



Laboratório de Materiais Poliméricos e Biossorventes

SORPTION OF Cu(II), Fe(II), Zn(II), AND Mn(II) FROM AQUEOUS MEDIUM USING LETTUCE ROOTS AND SUGARCANE BAGASSE



5th International Conference
on
Sustainable Solid Waste
Management

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Toxic metals are cumulative, not naturally degraded, either biologically or chemically, and require special treatment as they are harmful to living organisms.





Bioremediation and Bioeconomy

M.N.V. Prasad



A VERY IMPORTANT FIELD



Bioremediation and Bioeconomy

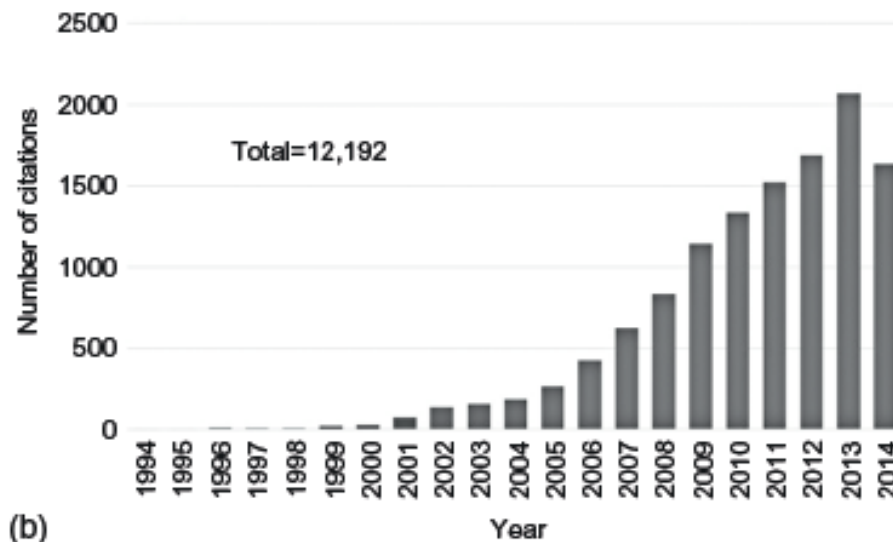
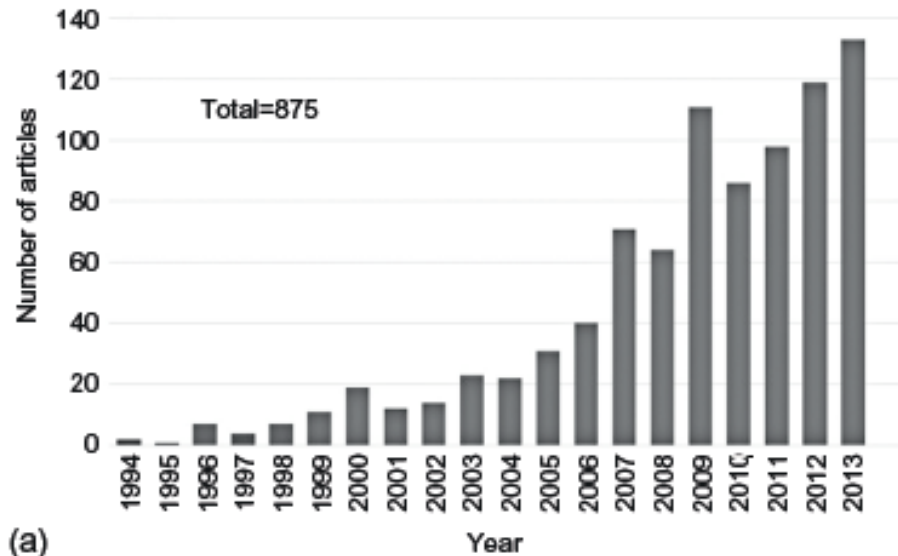
2016, Pages 569–588



Chapter 22 – Bioremediation in Brazil: Scope and Challenges
to Boost Up the Bioeconomy

G. Labuto¹, E.N.V.M. Carrilho²

RESEARCH ON THE USE OF BIOMASS



Bioremediation and Bioeconomy

2016, Pages 569–588



Chapter 22 – Bioremediation in Brazil: Scope and Challenges to Boost Up the Bioeconomy

G. Labuto¹, E.N.V.M. Carrilho²

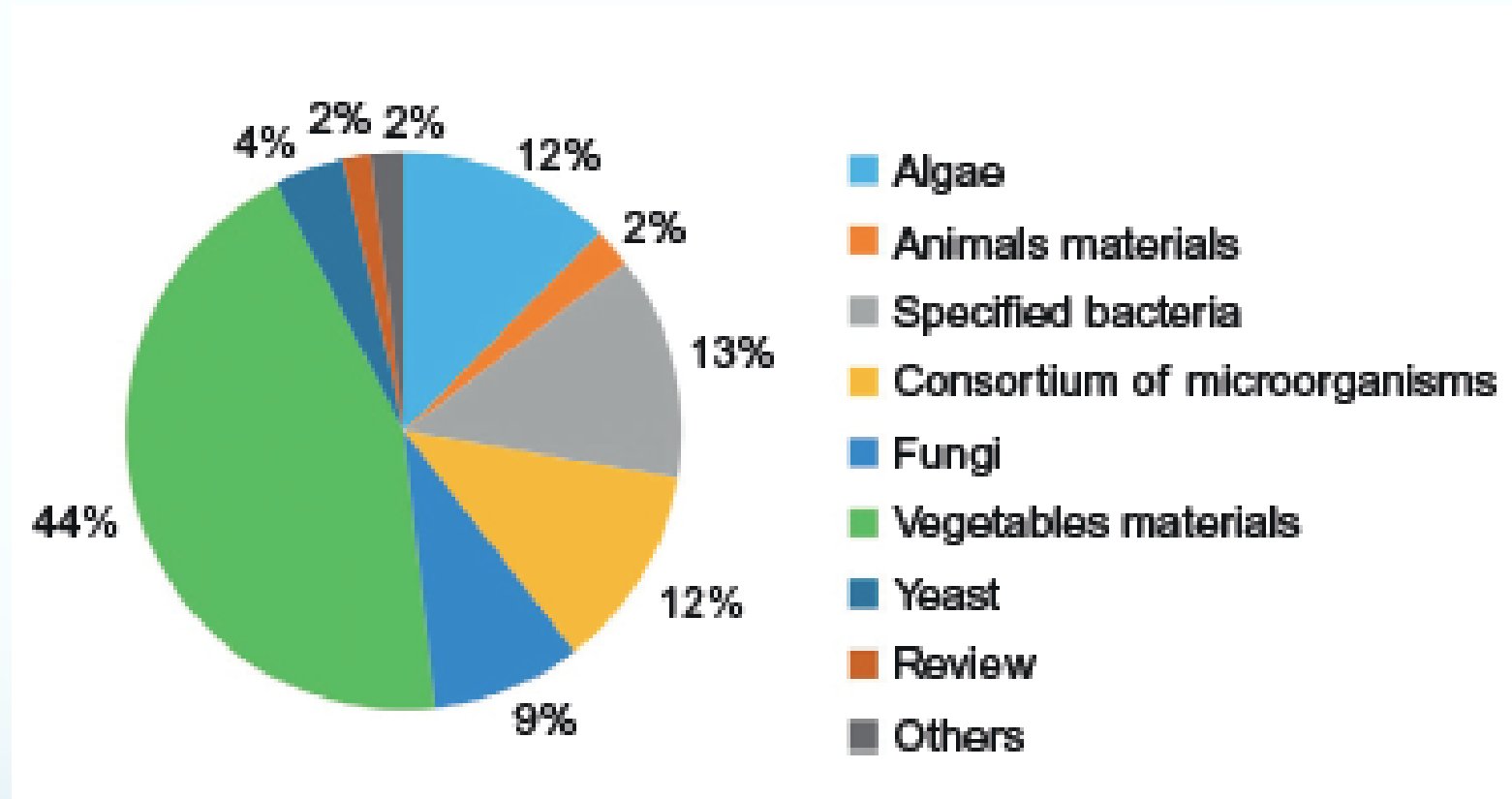
(a) Number of articles published by Brazilian scientists;

(a) Number of citations on articles published by Brazilians over the last 20 years.

Keywords searched: Brazil, biosorption, phytoremediation, and bioremediation.

Source: Web of Science and Scopus websites in 11/30/2014.

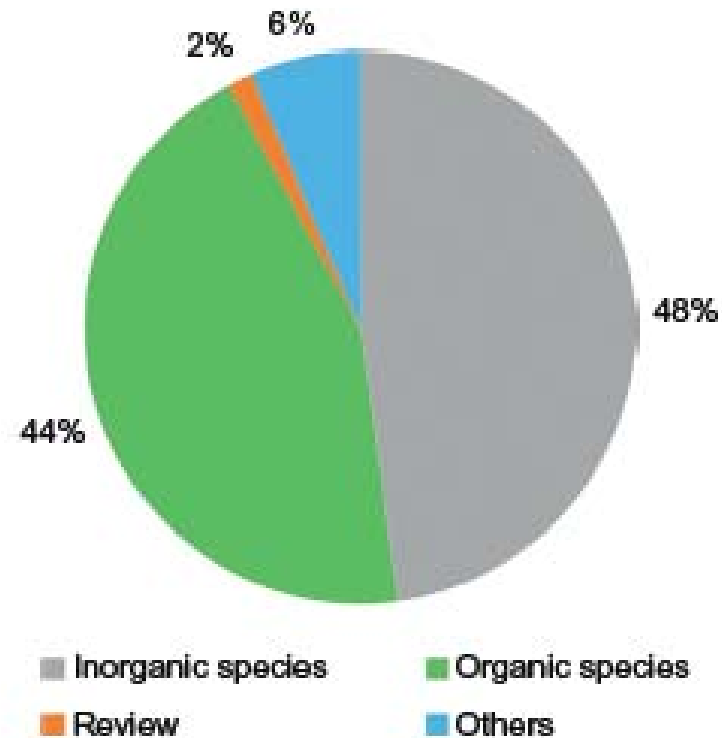
Biomasses used as biosorbents in articles published by Brazilians between 1994 and 2014



Keywords searched: phytoremediation, bioremediation, and biosorption.

Source: Web of Science and Scopus websites in 11/30/2014.

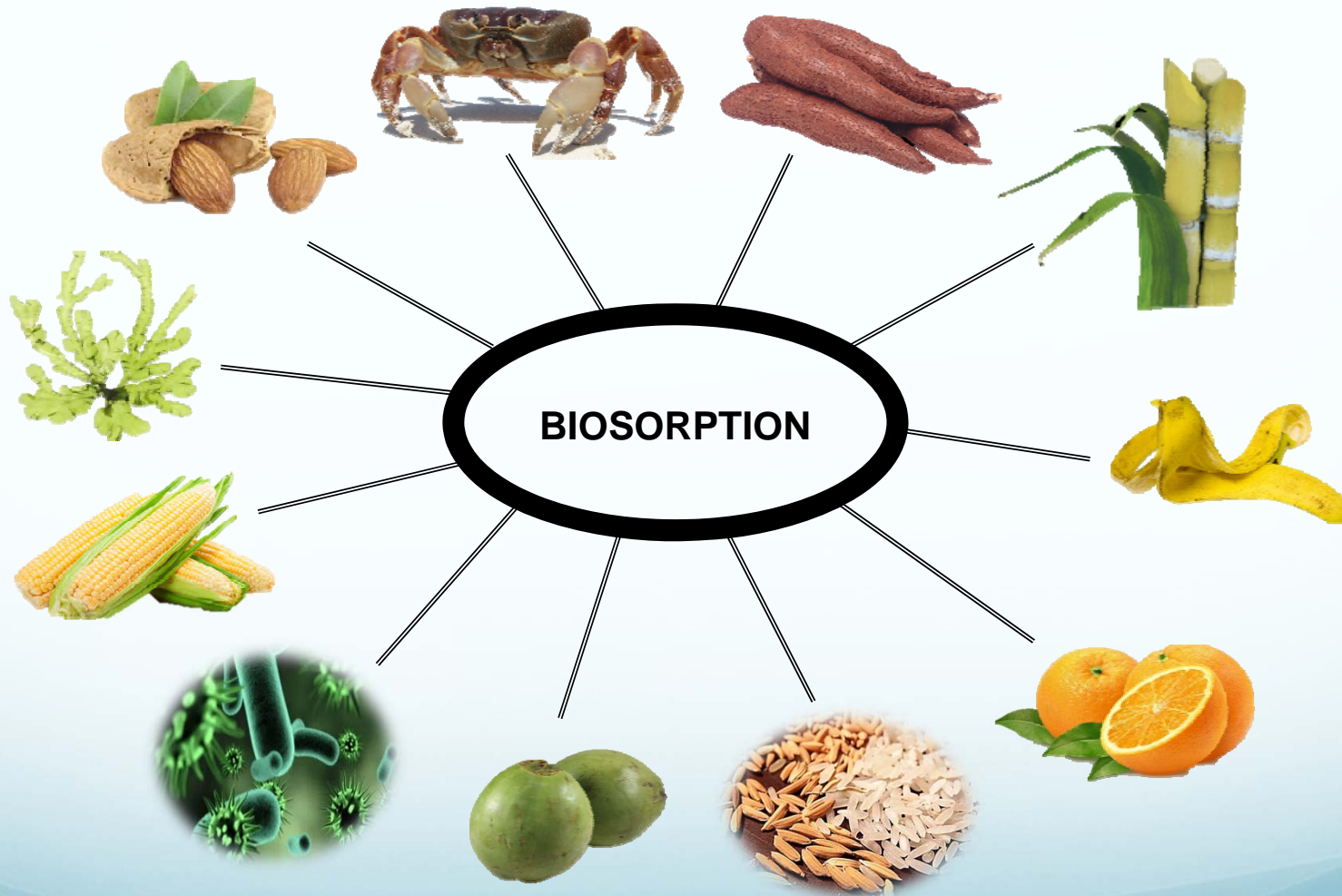
Contaminants or analytes of interest in biosorption studies published by Brazilians between 1994 and 2014



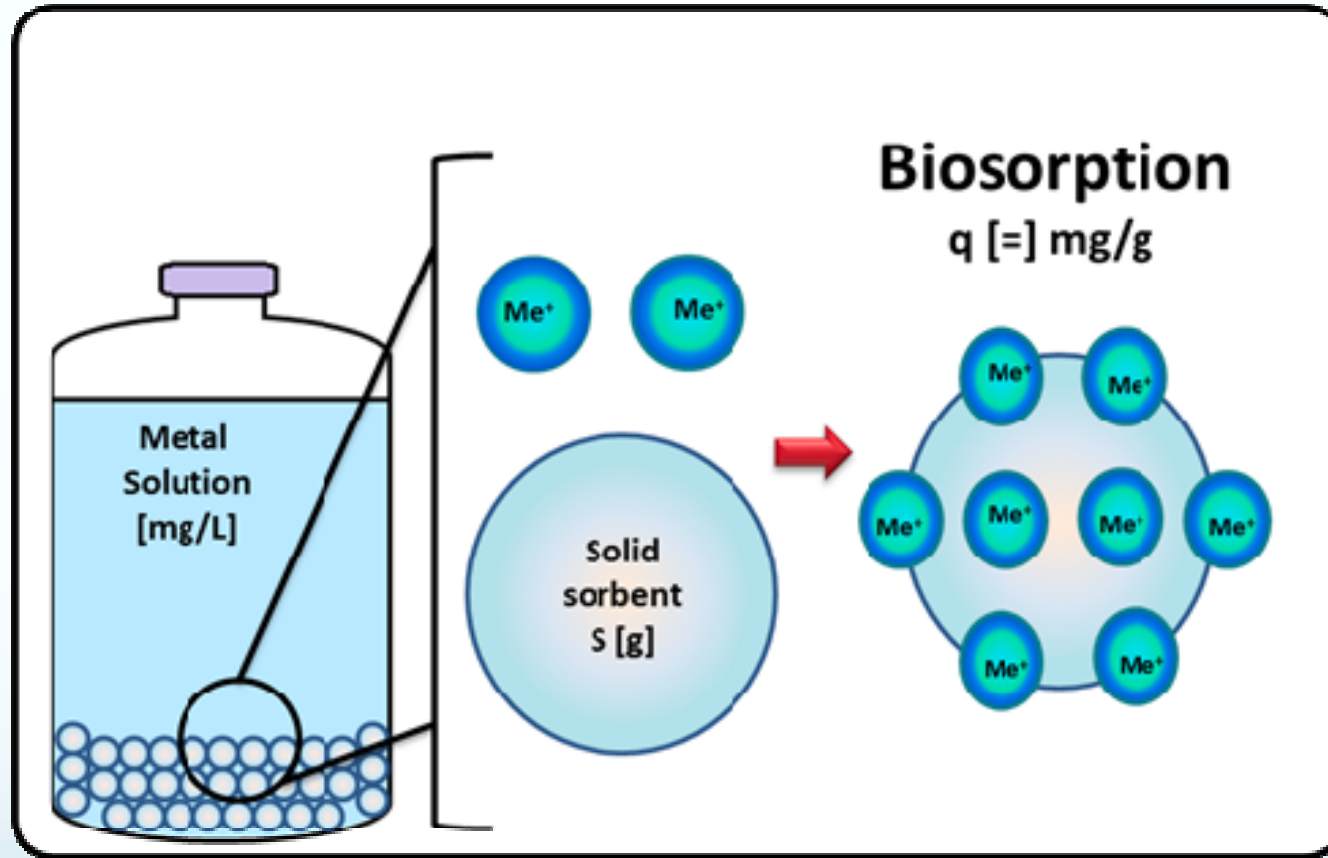
keywords: phytoremediation, bioremediation, and biosorption.

Source: Web of Science and Scopus websites in 11/30/2014.

CHOICES OF BIOSORBENTS



METAL BIOSORPTION MECHANISM



Efficient option to remove metals from aqueous medium.

LETTUCE



1.27 million tons/year in 2012/13

SUGARCANE



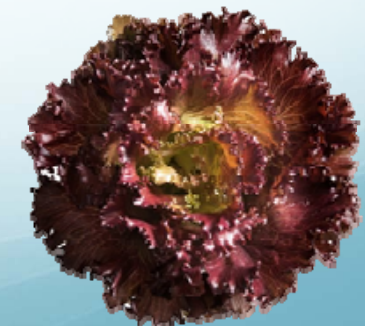
685 millions of tons 2016/17

Assessment of biomasses in the sorption of Cu(II), Fe(II), Mn(II) and Zn(II) from multielement solution and lake water.

THE UNIVERSITY FARM – SUGARCANE CROP



THE UNIVERSITY FARM – HYDROPONIC LETTUCE



BIOMASSES USED



Sugarcane Bagasse



Lettuce Roots

**Cleaning with
purified H₂O**

Drying at 50 °C

**Ground to 0.5 mm
to 1 mm**

1.5 g of biomass

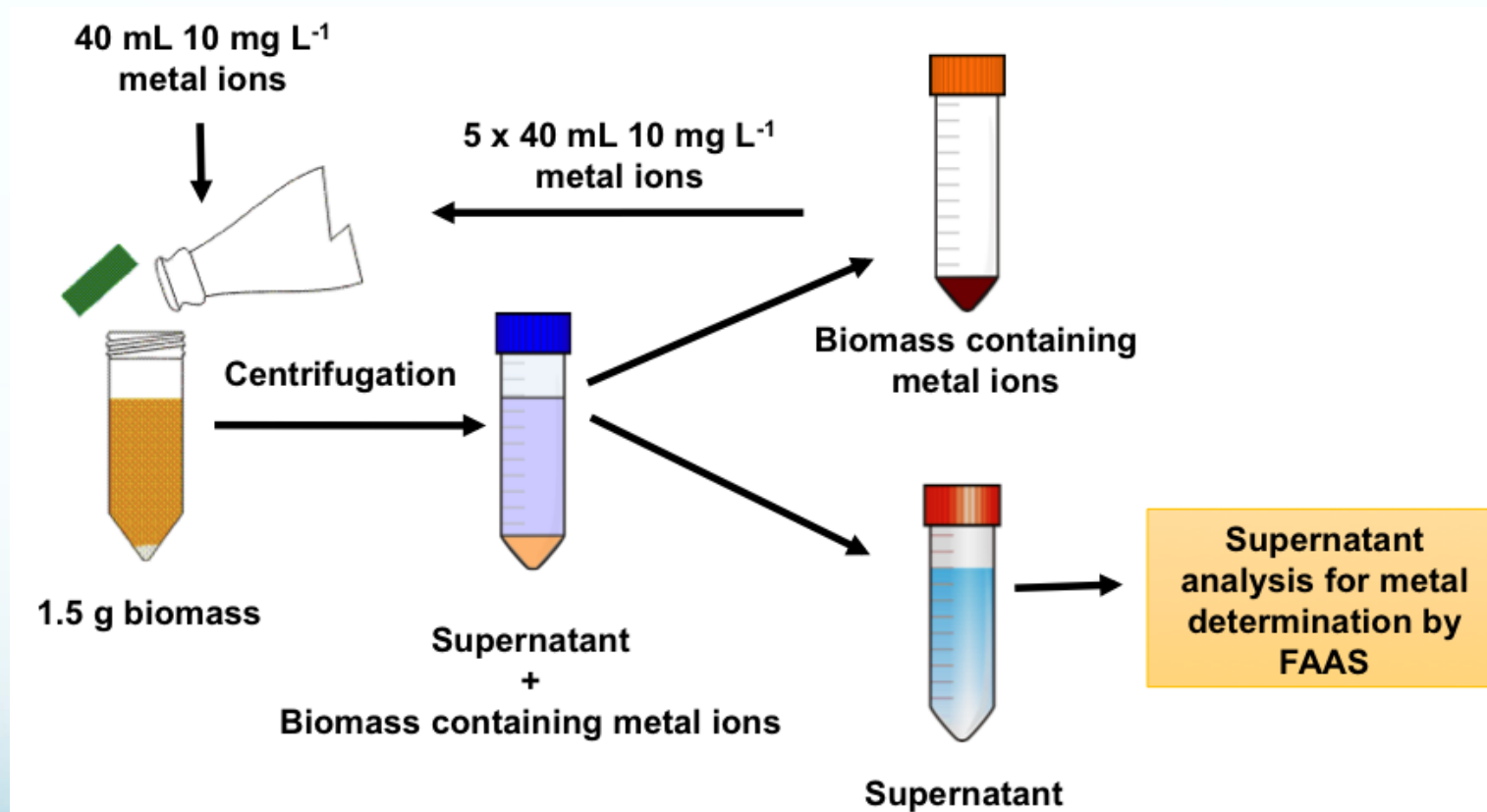
**Leaching with HNO₃
1 mol/L**

**Conditioned with solution
KCH₃COO/CH₃COOH 0.005
mol/L at pH 5.5**

BIOMASS LEACHING WITH HNO₃

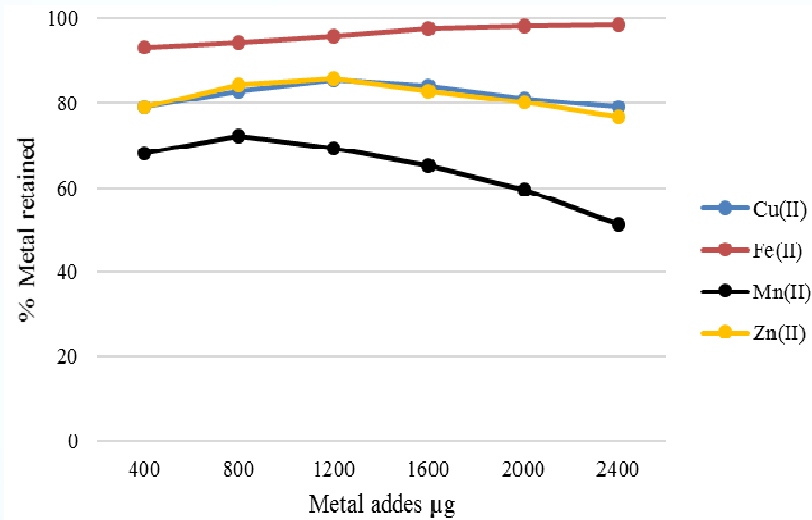
Element	Elements Contents of the Biomasses (mg/g ± SD)			
	NRL	MRL	NSB	MSB
Na	0.45 ± 0.02	0.04 ± 0.01	0.06 ± 0.01	0.04 ± 0.00
Ca	19.99 ± 0.83	0.03 ± 0.01	0.21 ± 0.04	0.002 ± 0.001
Mg	1.91 ± 0.04	0.16 ± 0.00	0.12 ± 0.01	0.004 ± 0.002
P	3.52 ± 0.13	0.81 ± 0.02	0.06 ± 0.01	0.05 ± 0.002
K	0.23 ± 0.01	0.006 ± 0.001	0.04 ± 0.01	0.003 ± 0.001
S	6.58 ± 0.11	5.94 ± 0.22	0.64 ± 0.14	0.58 ± 0.04
Cu	25.68 ± 0.74	0.97 ± 0.02	0.76 ± 0.08	0.15 ± 0.04
Fe	106.74 ± 1.20	115.92 ± 2.44	130.89 ± 3.47	105.53 ± 0.71
Mn	99.94 ± 0.58	0.003 ± 0.001	6.69 ± 0.25	0.05 ± 0.01
Zn	396.15 ± 4.37	3.06 ± 0.49	8.71 ± 0.97	1.56 ± 0.12

SORPTION BATCH PROCEDURE OF Cu(II), Fe(II), Zn(II), AND Mn(II) BY *in natura* AND MODIFIED BIOMASS

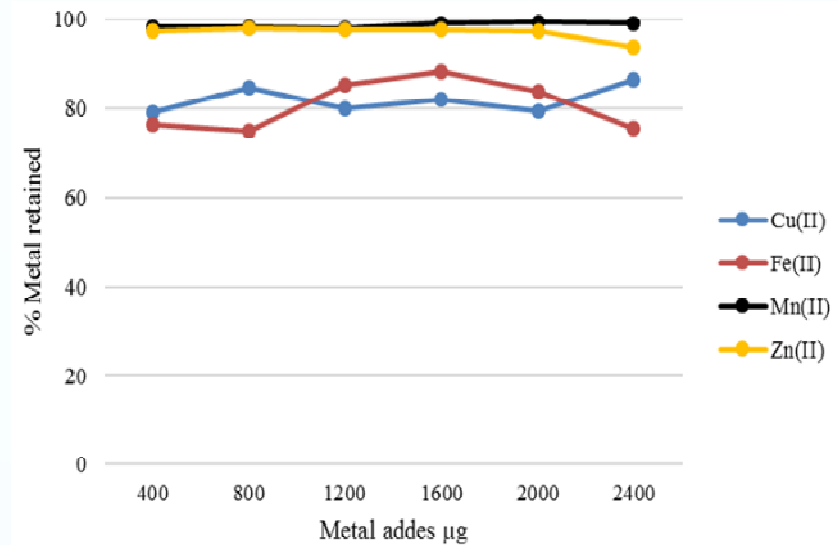


EFFECT OF BIOMASS MODIFICATION

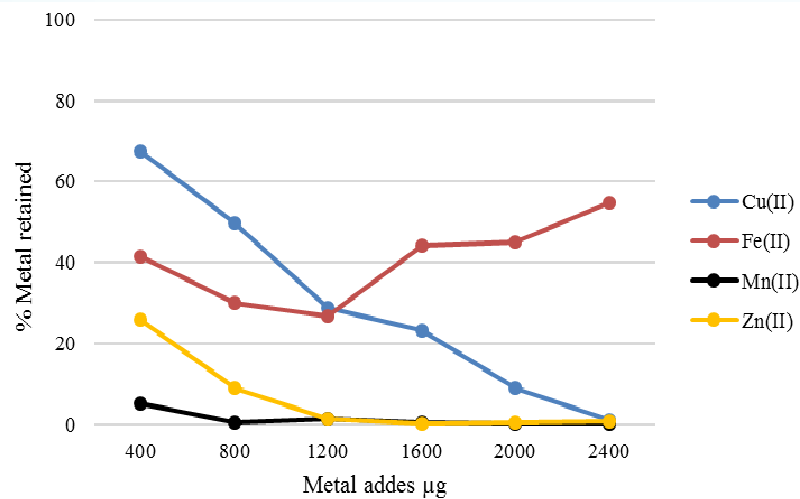
in natura lettuce roots



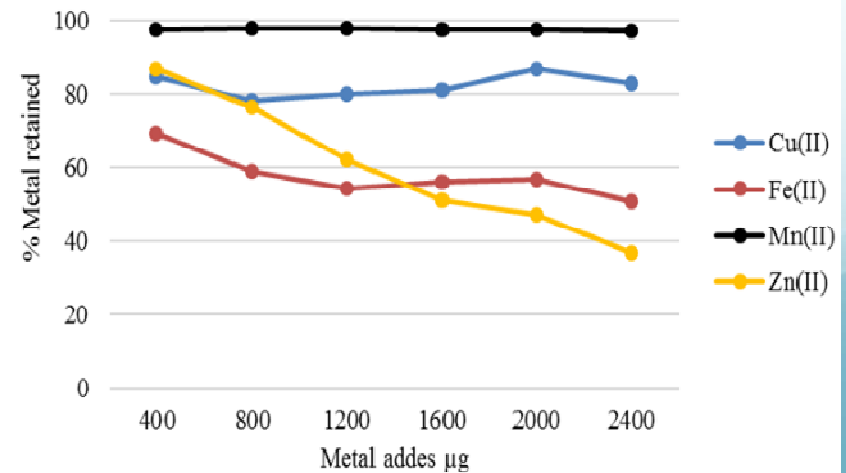
modified lettuce roots



in natura sugarcane bagasse



modified sugarcane bagasse



Error analysis and competitive Langmuir calculated sorption isotherm for Cu(II), Fe(II), Zn(II), and Mn(II)

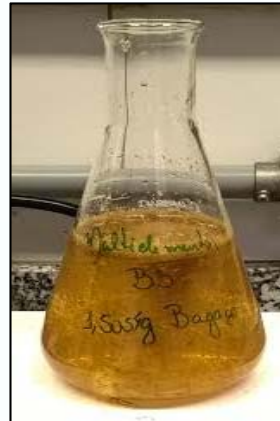
Parameters	NSB				MSB			
	Cu(II)	Fe(II)	Mn(II)	Zn(II)	Cu(II)	Fe(II)	Mn(II)	Zn(II)
$q_{\max}(\text{mg/g})$	0.92	3.94	0.03	0.18	54.11	6.52	16.7	1.26
b (L/mg)	0.1414	0.02	0.16	0.3271	0.0022	0.009	0.075	0.153
χ^2	0.0024	0.400	0.0001	0.0002	0.0100	0.0030	0.0200	0.0090
$r^{2(*)}$	0.9964	0.1485	0.9999	0.9987	0.9895	0.9982	0.9973	0.9921
Parameters	NLR				MLR			
	Cu(II)	Fe(II)	Mn(II)	Zn(II)	Cu(II)	Fe(II)	Mn(II)	Zn(II)
$q_{\max}(\text{mg/g})$	35.86	31.42	3.33	24.07	25.36	27.95	14.06	6.43
b (L/mg)	0.0194	0.0801	0.1111	0.0063	0.0047	0.0041	0.1390	0.2060
χ^2	0.60	1.37	0.65	0.03	0.01	0.06	0.15	0.03
$r^{2(*)}$	0.9323	0.0242	0.9737	0.9953	0.9959	0.9789	0.9354	0.9998

(*) corresponds to the linear fitting by plotting $q_{\text{exp}} \times q_{\text{calc}}$ obtained from the model adjustment.

KINETIC STUDIES



1.5g de biomass



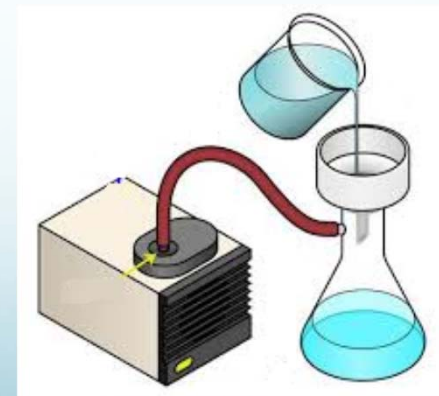
500 mL de
Multielement solution



20 mL aliquots at 5, 10,
30, 60, 90, and 1440 min



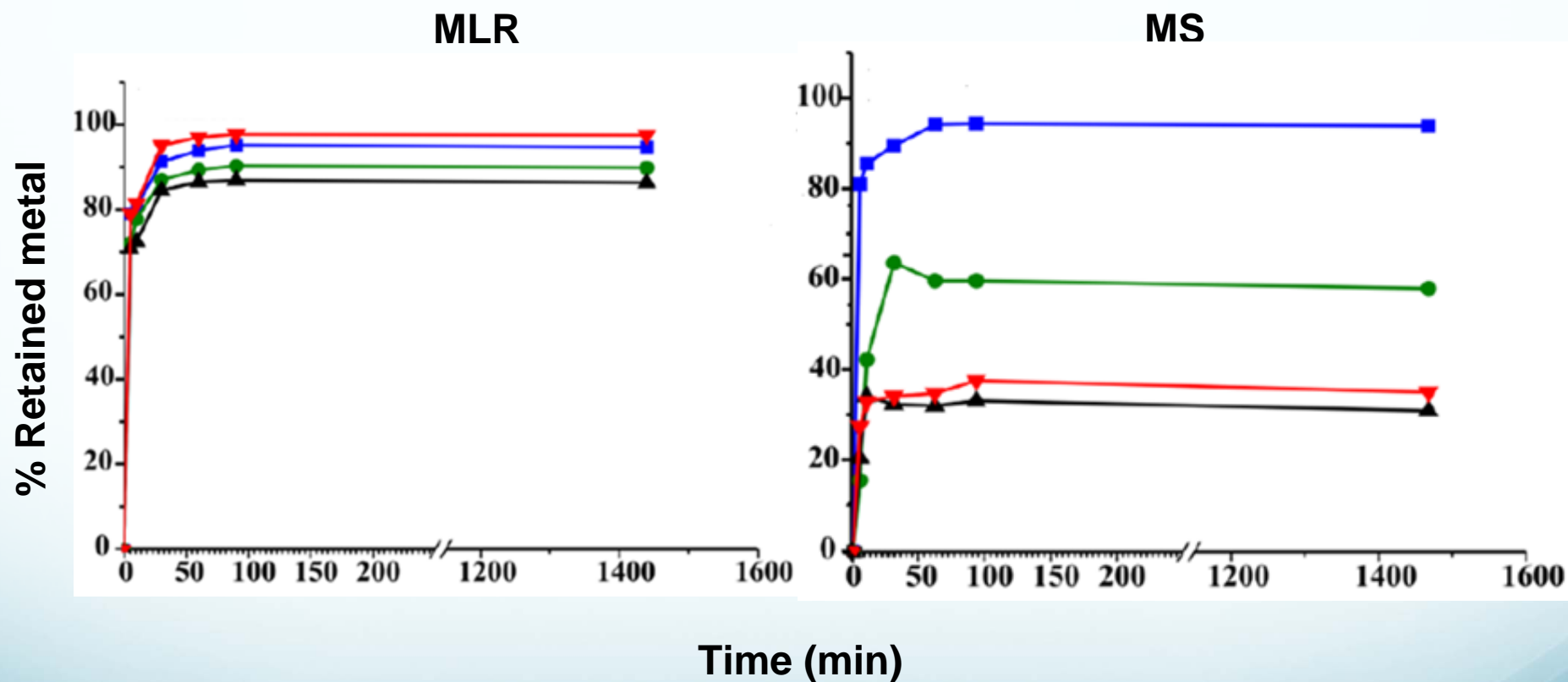
Flame Atomic Absorption
Spectrometry



Vacuum filter



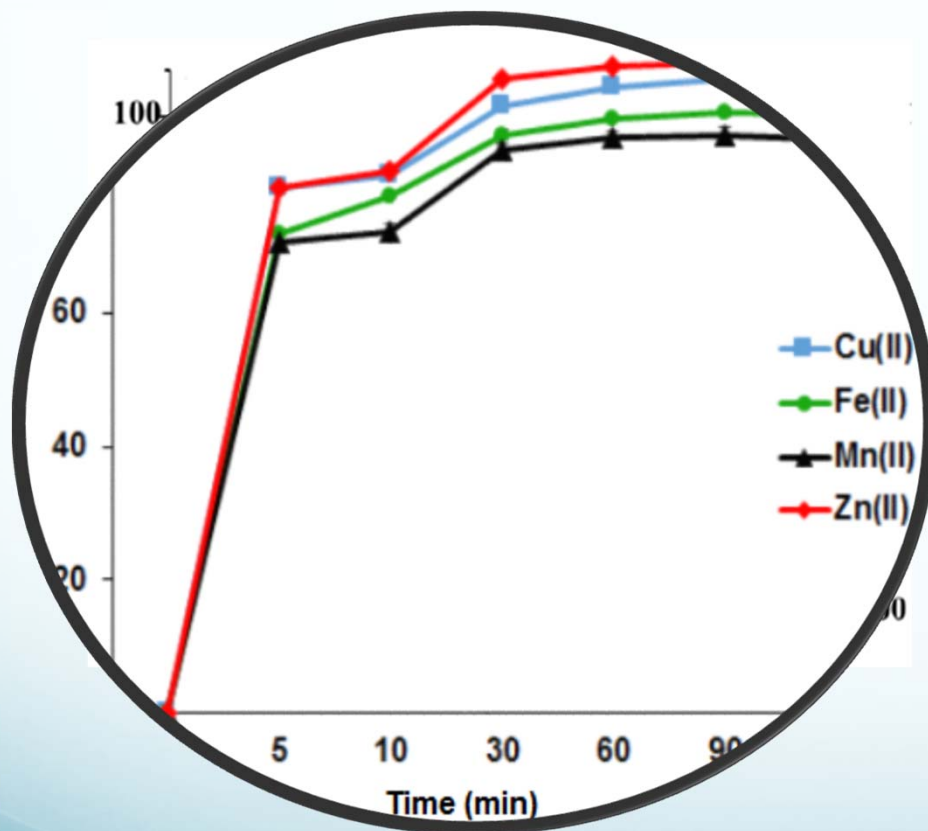
SORPTION KINETICS OF Cu(II), Fe(II), Mn(II), AND Zn(II) USING MODIFIED LETTUCE ROOTS (MLR) AND SUGARCANE BAGASSE (MSB)



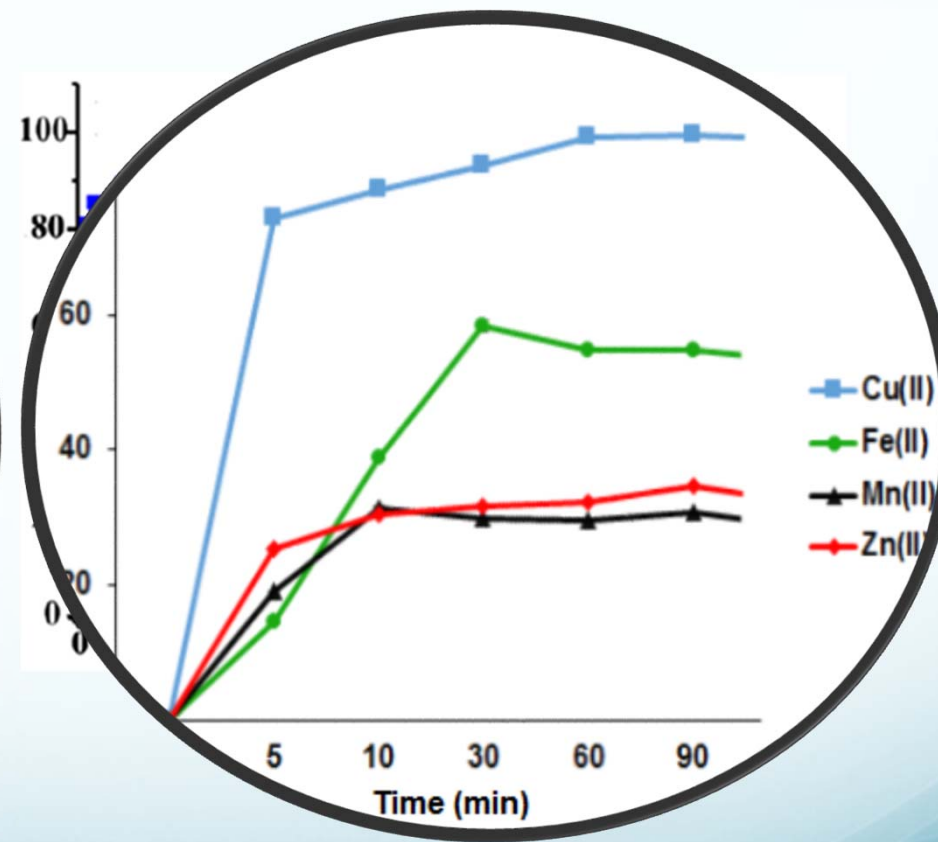
—■— Cu(II) —●— Fe(II) —▲— Mn(II) —▼— Zn(II)

SORPTION KINETICS OF Cu(II), Fe(II), Mn(II), AND Zn(II) IN MRL AND MSB

% Retained metal by MLR



% Retained metal by MSB



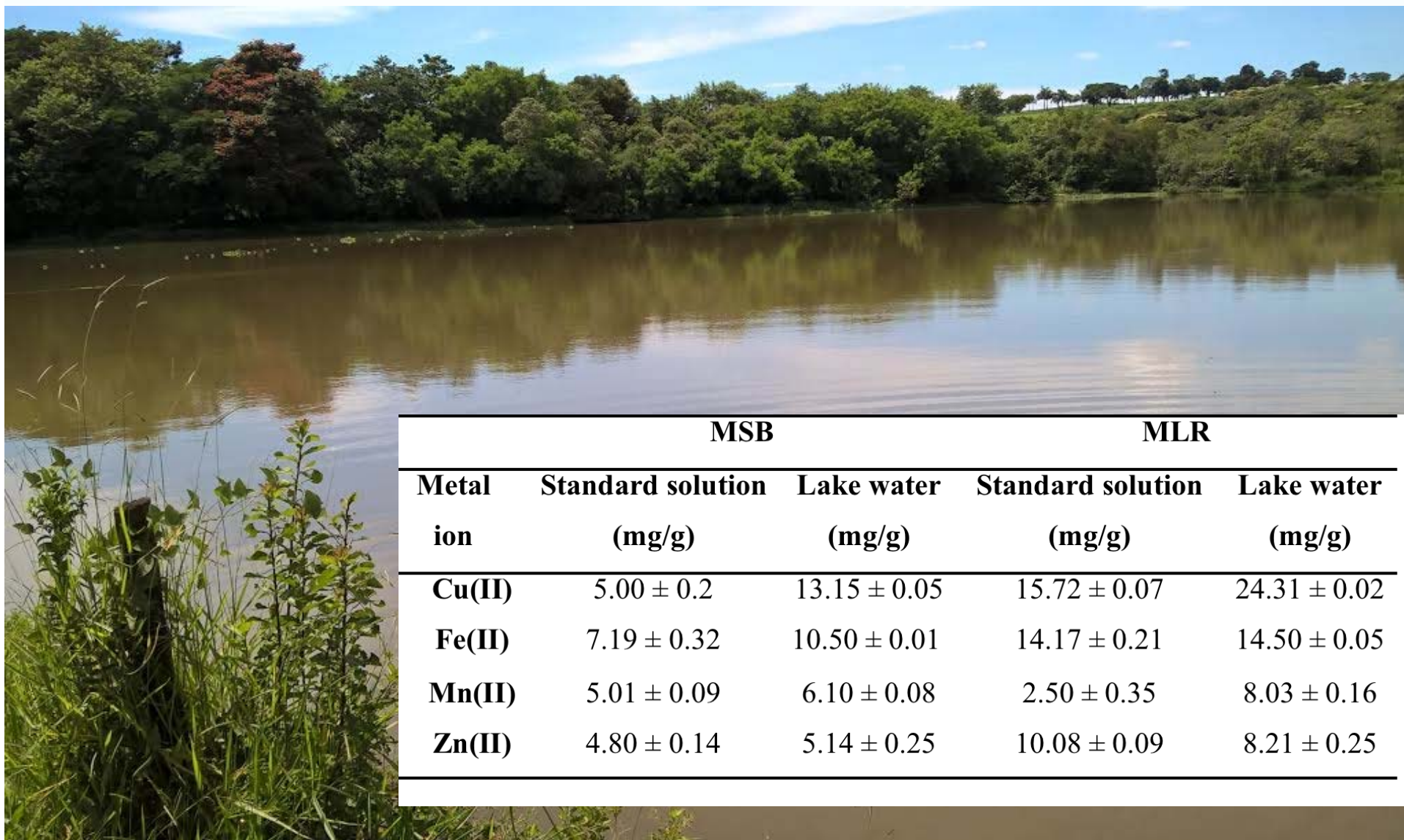
■ Cu(II) ● Fe(II) ▲ Mn(II) ▼ Zn(II)

EQUATIONS AND THEIR CORRELATION COEFFICIENTS FOR KINETICS SORPTION OF MULTIELEMENTAL SOLUTIONS BY MODIFIED BIOMASSES

	MSB		MLR	
	pseudo 1 st order	pseudo 2 nd order	pseudo 1 st order	pseudo 2 nd order
Cu(II)	$y = -1.6132x + 2.4689$	$y = 0.1426x + 0.1796$	$y = -0.0502x + 0.5011$	$y = 0.1292x + 0.2108$
	$r^2 = 0.8936$	$r^2 = 0.9998$	$r^2 = 0.9850$	$r^2 = 0.9999$
	$k_1 = 0.16$	$k_2 = 1.56$	$k_1 = 0.006$	$k_1 = 0.98$
Fe(II)	$y = -2.6053x + 5.0601$	$y = 0.1814x + 1.5368$	$y = -0.0774x + 0.8406$	$y = 0.1219x + 0.1977$
	$r^2 = 0.8227$	$r^2 = 0.9971$	$r^2 = 0.9999$	$r^2 = 1.000$
	$k_1 = 0.08$	$k_2 = 1.02$	$k_1 = 0.60$	$k_2 = 0.41$
Zn(II)	$y = -0.7672x - 0.02$	$y = 0.3922x + 0.9451$	$y = -0.0917x + 0.8823$	$y = 0.1374x + 0.2284$
	$r^2 = 0.9703$	$r^2 = 0.9975$	$r^2 = 0.9965$	$r^2 = 0.9999$
	$k_1 = 0.07$	$k_2 = 1.51$	$k_1 = 0.01$	$k_2 = 0.83$
Mn(II)	$y = 0.0279x - 0.1184$	$y = 0.4092x + 0.3917$	$y = -0.9895x + 1.5884$	$y = 0.1409x + 0.2304$
	$r^2 = 0.5333$	$r^2 = 0.9985$	$r^2 = 0.9485$	$r^2 = 0.9999$
	$k_1 = 0.32$	$k_2 = 1.41$	$k_1 = 0.005$	$k_2 = 1.12$

MSB: Modified Sugarcane Bagasse; MLR: Modified lettuce roots; For pseudo 1st order the slope = k_1 (min⁻¹). For pseudo 2nd order the angular parameter = k_2 (g mg⁻¹ min⁻¹), $n = 3$.

EFFECT OF WATER MATRIX ON METAL IONS SORPTION BY MODIFIED BIOMASSES



Metal ion	MSB		MLR	
	Standard solution (mg/g)	Lake water (mg/g)	Standard solution (mg/g)	Lake water (mg/g)
Cu(II)	5.00 ± 0.2	13.15 ± 0.05	15.72 ± 0.07	24.31 ± 0.02
Fe(II)	7.19 ± 0.32	10.50 ± 0.01	14.17 ± 0.21	14.50 ± 0.05
Mn(II)	5.01 ± 0.09	6.10 ± 0.08	2.50 ± 0.35	8.03 ± 0.16
Zn(II)	4.80 ± 0.14	5.14 ± 0.25	10.08 ± 0.09	8.21 ± 0.25

CONCLUSIONS

Biomasses

- ✓ Lettuce roots and sugarcane bagasse have great potential in the sorption of Cu(II), Fe(II), Mn(II), and Zn(II) in aqueous solutions and lake water.
- ✓ Lettuce roots presented higher adsorption capacity for the investigated metals.

Chemical Modification

- ✓ The chemical modification of the biomass was efficient to increase the maximum capacity of multielementar adsorption of all elements for sugarcane bagasse.

Adsorption

Capacity

- ✓ High adsorption capacity was found for both biomasses using the Langmuir isothermal model.

Industrial Application

- ✓ Due to the high sorption capacity in both *in natura* and modified lettuce roots this is expected to be a promising biosorbent.



Federal University of São Carlos

THE BIOSORPTION GROUP



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Efharistó



Thank You

Obrigada