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IMPROVING THE ADSORPTIVE PROPERTIES OF BIOMATERIALS FOR THE REMOVAL OF HEAVY METALS

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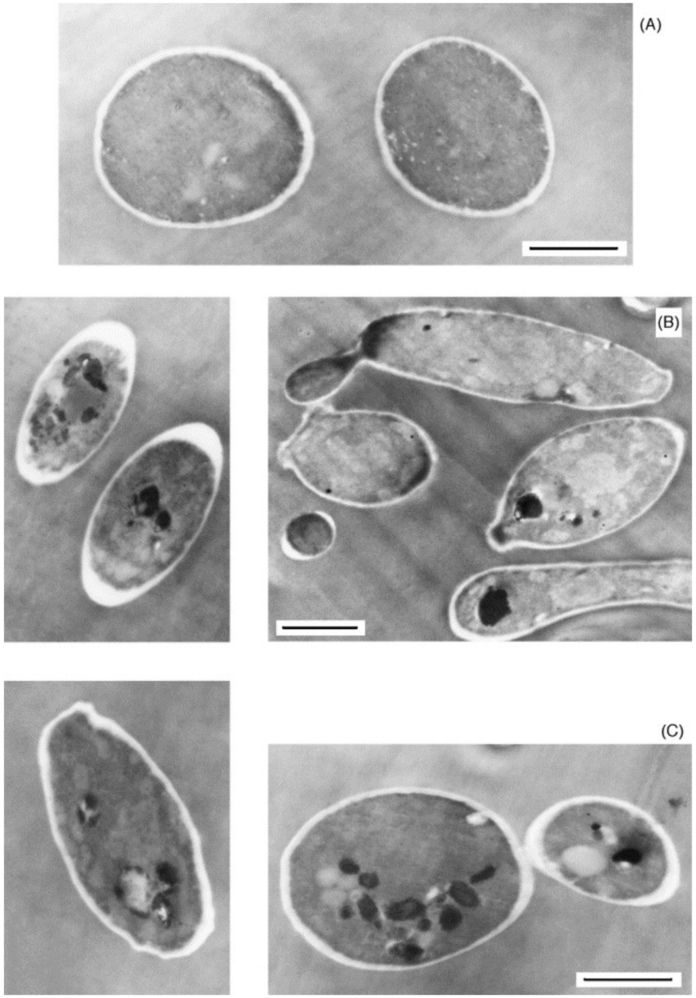
PROBLEM

Heavy Metals

- Present in human activities, from food to metal-mechanic and paints.
- Are not biodegradable
- Can be bioaccumulated and transferred to humans through the food chain.
- Copper, Zinc, Cobalt, and Iron. Most toxic: Lead, Cadmium, Mercury and Chromium.

BIOREMEDIATION

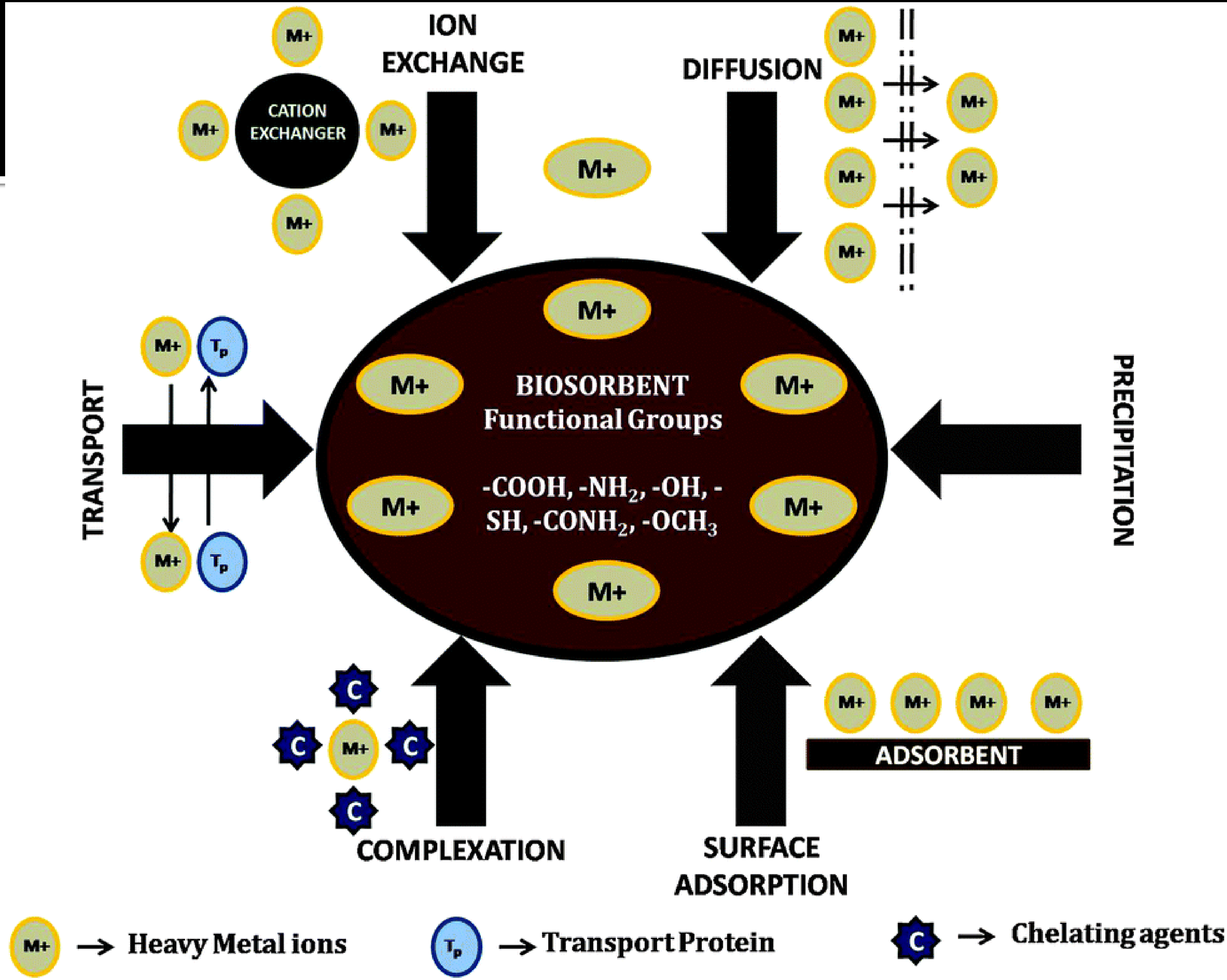


Use of biological techniques to remove pollutants from air, soil and water.

- Bioaccumulation: Living organism
- Biosorption: Dead biomass

BIOSORPTION

- Use of non-living biomasses to passively remove pollutants
- Driven by physico-chemical processes
- Algae, crustacean shells, eggshell, nutshell, fruit peels, fruit seeds, TEALEAVES.
- Fast kinetics (saturation time).
- Potential recyclability of waste


ION EXCHANGE
CATION EXCHANGER
M+
DIFFUSION
TRANSPORT
Tp
BIOSORBENT Functional Groups
-COOH, -NH2, -OH, -SH, -CONH2, -OCH3
PRECIPITATION
C
COMPLEXATION
SURFACE ADSORPTION
ADSORBENT
M+ → Heavy Metal ions
Tp → Transport Protein
C → Chelating agents

ADVANTAGES

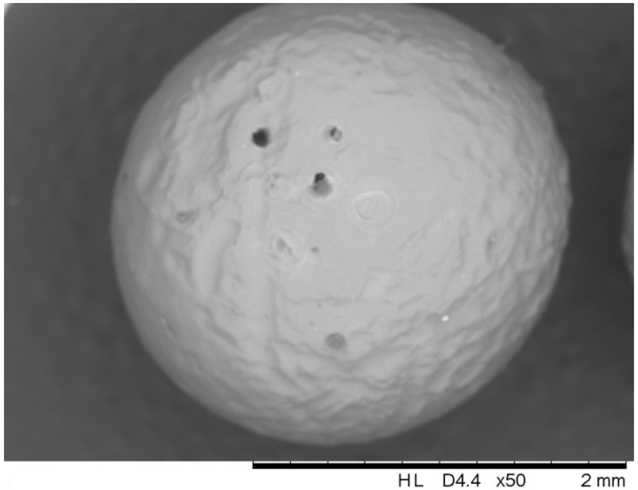
- Competitive performance.
- Pollutant selectivity.
- Cost effectiveness.
- Pollutant recovery.
- No sludge generation.

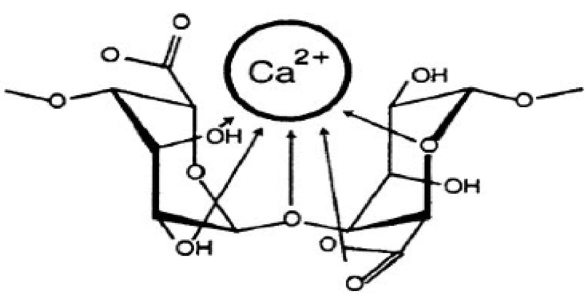
OUR ADSORBENTS

- Domestic waste found in the kitchen:
- Why? High content of functional organic groups such as alcohol (fiber and carbohydrates), carboxylic acids and amines (structural polysaccharides).
- Why? Easy preparation and massive collection.
- Widespread use of green tea as a hot/cold drink. Massive collection from green tea industries (i.e. Arizona and other bottled tea-based drinks).

ALGINATE BEADS

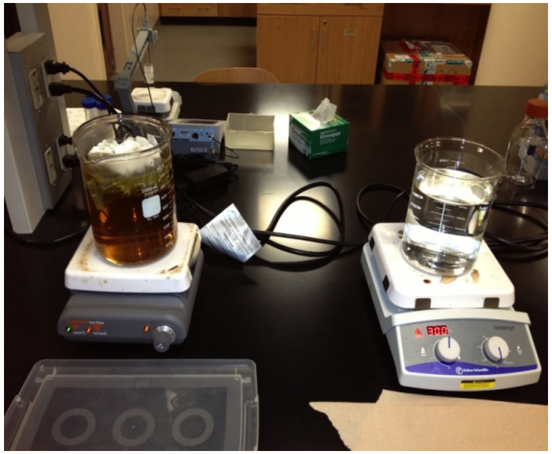
- Alginate and other polymers gelify in contact with divalent cations (Calcium ions).
- High porosity and stability.
- Encapsulating matrix

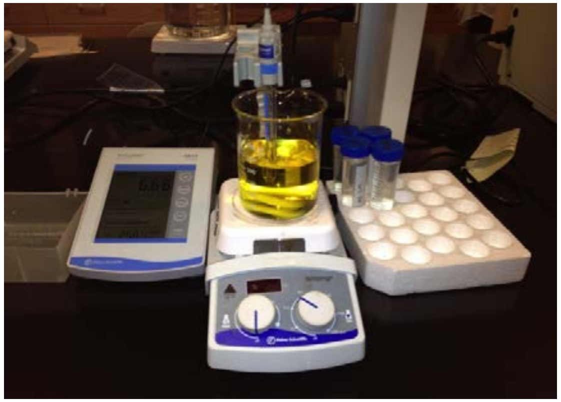




METHODOLOGY

- Teabags were boiled, dried, stored and used in adsorption experiments.
- Solutions of pollutants were prepared and taken to proper pH, mass of adsorbent, dye concentrations, salinity, and crowding.

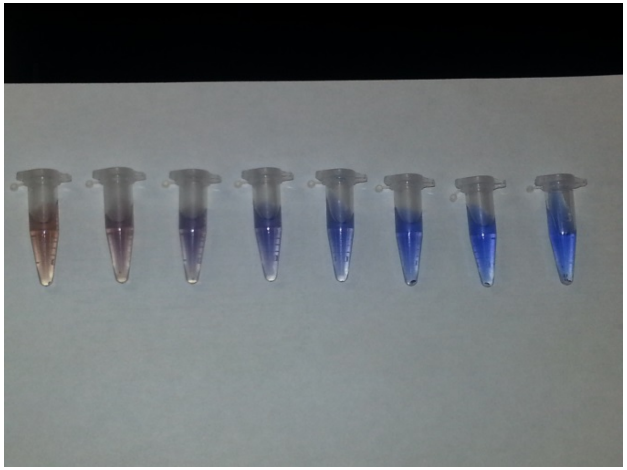


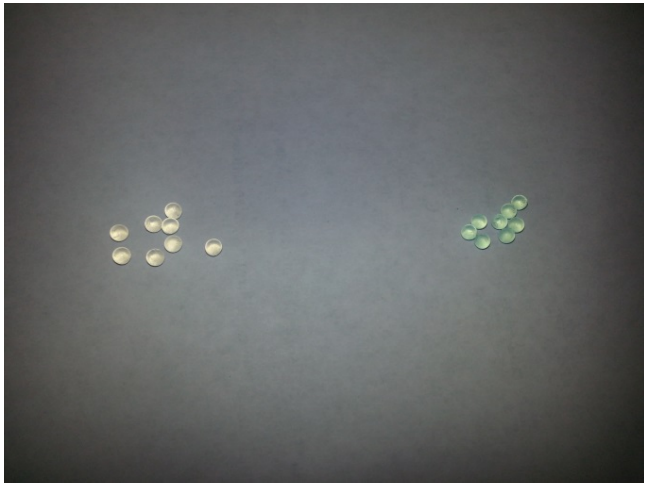


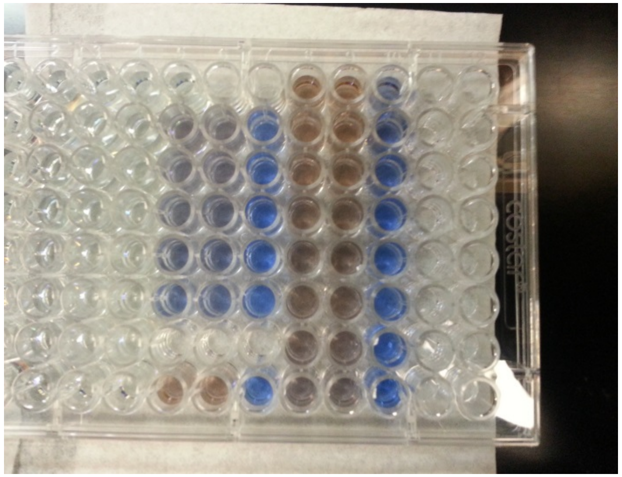
METHODOLOGY

- Duplicate experiments were carried out at room temperature and shaken during 24h.
- Metal concentrations were measure by the color of the complex with Zincon.
- Adsorbents were characterized using Thermogravimetric analysis (TGA), Scanning Electron Microscopy (SEM), Infrared Spectroscopy (FTIR), X-ray Energy Dispersion Spectroscopy (EDS). Surface and porosity were determined by colorimetric and redox experiments.

METHODOLOGY







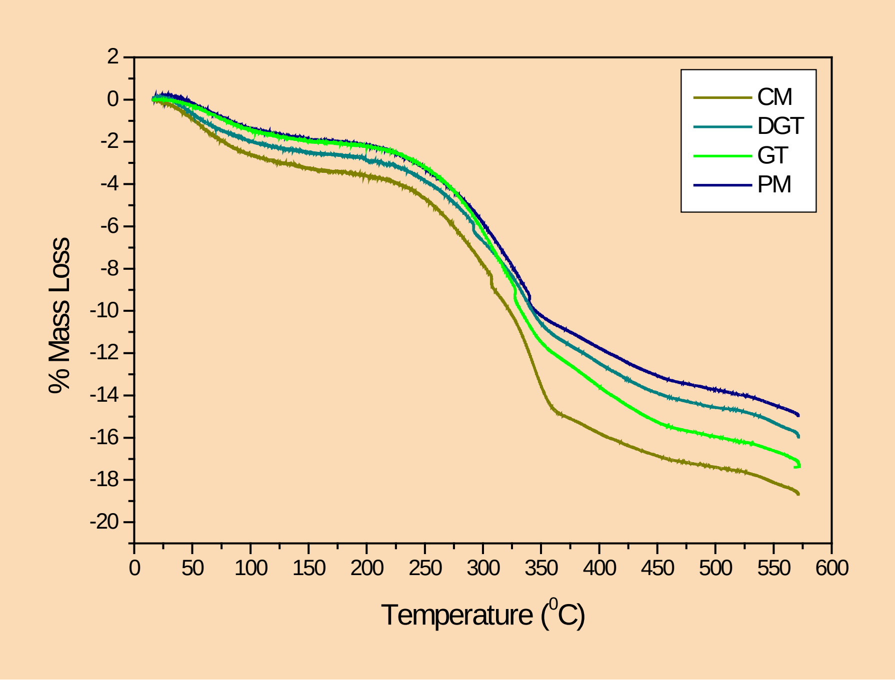
RESULTS

Characterization of the Adsorbents

TGA: Temperature resistance and presence of volatile compounds

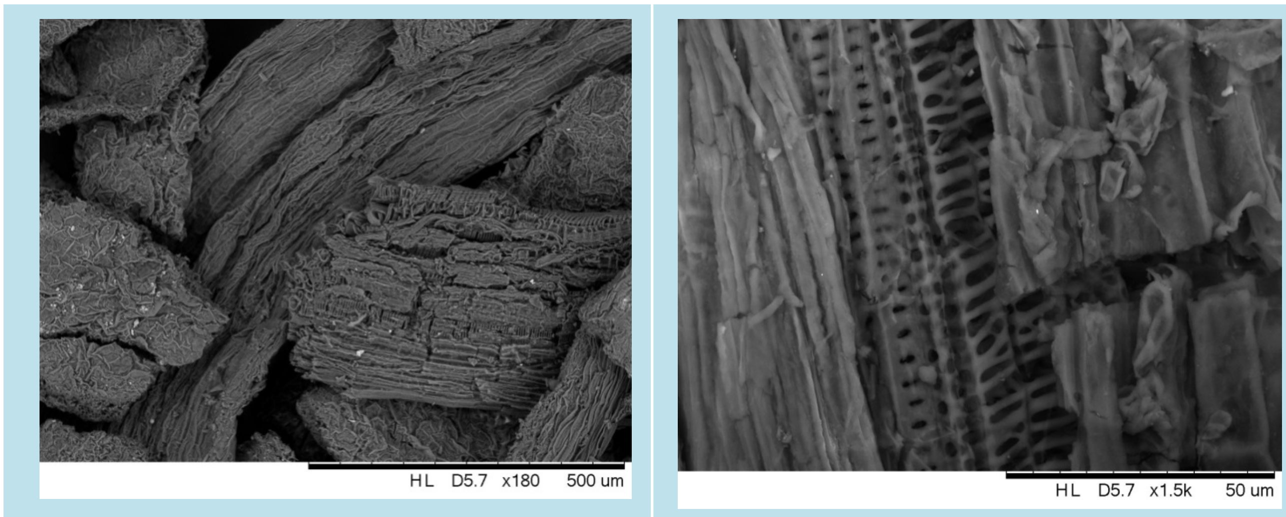
Surface Area and Porosity: Compared to Activated carbon (SA+ 1000 – 2500 cm²/g

ADSORBENT	Surface Area (m^2/g)	Micropore Volume (cm^3/g)	Total Pore Volume (cm^3/g)
AB	228	0.056	0.137
CM	1063	0.397	0.578
CT	231	0.149	0.529
DGT	274	0.219	0.592
GT	2736	0.692	1.106
PGT	221	0.058	0.411
PM	946	0.892	0.961

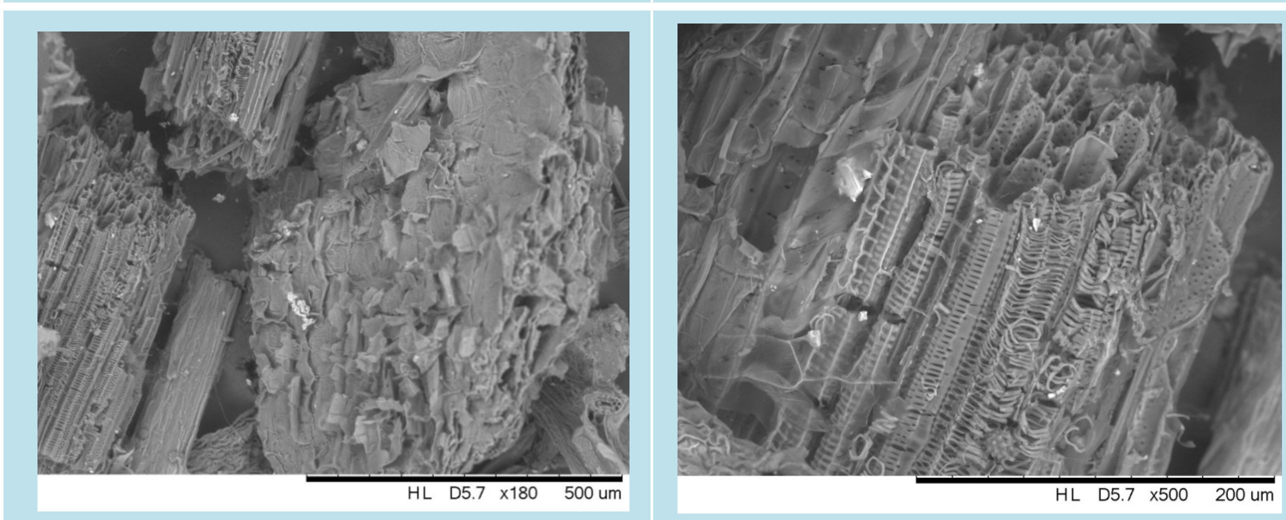


RESULTS

PM



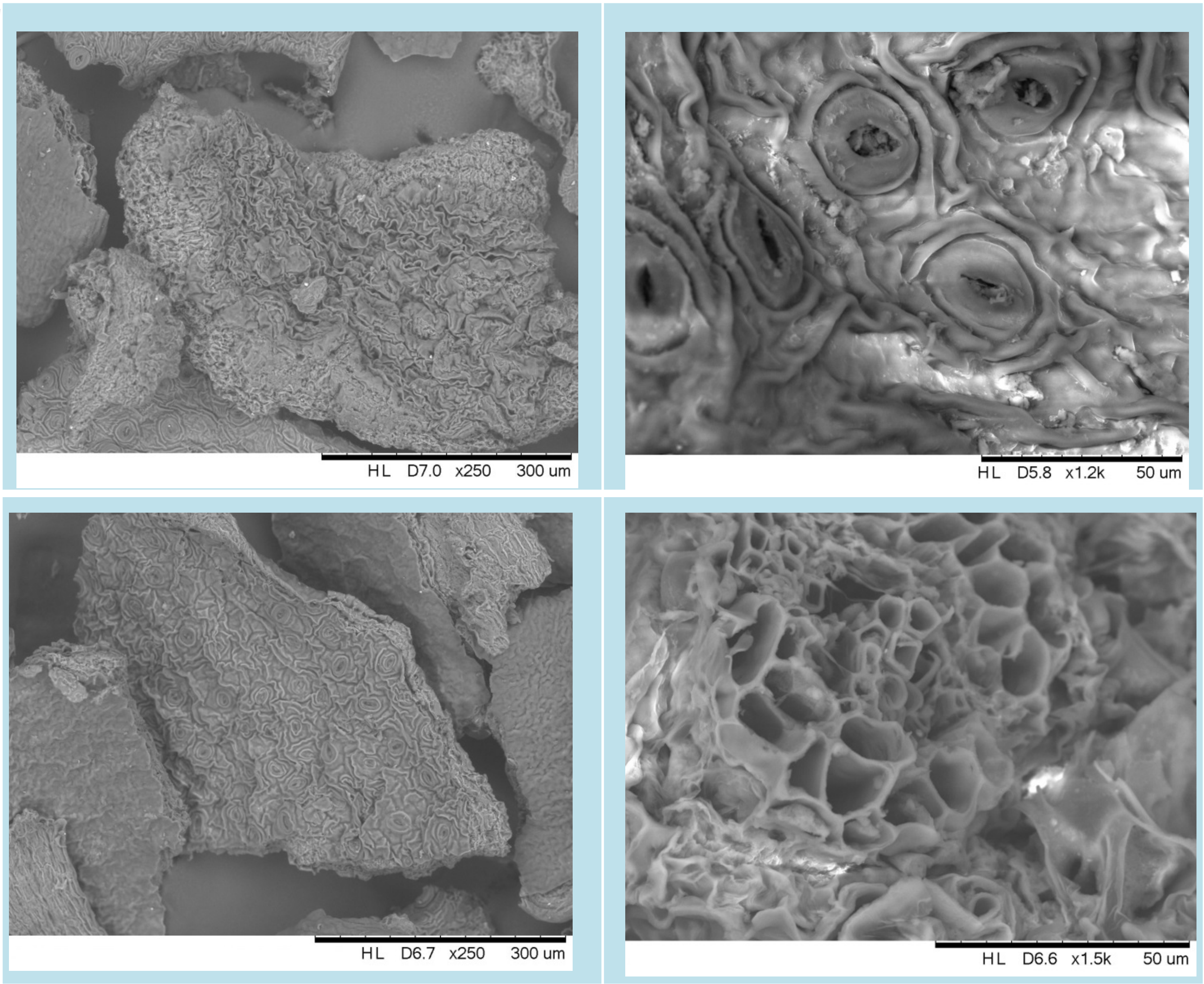
CM



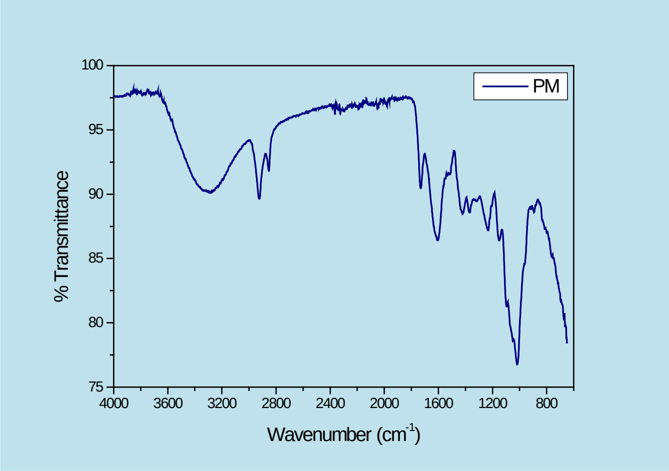
RESULTS

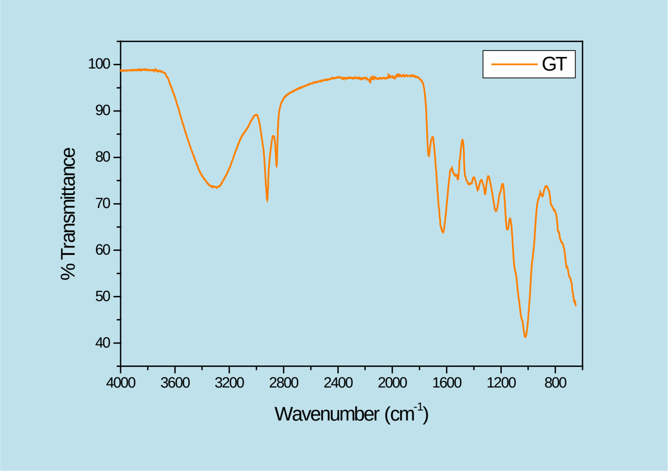
GT

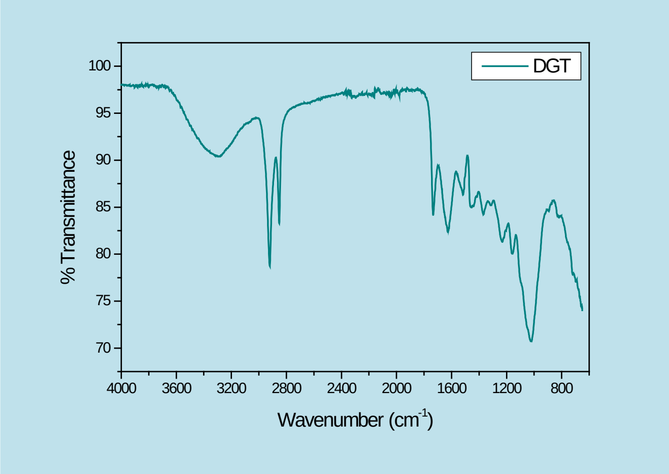
DGT

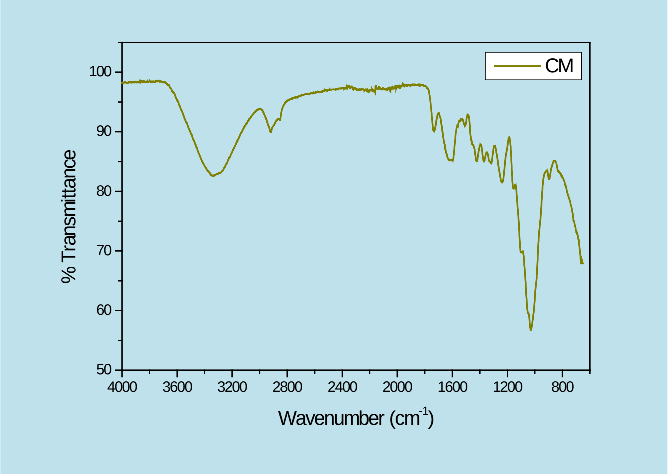


RESULTS

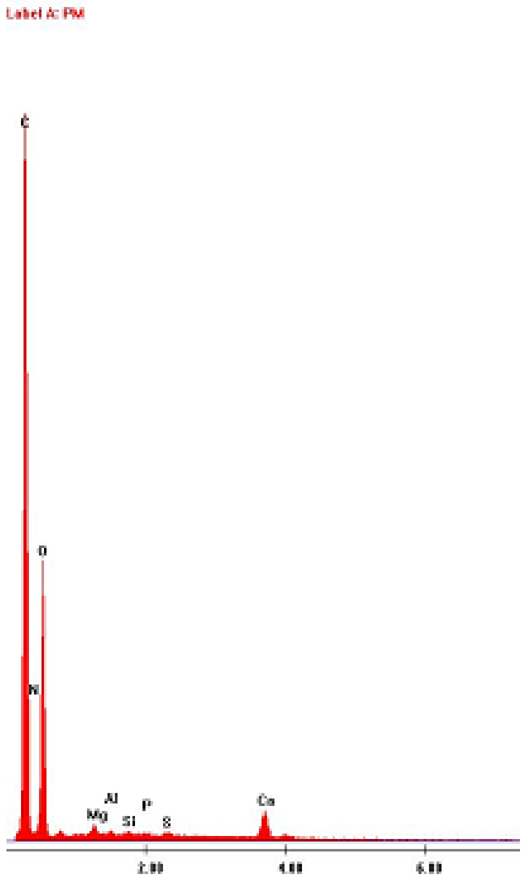

PM
% Transmittance
100
95
90
85
80
75
4000 3600 3200 2800 2400 2000 1600 1200 800
Wavenumber (cm-1)


GT
% Transmittance
100
90
80
70
60
50
40
4000 3600 3200 2800 2400 2000 1600 1200 800
Wavenumber (cm-1)

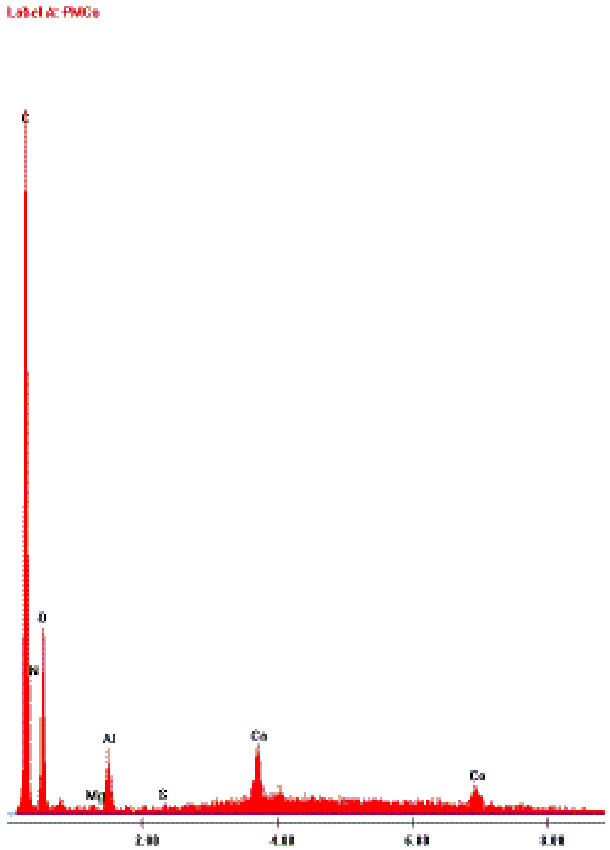

DGT
% Transmittance
100
95
90
85
80
75
70
4000 3600 3200 2800 2400 2000 1600 1200 800
Wavenumber (cm-1)


CM
% Transmittance
100
90
80
70
60
50
4000 3600 3200 2800 2400 2000 1600 1200 800
Wavenumber (cm-1)

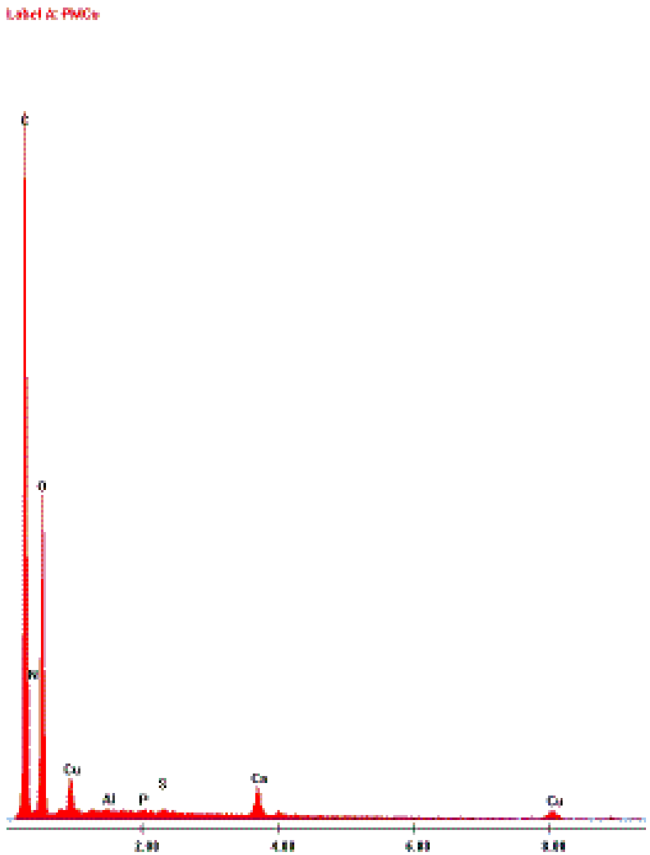
X-RAY EDS – ADSORPTION



PM



PM + Co

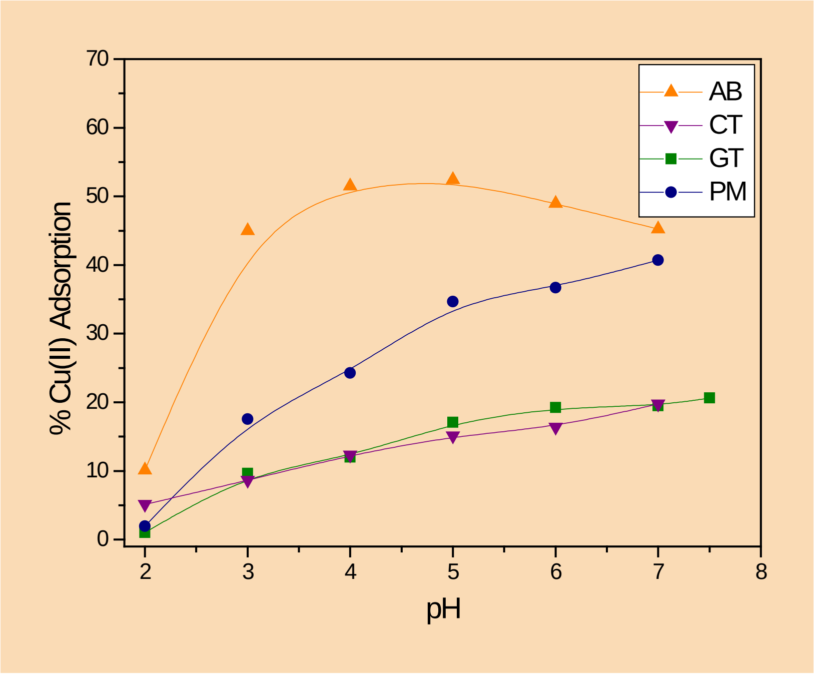


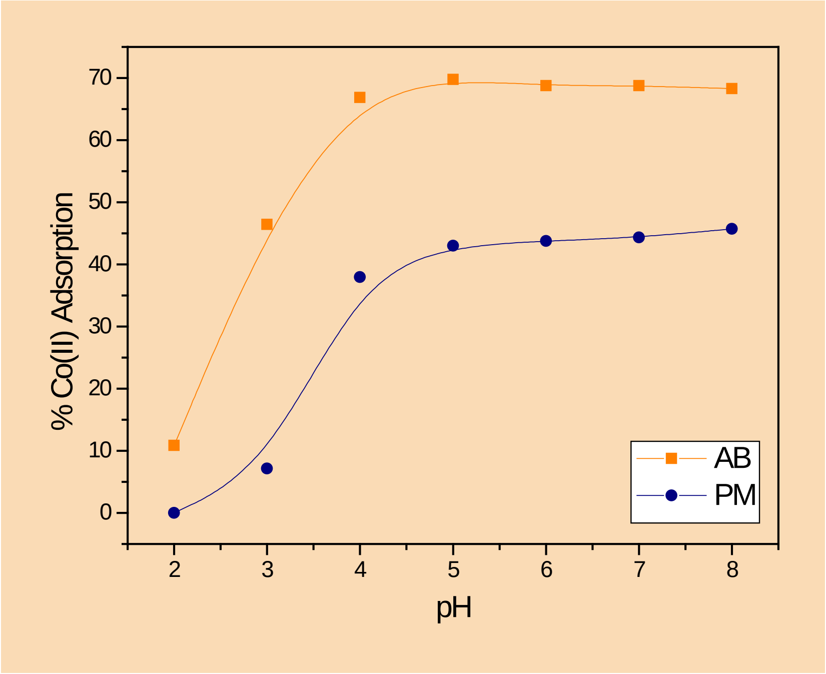
PM + Cu

RESULTS

pH Effect

- Ionization of adsorbent's surface and metals (aquo- and hydroxo-complexes.
- Higher pH promotes higher adsorption.

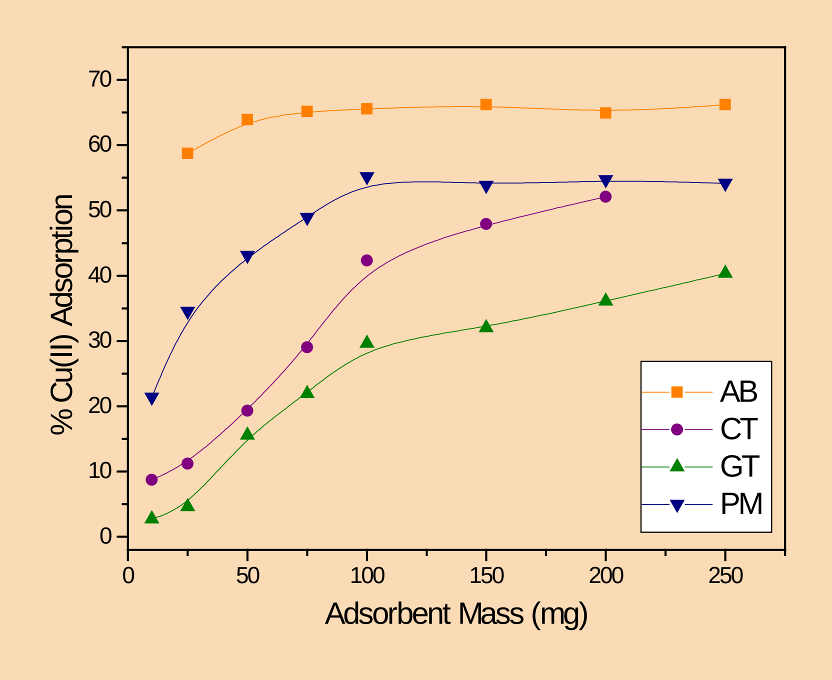




RESULTS

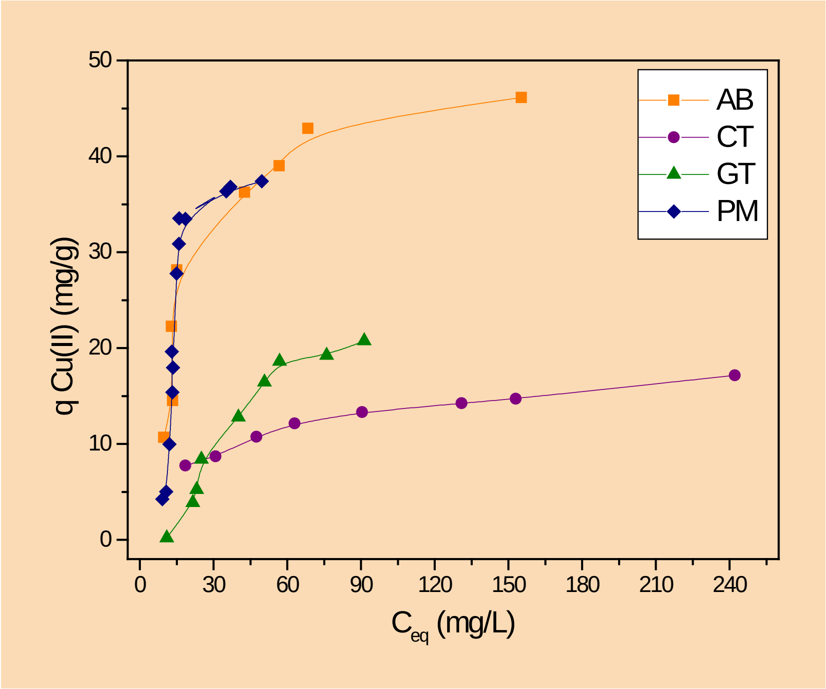
Mass Effect

- Minimize amount of adsorbent.
- Higher adsorption promotes formation of aggregates.



RESULTS

- Isotherms were modeled by Langmuir, Freundlich, Dubinin-Radushkevich and Temkin theories.



RESULTS

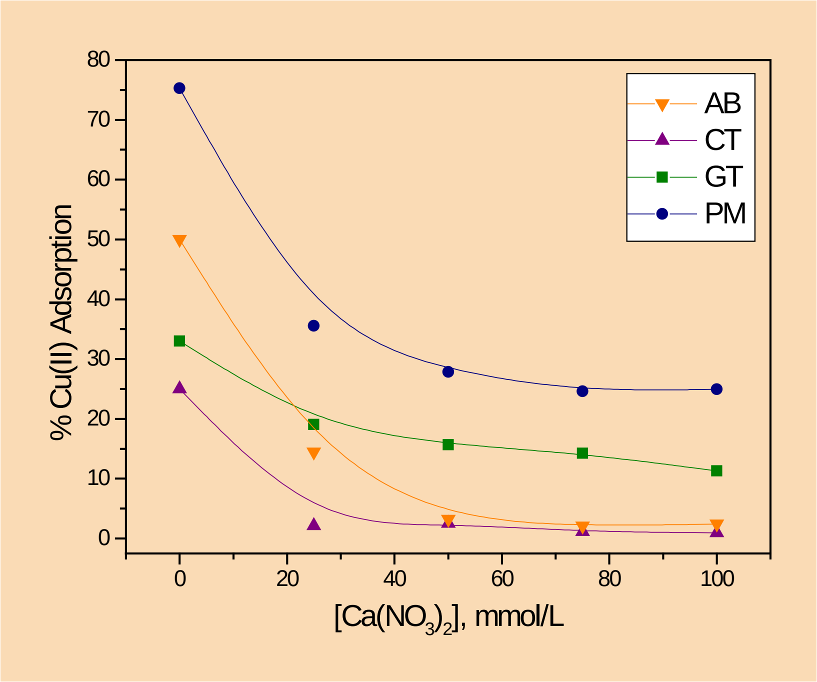
Isotherm Theory	Equation
Langmuir	$q = \frac{q_{max} \text{ x } b \text{ x } C_{eq}}{1 + b \text{ x } C_{eq}}$
Freundlich	$q = k_F \text{ x } C_{eq}^{1/n}$
Dubinin-Radushkevich	$q_{e=} q_{DR} \text{ x } \exp\ (-K_{DR} \text{ x } \varepsilon^2)$
Temkin	$q_e = \frac{RT}{b_t} \ln\ (a_t \text{ x } C_{eq})$

Adsorption Isotherm	Parameters	AB	CT
Langmuir	q_{max} (mg/g)	79.87	16.28
	b (L/mg)	0.0162	0.045
	p-value	< 0.0001	< 0.0001
	R^2	0.984	0.930
Freundlich	k_F (L/g)	2.045	3.142
	n	1.349	3.199
	p-value	0.00062	< 0.0001
	R^2	0.959	0.982
Dubinin-Radushkevich	q_{DR} (mg/g)	46.84	14.59
	B x 10^{-4} ($mol^2.J^2$)	0.235	0.892
	E (J/mol)	146	75
	p-value	< 0.0001	0.00186
	R^2	0.969	0.823
Temkin	a_T	0.291	0.406
	b_T x 10^{-4} (J/mol)	0.312	1.104
	p-value	0.00055	< 0.0001
	R^2	0.924	0.987

RESULTS

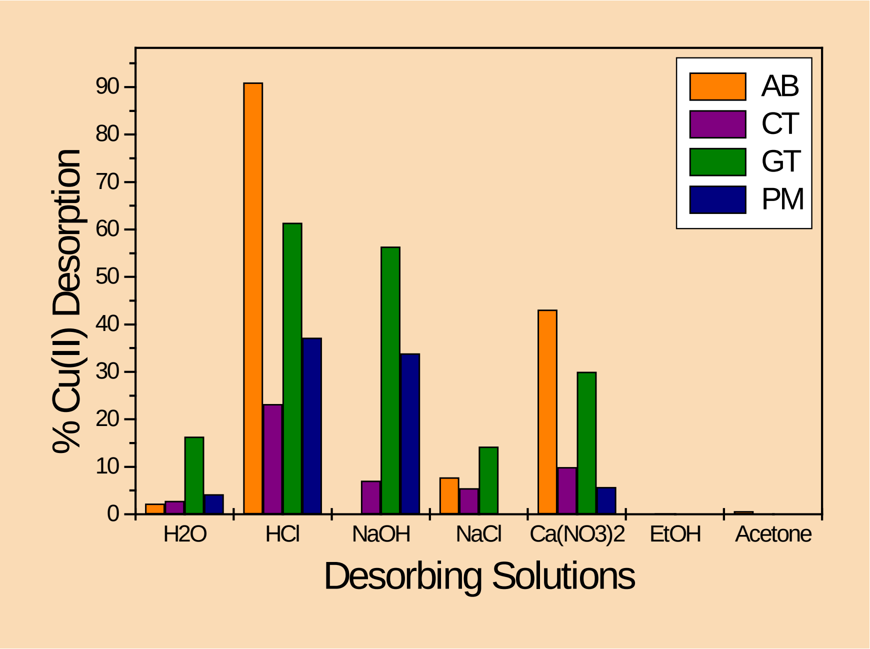
Salinity Effect:

- Decreases adsorption due to competition for the adsorption sites.
- Higher the charge, the stronger the effect.

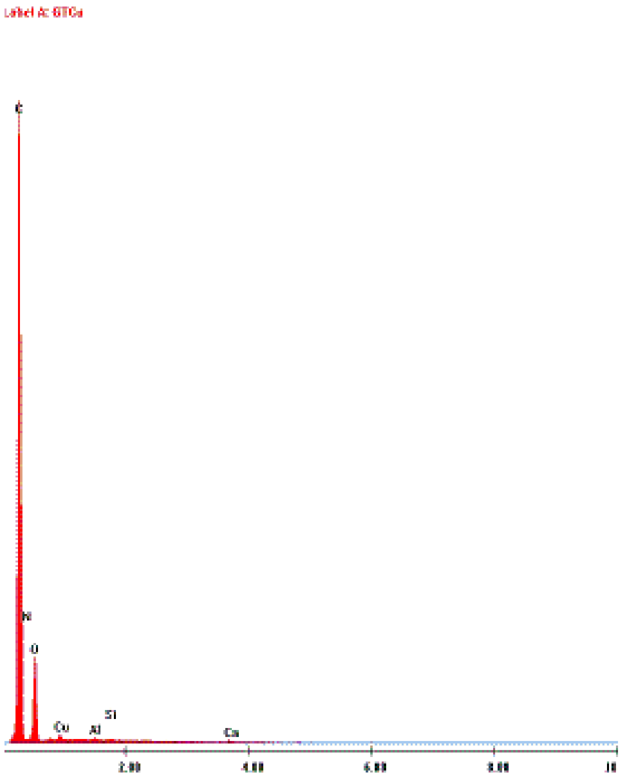


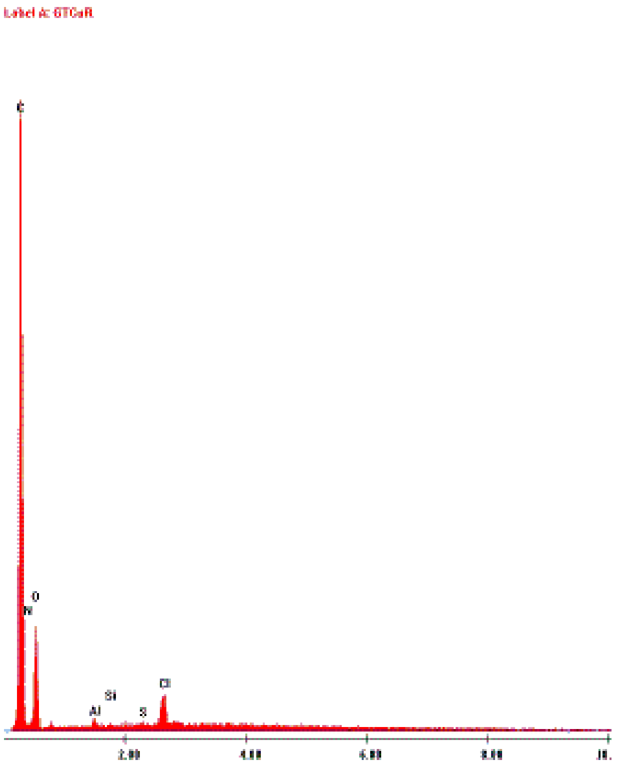
RESULTS

- Mild acidic conditions were enough to desorb both dyes.
- Competition of hydronium for active sites.
- Water has weak desorbing properties.



X-RAY EDS – DESORPTION (HCl treatment)





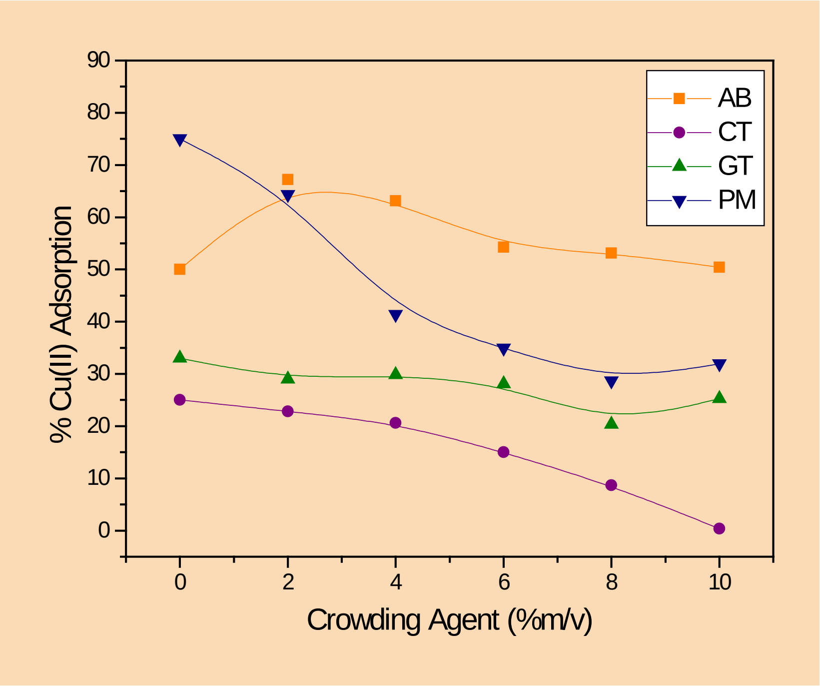
GT

GT + Cu

GT – 5 cycles

RESULTS

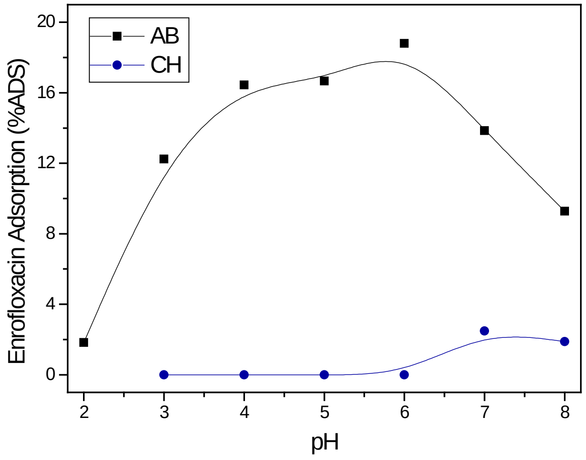
- Challenge in Remediation: Real Conditions.
- Crowding Agent: Ficoll, Polyethylene glycol.
- Steric Hindrance, access to active sites

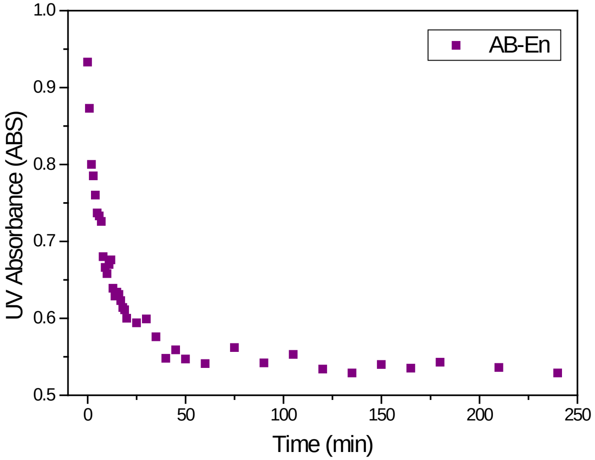


FUTURE WORK

- Mixtures of metals: Cu + Zn
- Explore other more toxic metals, proteins, PAHs, **emerging pollutants**.
- **Column studies**
- **Chemical modification of adsorbents**
- Characterization: Elemental Analysis, Potentiometric Titration, BET, AFM.

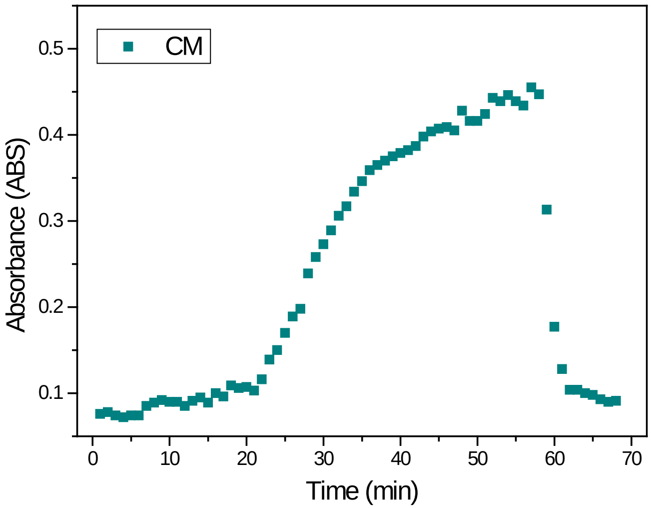
NEW DIRECTIONS





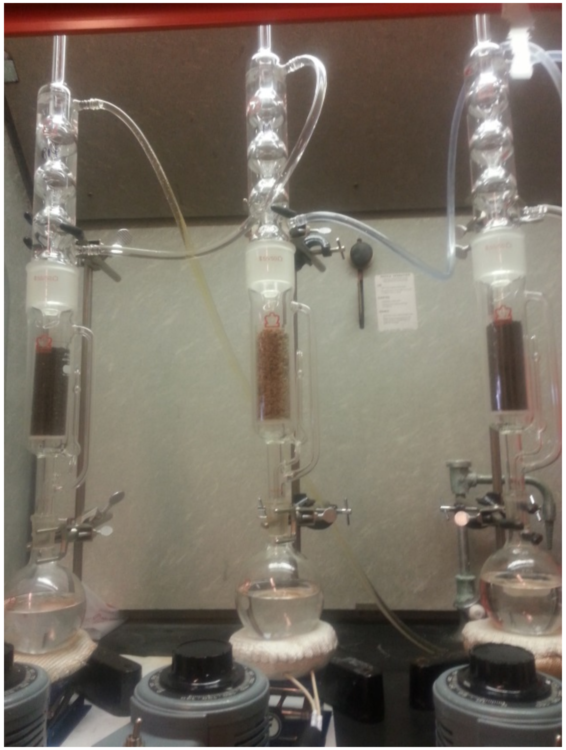
Emerging Pollutants – Antibiotic Enrofloxacin

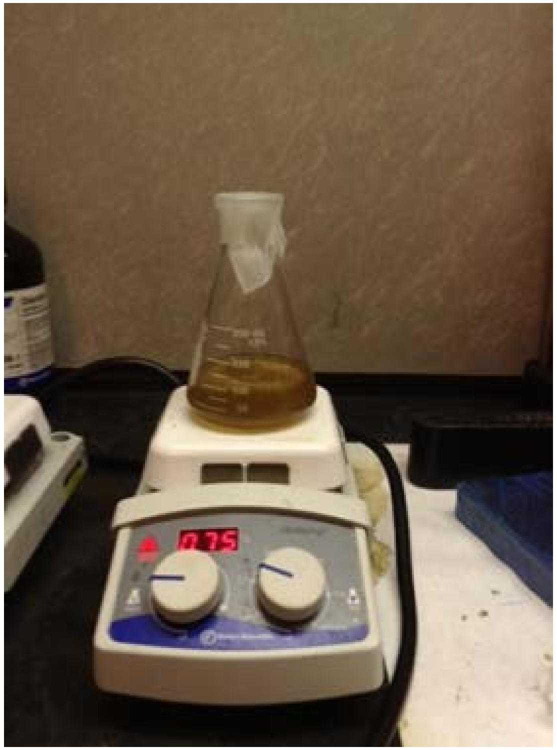
pH effect and kinetics



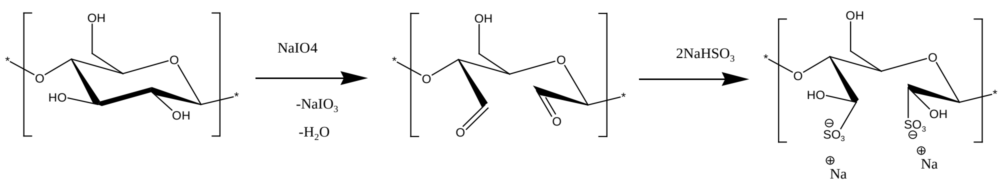
Continuous-flow experiment: Chamomile as an adsorbent of Cu(II) ions. Conditions: 1.8g of CM, flow 7mL/min, pH 6, 100ppm Cu(II).

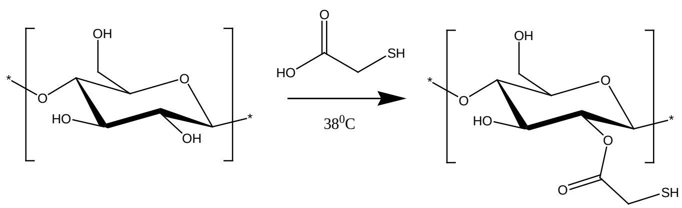
NEW DIRECTIONS





NEW DIRECTIONS

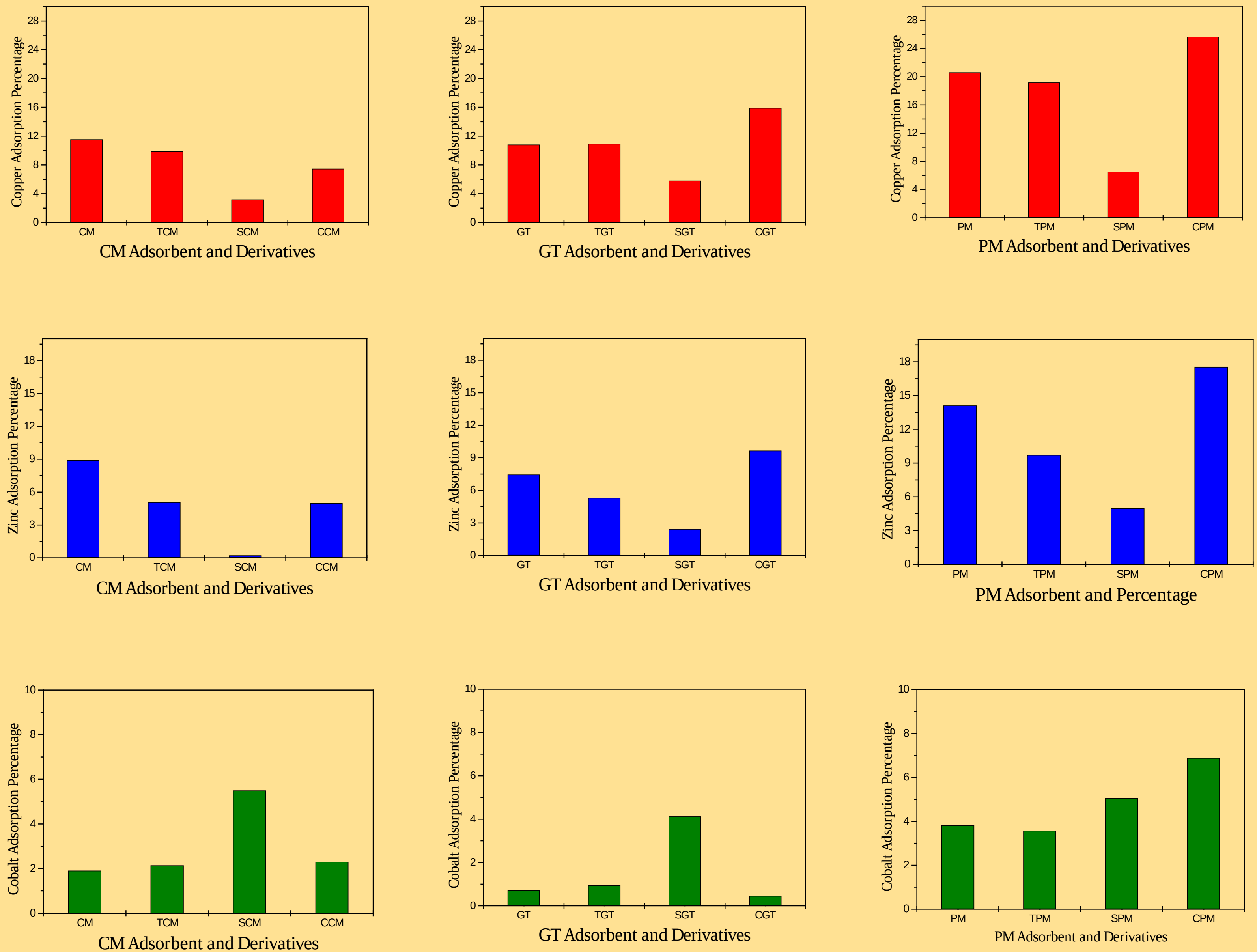




Enhance adsorption affinity by the incorporation of more reactive functional groups: Carboxyl, thiol, sulfonic

ADSORBENT	C_{COOH} (mmol/g)	ADSORBENT	C_{COOH} (mmol/g)	ADSORBENT	C_{COOH} (mmol/g)
CM	1.36	GT	1.72	PM	1.4
TCM	1.48	TGT	1.88	TPM	2
SCM	1.76	SGT	1.92	SPM	1.48
CCM	1.08	CGT	1.72	CPM	1.36

Table: Acidic Group content (mmol/g) of all the adsorbents



Adsorption of heavy metals onto raw and modified adsorbents: Copper (red), Zinc (blue), and Cobalt (green) at pH 6, using 50mg of adsorbent in a 100 ppm metal solution.

CONCLUSIONS

- Tealeaves have proven to be promising adsorbents for model metals and other pollutants. They also serve as scaffold for chemical modifications.

- Characterization studies report advantages of tealeaves and alginate beads as an alternative adsorbent.

- pH has a strong effect on the adsorption. Likewise, salinity and crowding effects have a negative impact.

- Carboxylation and sulfonation improve the adsorption of metals.

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- Diaz, C., Jacinto, C., Medina, R., **Navarro, AE., Cuizano, N., Llanos, B. Study of the biosorption of chromium (VI) on cross linked quaternary chitosan for their application on the bioremediation of wastewaters. *Rev. Soc. Quím. Perú, 2013, 79(4): 304-318.***

Acknowledgements

Group Members:

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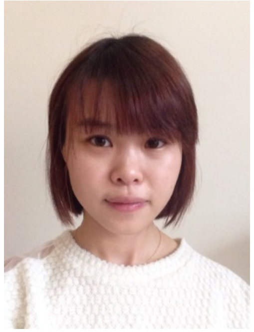

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