SYNTHESIS, CHARACTERIZATION, AND USE OF NANOMODIFIED SUGARCANE BAGASSE FOR THE SORPTION OF HEXAVALENT CHROMIUM

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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.

HOME SEARCH The New York Times

Chromium and Worry Rise in Jersey City

By ROBERT HANLEY JUNE 26, 1989

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The New York Times
Metropolitan News
Helmsley Case On Taxes Goes To Trial Today
Women Work To Recapture Lost Momentum
Chromium and Worry Rise in Jersey City
A potent carcinogen bubbles up in parks and seeps into homes.

Still Toxic After All These Years

Nearly a quarter-century after winning millions from PG&E, the 'Erin Brockovich' town continues its fight for clean water.

By Max Genecov on Jan 29, 2019

Over six times the normal level of hexavalent chromium detected at arena construction site in Okinawa City

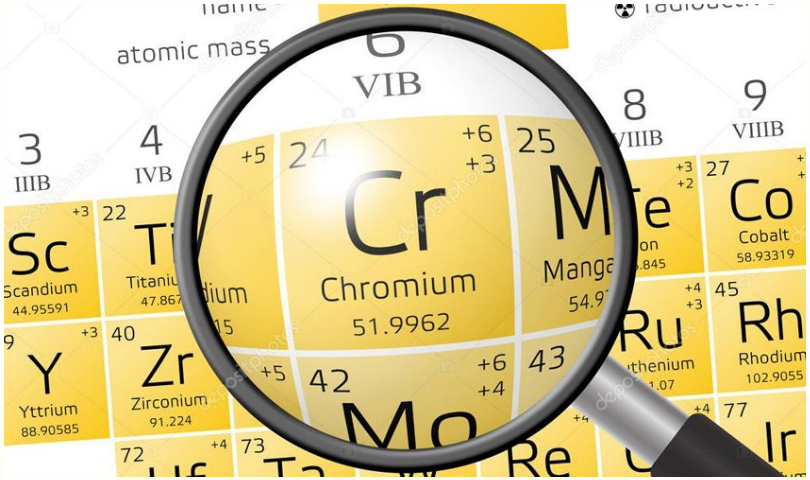
May 17, 2019 Ryukyu Shimpo

Okinawa City – Over six times the standard level of hexavalent chromium was detected at the construction site where Okinawa City is planning to build a 10,000 person-capacity multi-purpose arena on May 16. Hexavalent chromium is sometimes found in the ground at construction sites, as it exists in cement. However, in Okinawa it is mainly discovered coming from U.S. military bases, or as ground pollution in the remains of past U.S. bases, and some are concerned that this current case of pollution is coming from U.S. military waste.


The arena construction site where hexavalent chromium was detected. May 16, Yamauchi, Okinawa City.

The construction site for the arena in Yamauchi, Okinawa was used as a garbage incineration plant until 1970, when it was repurposed as a bullfighting ring run by Koza City in 1972. In 2018, the bullfighting ring was demolished to make way for the arena, and in the remains large amounts of waste material was found mixed into the soil.

HEAVY METAL – CHROMIUM



Cr(III) is considered an essential nutrient to humans

Cr(VI) is considered a **toxic and carcinogenic** agent

HEXAVALENT CHROMIUM – Applications

Stainless steel industries, electroplating processes, dyes and leather tanneries, and in wood preservation processes

In aqueous solution:

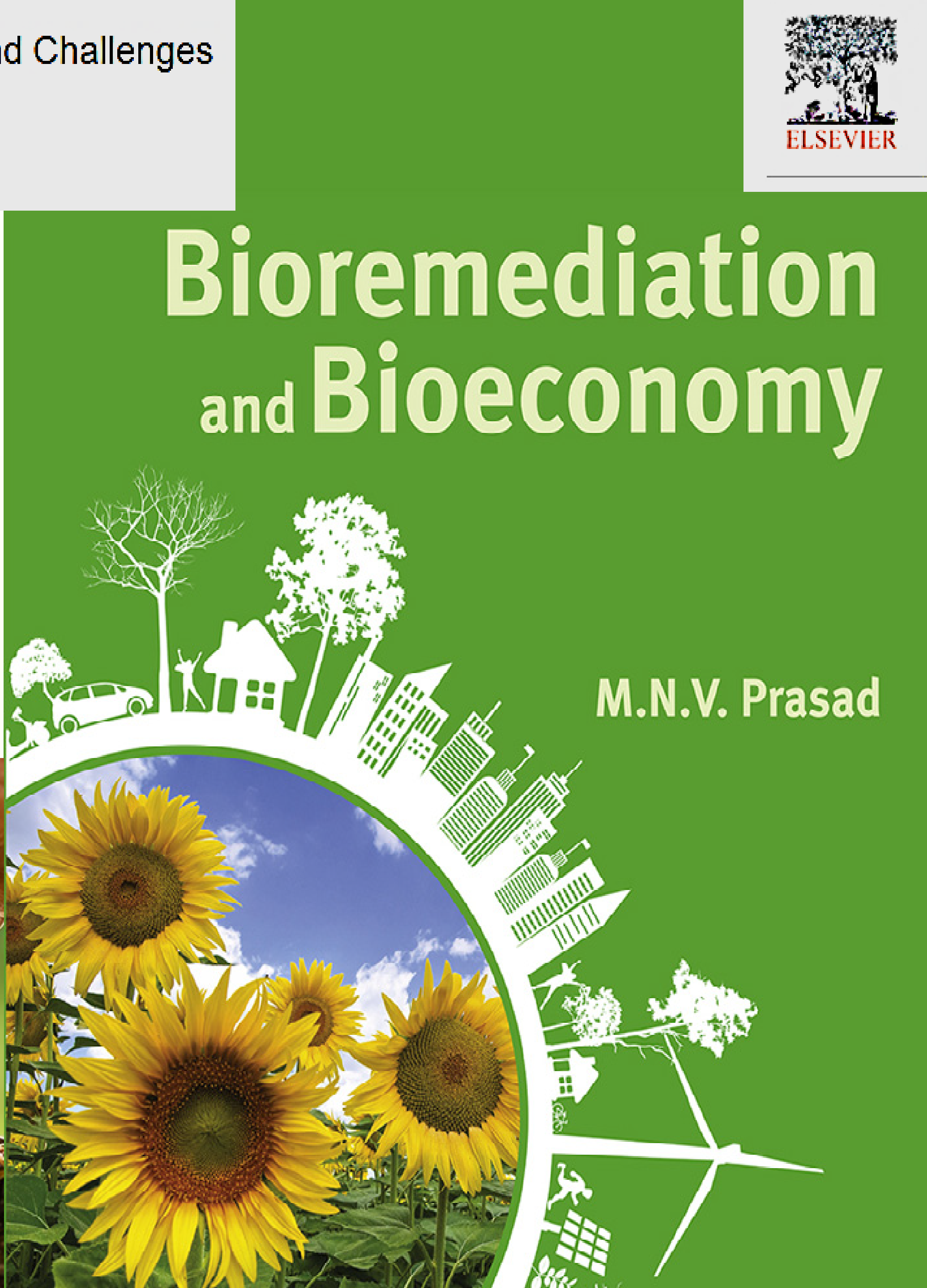
$H_2CrO_4 \rightarrow H^+ + HCrO_4^-$ **(pH = 1 – 6)**

$HCrO_4 \rightarrow H^+ + CrO_4^{2-}$ **(pH > 7)**

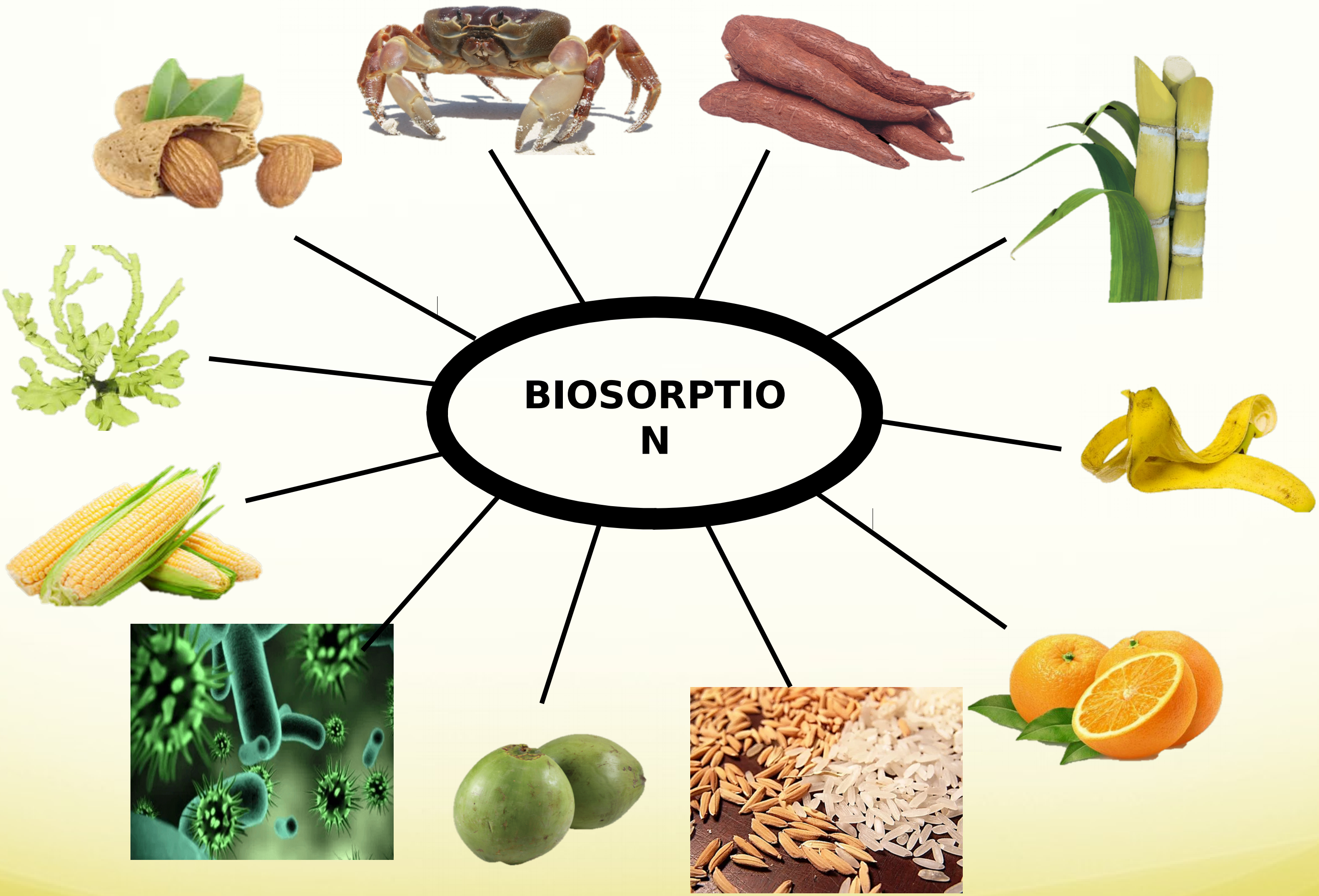
Chapter 22 – Bioremediation in Brazil: Scope and Challenges to Boost Up the Bioeconomy

G. Labuto[1], E.N.V.M. Carrilho[2]

AN IMPORTANT FIELD



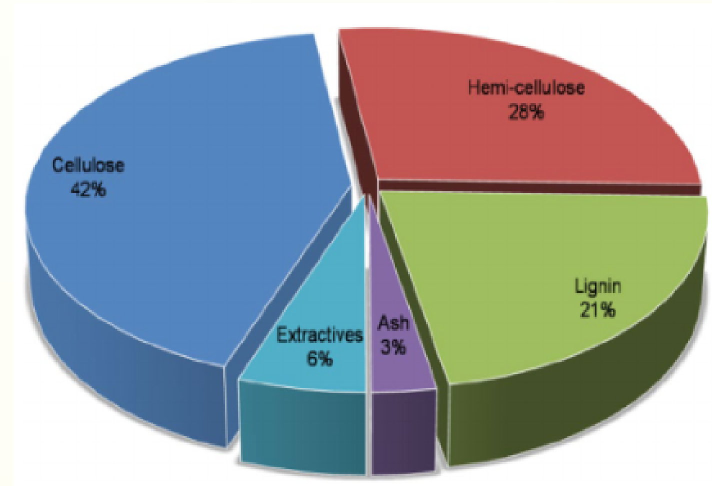
CHOICES OF BIOSORBENTS



SUGARCANE

Dried powdered bagasse

616 millions of tons 2018/19



Sarker, et al., 2017

Assessment of biomasses in the sorption of Cr(VI) from aqueous medium

THE UNIVERSITY FARM – SUGARCANE CROP

BIOMASSES USED

Cleaning with purified H_2O

Drying at 50 ºC

Ground to 0.12 mm

1.5 g of biomass

Sugarcane Bagasse

Modification

Leaching with HCl 1 mol/L

Conditioned with 0.005 mol/L KCH_3COO/CH_3COOH solution at pH 5.5

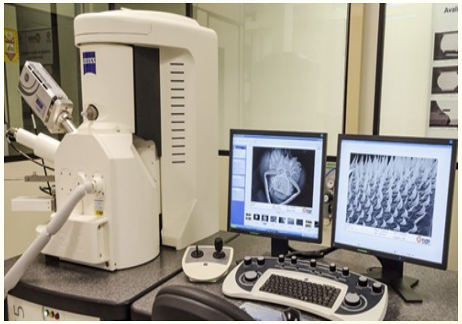
CHARACTERIZATION OF THE ADSORBENTS

- **X-Ray Diffraction (XRD)**

Identification of crystalline structures of the materials;

- **Scanning Electron Microscopy (SEM)**

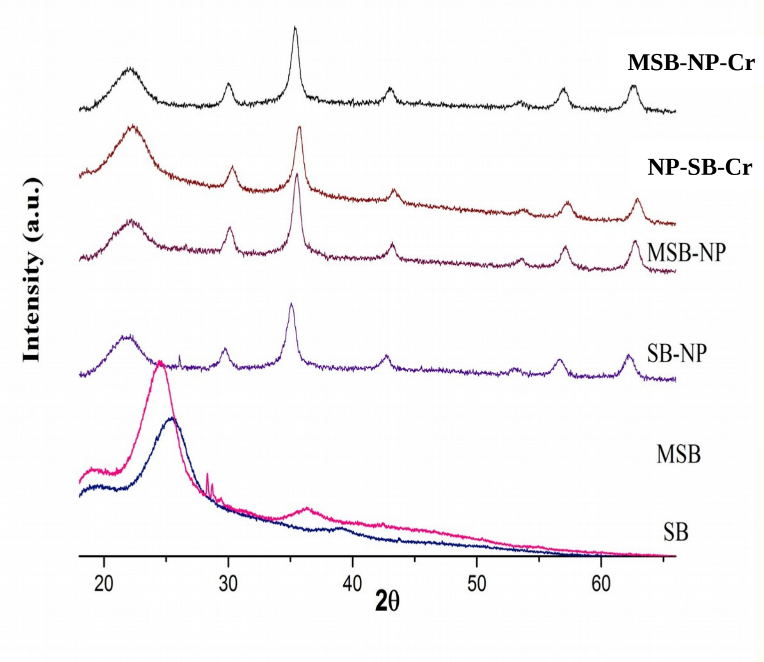
It is possible to obtain external images showing the surface of the materials;



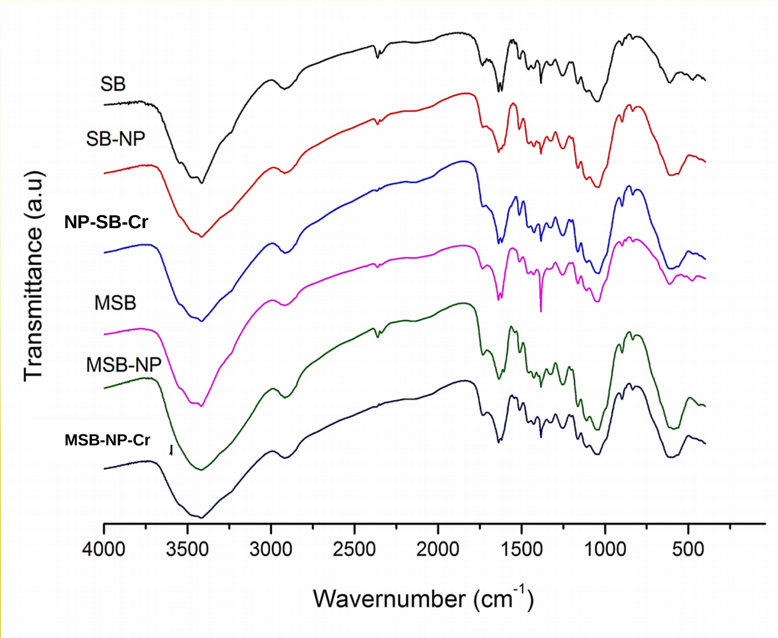
- **Fourier Transform Infrared Spectroscopy (FTIR)**

Detects the absorption in a characteristic region, identifying the functional groups in the materials.

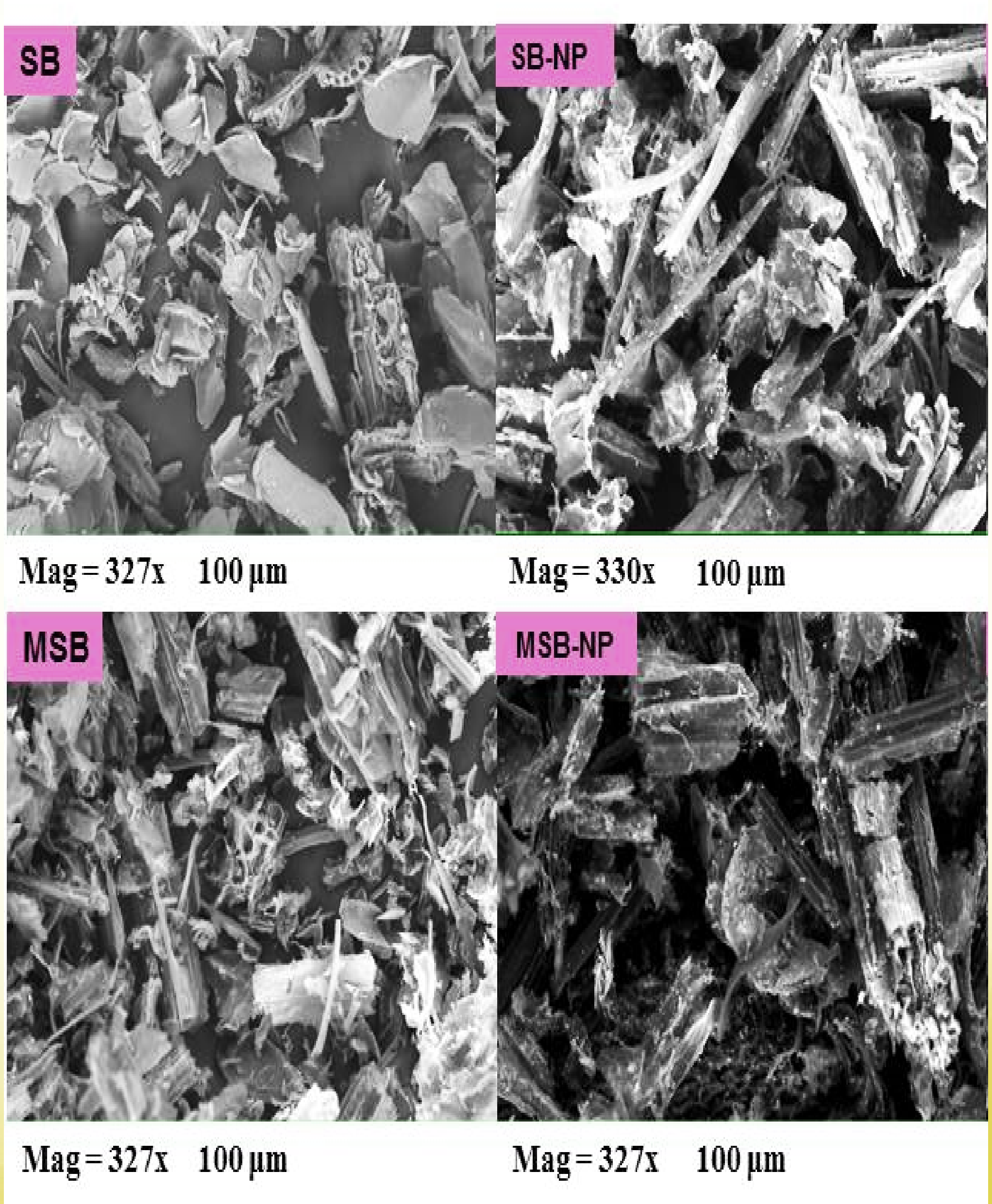
X-Ray Diffraction (XRD)



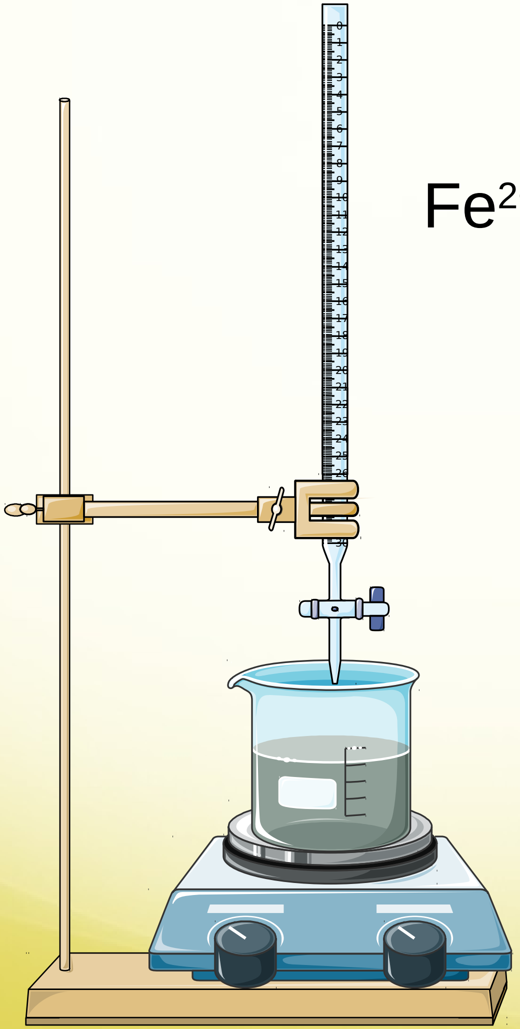
Fourier Transform Infrared Spectroscopy



Scanning Electron Microscopy



SYNTHESIS OF MAGNETITE NANOPARTICLES



30 min

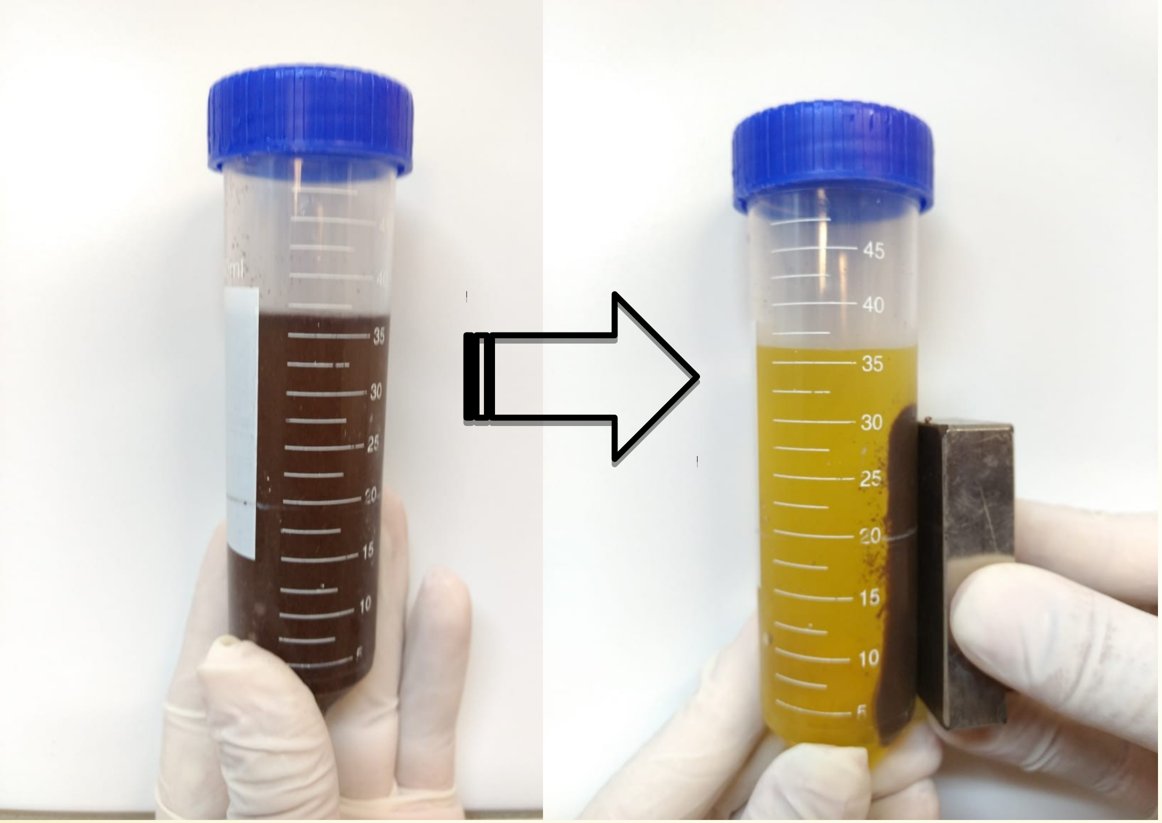
$$Fe^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} + 8\ OH^{-}_{(aq)} \rightarrow \mathbf{Fe_3O_{4\ (s)}} + 4H_2O_{(l)}$$

30 min 80 ºC

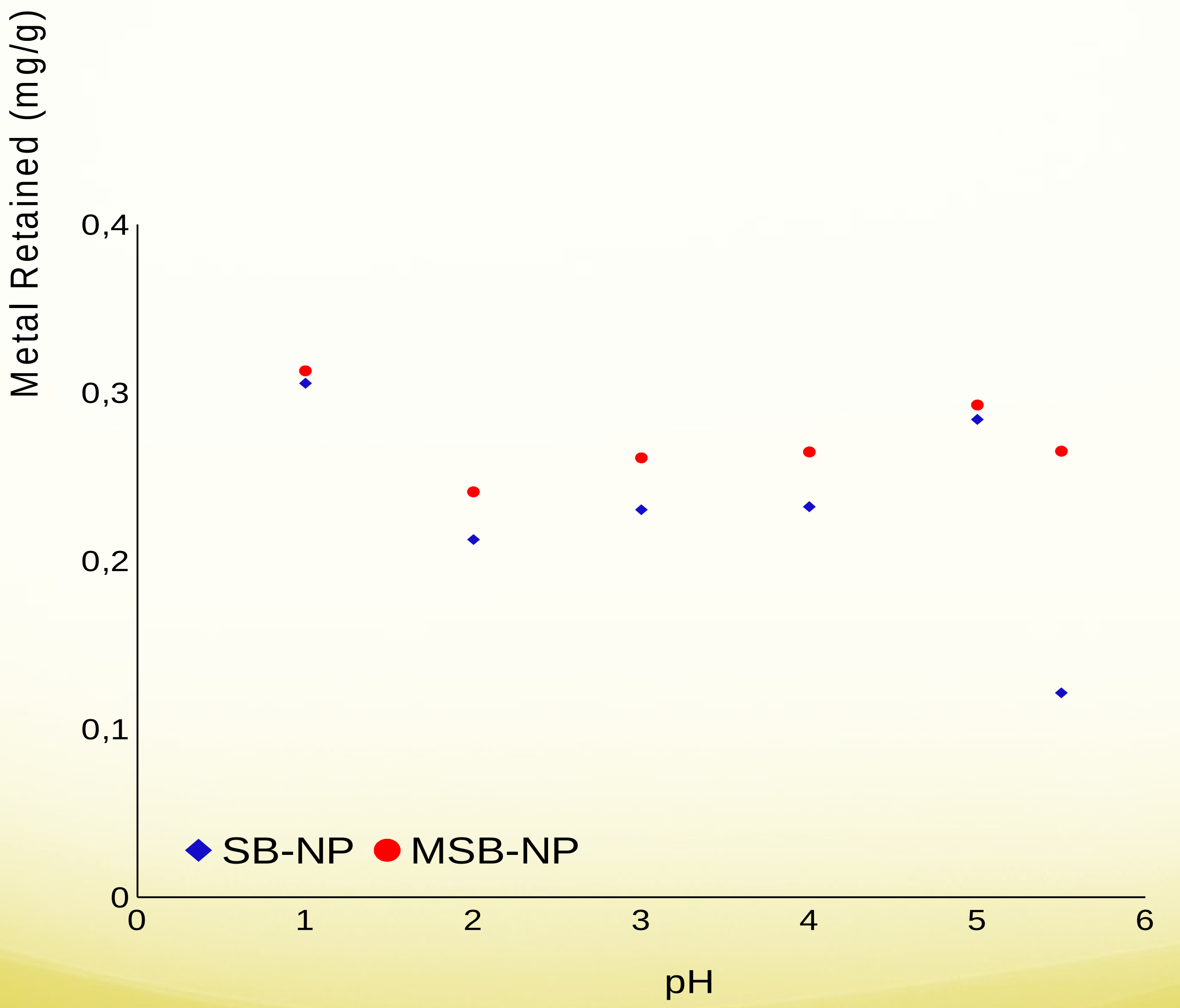
$$Fe_3O_{4\ (s)} + SB_{\ (s)} \rightarrow \mathbf{SB\text{-}Fe_3O_4}_{\ (s)}$$

(Biomass impregnated with magnetite)

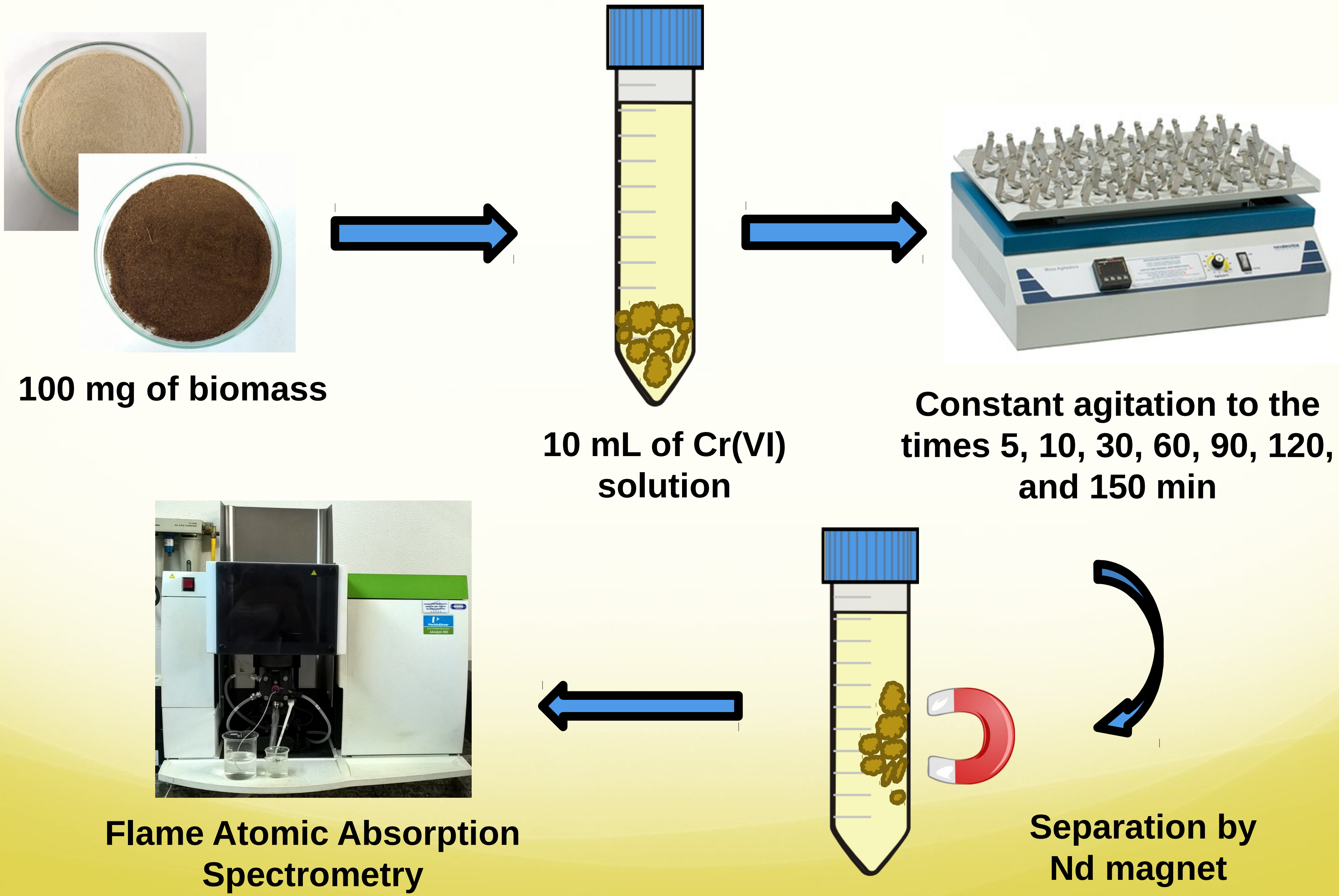
EFFECT OF MAGNETIZATION



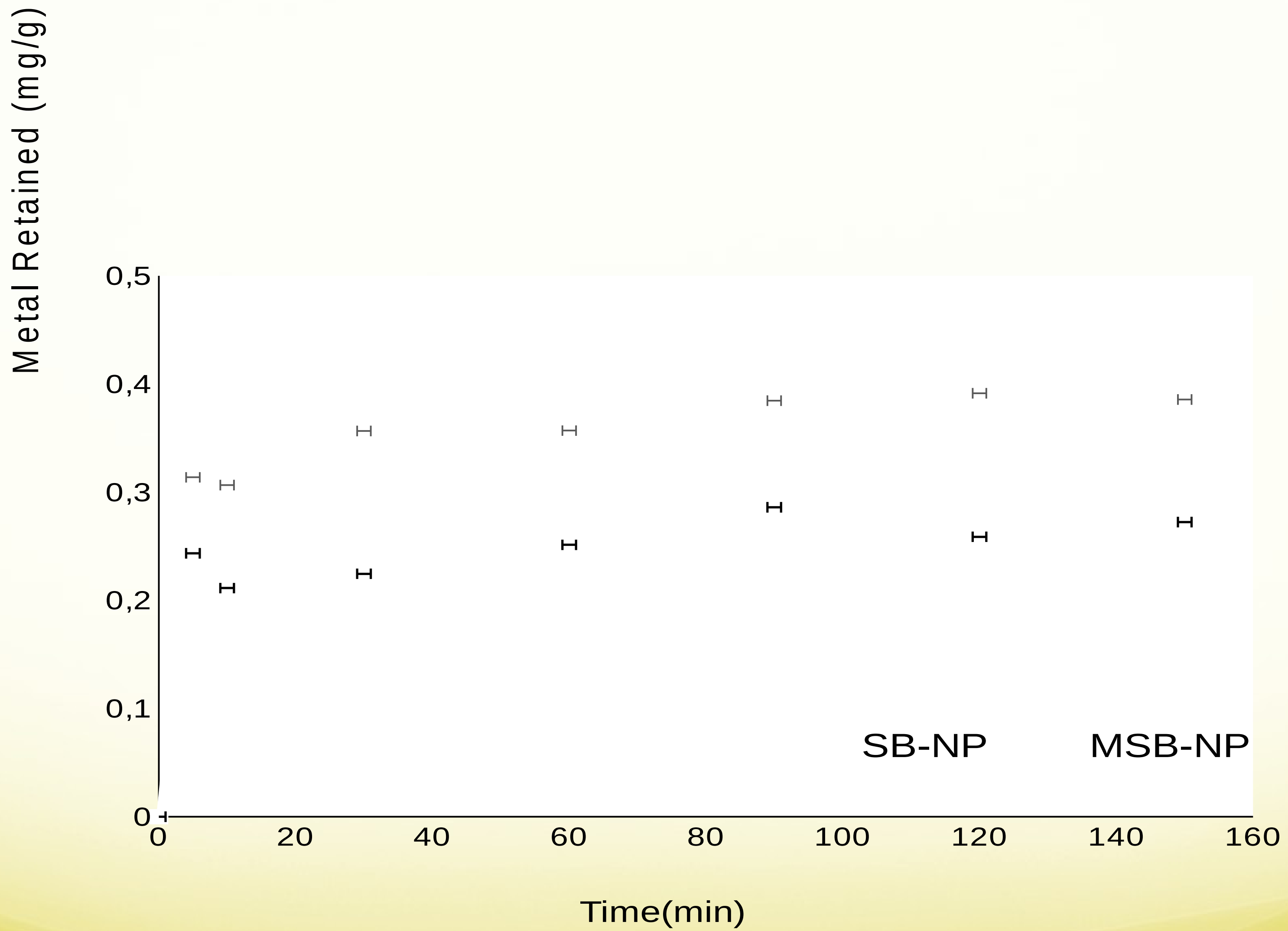
pH ASSESSMENT

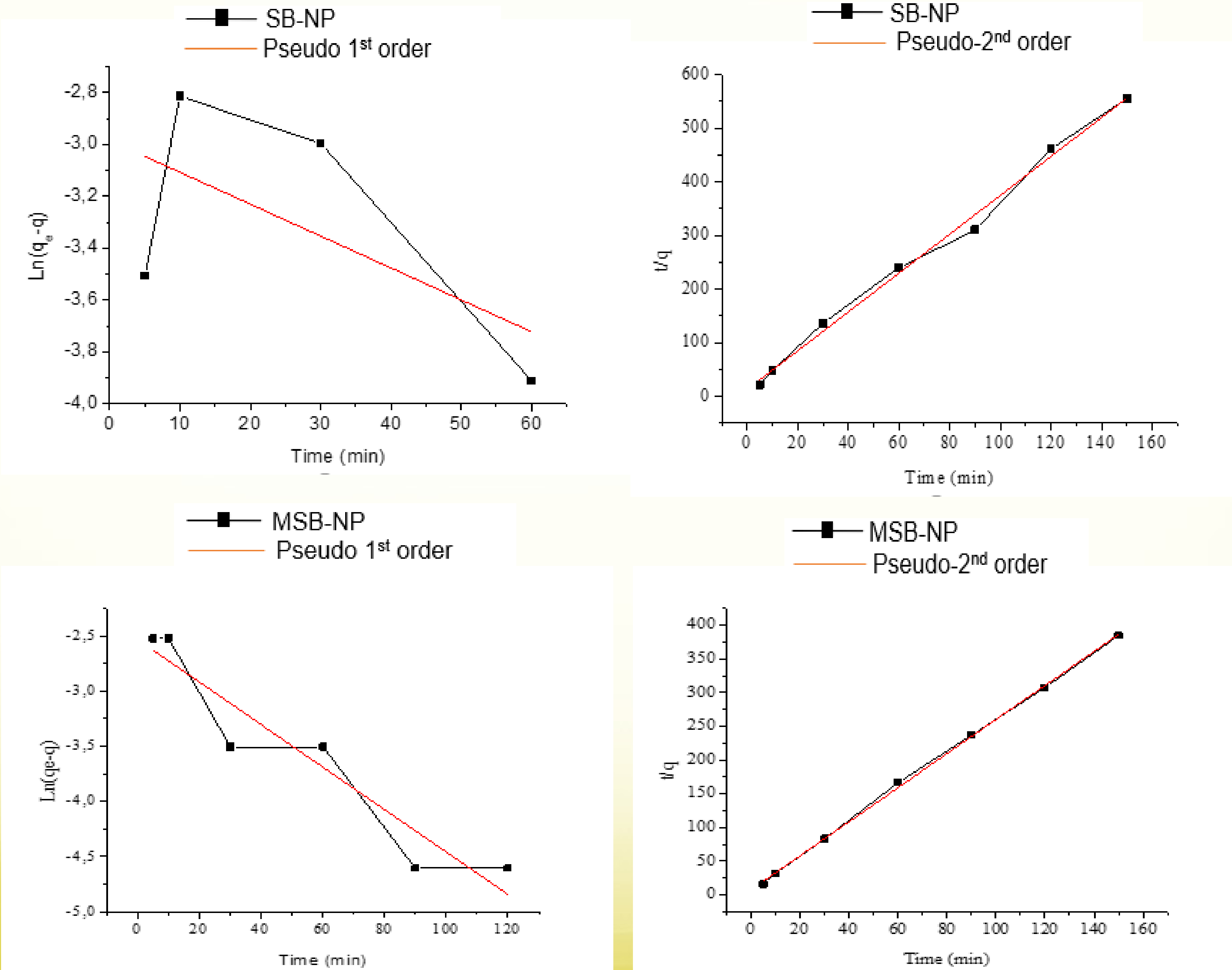


KINETIC STUDIES



KINETICS OF Cr(VI) SORPTION BY *in natura* AND ACID WASHED NANOMODIFIED SUGARCANE BAGASSE




SB-NP
Pseudo 1st order
Ln(q_e-q)
Time (min)
SB-NP
Pseudo-2nd order
t/q
Time (min)
MSB-NP
Pseudo 1st order
Ln(qe-q)
Time (min)
MSB-NP
Pseudo-2nd order
t/q
Time (min)

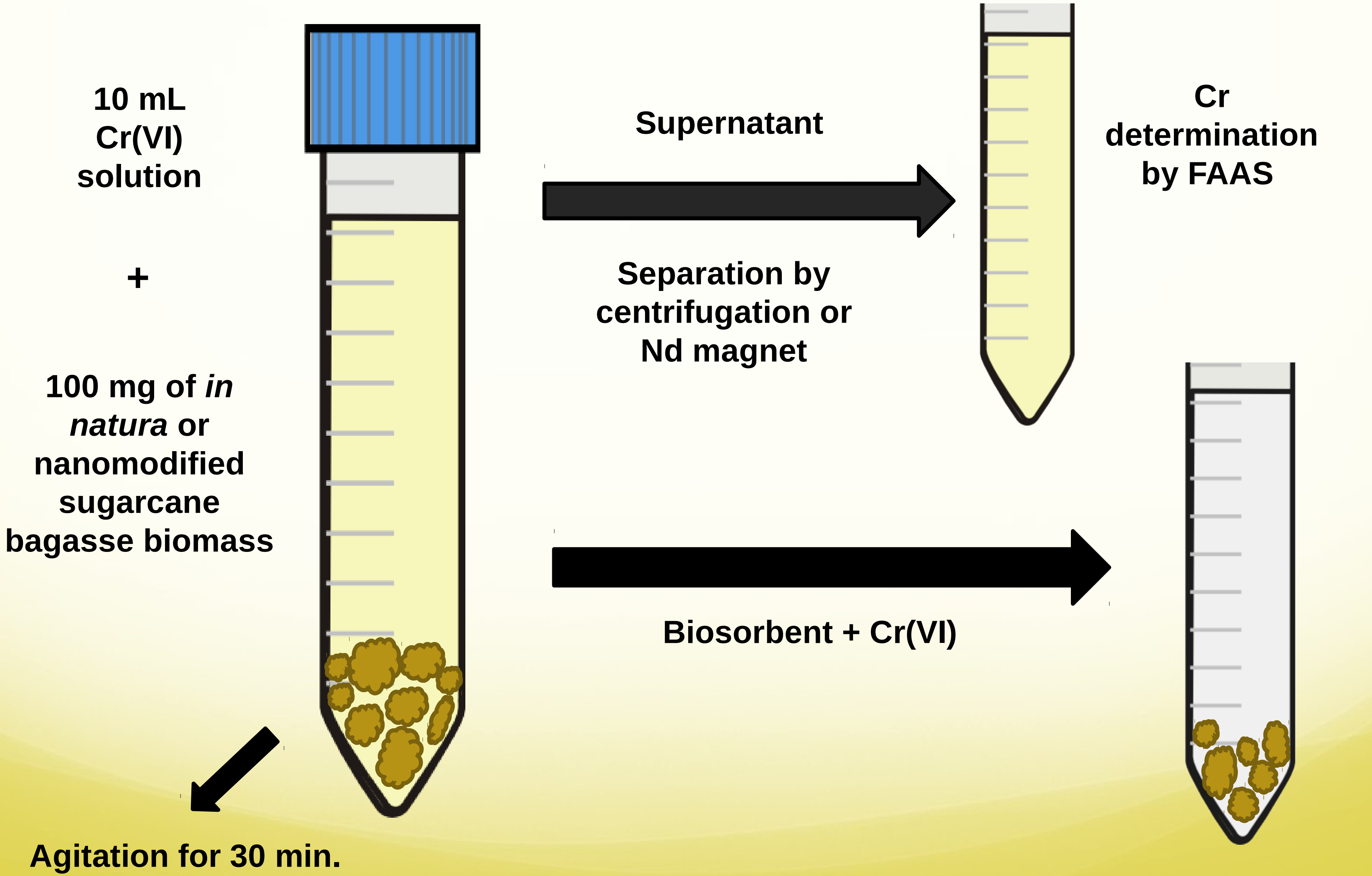
Data of pseudo-first and pseudo-second order kinetics of *in natura* (SB-NP) and acid washed (MSB-NP) nanomodified sugarcane bagasse.

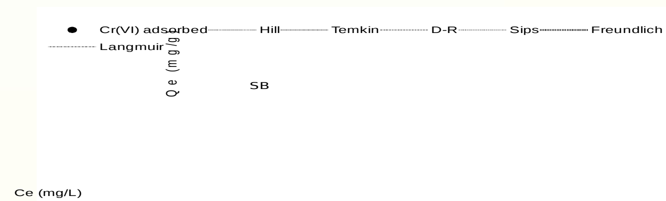
	Pseudo 1st order			Pseudo 2nd order		
	r^2	K_1 (min^{-1})	q_{exp} (mg/g)	r^2	K_2 (g/mg min)	q_{exp} (mg/g)
SB-NP	0.071	0.012	0.051	0.9931	1.09	0.27
MSB-NP	0.88	0.019	0.079	0.9991	0.83	0.40

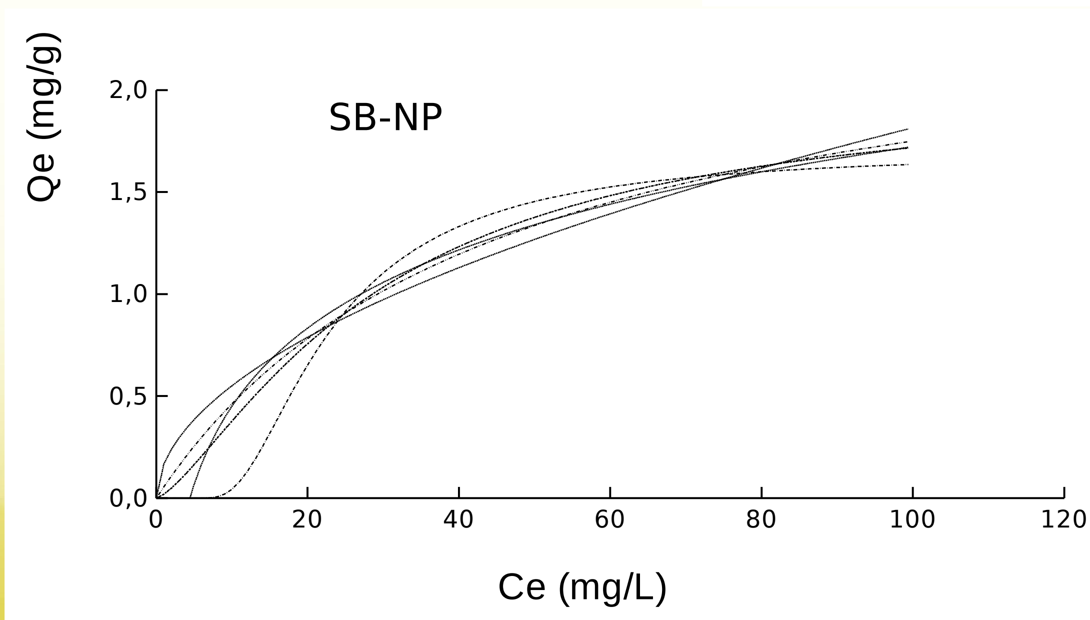
CHEMICAL NATURE

In natura (SB-NP) and acid washed (MSB-NP) nanomodified sugarcane bagasse;
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.

BATCH PROCEDURE FOR Cr(VI) SORPTION BY *in natura* OR NANOMODIFIED SUGARCANE BAGASSE




Cr(VI) adsorbed
Hill
Temkin
D-R
Sips
Freundlich
Langmuir
Qe (mg/g)
SB
Ce (mg/L)


SB-NP
Qe (mg/g)
Ce (mg/L)
2,0
1,5
1,0
0,5
0,0
0
20
40
60
80
100
120

Values of experimental sorption capacity (Q_{exp}), isotherms parameters and χ^2 error evaluation for Cr sorption by NP SB, and SB-NP

NP – magnetic nanoparticles
SB – sugarcane bagasse
SB-NP – nanomodified sugarcane bagasse

SD = Standard Deviation;
SE = Standard Error provided by fitting the model to the experimental data;
n = 3.

The lower the χ^2, higher similarities between the experimental isotherms and the predicted model

	SB	SB-NP
Q_{exp} (mg/g)	1.49 ± 0.06 (SD)	1.60 ± 0.08 (SD)
Langmuir Isotherm Model		
Q_{max} (mg/g)	2.4 ± 0.5 (SE)	2.5 ± 0.2 (SE)
b (L/g)	0.0176 ± 0.0067 (SE)	0.0223 ± 0.0047 (SE)
r^2	0.9350	0.9772
χ^2	0.020	0.0086
Freundlich Isotherm Model		
K_f (L/mg)	0.1235 ± 0.0445 (SE)	0.17 ± 0.047 (SE)
n_f	1.80 ± 0.28 (SE)	1.93 ± 0.26 (SE)
r^2	0.9320	0.9507
χ^2	0.0208	0.0186
D-R Isotherm Model		
Q_{DR} (mg/g)	1.50 ± 0.13 (SE)	1.70 ± 0.09 (SE)
B_{DR} (mol²/kJ)	$7.46 \times 10^{-5} \pm 2.4 \times 10^{-5}$ (SE)	$6.56 \times 10^{-5} \pm 1.3 \times 10^{-5}$ (SE)
E (kJ/mol)	57.5	87.7
r^2	0.8566	0.9409
χ^2	0.0439	0.0223

Values of experimental sorption capacity (Q_{exp}), isotherms parameters and χ^2 error evaluation for Cr sorption by NP, SB, and SB-NP

NP – magnetic nanoparticles
SB – sugarcane bagasse
SB-NP – nanomodified sugarcane bagasse

SD = Standard Deviation;
SE = Standard Error provided by fitting the model to the experimental data;
n = 3.

The lower the χ^2, the higher similarities between the experimental isotherms and the predicted model

	SB	SB-NP
Q_{exp} (mg/g)	1.49 ± 0.06 (SD)	1.60 ± 0.08 (SD)
Sips Isotherm Model		
Q_{max} (mg/g)	3.06 ± 3.23 (SE)	2.03 ± 0.25 (SE)
K_s	0.011 ± 0.0026 (SE)	0.034 ± 0.0076 (SE)
n	0.85 ± 0.50	1.38 ± 0.56
r^2	0.9252	0.9795
χ^2	0.0229	0.0077
Temkin Isotherm Model		
b_T	$1.89 \times 10^5 \pm 2.6 \times 10^4$ (SE)	$1.65 \times 10^5 \pm 1.4 \times 10^4$ (SE)
K (L/mg)	0.22 ± 0.71 (SE)	0.22 ± 0.043 (SE)
r^2	0.9144	0.9671
χ^2	0.0262	0.012
Hill Isotherm Model		
Q_H (mg/g)	3.06 ± 3.17 (SE)	2.03 ± 0.25 (SE)
n_H	0.85 ± 0.49 (SE)	1.4 ± 0.29 (SE)
K_H	48.3 ± 27.5 (SE)	103.7 ± 79.4 (SE)
r^2	0.9250	0.9709
χ^2	0. 0229	0.0077

CONCLUSIONS

Biomass

- ✓ Sugarcane bagasse showed great potential in the sorption of Cr(VI) in aqueous medium.

Chemical Modification

- ✓ Chemical modification did not show significant improvement in the sorption of Cr(VI) – Sugarcane bagasse can be used *in natura*!!!

Magnetization of the biomass

- ✓ The magnetite, besides facilitating the removal of the biosorbent from the medium, increases the sorption capacity;

Industrial Application

- ✓ Both *in natura* and nanomodified sugarcane bagasse can be used for water decontamination.

THE BIOSORPTION GROUP

Federal University of São Carlos

Polymer Materials and Biosorbents Laboratory

Ef’rraristó

ευχαριστώ

Thank You

Obrigada