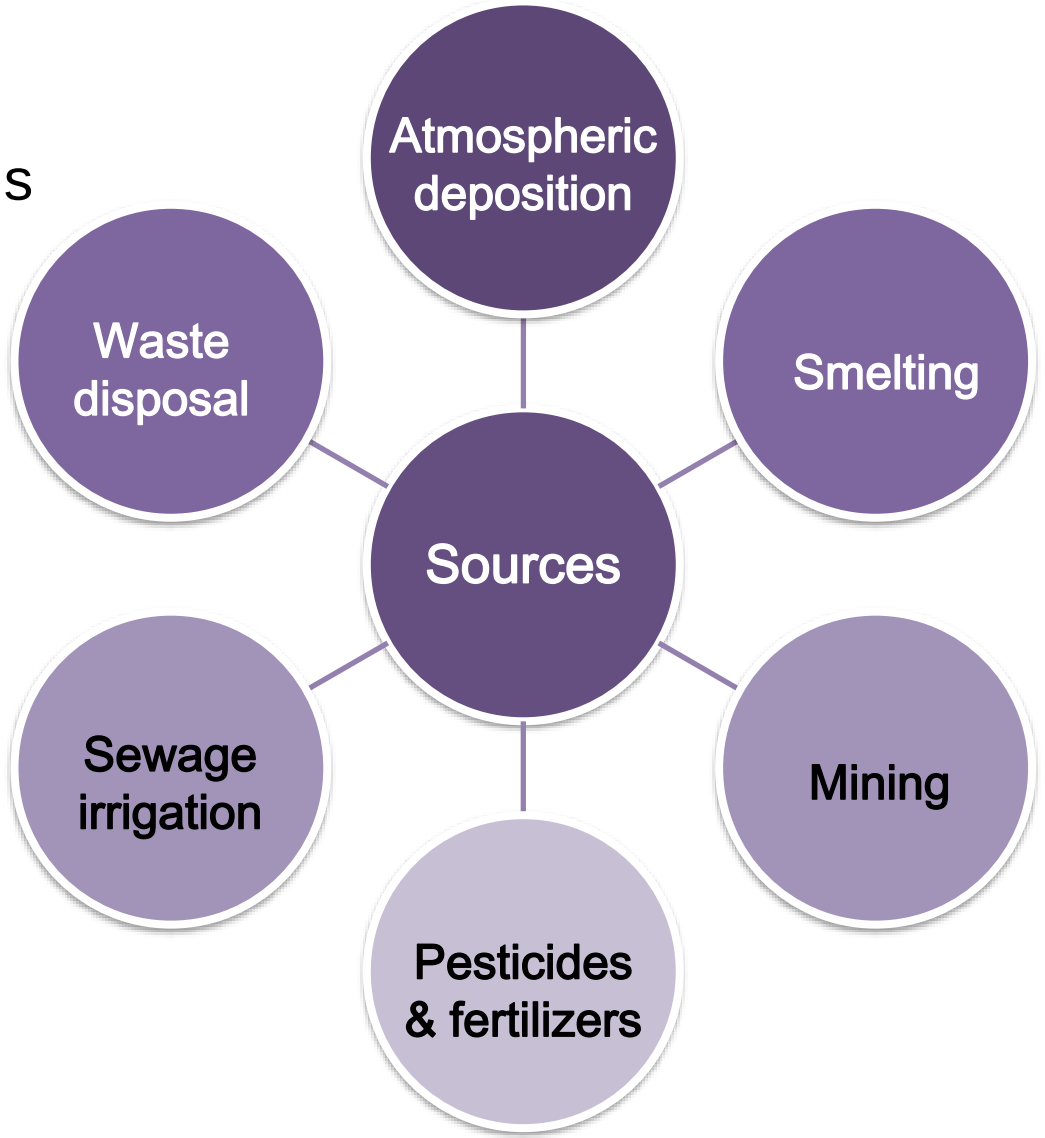
- Hazardous metal pollution
- Non-biodegradable & accumulate in living organisms



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Introduction

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- Humic substances: organic compounds naturally occur in soils, waters and sediments
- Three types: 1) **humic acid (HA):** soluble under alkaline conditions; 2) fulvic acid (FA): soluble under all pH conditions; 3) humin: insoluble
- HA: abundant functional groups

  (*eg.* COOH, amino, aliphatic- and phenolic-OH and carbonyl,etc)

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High binding ability with metal ions

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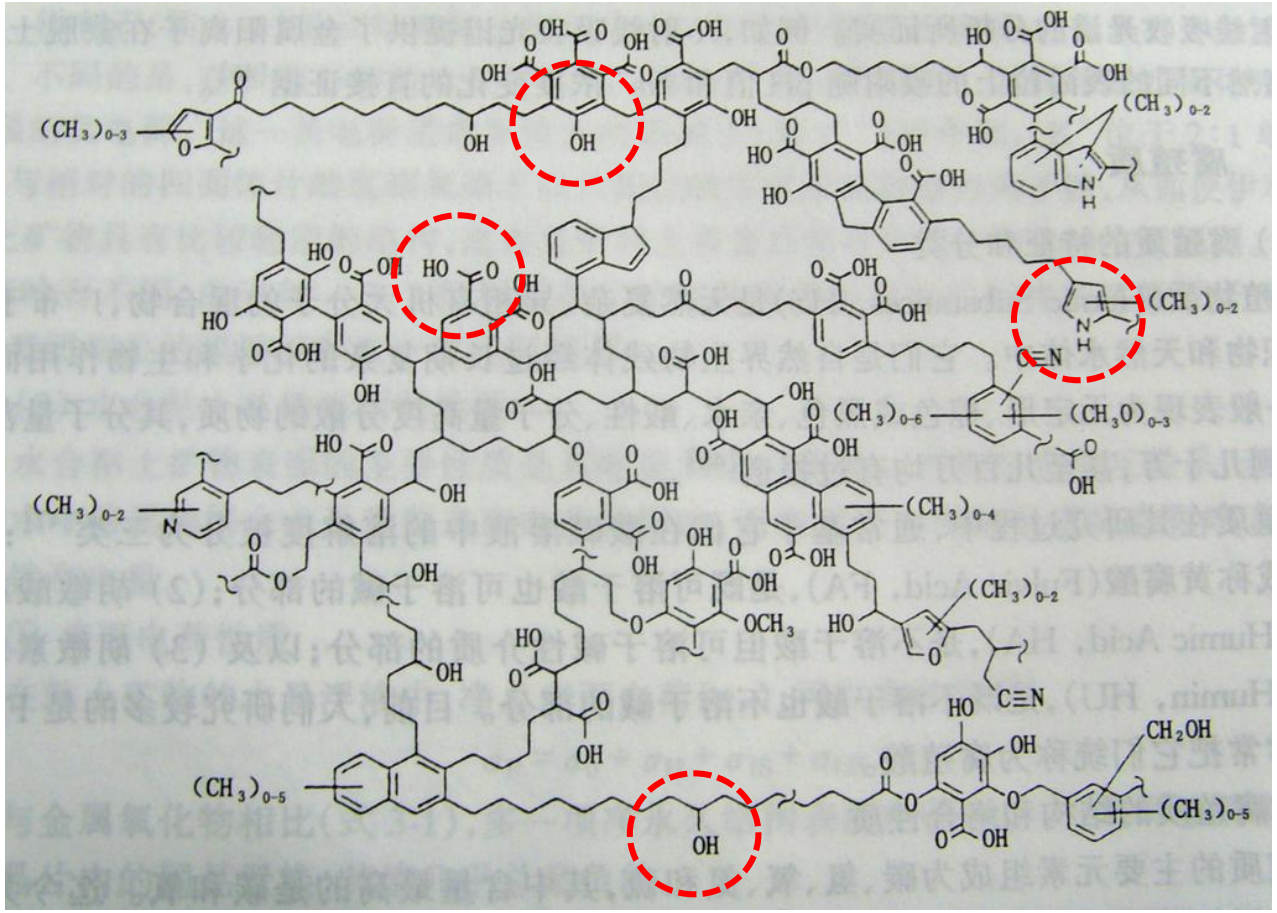
Adsorbent in water/wastewater treatment



Humic Acid

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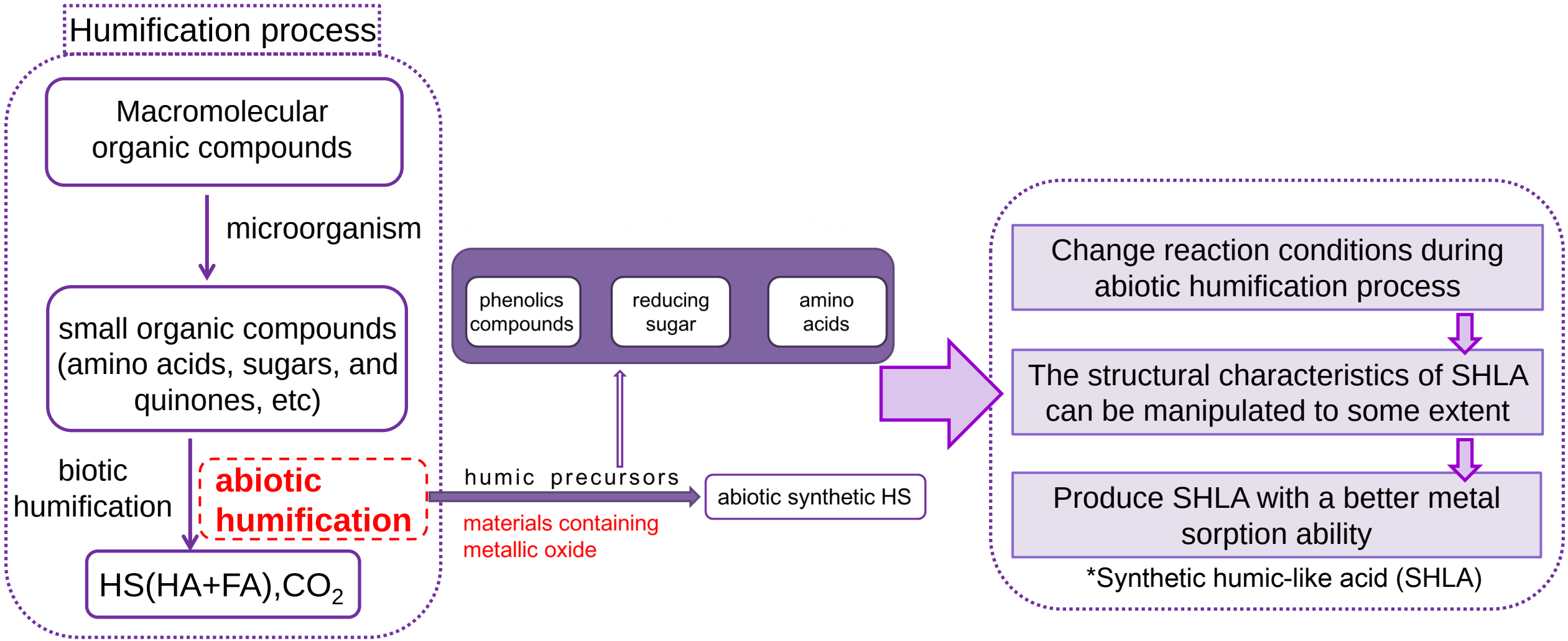

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Introduction

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- Research aims
  - A synthetic humic-like acid (SHLA) with a high COOH content was prepared.
  - Determined adsorption efficiency, kinetics, isotherms, thermodynamics, and desorption behaviour of SHLA in the single metal (Cu^{2+}) system.
  - Determined the adsorption efficiency of SHLA in the multi-metal system.

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Research process

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Prepare optimal synthetic humic-like acid (SHLA)

1 L autoclaved phosphate buffer
pH=8 0.2 M Na_2HPO_4 / NaH_2PO_4)

Thimerosal (0.02% w/v)

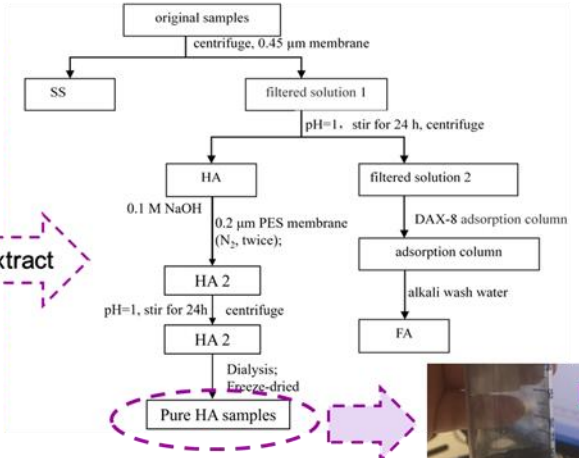
Precursors: Catechol (0.25 mol/L)
Glycine (0.25 mol/L)

Catalyst: MnO_2 (25 g/L)

Shake in dark; 240h; 25℃

High COOH content

Extract



Multi-metal system

Cu Pb Cr Ni Zn Cd Co

Single metal system (Cu^{2+})

Adsorption efficiency	Adsorption kinetics	Adsorption isotherms	Adsorption thermodynamics	Desorption and regeneration
pH	Pseudo-first-order model	Freundlich model	Δ°G	Eluant agent
Temperature	Pseudo-second-order model	Langmuir model	Δ°S	Adsorption-desorption cycles
Cu^{2+} concentration	Intraparticle diffusion model	bi-Langmuir model	Δ°H	
SHLA addition dose	Elovich model			

Results and Discussion

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Single metal system

- Characterization of SHLA
- Adsorption kinetics and efficiency
- Adsorption isotherms
- Desorption and reusability

Multi-metal system

- Multielement adsorption

Characterization of SHLA

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Elemental composition

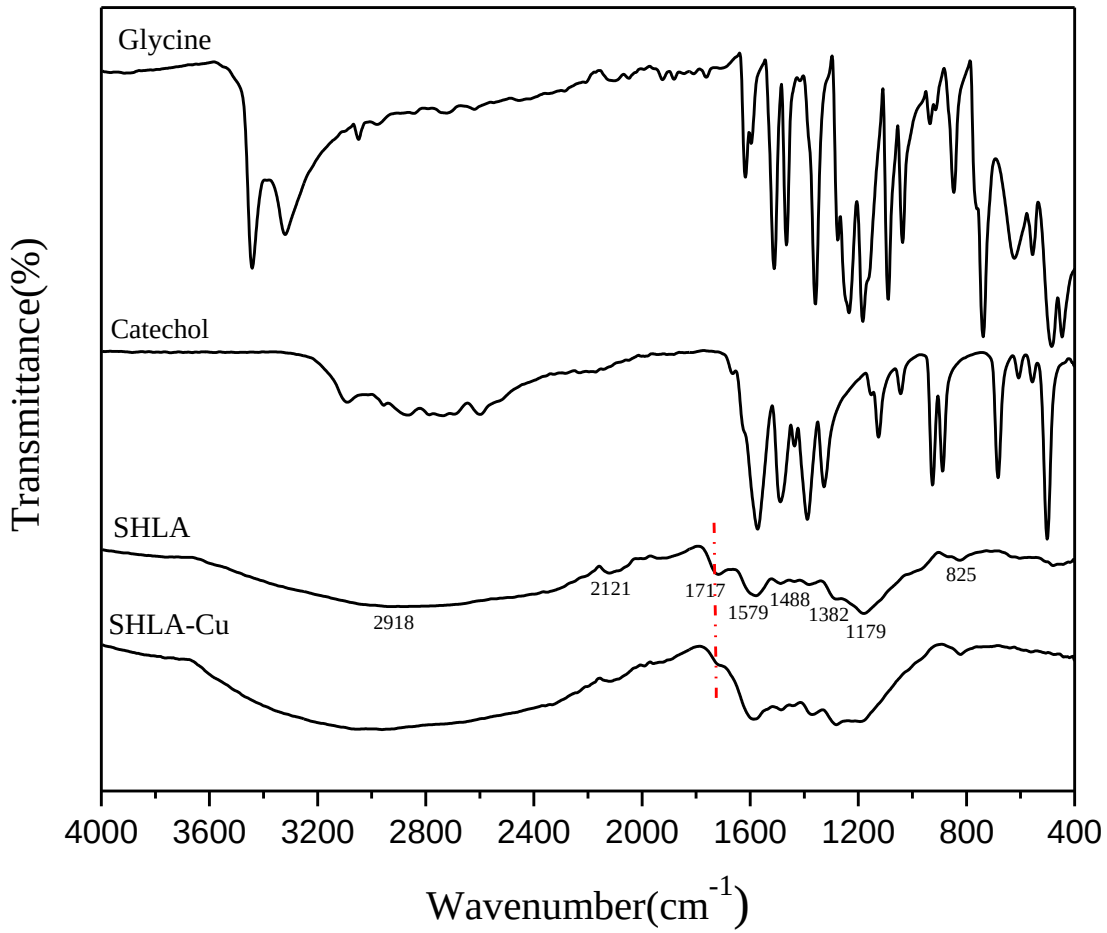
N/%	C/%	H/%	O/%	N/C	H/C	O/C
5.14	47.68	2.96	44.23	9.28	16.13	0.93

Acidic functional group content and E_4/E_6

COOH (mmol/g)	Phenolic-OH (mmol/g)	Total acidity (mmol/g)	E_4/E_6
5.03±0.34	6.65±0.34	11.58±0.68	3.2±0.0

FTIR

Wavenumber/cm^{-1}	Assignment
2918	C-H stretching of aliphatic structures
2121	C≡C stretching and the presence of cyano group
1717	C=O stretching of carbonyl groups
1579 &1493	C=C ring stretching, symmetric C–O stretch of COO- and N-H deformation and C=N stretching (amide II band)
1382	O-H deformation of phenols, C-H deformation, symmetric and asymmetric stretching of CH_3 and C-O stretch of COO-
1179	C–O stretching and C–O–H deformation of alcohols, phenols and ethers



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Adsorption kinetics and efficiency

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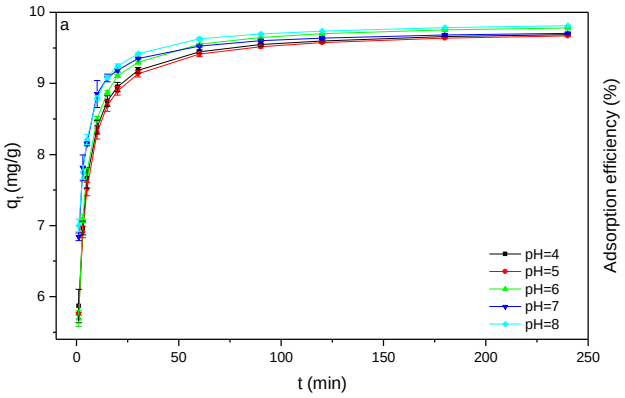

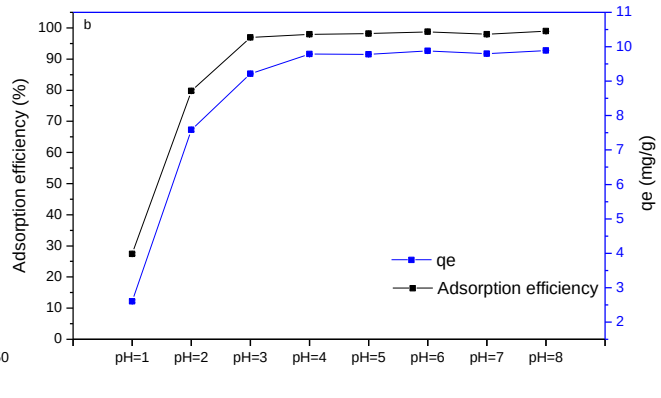

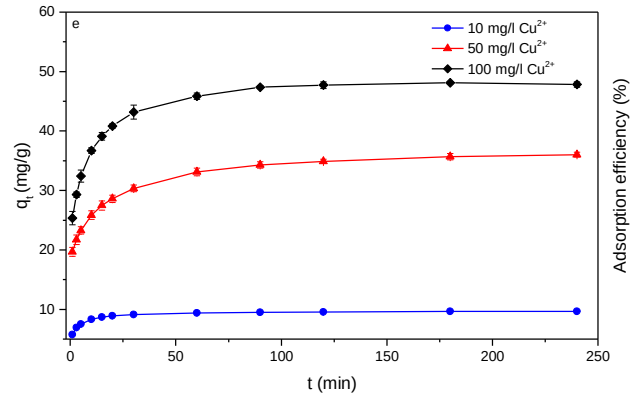

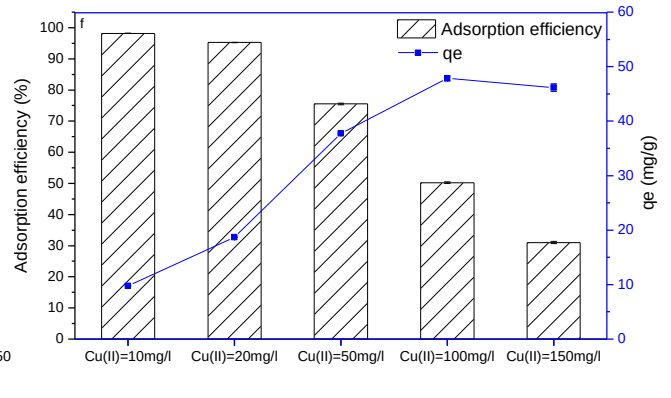

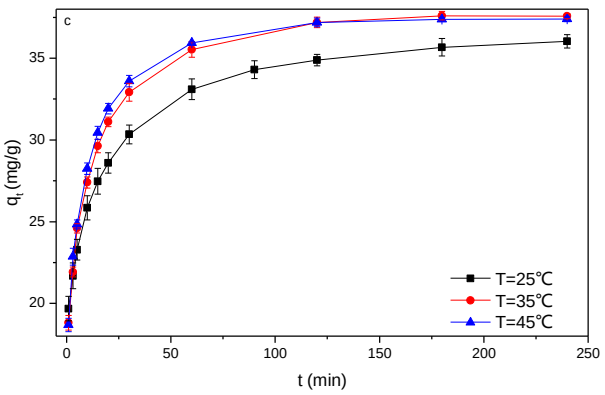

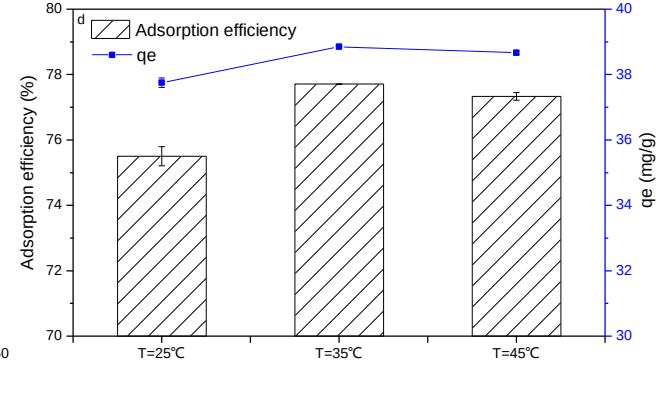

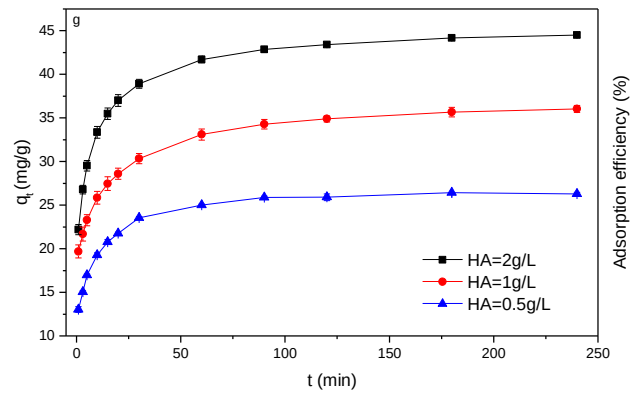

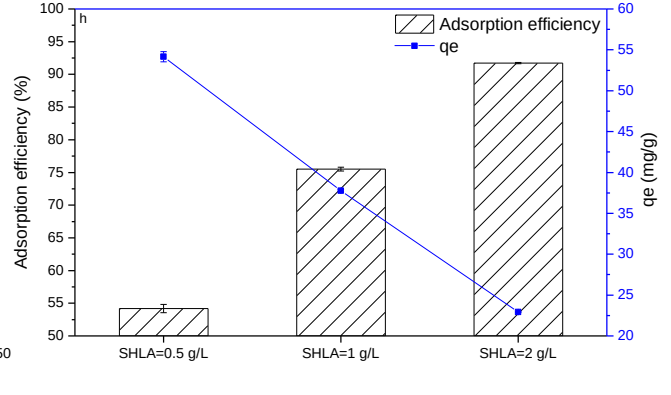

- Adsorption efficiencies: 27% - 99%; pH ↑, temperature ↑, SHLA dose ↑ , Cu^{2+} concentration↓,→ adsorption efficiency ↑
- Pseudo-second-order model fit BEST → Chemisorption

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Adsorption isotherms

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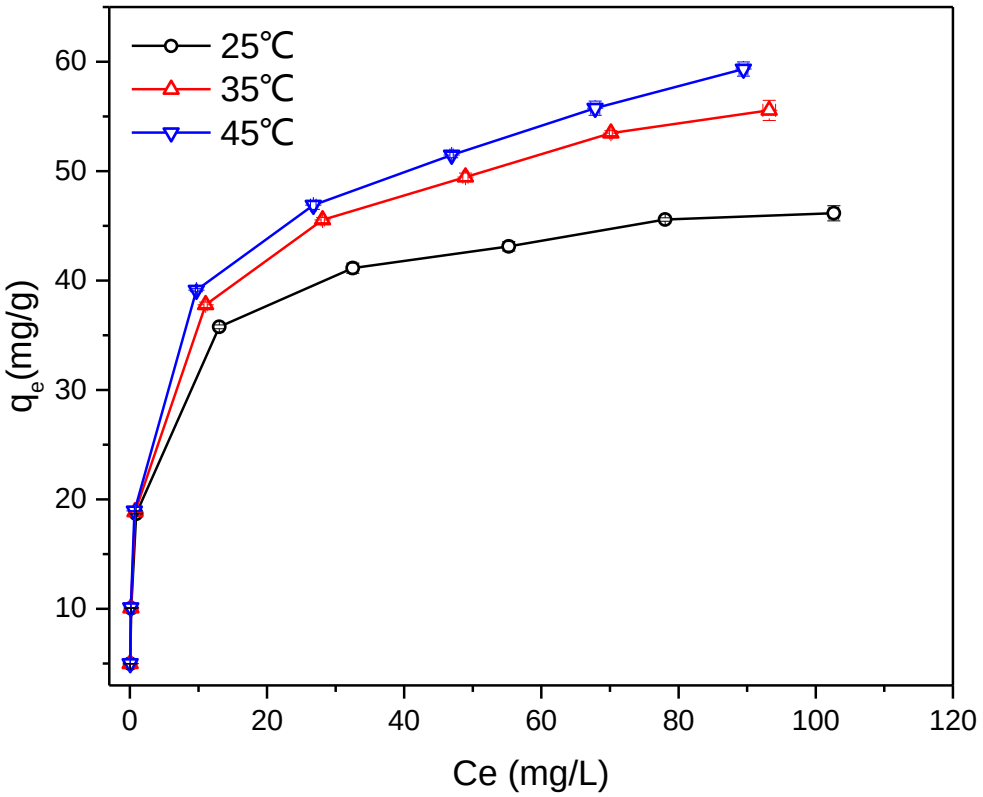

- Both Langmuir and Freundlich models fit data well.
- Carboxylic groups could bind with Cu^{2+} by:

  1) Surface complexation 2) Electrostatic attraction.
- q_m: 58.8 mg/g

Langmuir and Freundlich models

Temperature /℃	Langmuir					Freundlich			
	q_m (mg/g)	K_L (L/mg)	R^2	p	R_L	K_f (mg/g(L/mg)$^{1/n}$)	n	R^2	p
25	46.45 ±0.79	0.466 ±0.129	0.9982	<0.0001	0.0142-0.2985	14.488 ±1.206	3.527 ±0.303	0.9497	<0.0001
35	55.62 ±1.58	0.344 ±0.102	0.9949	<0.0001	0.0192-0.3656	15.704 ±1.204	3.264 ±0.245	0.9616	<0.0001
45	58.79 ±1.98	0.336 ±0.106	0.9928	<0.0001	0.0196-0.3711	16.711 ±1.191	3.276 ±0.231	0.9667	<0.0001

bi-Langmuir model

Temperature /°C	$q_{m,1}$ (mg/g)	$K_{L,1}$ (L/mg)	$q_{m,2}$ (mg/g)	$K_{L,2}$ (L/mg)	R^2	p
25	20.77±1.58	4.338±0.719	27.92±1.44	0.0892±0.014	0.9995	<0.0001
35	24.21±2.69	3.807±0.930	37.38±2.23	0.0501±0.012	0.9990	<0.0001
45	26.41±4.66	3.969±1.591	39.98±3.74	0.0442±0.019	0.9971	<0.0001

Desorption and reusability of SHLA

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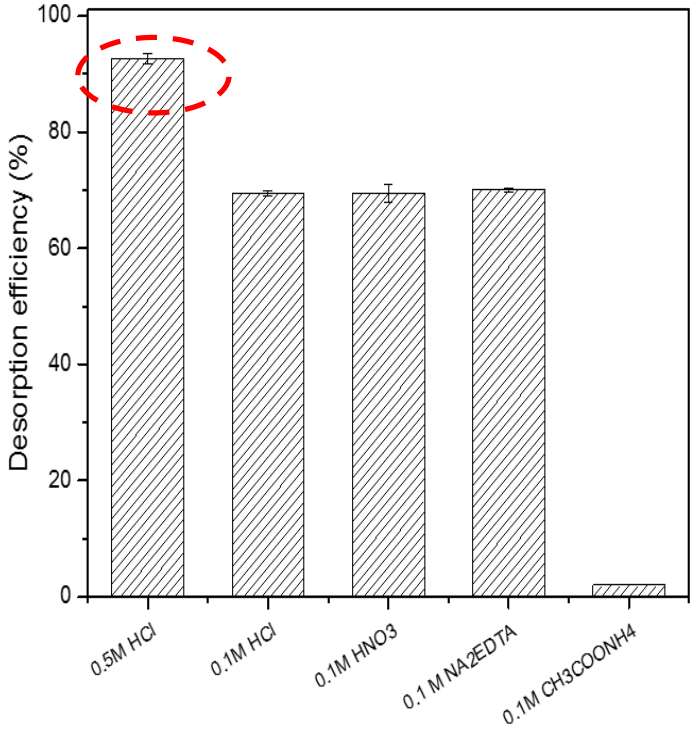

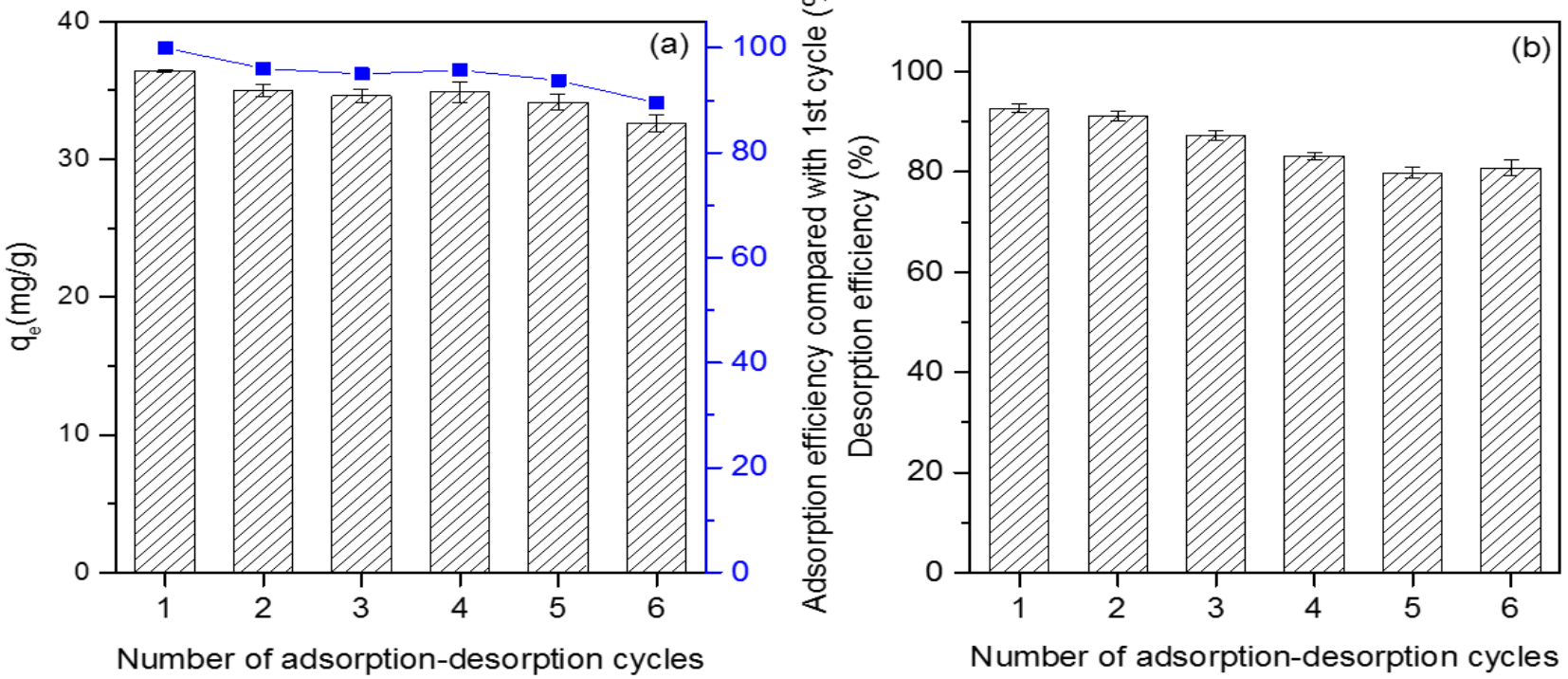

- Eluant selection: 0.5 M HCl
- q_e: decreased just 10% after 6 cycles
- Good regeneration performance

Multielement adsorption

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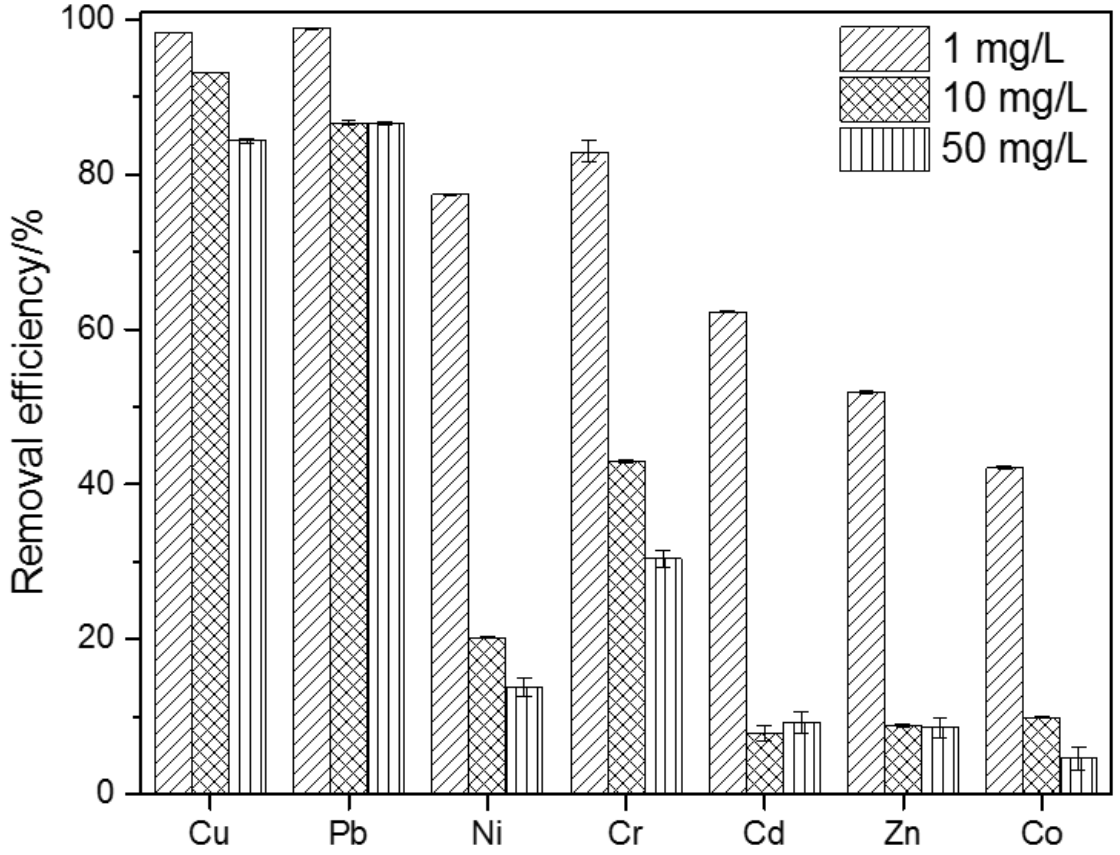

- Adsorption efficiencies:

  84.3-98.3% for Cu, 86.6-98.8% for Pb,

  30.4-82.9% for Cr, 13.8-77.4% for Ni,

  9.2-62.3% for Cd, 8.6-51.9% for Zn,

  and 4.6-42.1% for Co.

- Metal removal efficiency order (based on 1 mg/L system):

  Cu ≈ Pb > Cr > Ni > Cd > Zn > Co

Conclusions

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- The optimal SHLA worked well in both single metal system and multi-metal system.
- A pseudo-second-order kinetic model fit best → chemisorption.
- The maximum adsorption capacity of the SHLA was 58.8 mg/g at 313 K.
- The adsorption of Cu^{2+} onto SHLA was favourable, spontaneous and endothermic in nature.
- The Cu^{2+} adsorption capacity of SHLA was much higher than most of the humic acid-based materials.

SHLA has significant potential for use as an adsorbent for the clean up of metal-contaminated waters.

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Thanks !

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