

REPUBLIQUE ALGERIENNE DEMOCRATIQUE ET POPULAIRE
MINISTERE DE L'ENSEIGNEMENT SUPERIEUR ET DE LA RECHERCHE
SCIENTIFIQUE

UNIVERSITE AMAR TELIDJI DE LAGHOUAT
FACULTE DES SCIENCES
DEPARTEMENT DE GENIE DES PROCEDES



THESE

Présenté pour l'obtention du diplôme de Doctorat en D.LMD

Filière : Génie des procédés

Par : Mlle. NOUACER Imane

Thème

**Contribution a la valorisation d'un biosorbent
local dans le traitement des eaux usées par le gaz
naturel**

Mr. DEJEDID Mebrouk	Pr	UAT- Laghouat	Président
Mr. FODILI Mokhtar	Pr	UZA – Djelfa	Examineur
Mr. CHABIRA Salem Fouad	Pr	UAT- Laghouat	Examineur
Mr. BELKHEIRI Nadji	MCA	UZA – Djelfa	Examineur
Mr. BENALIA Mokhtar	Pr	UAT- Laghouat	Directeur de thèse
Mrs. HENINI Ghania	Pr	UHB-Chlef	Co-Directeur de thèse

Année 2021- 2022

Acknowledgment

My deepest gratitude goes first and foremost to Prof. BENALIA Mokhtar, my supervisor, for his countless support, constant encouragement and invaluable advice and guidance throughout the course of my research work. Without his patient instruction, insightful criticism and expert guidance, the completion of this thesis would not have been possible. During this time, I have learnt from him a lot not only about professional knowledge, but also the truth in life.

I am deeply grateful to all members of the jury Prof. CHABIRA Salem Fouad, Prof. FODILI Mokhtar, Dr. BELKHIERI Nadji Dr. DJEDID Mebrouk for agreeing to read the manuscript and to participate in the defense of this thesis. I extend my sincere thanks to all members of the department of process engineering, and all those who contributed directly or indirectly to the dissertation.

I would like to express my heartfelt gratitude to Dr. DJEDID Mebrouk, who triggered my love of scientific research. His rigorous, meticulous, serious, and responsible academic attitude has always been my role model. I am also extremely grateful to Prof. TOUCHAN Ramzi, Research Professor at the Laboratory of Tree-Ring Research, University of Arizona, who furthered my motivation and guided during my doctoral thesis.

I am deeply indebted to Prof. CHABANI Malika from USTHB University, whose valuable ideas and suggests with her profound knowledge and rich research experience are indispensable to the completion of this thesis.

I take this opportunity to record my sincere thanks to all the members of process engineering la laboratory (USTHB) for their help and encouragement. My work could not have been conducted without the assistance of several key staff members.

I sincerely thank my fellow doctoral colleagues, HAMMADI Soumia and MATALAH Messouda for their joyous company and moral support.

Furthermore, I would especially like to thank my parents, my sisters and my best friend OULEDELMIR Nawal. I always remember, every step forward, all carrying their silent love and continuous support. They have always been there to support me, I hope they always healthy and happy. Also, thanks to everyone who encouraged me, helped me, and gave me passion and encouragement when I was down and lost.

I dedicate this work to:

*the memory of my mother KRAMI Fatima, who
thought me about dreams and how to catch them.*

NOUACER Imane

Contents

Contents

Abstract	
Dedication, Acknowledgements	
List of symbol.....	I
List of figures.....	II
List of tables.....	III
General introduction.....	1
Chapter I: Literature review	
I.1. Introduction.....	4
I.2. Heavy metals pollution from queues solution.....	4
I.3. Heavy metals pollution from industrial wastewater of HASSI R'MEL(Algeria).....	7
I.4. Methodologies for removal of heavy metal ions from wastewater.....	8
I.5. Heavy metal removal from wastewater using various biosorbents.....	11
I.6. Heavy metal removal from wastewater using Luffa Cylindrica.....	17
I.7. Research main objectives.....	19
Bibliography.....	19
Chapter II: Adsorption	
II.1. Introduction.....	23
II.2. Definition of adsorption.....	23
II.2.1. Physical Adsorption.....	23
II.2.2. Chemical Adsorption.....	23
II.3. Adsorption Mechanisms.....	24
II.4. Adsorption kinetics.....	25
II.5. Thermodynamic study.....	25
II.6. Equilibrium adsorption isotherm models.....	26
II.6.1. One-two parameter isotherm models.....	26
II.6.1.1. Henry's isotherm model.....	26
II.6.1.2. Langmuir model.....	27
II.6.1.3. Freundlich model.....	27
II.6.1.4. Temkin model.....	28
II.6.1.5. Elovich model.....	28
II.6.1.6. Fowler-Guggenheim model.....	28
II.6.1.7. Kiselev model.....	29

Contents

II.6.1.8. Hill-de Boer model.....	29
II.6.1.9. Flory – Huggins model.....	29
II.6.2. Three parameter isotherm models.....	29
II.6.2.1. Redlich–Peterson model.....	29
II.6.2.2. Sips model.....	30
II.6.2.3. Koble–Carrigan model.....	30
II.6.2.4. Toth model.....	31
II.6.2.5. Khan model.....	31
II.6.3. Four-five parameter isotherm models.....	31
II.6.3.1. Baudu model.....	31
II.6.4.2. Fritz-Schlünder (IV) model.....	32
II.6.4.3. Fritz-Schlünder (V) model.....	32
II.7. Error functions.....	34
Bibliography.....	35

Chapter III: Methodology

III.1. Chemicals.....	36
III.2. Biosorbent and treatment of biosorbent.....	36
III.2.1. Native biosorbent.....	36
III.2.2. Chemical treatment of biosorbents.....	36
III.2.2.1. Organism and culture medium.....	37
III.2.2.2. Preparation of <i>C. Pyrenoidosa</i> -luffa cylindrica immobilized discs.....	37
III.3. Chemical analysis.....	37
III.3.1. Analysis of extractives.....	37
III.3.2. Analysis of hemicelluloses.....	38
III.3. 3. Analysis of lignin and cellulose.....	38
III.4 Characterization.....	38
III.4.1 Equipment.....	38
III.4.2. Fourier Transform Infrared Ray (FTIR) analysis.....	39
III.4.3. SEM – EDS analysis.....	39
III.4.4. XRD analysis.....	39
III.4.5. TGA/DTG analysis.....	40
III.4.6. pH of point zero charge (pHpzc).....	40
III.5 Batch experiments.....	40

Contents

III.5.1 Influence of the initial metal concentrations.....	41
III.5.2 Influence of the biosorbent dosage.....	41
III.5.3 Desorption, regeneration and reuse.....	41
III.5.4 Kinetic study.....	42
III.5.5 Isotherm study.....	42
Bibliography.....	42
Chapter IV: Results and discussion	
IV.1. Biosorption of heavy metals by <i>Luffa Cylindrica</i>	43
IV.1.1. Characterization of <i>luffa cylindrica</i>	43
IV.1.1.1. Chemical analyses.....	43
IV.1.1.2. FTIR study	43
IV.1.1.3. SEM-EDS study.....	46
IV.1.1.4. X-Ray Diffraction analysis.....	48
IV.1.1.5. Thermogravimetric analysis.....	50
IV.1.1.6. Point of zero charge (pHpzc).....	51
IV.1.2. Biosorption optimization.....	52
IV.1.2.1. Effect of contact time.....	52
IV.1.2.2. Effect of pH solutions.....	53
IV.1.2.3. Effect initial concentrations of metal ions.....	56
IV.1.2.4. Effect of <i>Luffa Cylindrica</i> concentrations.....	57
IV.1.2.5. Effect of temperature and thermodynamics of adsorption	58
IV.1.3. Biosorption kinetics.....	60
IV.1.4. Adsorption isotherms.....	63
IV.1.5. Recycling of <i>luffa cylindrica</i>	67
IV.1.5.1. Desorption of metals ions loaded on the <i>luffa cylindrica</i>	65
IV.1.5.2. Regeneration and reusability of the <i>Luffa cylindrica</i>	68
IV.1.6. Comparison of metals biosorption with different biosorbents.....	69
IV.1.7. Application the optimum conditions in industrial sample(Hassi R'mel).....	71
IV.2. Biosorption of lead ions onto immobilized <i>luffa cylindrica</i>	72
IV.2.1. Characterization of l immobilized <i>Luffa cylindrica</i>	72
IV.2.1.1. FTIR study.....	72
IV.2.1.2. SEM-EDS study.....	73
IV.2.1.3. Thermogravimetric analysis.....	75
IV.2.1.4. Point of zero charge (pHpzc).....	76

Contents

IV.2.2. Biosorption optimization.....	76
IV.2.2.1. Effect of pH.....	76
IV.2.2.2. Effect of initial concentration.....	79
IV.2.2.3. Effect of temperature and thermodynamic parameters.....	80
IV.2.3. Biosorption kinetic.....	81
IV.2.4. Isotherm models.....	82
IV.2.4.1. One- and two-parameter models.....	86
IV.2.4.2. Three -parameter models.....	89
IV.2.4.3. Four- and five-parameter models.....	92
IV.2.5. Regeneration study.....	97
IV.2.6. Comparison of immobilized <i>C. pyrenoidosa</i> with other biosorbent.....	98
IV.2.7. Application the optimum conditions in industrial sample (Hassi R'mel).....	99
Bibliography.....	100
Conclusion.....	105
Annexes.....	106

Contents

List of figures

Figures	page
Fig. I.1: Various techniques of heavy metal removal from effluent.	10
Fig. I.2: Possible binding modes between functional groups and metal ions.	13
Fig. II.1: Illustration of interaction between adsorbate and adsorbent surface. Figures (a) and (b) are the physical (a) and the chemical (b) adsorption.	24
Fig.II.2. Schema of the mechanism of molecule adsorption using microporous adsorbent.	24
Fig. IV.1: FTIR spectrum. A: LC, B: LC-Pb (II), CLC-Pb-Zn (II), D: LC-Cu (II), E: LC- Cr (VI)	46
Fig. IV. 2 : SEM micrographs of Luffa cylindrica.	47
Fig. IV.3: EDS spectrum from the Luffa cylindrica.	48
Fig. IV. 4: X-Ray Diffraction patterns of free and loaded luffa cylindrica.	49
Fig. IV. 5: TGA/DTG analysis of Luffa cylindrica.	51
Fig. IV.6 : The determination of the point of zero charge (pH_{PZC}).	52
Fig. IV.7: Effect of contact time: initial concentration 10 mg/L; pH 5; biosorbent dose:1 g/100mL; temperature: 298K.	53
Fig. IV.8: Effect of pH solution: (A) LC-Pb (II), (B) LC-Zn (II), (C) LC-Cu (II), (D) LC-Cr (VI). (initial concentration 10 mg/L; contact time: 120 min; biosorbent dose:1 g/100mL; T: 298 K).	56
Fig.IV.9: Effect of initial metal ion concentration onto LC.	57
Fig. IV.10: Effect of adsorbent dosage on metal ion adsorption onto LC.	58
Fig. IV.11: Effect of temperature on the percentage removal of Pb (II), Zn (II), Cu (II) and Cr (VI) onto LC.	59
Fig. IV.12: Adsorption kinetic models of Pb, Zn, Cu and Cr ions by LC.	62
Fig. IV.13: Adsorption isotherm models of Pb, Zn, Cu and Cr ions by LC.	66
Fig. IV.14: Desorption of Pb (II), Zn (II), Cu (II) and Cr (VI) ions adsorbed on LC.	68
Fig. IV.15: FTIR spectrum of: L C, CP, CP-Pb (II), CP-LC, and CP-LC Pb (II).	73
Fig. IV.16: (A) SEM of <i>C. pyrenoidosa</i> cells. (B) SEM of Luffa Cylindrica fiber. (C) SEM of <i>C. pyrenoidosa</i> immobilized in luffa cylindrica.	74
Fig. IV.17: EDS spectrum from the CP-LC.	75
Fig. IV.18: Curves of thermo-gravimetric analysis (TG and DTG) of CP-LC.	76
Fig. IV.19: Effect of initial pH of the solution on the biosorption of Pb (II) by CP and CP-LC. (initial concentration 10 mg/L; contact time: 40 min; biosorbent dose:1 g/L; temperature: 298 K).	78

List of figures

Fig. IV.20: Distribution of lead (II) species in aqueous solution as a function of pH.	78
Fig. IV.21: Effect of the initial concentration of Pb (II) biosorption onto CP and CP-LC. (pH 5.0, time 40 min., temp. 298 K).	80
Fig. IV.22: Adsorption kinetic models of Pb (II) by CP-LC.	82
Fig. IV.23: Comparative non-linear plots for eight two-parameter isotherm models; (a) biosorption of Pb (II) onto CP, (b) biosorption of Pb (II) onto CP-LC.	88
Fig. IV.24: Comparative non-linear plots for six three-parameter isotherm models; (a) biosorption of Pb (II) onto CP, (b) biosorption of Pb (II) onto CP-LC.	92
Fig. IV.25: Comparative non-linear plots of four and five parameter isotherm models; (a) biosorption of Pb (II) onto CP, (b) biosorption of Pb (II) onto CP-LC.	96
Fig.26: Non-linear isotherm representations of modified Schlünder (V); (a) biosorption of Pb (II) onto CP, (b) biosorption of Pb (II) onto CP-LC.	97
Fig. IV.28: Desorption of Pb (II) ions adsorbed on CP-LC.	98

List of tables

Tables	Page
Tab. I.1: Classification of heavy metals based on toxicity.	4
Tab. I.2 (a): Sources and impact of heavy metals.	5
Tab. I.2 (b): Sources and impact of heavy metals.	6
Tab. I.3: Characteristics of wastewater of SONATRACH in HRM (Algeria).	7
Tab. I.4: Removal of metal ions from wastewaters.	9
Tab. I.5: The ligands present in biological systems and classes of metals.	11
Tab. I.6: The representative functional groups and class of organic compounds in biomass.	12
Tab. I.7 (a): Performance of various for heavy metal removal in batch process.	15
Tab. I.7 (b): Performance of various for heavy metal removal in batch process.	16
Tab. I.8 (a): Comparative Summary of Biosorption of Metals by <i>Luffa Cylindrica</i> , and <i>Luffa</i> -Immobilized Fungi and Algae for the Remediation of Contaminated Water.	18
Tab. I.8 (b): Comparative Summary of Biosorption of Metals by <i>Luffa Cylindrica</i> , and <i>Luffa</i> -Immobilized Fungi and Algae for the Remediation of Contaminated Water.	19
Tab. II.1: Illustration of the linear forms, nonlinear forms and plot of kinetic models analyzed for optimization studies.	25
Tab. II.2 (a): Illustration of the linear forms, nonlinear forms and plot of various isotherm models analyzed for optimization studies.	32
Tab. II.2 (b): Illustration of the linear forms, nonlinear forms and plot of various isotherm models analyzed for optimization studies	33
Tab. II.3: Error functions used in the study.	35
Tab. IV.1: Chemical analyses used in this study.	43
Tab. IV. 2: Principal elements identified on the biomass surface by SEM/EDS.	48
Tab IV. 3: Crystallinity index LC and LC-Metals.	50
Tab.IV.4: Thermodynamic parameters of Pb, Zn, Cu and Cr ions removal from aqueous solution by LC.	59
Tab.IV.5: Kinetic parameters of Pb, Zn, Cu and Cr ions removal from aqueous solution by LC.	63
Table.IV.6: Isotherm parameters of Pb, Zn, Cu and Cr ions removal from aqueous solution by LC.	66
Table.IV.7. Comparison of other biosorbents from selected literature with the present	70

List of tables

work.	
Tabl.IV.8. Adsorption of Pb (II), Zn (II), Cu (II) and Cr (VI) ions in the industrial waste water.	71
Tab.IV.9: Thermodynamic parameters of Pb (II) biosorption onto CP-LC at different T.	80
Table.IV.10: Kinetic parameters of Pb (II) biosorption by CP-LC.	82
Tab.IV.11 (a): Isotherm constants of two-parameter models for Pb (II) biosorption onto CP and CP-LC.	86
Tab.IV.11 (b): Isotherm constants of two-parameter models for Pb (II) biosorption onto CP and CP-LC.	87
Tab.IV.12: Isotherm constants of three-parameter models for Pb (II) biosorption onto CP and CP-LC.	90
Tab.IV.13: Isotherm constants of multi-parameter models for Pb (II) biosorption onto CP and CP-LC.	94
Tab.IV.14: Adsorption, desorption and desorption/ reloading ratio of Pb (II) in five seductive	98
Tab. IV.15: Comparison of the maximum biosorption capacity of immobilized chlorella pyronoidosa in Luffa Cylindrica for Pb (II) with other biosorbents	99

Nomenclature

AAS: Atomic absorption spectrophotometer.

A_k (mg/g): Koble-Carrigan isotherm constant.

ASTM: American Society for Testing and Materials.

a_e (-): Activity of Metal in solution at equilibrium.

a_{kh} (-): Constant in Khan isotherm.

a_R (L/g) : Constant in Redlich–Peterson isotherm.

ARE: average relative error.

A_T (L/g): Equilibrium binding constant.

a_s : Activity of adsorbed Metal.

b_o (L/g) Constant in Baudu isotherm.

B_k (L/g): Koble-Carrigan isotherm constant.

b_{KH} (L/g) : Constant in Khan isotherm.

b_R (-) : Constant in Redlich–Peterson isotherm.

B_T (Kj/mol): Temkin constant.

b_T (Kj/mol): Adsorption energy.

C (L/g): Fritz-Schlünder (IV) constant.

C° : Total normality of solution (in milliequivalents per liter)

C_0 (mg/L): Initial Metal ion concentration.

C_e (mg/L): Metal ion concentration in solution at equilibrium.

C_L : Light metal normality (in milliequivalents per liter).

CM: Heavy metal normality (in milliequivalents per liter)

C_s (mg/g): Metal adsorbed on BIOSORBENT

CP: *Chlorella pyrenoidosa*.

CP-LC: *Chlorella pyrenoidosa* immobilized in *luffa cylindrica*.

Nomenclature

D (L/g): Fritz-Schlünder (IV) constant.

ERSQ (-): Sum of the squares of the errors.

FTIR Fourier transform spectrometer.

G_0, G_1, G_2, G_4 : masses of biosorbent during extraction analyse.

GM: Growth medium.

HYBRID: Hybrid fractional error function.

IUPAC: International union of pure and applied chemistry

k : Affinity constant

K (-): Henry's isotherm model adsorption constant.

K_1 (1/min): The rate constant of pseudo first-order model.

K_2 (g/mg/min): the rate constant of pseudo second-order model.

K_c (-): The distribution constant.

K_{K1} (L/g): Kiselev equilibrium constant.

K_{K2} (-): Constant of complex formation between adsorbed molecules.

K_E (L/mg): Elovich constant.

K_F (mg/g)(L/g)^{1/n} : Adsorption capacity.

K_{FH} (L/g): Flory–Huggins equilibrium constant.

K_{FG} (L/g): Fowler–Guggenheim equilibrium constant.

K_{FS1} (L/g): Fritz-Schlünder (v) equilibrium constant.

K_{FS2} (L/g): Fritz-Schlünder (v) equilibrium constant

K_H (L/g): Hill–de Boer constant.

K_L (L/mg): Constant in Langmuir isotherm.

K_n (kJ/mol): Energetic constant of the interaction between adsorbed molecules.

K_R (L/g): Constant in Redlich–Peterson isotherm.

K_{RP} (L/g): Constant in Radke–Prausnitz isotherm.

k_s (L/g) : Constant in Sips isotherm.

Nomenclature

K_T (L/g): Constant in Toth isotherm.

m (g/L) : Dose of free or immobilized cells.

M_1, M_2 (-): Constants in Fritz-Schlünder model.

MPSD: Marquardt's percent standard deviation.

MT: mass titrations.

N (-): Number of observations in the experimental isotherm.

n (-) : Constant in Freundlich isotherm.

n_{FH} (-) : Number of adsorbates occupying adsorption sites.

n_K (-): Noefficient in Koble-Carrigan isotherm.

n_R (-) : Constant in Radke–Prausnitz isotherm.

n_S (-): Coefficient in Sips isotherm.

n_T (-) : Constant in Toth isotherm.

P (-) : Number of parameters in the regression model.

pH_{pzc} : pH point of zero charge.

pHs: pH solution.

Q : Total number of ion exchangeable binding sites (in milliequivalents per gram)

q_{cal} (mg/g): Estimate from the isotherm for corresponding q_{exp} .

q_e (mg/g) : Adsorption capacity.

q_{exp} (mg/g): Observation from the batch experiment.

q_L Light metal concentration in the solid phase (in milliequivalents per gram).

q_{mKH} (mg/g): Maximum adsorbate uptake from Khan model.

q_M Heavy metal concentration in the solid phase (in milliequivalents per gram)

q_m (mg/g): Maximum adsorbate uptake from Radke–Prausnitz model.

q_{mb} (mg/g): Maximum adsorbate uptake from Baudu model.

q_{max} (mg/g) : Maximum adsorbate uptake from Langmuir model.

q_{mE} (mg/g) :Maximum adsorbate uptake from elovich model.

Nomenclature

q_{mFS} (mg/g): Fritz-Schlünder (v) maximum adsorption capacity.

q_{mk} (mg/g) : Maximum adsorbate uptake from Toth model.

q_{mS} (mg/g) :Maximum adsorbate uptake from sips model.

R (J/mol K) : Ideal gas constant.

R^2 (–) : Coefficient of determination.

R_L (–): Separation factor.

S^2 : Residual variance.

SEM: Scaninig electron microscopy.

t (min) : Time.

T (K): Temperature.

TGA: Thermal gravimetric analyzer.

W (KJ/mol): Interaction energy between adsorbed molecules.

WHO: World health organization.

x : Constants in Baudu isotherm.

x_L :Light metal equivalent fraction in the liquid.

x_M :Heavy metal equivalent fraction in the liquid.

y_L :Light metal equivalent fraction in the solid.

XRD: X-Ray analysis.

y_M :Heavy metal equivalent fraction in the solid.

y (–):Constants in Baudu isotherm.

Y_e (–) : Activity coefficient of Metal in equilibrium solution.

Y_s (–) : Activity coefficient of adsorbed Metal.

W_1 : The percentage of extractive materials.

W_2 : The percentage of hemicellulose.

W_3 : The percentage of lignin.

W_4 : The percentage of cellulose.

Nomenclature

ΔH° (kJ/mol): Enthalpy change.

ΔS° (J/mol K): Entropy change.

ΔG° (kJ/mol): Gibbs free energy change (kJ/mol).

Greek symbols

θ (–) : Surface coverage of the adsorbent.

α, β (–): Constant in modified Fritz-Schlunder (v).

General introduction

In recent years, natural ecosystems have been worsened due to the massive increase in pollution generated mainly by neo-industrial activities such as metal surface treating, electro-osmosis, metallurgy, mining industry, aerospace and atomic energy installations, wastes containing different heavy metals are discharged directly or indirectly into the natural environment [1]. It is mainly important to control concentrations of metals ions which are one of the most environmentally dangerous and toxic elements of wastewater effluents. In general the heavy metals are considered as group of trace elements because of their existence in very low concentrations metals in environment with an atomic density greater than $5 \pm 1 \text{ g/cm}^3$, Pb, Ni, Cu, Zn, Cr, Hg, Cd, Sn, Fe, Mn, Ag, Co, As, Al etc. These metal ions are mainly considered as the most commonly toxic metal contaminants of water systems [2]. Due to stability, high solubility and migration activity of heavy metals in aqueous media, untreated or insufficiently treated heavy metal-contaminated wastewater discharges cause a variety of environmental and health impacts when discharged into water bodies [3]. The bioaccumulation and bio-augmentation of these metals by the food chain in living species could damage normal physiological activity and endangering human life [4]. Among these toxic metals, lead, zinc, copper and chromium have a very high solubility in waste media. However, these metal ions accumulate mainly in the muscles, bone, kidney, and central nervous system and the augment in metal concentrations can provoke many adverse health impacts like, kidney damage, anemia, gastrointestinal diseases, nervous disorders, liver toxicity and corrosive to skin and eye [5]. It is, therefore, essential to sequester these toxic metals from contaminated water before disposal. Due to these reasons, a wide variety of conventional processes have been studied in detail to achieve the aim of metal removal from contaminated aqueous media. Some of the treatment methods used to overcome this environmental problem are ion exchange, reverse osmosis, membrane separation method, flocculation, chemical precipitation, electro-coagulation, ultra-filtration, adsorption on activate carbon, etc [6]. Unfortunately, using chemical precipitation and electrochemical treatment is ineffective for solutions with low concentration of metal ions (1 to 100 mg/L), they also produce large quantities of sludge to be treated with big difficulties. Ion exchange, membrane technologies and activated carbon adsorption methods are prohibitively expensive, especially when treating a large volume of water and wastewater contaminated with toxic metals in low concentration, so all these methods cannot be used at wide-scale. Alternative treatment process to sequester heavy metals is biosorption, which utilizes various inexpensive biomass of biological origin, including plants, bacteria, fungi, algae, yeast, etc [7]. These bio-adsorbents possess metal removing

Introduction

properties and can decrease the concentration of metals ions in aqueous solution from ppm to ppb level. They can effectively eliminate dissolved heavy metal ions out of dilute solutions with greater effectiveness and quickly. Therefore biosorption is an ideal process for the treatment of high volume and low concentration complex wastewaters [2]. The main aim of this research was to investigate the efficiency and the practical applicability of locally abundant low-cost biosorbents *luffa cylindrica* as free and immobilized with microalgal *chlorella pyrenoidosa* for the single or/and multicomponent removal of heavy metals (Pb (II), Zn (II) Cu(II) and Cr(VI)) from constituted industrial wastewater.

The thesis, presented as a compendium of publications, is divided in the following chapters: General Introduction Objectives and Thesis outline, Literature review, Materials and Methods, Results and Discussion and finally Conclusion.

The literature review, presented in chapter 1: highlights those aspects which are more significant for the present experimental work understanding. This chapter is devoted to the toxicity of heavy metals and various experimental technique used for the treatment of contemned wastewater, mainly treatment using the *luffa cylindrica* as biosorbent.

Chapter II: The adsorption process is thoroughly reviewed in this chapter. The basic concepts and tools are considered. These are kinetics, thermodynamic and isotherm model in batch mode.

Materials and methods implemented to carry out this work are the focus of the chapter 3. This chapter is included into the thesis in order to extent and detail the experimental section of publications, thus facilitating repeatability and further research in the application field.

The fourth chapter is devoted to the presentation of experimental results and their discussion; it compromises the following tree publications articulated the biosorption of heavy metal onto free and immobilized *luffa cylindrica*.

The conclusion summarize the main results of this study

Bibliography

[1] - Wei BG, Yang LS, **2010**, *Microchem J*, 94:99–107.

[2] - Wang J, Chen C, **2006**, *Biotechnol Adv*, 24(5):427-51.

[3] - Abhari PS, Manteghi F, Tehrani Z , **2020**, *Nanomaterials*, 10 (9):1647.

[4] – Agarwal A, Upadhyay U, Sreedhar I, Singh SA, Patel, CM , **2020**, *J. Water Process. Eng*, 38: 101602.

Introduction

[5] - Moreira VR, Lebron YAR, Freire SJ, Santos LVS, Palladino F, Jacob R S , **2019**, Microchemical Journal 145: 119-129.

[6] - Vidal CB, Melo DQ, Raulino GSC, da Luz AD, da Luz C, Nascimento RF , **2016**, Desalin. Water Treat 57(19): 9001–9008.

[7] - Kumar KV, **2006**, J. Hazard. Mater, 136: (21) 197-202.

Chapter I:

Literature review

I.1. Introduction

With the development of industrial activities an increasing amount of toxic effluents containing organic and inorganic substances especially heavy metal is directly or indirectly released into the environment, either freshwater or marine environment [1]. The metal ions pollution has become one of the major environmental problems nowadays. In Algeria, the discharges, leaks and waste resulted from neo-industrial activity act as sources of metal ions pollution for different water systems, affecting 2.9% of coastal waters, 6.7% of rivers and 64.2% of groundwater [2]. Facing with this problem, it has been growing concern about the toxic impacts of metal ions in the aqueous media and the sequestration of these toxic substances from water and wastewater. Heavy metal pollution in waste water will be introduced from the following elements, starting with the toxicity and origin of metal effluents, then an overview of their treatment technology, then introduction of a new biosorbent using native and immobilized *Luffa cylindrica* in *Chlorella pyrenoidosa* (microalgal) for metals removal from industrial wastewaters.

I.2. Heavy metals pollution

Heavy Metal pollutants are among the major toxic and persistent effluents in aquatic environment [3]. Metal pollution occurs directly or indirectly by effluent outfalls from neo-industries. Unfortunately, many aquatic ecosystems face metal ions concentrations that exceed aqueous media criteria designed to preserve the natural environment, humans and animals. Most metals are transition substances with incompletely filled *d* orbitals. These orbitals allow heavy metal cations in solutions with the ability to form complex substances which may or may not be redox-active. Heavy Metal cations play a major role as groups of trace elements in sophisticated bio-chemical reaction, though some of them are necessary for many organisms. Consequently, heavy metals are extremely dangerous to plants, animals and human and because of their augmentation and accumulation (over at various limiting concentration levels depending of the heavy metal). The toxicity of metal ions occurs even in very low concentrations of about 1.0-10 ppm, which are classified based on toxicity are presented in table. I.1 [4].

Tab. I.1: Classification of heavy metals based on toxicity.

Heavy metals	Toxicity
Mn, Fe, Mo	Low toxicity
Cr , Zn, Ni, V, Co, W, Cu	Average toxicity
As, Ag, Sb, Cd, Hg, Pb, U	High toxicity

Metal ions can be accumulated into food chains and concentrated in aquatic media to a level that impacts their physiological state. Due to their non-biodegradable characteristics, carcinogenicity and toxicity to living organisms, many heavy metals are regarded as priority effluents [5]. Among them, the toxic heavy metals of particular concern in treatment of industrial wastewaters include, copper, lead, cadmium, arsenic, chromium, mercury, Selenium, zinc, nickel. Some of the common sources and impact of heavy metals are present in table. I.2 [5].

Tab. I.2 (a): Sources and impact of heavy metals.

Sl.	Heavy metals	Sources of Metal contamination	Adverse health effects	Allowed limits WHO (ppm)
1	Copper	Dental products, Corrosion of household, plumbing, erosion of natural deposits , alloy, electroplating,	Gastrointestinal (GI) irritation and Liver toxicity, lung neoplasms, , kidney damage	1.0-1.3
2	Lead	Lead-acid battery production, Plumbing systems , pigment, pesticides industry	Delayed development in children, anemia, vomiting, kidney damage, high blood pressure Memory loss and effect on central nervous system,, gastrointestinal diseases,	0.005-0.015

Tab. I.2 (b): Sources and impact of heavy metals.

Sl.	Heavy metals	Sources of Metal contamination	Adverse health effects	Allowed limits WHO (ppm)
4	Arsenic	Electroplating, industrial fuel, mining, battery manufacturing Erosion of natural deposits, runoff, pigment	Cancer, skin damage, circulatory system problems	0.01
5	Chromium	Steel industry, Electro plating, pulp mills, erosion leather tannery facilities, steel welding, paints, chromate and ferrochrome production	Diarrhea, skin and eye irritation, kidney dysfunction, ulcer, irritation in respiratory track Allergic dermatitis, hemolysis, renal failure	0.05-0.25
6	Antimony	Petroleum refineries, fire retardants, ceramics, electronics, solder	Increased blood cholesterol, decreased blood sugar	0.006
7	Mercury	Erosion of natural deposits, discharge from refineries and factories, runoff from landfills, croplands	Hypersensitivity, fever, vomiting, neurasthenia	0.002
8	Mercury	Petroleum refineries, erosion, discharge from mines	Hair and finger nail loss, red skin, numbness in fingers and toes, caustic burns, circulatory problems	0.01-0.05
9	Zinc	Electroplating industry, galvanized metal surfaces, motor oil and hydraulic fluid, tire dust	Corrosive to skin and eye, zinc pox, sweet taste, throat dryness, cough, weakness, generalized aching, chills, fever, nausea, vomiting	5

Based on that, the sequestration of heavy metals from aqueous media has attracted attention by researchers, for the preservation of public health and ecosystems, so, it is essential to remove these toxic metals before discharge.

I.3. Heavy metals pollution from industrial wastewater of HRM (Algeria)

The wastewater from a petroleum industry consists a wide variety of pollutants like petroleum hydrocarbons, mercaptans, oil and grease, phenol, ammonia, sulfide, inorganic and other organic compounds. All these compounds are present as very complex form in discharged water of petroleum industry, which are harmful for environment directly or indirectly.

The current study was investigated to establish the concentration of some heavy metals in samples of wastewater obtained from the boosting of SONATRACH in HASSI R'MEL. (Algeria). Clogged wastewater channels increase overflow of the wastewater into the neighboring areas through surface water when it rains. The analysis of the wastewater is given in table. I. 3. Based on this analysis, we chose Pb (II), Cu (II), Zn (II) and Cr (VI) for this research for removing from industrial wastewater (SONATRACH) using local biosorbents. Consequently, the present study aims to highlight the impact health risks that may happen when humans, crops and livestock become exposed to the toxic metal contaminated soils and wastewater. It is evident that the results obtained from the research will justify and inform on the need to adopt effective wastewater management containing prioritizing on good wastewater treatment and reuse in Algeria major urban areas.

Tab. I.3: Characteristics of wastewater of SONATRACH in HASSI R'MEL. (Algeria).

Characteristics	value
pH	5.3
Lead (ppm)	226.4
Zinc (ppm)	11.2
Chromium (ppm)	5.3
Copper (ppm)	7
Mercury (ppm)	0.001
Aluminum (ppm)	0.001

I.4. Methodologies for removal of heavy metal ions from wastewater

Various conventional methods have been used for the treatment of toxic metal pollutions in different contaminated water, which usually include membrane filtration (nanofiltration, reverse osmosis, etc.), chemical precipitation (sulfides, hydroxides, etc.), ion exchange, solvent extraction and adsorption (Fig. I.1). Table I.4 compares selective technologies used [6]. Chemical precipitation and electrochemical treatment are unsuccessful, especially when dissolved metal concentration in aqueous solution is inferior to 100 ppm, and also produce large amount sludge required to removal with great difficulty. Ion exchange, membrane filtration and solvent extraction are expensive when treating large quantity of wastewaters containing dissolved metal at low concentration, so they cannot be applied at large scale [7]. In addition, most of these methods have some inconvenient such as complicated treatment systems, high energy and cost use. Adsorption has considered best alternatives technique for such situations due to cost-effective process and ease of operation [8]. Various materials have been used as adsorbents for the sequestration of metal ions. In particular, activated carbon has been developed as an effective adsorbent for the removal of toxic metal contaminants [9]. Its usefulness derives mostly from its large micro-pore and meso-pore volumes and the resulting high adsorptive capacity, high surface area, and degree of surface reactivity [10]. Furthermore, activated carbon is expensive, and it is relatively difficult to elute heavy metals from it and recycle the activated carbon as adsorbent due to the strong interaction between adsorbent-adsorbate. Moreover, the application of expensive synthetic adsorbent also has similar problems like economic or technical constraints [11]. Thus, the main study focus is studying for low-cost, regenerable and adsorbent materials which are capable of isolating metal ions from wastewaters [12]. In general, the adsorbents can be used as “low cost” if it needs little processing, is abundant in environment or waste material from industry [13]. For that reason, hundreds of researches on the conducted of low-cost material have been published. Natural substances, industrial byproducts and agricultural wastes, have been studied as adsorbents for the toxic metal wastewater treatment. Several research are available that discuss the applicant of low-cost adsorbents for the removal of heavy metals from aqueous solution, including zeolites, chitosan, clay, peat moss, coal, fly ash, natural oxide and industrial waste and so on [14].

Tab. I.4: Removal methods of metal ions from wastewaters.

Method	Advantage	Disadvantage
Chemical precipitation	Simple Inexpensive Most of metals can be removed	Large amounts of sludge produced Disposal problems
Chemical coagulation	Sludge settling Dewatering	High cost Large consumption of chemicals
Membrane process and ultra filtration	Less solid waste produced Less chemical consumption High efficiency (>95% for single metal)	High initial and running cost Low flow rates Removal (%) decrease with the presence of other metals
Electrochemical methods	Metal selective No consumption of chemicals Pure metals can be achieved	High capital cost High running cost Initial solution pH and Current density
Ion-exchange	High regeneration of materials Metal selective	High cost Less number of metal ions removed
Adsorption using activated carbon	Most of metals can be removed High efficiency (>99%)	Cost of activated carbon No regeneration Performance depends upon adsorbent
Adsorption using natural zeolite	Most of metals can be removed Relatively less costly materials	Low efficiency

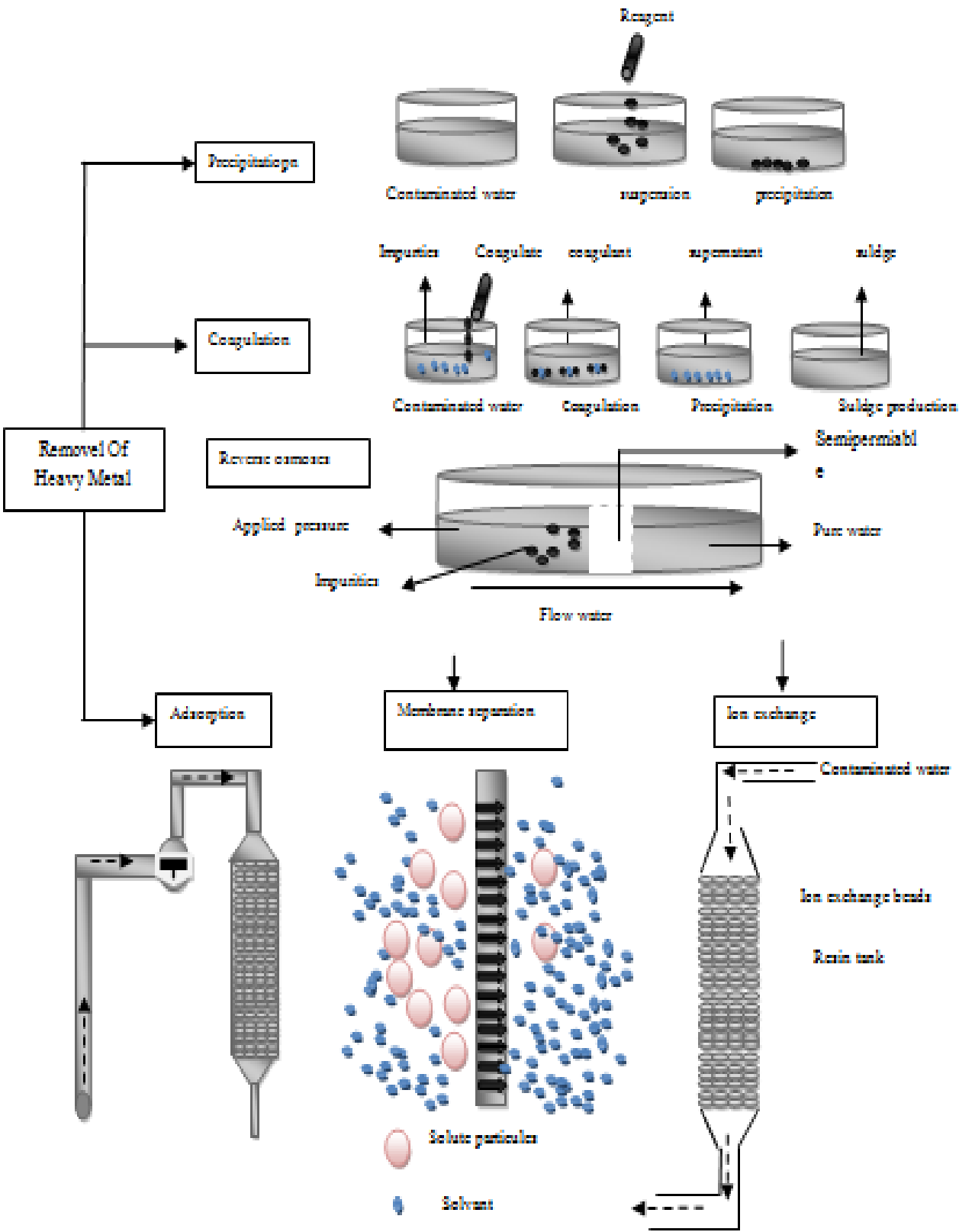


Fig. I.1: Various techniques of heavy metal removal from effluent.

I.5. Heavy metal removal from wastewater using various biosorbents

In recent times, applying biotechnology in controlling and sequestering metal ions pollution has been attract much attention, and becomes hot topic in metal pollution field because of its potential application [15]. An alternative technique is the biosorption, which can be used as the removal of metal or metalloid elements, compounds and particulates from solution by several biomaterials [16]. According to the heavy metal classification by Pearson [17] as well as by Richardson and [18], Nieboer metal affinity for ligands is assumed and illustrated in Table. I.5 [19]. The symbol (R) represents an alkyl radical. Class A metal ions selected to bind the ligands of (I) via oxygen. Class B metal ions elucidate high affinity for type (III) of ligands, but also form adhesive binding with the ligands with type (II) of ligands.

On the report of the Hard and Soft Acid Base Principle “HSAB principle”, hard ions which attach F^- strongly, such as Na^+ , Mg^{2+} , Ca^{2+} may form stable bonds with $=C=O$, $R-COO^-$, OH^- , HPO_4^{2-} and CO_3^{2-} , which are oxygen-containing ligands. whilst soft ions like heavy metal ions such as Pb^{2+} and Hg^{2+} form strong bond with SH^- , CN^- , $-NH^-$, $R-S^-$, and imidazole, which are groups including sulfur and nitrogen atoms. Hard ions mostly show ionic form of binding, while soft ions binding reveal a more covalent degree [20]. Intermediate metal ions such as Cu^{2+} , Ni^{2+} and Zn^{2+} are less toxic, and can act as soft or hard ions depending on the nature of the ligands or chemical groups present in aqueous media.

Heavy Metal biosorption by biomaterials mainly depend on the functional groups. The major important of these groups including carboxyl, carbonyl (ketone), sulfonate, sulfhydryl (thiol), amide, thioether, amine, amine imidazole, secondary amine, phosphonate and phosphor-diester are mentioned by Volesky [21]. Table. I.6 offers some functional groups and classes of organic compounds in biomaterial. The symbol (R) is shorthand for residue, and its placement in a structure indicates that what is attracted at that site varies from one substance to another [22].

The biosorption of metal ions by biomaterials might be attributed that these biomass, mainly composed of lipids, proteins and polysaccharides have hydroxyl, carboxyl, phosphate, sulfhydryl, amino groups and carbonyl, can bind metals involving valance forces via sharing or exchange of electrons between biomass and metal ions (Fig. I.6). However, these biomaterials can also passively bind heavy metals though various physico-chemical mechanisms. Mechanisms responsible for biosorption phenomena, although understood to a limited extent, could be one or a combination of complexation, ion exchange, coordination, adsorption, microprecipitation and electrostatic interaction. There are some evidences to confirm that the N-, S-, O-, or P- containing

Chapter I: Literature review

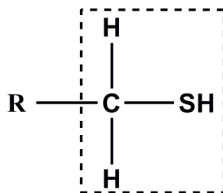
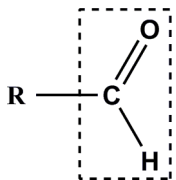
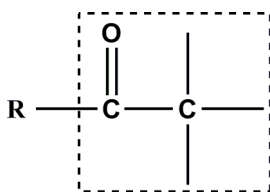
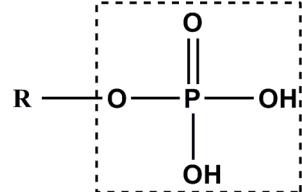
functional groups participate directly in binding some metals [23].

Tab. I.5: The ligands present in biological systems and classes of metals.

Ligand class	Ligands	Metal classes
I: Ligands Preferred to Class A	F^- , O^{2-} , OH^- , CO_3^{2-} , SO_4^{2-} , $ROSO_3^-$, NO_3^- , HPO_4^{2-} , PO_4^{3-} , ROH , $RCOO^-$, $C=O$, ROR	Class A: Li, Be, Na, Mg, K, Ca, Sc, Rb, Sr, Y, Cs, Ba, La, Fr, Ra, Ac, Al. Lanthanides, Actinides
II: Other Important Ligands	Cl^- , Br^- , N_3^- , NO_2^- , S^{2-} , NH_3 , N_2 , RNH_2 , R_2NH , R_3N , $=N-$, $-CO-N-R$, O_2 , O_2^- , O_2^{2+}	Borderline ions: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Cd, In, Sn, Sb, As
III: Ligands preferred to Class B	H^- , I^- , R^- , CN^- , CO , S^{2-} , RS^- , R_2S , R_3As	Class B: Rh, Pd, Ag, Ir, Pt, Au, Hg, Tl, Pb, Bi

Tab. I.6: The representative functional groups and class of organic compounds in biomass.

Formula of functional group	Name	Class of compounds
$R^* - \boxed{O - H}$	Hydroxyl	Alcohols, carbohydrates
$R - \boxed{\begin{array}{c} O \\ // \\ C \\ \backslash \\ OH \end{array}}$	Carboxyl	Fatty acids, proteins, organic acids
$R - \begin{array}{c} H \\ \\ C - \boxed{NH_2} \\ \\ H \end{array}$	Amino	Proteins, nucleic acids
$R - \boxed{\begin{array}{c} O \\ // \\ C \\ \backslash \\ O - R \end{array}}$	Ester	Lipids

	Sulfhydryl	Cysteine (amino acid), proteins
	Carbonyl, terminal end	Aldehydes, polysaccharides
	Carbonyl, internal	Ketones, polysaccharides
	Phosphate	DNA, RNA, ATP

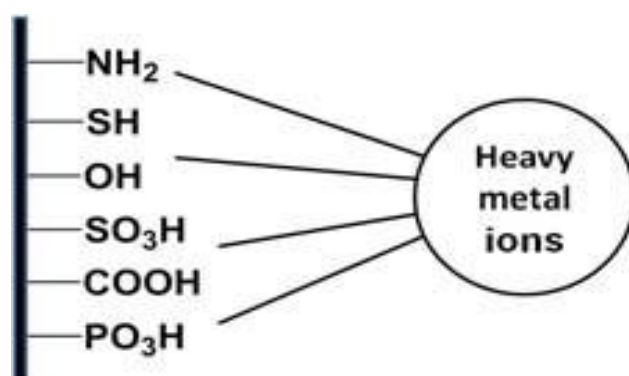


Fig. I.2: Possible binding modes between functional groups and metal ions.

A large amount of biomaterials types has been investigated as biosorbents for the sequestration of heavy metals, for their metal ions binding capacity under several conditions. Waste biomasses are considered good alternatives as low-cost biosorbents for the sequestration of metal ions from low strength contaminated water due to quite efficient adsorption rate. A vast array of low-cost waste biomass from large-scale industrial has also effectively been e

employed as biosorbents for the sequestration of heavy metals from aqueous media [24]. Although many biomasses can bind heavy metals, only those with sufficiently high metal ions binding capacity and selectivity for metals are suitable for use in a full-scale biosorption system [25]. Table .I.7 gives the complete overview of all the recent studies where biosorbents were developed for heavy metal removal and subsequent subsections point out the major findings and trends that were realized during the composition of this table .

Among the several biosorbents used, cellulosic waste biomasses are the major abundant for the sequestration of heavy metals, which involve agricultural waste. Cellulosic waste biomaterials usually are composed of cellulose and lignin as mainly constituents and may also involve other polar groups of lignin, which involves alcohols, ketones, aldehydes, phenolic, carboxylic and other group. These functional groups have the capacity to extent to bind metal ions by donation of an electron pair from these functional groups to complexes with the heavy metals in liquid phase [26]. As a kind of abundant natural source of lignocelluloses are *Luffa Cylindrica* biomaterials which are currently being investigated as biosorbents for the sequestration of heavy metal ions from solution and wastewater, which are relatively abundant and low-cost materials. *Luffa cylindrica* used as effective biosorbents, either directly or after chemically or biologically activation, to remove metal ions due to their high contents of hydroxyl, carboxyl, amino and sulfur-containing functional groups (Table .I.8) [27]. This biosorbent has showed significant potentials of sequestering metal ions from aqueous media. Considered the importance of *luffa Cylindrica* biomaterials as biosorbents for the removal of metal ions from wastewater, an overview of summarized information concerning the application of *luffa Cylindrica* materials based on recent research is presented in the following part and their biosorption capacity, influencing factors of the metal ions biosorption process, the biosorption mechanism and the favorable factor, etc., are here discussed.

Chapter I: Literature review

Tab. I.7 (a): Performance of various for heavy metal removal in batch process.

Metal removed	Source/ Effluent	Biosorbent Composition	Modification	Synthesis	Process Parameter	rate or removal capacity (mg/g)
Cr (VI)	Lab Solution	Ficus auriculata	Unmodified	Collect→was h with DDDW →air dry →Oven dry →crush	T ~30 °C P-atm AD- 0.5 g/L Rotation: 120 rpm time: 1 h pH:2	94.30 %
Pb(II) Cd (II) Mn (II) Co (II) Ni (II)	Metal industry	Peanut Husk	Washed with HCl and NaOH	Collect→ Washed with tap water and DDDW→ Oven dried →Grind→ Sieve→ Wash with DDDW, HCL and	T- P-1 atm AD-5 g/L Shaking:250 rpm time: 1 h pH: ~6	Pb(II):27.03 Cd(II):11.36 Mn(II):14.29 Co(II):6.10 Ni(II):56.82
Cu (II) Ni (II) Zn (II) Pb (II)	Lab Solution	Coconut Husk	Unmodified	Cut into small pieces→	T ~30 °C P- atm AD- 1 g/L Rotation:120 rpm time: 40 min pH:6	Cu(II):443.3 Zn (II):338.0Ni (II):404.5 Pb (II):362.2
Cr(VI)	Lab Solution	Milled olive stones	Unmodified	4 Separate olive oil from solid	T- P-atm AD- 10 g/L Rotation:120 rpm time: 2 h pH:2	Cr(VI):2.34
Pb (II) Cu (II) Zn (II)	Lab Solution	Raw sugarcane bagasse	Pre-treated with NaOH followed by epoxidation amination and sulfonation reaction	pre-treated with NaOH in homogenizer → add epichlorohydrin and ethanol → wash with	T-35C- 49C P-atm AD-1.25 g/L Rotation:120 rpm time: 50 min pH:5	Pb(II):558.9 Cu(II):446.2 Zn(II):363.3

Tab.
I.7:

Chapter I: Literature review

Tab. I.7 (b): Performance of various for heavy metal removal in batch process.

Metal removed	Source/ Effluent	Biosorbent Composition	Modification	Synthesis	Process Parameter	rate or removal capacity (mg/g)
Cr (VI)	Lab Solution	4 Olive stone (OS) And Date pit (DP)	Grafting using DETA and crosslinking with epichlorohydrin	NaOH + epichlorohydrin→ Mix →filter→Wash with DDDW→Oven dry → Mix75 mL of NaOH+12.5 mL of DETA + dried biosorbent →wash with DDDW →Dry → Store	T~30C P-atm AD- 11 g/L(OS) and 10 g/L (DP) Rotation: time: pH:2	(OS) Cr(VI): 53.31 (DP) Cr (VI):82.63
Cu (II) Cd (II) Pb (II)	Lab Solution	Oiltea Shell	Unmodified	Collect→ Wash with	T~25C P-atm AD:2 g/L Shaking: 130 rpm time:6 h pH:5 (Cu2+) & 9(Cd2+)	Pb(II):22.4 Cu(II):12.1, Cd(II):14.2
Pb (II) Cu (II) Ni (II)	Lab Solution	Casuarina equisetifolia leaves	Treated with sodium aluminate	Collect→crush and sieve →Wash with DDDW→Add aq. sol.of sodium aluminate→ filter→Wash with DDDW→Oven dry →store in desiccator.	T~25C P-atm AD:18.89 g/L Shaking: 130 rpm time:104.7 min pH:4	Cu(II):44.0 Ni(II):39.0 Pb(II):28.0

I.6. Heavy metal removal from wastewater using *Luffa Cylindrica*

Proximate analysis of *Luffa Cylindrica* shows it to contain 37.81% carbohydrate, 55.78% fiber, 4.2% protein, 1.04% ash and 1.08% lipid [28]. The fibers of LC are principally made up of cellulose, hemicelluloses and lignin with can range, respectively, from 50-60%, 25-29% and 10-11% [29]. Chemical composition and the breakup of main constituents of the ligno-cellulosic fibers have not been studied in much detail, but these researchers have reported hemicelluloses in LC to contain xylose, arabinose, galactose, and glucose sugars in the molar proportions of 1:95:2:1, and 10% uronic acid. Another research has shown the fibers to be made up of 79.5% hollocellulose, 58.3% α -cellulose, 15.0% pentosans, 13.6% lignin and 1.8% ash [30]. The surface functional group analysis of the fibers indicated the function groups to be predominantly acidic; strongly acidic (carboxylic group) 0.52 meq/g, weakly acidic (lactonic, enolic, carboxylic) 0.53 meq /g, and phenolic 0.88 meq /g, whereas the magnitude of the basic functional groups of 0.13 meq /g was very low [34]. The predominance of the acidic groups on the surface of *Luffa Cylindrica* is due to the polar functional groups of these acidic groups are available to involve in ion exchange reactions. The *Luffa cylindrica*, morphologically, is the placental cushion of the ovary bearing seeds, which is obtained by separating it from the outer soft integuments of the matured dried fruit and seeds. It consists of peripheral portion, a core portion and three hollows in the cross section. The cushion shows a multilayered mesh with pore size from 2.0 to 4.0 mm, overlapping each other. The cushion of LC is the lignified endocarp, made up of an organized fibrous network. The fibers are of different sizes varying from 150 to 800 μm . The LC is characterized by a remarkable lightness, owing to its honeycomb conformation of the intermingled fibers. Specific gravity of LC is 0.92 g/cm^3 . The LC sponge has specific surface area of 840 m^2/m^3 and empty volume of 92%.[35]. *Luffa cylindrica* is light, made up of an interconnecting void within an open network of biomaterial [36]. On account of the random lattice of small cross sections coupled with high porosity (79-93%), low density (0.02-0.04 g/cm^3), and high specific pore volume (22-29 cm^3/g) [37]. In addition, the large void spaces that provide for the growth of immobilized cells fixed with high densities offer the prospect of high metabolite yields. *Luffa Cylindrica* is thus a suitable bio-structure for cell immobilization and biosorption process activities [38].

Owing to the advantages available in the bio-structure of LC, several studies have been reported on the utilization of this unique fibrous structure in many biotechnological techniques, especially for

Chapter I: Literature review

the immobilization of diverse kinds of cells (including filamentous and microalgae, yeasts, fungi, higher plants, bacteria, rat, and human cell types) [39]. In all of these researches the potential of cells immobilized in LC performed more than free suspended cultures and other immobilization bio-matrices. The LC-immobilized cells have effectively performed in the elimination and biodegradation of toxic heavy metals, chlorinated chemicals and dyes [40]. These processes have been also utilized in the bio-degradation of a herbicide and a fungicide. *Luffa Cylindrica*, further, was noted to be a good biosorbent for the amelioration of bio-films for the wastewaters treatment and industrial effluents.

Based on that, the *Luffa Cylindrica* is a more suitable material for cell immobilization. The LC has been utilized to immobilize cells belonging to various classes of organisms in a bioactive state. LC-immobilized have employed to produce a variety of bio-chemicals, in the remediation of wastewaters through sorption of metals and in the bio-degradation of herbicide and fungicide. It is deduced in summation that *Luffa Cylindrica* is an eco-friendly, renewable, and a competitive biomaterial for cell immobilization

Tab. I.8 (a): Comparative Summary of Biosorption of Metals by *Luffa Cylindrica*, and *Luffa*-Immobilized Fungi and Algae for the Remediation of Contaminated Water.

Biosorbent /metal system	Contact time (h)	C (mg/L)	Q_{max} (mg/g)	Refs
Ca-alginate beads/ Cd^{2+}	0.5	10-500	88	[41]
<i>C. sorokiniana</i> / Ni^{2+}	0.5	10-300	58.7	[42]
<i>C. sorokiniana</i> / Cd^{2+}	0.083	10-150	116.5	[43]
LC- <i>C. sorokiniana</i> / Pb^{2+}	0.25	10-300	112.8	[44]
LC- <i>C. sorokiniana</i> / Cr^{3+}	0.33	10-300	69.26	[45]
LC- <i>Synechococcus</i> / Cd^{2+}	0.083	2-200	47.73	[46]
LC/ Cd^{2+}	1	10-500	10.5	[47]

Tab. I.8 (b): Comparative Summary of Biosorption of Metals by *Luffa Cylindrica*, and *Luffa*-Immobilized Fungi and Algae for the Remediation of Contaminated Water.

Biosorbent /metal system	Contact time (h)	C(i mg/L)	Q _{max} (mg/g)	Refs
LC-P. chrysosporium /Cr ³⁺	0.25	10-300	74.0	[48]
LC -P. chrysosporium /Cd ²⁺	1	50-200	59.9	[49]
LC -P. chrysosporium/ Ni ²⁺	1	10-300	71.3	[50]
LC-P. chrysosporium/Cr ³⁺	1	10-500	76.95	[51]
LC-P. chrysosporium/ Cd ²⁺	0.25	10-500	88.16	[52]

I.7. Research main objectives

Based on this analyze mentioned above, the main objective of this study was to investigate heavy metals removal from aqueous solutions by using native and immobilized *luffa cylindrica* under different experimental conditions. In this regard, biosorption of heavy metals from aqueous media is here investigated under various conditions such as contact time, pH of solution, biosorbent dosage and initial metal concentration to achieve the optimized conditions. Moreover, the kinetics, thermodynamic and isotherm models (different models involved and new mathematical model was developed in this study) are carefully studied to understand the biosorption mechanism.

Bibliography:

- [1] - Farhan SN, Khadom AA , **2015**, Int J Ind Chem, **6**: 119–130.
- [2] - Abhari PS, Manteghi F, Tehrani Z , **2020**, Nanomaterials, 10 (9):1647.
- [3] - garwal GS., Bhuptawat HK., Chaudhari S, **2006**, Bioresour. Technol, 97: 949-956.

Chapter I: Literature review

- [4] - Bhatnagar A, Kaczala F, Hogland W, Marques M, Paraskeva CA, Papadakis VG, Sillanpaa M, **2014**, Environ. Sci. Pollut. Res, 21: 268-298.
- [5] – Edgar J, Simpson W, **1975**, Textile Research Journal, 45 (4): 281-284.
- [6] - Hsieh CY, Tsai MH, Ryan DK, Pancorbo OC, **2004**, Sci. Total Environ, 320: 37-50.
- [7] - Hastuti B, Mudasir D, Triyono S, **2013**, Int. J. Chem. Eng. Appl, 4: 349-353.
- [8] - Nieboer E, Richardson D S, **1980**, Environmental Pollution 1 (Series B) : 3-26.
- [9] – Ahalya N, Ramachandra T, Kanamadi R, **2003**, Res. J. Chem. Environ, 7 (4): 71-79.
- [10] – Demirbas A, **2008**, Journal of Hazardous Materials, 157 (2–3): 220-229.
- [11] – Sud D, Mahajan G, Kaur M P, **2008**, Bioresource Technology, 99 (14) : 6017-6027.
- [12] – Basci N, Kocadagistan E, Kocadagistan B, **2004**, Desalination, 164 (2) : 135-140.
- [13] – Farooq U, Kozinski JA, Khan MA, Athar M, **2010**, Bioresource Technology, 101 (14): 5043-5053.
- [14] – Ahmaruzzaman M, Gupta V K, **2011**, Industrial & Engineering Chemistry Research, 50 (24): 13589-13613.
- [15] - Vázquez G, Antorrena G, González J, Doval MD, **1994**, Bioresource Technology, 48 (3): 251-255.
- [16] – Shukla SS, Yu LJ, Dorris KL, Shukla A, **2005**, Journal of Hazardous Materials, 121: (1–3), 243-246.
- [17] – Bulut Y, Tez Z, **2007**, Journal of Environmental Sciences, 19 (2): 160-166.
- [18] – Crini G, **2005**, Progress in Polymer Science, 30 (1): 38-70.
- [19] - Yang TC, Zall RR, **1984**, Industrial & Engineering Chemistry Product Research and Development, 23 (1): 168-172.
- [20] – Boddu V.M, Abburi K, Talbott JL, Smith ED, Haasch R, **2008**, Water Research, 42 (3): 633-642.

Chapter I: Literature review

- [21] – Tran HV, Tran LD, Nguyen T N, C **2010**, Materials Science and Engineering, 30 (2): 304-310.
- [22] – Li N, Bai R, **2005**, Separation and Purification Technology, 42 (3): 237-247.
- [23] – Sun X, Peng B, Ji Y, Chen J, Li D, **2009**, AIChE Journal, 55 (8) : 2062-2069.
- [24] – Zhou L, Xu J, Liang X, Liu Z, **2010**, Journal of Hazardous Materials, 182 (1–3): 518-524.
- [25] - Fujiwara, K, Ramesh A, Maki T, Hasegawa H, Ueda K, **2007**, Journal of Hazardous Materials, 146 (1–2): 39-50.
- [26] - Rouse JG, Van Dyke ME, **2010**, Materials, 3 (2): 999-1014.
- [27] – Agarwal A, Upadhyay U, Sreedhar I, Singh SA, Patel, CM , **2020**, J. Water Process. Eng, 38: 101602.
- [28] - Dąbrowski A, Hubicki Z, Podkościelny P, Robens E, **2004**, Chemosphere, 56 (2): 91-106.
- [29] - Balkose D, Baltacioglu H, **1992**, Journal of Chemical Technology and Biotechnology, 54 (4): 393-397.
- [30] - Shinoda K, Kikuyotani S, **1978**, Chem. Econ. Eng. rev, 10 (7): 43-47.
- [31] - Guthrie R, Laurie S **1968**, Australian Journal of Chemistry, 21 (10), 2437-2443.
- [32] - Brady P R, Freeland GN, Hine R J, **1974**, Hoskinson RM, Textile Research Journal, 44 (10): 733-735.
- [33] - Freeland GN, Hoskinson RM, Mayfield RJ, Environmental Science & Technology, **1974**, 8 (10): 943-944.
- [34] - Wei BG, Yang LS, **2010**, Microchem J, 94:99–107.
- [35] - Edgar J, Simpson W, **1975**, Textile Research Journal, 45 (4): 281-284.
- [36] - Iqbal M, Zafar SI, **2000**, Pak J Food Sci, 10:6-9.
- [37] - Kar S, Swain MR, Ray RC, **2009**, Appl Biochem Biotechnol, 152:177-188.
- [38] - Meagher MM, Reilly PJ, **1989**, Biotechnol Bioeng, 34: 689-693.
- [39] - Polakovic M, Bryjak J, **2004**, Biochem Eng J, 18: 57-64.
- [40] - Crabb WD, Shetty JK, **1999**, Curr Opin Microbiol, 2: 252-256.

Chapter I: Literature review

- [41] - Stamm AJ, Baechler RH, **1960**, Forest Prod J, 10:22-26.
- [42] - Norouzian D, Akbarzadeh A, Scharer JM, Young MM, **2006**, Biotechnol Adv, 24: 80-85.
- [43] - Federici RG, Federici F, Petruccioli M, **1990**, Biotechnol Lett, 12: 661-6.
- [44] - Kuek C, **1991**, Appl Microbiol Biotechnol, 35: 466-470.
- [45] - Slokoska LS, Angelova MB, **1998**, Zeitschrift fur Naturforschung, 53: 968-972.
- [46] - Satyanarayana T, Noorwez SM, Kumar S, Rao JLUM, Ezhilvannan M, Kaur P, **2004**, Biochem Soc Trans, 32: 276-279.
- [47] - Balasundaram B, Pandit AB, **2001**, Biochem Eng J, 8: 251-256.
- [48] - Marques LLM, Buzato JB, Celligoi MAPC, **2006**, Braz Arch Biol and Technol, 49: 873-880.
- [49] - Georgiev DI, Minkova KM, Petkova RA, **1987**, Biol Physiol, 40: 99-100.
- [50] - Vignoli JA, Celligoi MAPC, Silva RSF, **2006** Process Biochem, 41: 240-243.7
- [51] - Vignoli JA, Celligoi MAC, Silva RSF, Barros M, **2006**; BioTechnol, 49: 683-687.
- [52] - Amin HAS, Mohamed SS, **2012**, J Molecular Catalysis B: Enzymatic, 78: 85-90.

Chapter II:

Adsorption

II.1. Introduction

Adsorption process is considered as one of the most used separation and purification processes, in which adsorption occurs by the formation of the physical or chemical bonds between a porous solid medium and a mixture of liquid [1]. By taking into consideration the equilibrium data and the adsorption properties of both the adsorbent and the adsorbate, adsorption isotherm models can describe the interaction mechanisms between the adsorbent and the adsorbate at constant temperature. Therefore, understanding modeling of the equilibrium data is a very essential way of predicting the adsorption mechanisms of various adsorption systems. This chapter discusses the adsorption phenomena (kinetics and thermodynamic) and the guidelines using mono-parametric isotherm models. The aim of this chapter is to establish criteria for choosing the optimum isotherm model through a critical review of different adsorption models and the use of various mathematically error functions such as linear regression analysis, nonlinear regression analysis, and error functions for adsorption data optimization.

II.2. General definition of adsorption

Adsorption is a process in which a substance (adsorbate), in gas or liquid phase, accumulates on a solid surface. It is based on the capability of porous materials with large surfaces to selectively retain compounds on the surface of the solid (adsorbent). There are two types of adsorption; physical and chemical adsorption [2].

II.2.1. Physical Adsorption

Physical adsorption is achieved by Van der Waals forces, dipole interactions, and hydrogen binding. There is no electron exchange between adsorbent and adsorbate. Because there is no activation energy required for physical adsorption, the time needed to reach equilibrium is very short. Physical adsorption is a non-specific and a reversible process [3].

II.2.2. Chemical Adsorption

Chemical adsorption results from the chemical link between adsorbent and adsorbate molecule, therefore it is specific as well as irreversible and chemical as well as electronic properties of adsorbent are changed. Binding between adsorbent and adsorbate by covalent bond is called weak chemical adsorption, and that by ionic bonds is called strong chemical adsorption [4].

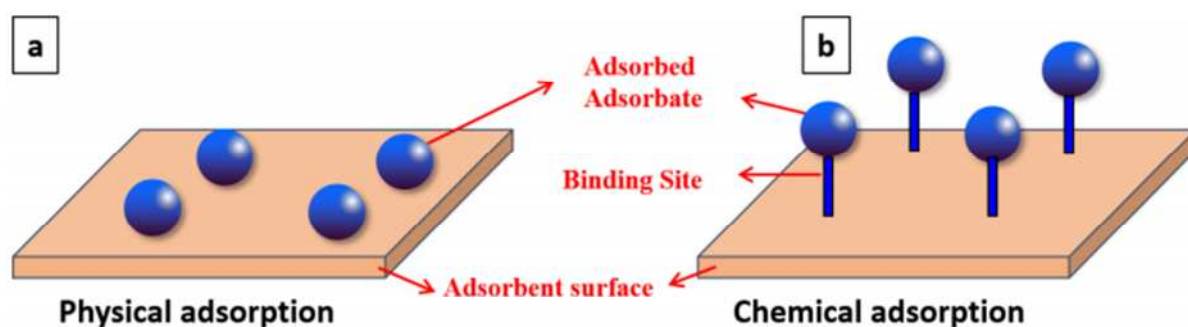


Fig. II.1: Illustration of interaction between adsorbate and adsorbent surface. Figures (a) and (b) are the physical (a) and the chemical (b) adsorption.

II.3. Adsorption Mechanisms

The adsorption process of the adsorbate molecules from the bulk liquid phase into the adsorbent surface is presumed to involve the following stages (Fig.II-1):

1. Mass transfer of the adsorbate molecules across the external boundary layer towards the solid particle.
2. Adsorbate molecules transport from the particle surface into the active sites by diffusion within the pore-filled liquid and migrate along the solid surface of the pore.
3. Solute molecules adsorption on the active sites on the interior surfaces of the pores.
4. Once the molecule adsorbed, it may migrate on the pore surface through surface diffusion [5].

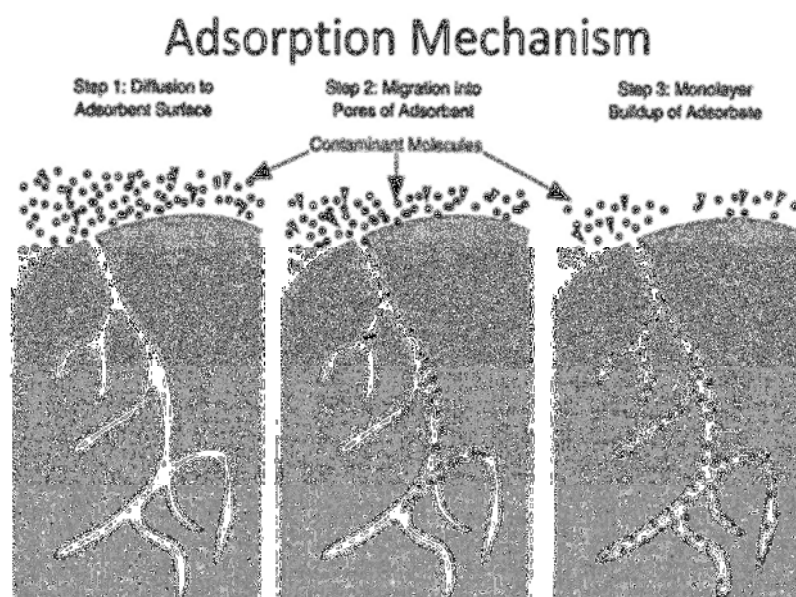


Fig.II.2. Schema of the mechanism of molecule adsorption using microporous adsorbent.

II.4. Adsorption kinetics

Adsorption kinetic expresses the mechanism of the adsorption. The solute sorbate can be transferred from the liquid phase to the surface of the adsorption in several steps, and the combination of one or more steps can be speed control mechanisms. The transfer of adsorbate can be either in the form of mass transfer of the solution surrounding the outside of the adsorbent via the outer boundary layer film, or diffusion of the sorbate molecules into a biosorption zone through solution absorption pores, or by a biosorbent surface diffusion mechanism, or chemical or physical (internal or external). [6]. In this study, pseudo-first order and pseudo-second order kinetics models were applied to investigate the potential speed control steps. Non-linear form and linear form equations of kinetic models are given in Table II.1:

Tab. II.1: Illustration of the linear forms, nonlinear forms and plot of kinetic models analyzed for optimization studies.

Kinetics model	Non-linear form	linear form	Refs
pseudo-first order	$q_t = q_e(1 - e^{-k_1 t})$	$\log(q_e - q_t) = \log q_e - K_1 \cdot t / 2.303$	[7]
pseudo-second order	$q_t = \frac{K_2 q_e^2}{1 + K_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	[8]

Where q_t and q_e is the biosorption capacity (mg/g) at equilibrium and at time t (min), respectively and k_1 (1/min) is the rate constant of pseudo-first order model K_2 (g/mg/ min) is the rate constant of pseudo-second order model.

II.5. Thermodynamic study

The thermodynamic parameters that shall be taken into consideration in order to qualify the adsorption processes are free energy of Gibbs or free adsorption enthalpy ΔG° (kJ / mol) due to the transfer of one mole of solute from the solution to the solid / liquid interface, the adsorption enthalpy; ΔH° (kJ / mol) as well as the adsorption entropy; ΔS° (J / mol / K). These quantities were calculated according to the following equations [7]:

$$\Delta G^\circ = -RT \ln K_c$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$K_c = \frac{as}{ae} = \frac{Ys}{Ye} = \frac{Cs}{Ce}$$

Where K_c is the distribution constant, as is activity of adsorbed metal, ae is activity of metal in solution at equilibrium, Ys is activity coefficient of adsorbed metal, Ye is activity coefficient of Pb (II) in equilibrium solution, Cs is metal adsorbed on CP-LC (mg/g), and Ce is metal concentration in equilibrium solution (mg/L). (ΔH°) (ΔS°) and (ΔG°) are enthalpy (kJ/mol), entropy (J/mol K) and change in Gibbs free energy (kJ/mol), respectively. R is the universal gas constant (8.314 J/mol K) and T is the temperature in Kelvin.

II.6. Equilibrium adsorption isotherm models

One of the fundamental criteria for adsorbent materials utility is its maximal sorption capacity, which is obtained based on the relationship between the mass of sorbate per mass unit of sorbent (mg/g) and the equilibrium concentration of sorbate (mg/L). The best design of the adsorption process requires a mathematical model description of an isotherm under equilibrium conditions. In this regard, several mathematical models of one-, two-, three-, four and five-parameter available for interpreting the experimental data. The parameters of each isotherm can provide insights into the circulation of solute sorption between the sorbent/sorbate phases, the adsorption mechanism, and the affinity of the adsorbent [7]. The linear and nonlinear mathematical equations of isotherm models are given in Table II.2 [8]. In the present study eighteen-different isotherm equations were studied for analyzing the experimental data. These models are: Henry, Langmuir, Freundlich, Temkin, elovich, Fowler-Guggenheim, kiselev, Hill de Boer, Flory-Huggins, Redlich-Peterson, Sips, Koble–Carrigan, Radke-Prausnitz, Toth, Khan, Baudu, Fritz-Schlünder (IV) and Fritz-Schlünder (V).

II.6.1. One-two parameter isotherm models

II.6.1.1. Henry's isotherm model

Henry's isotherm model is considered as the simplest adsorption isotherm model as the partial pressure of the adsorptive gas is proportional to the amount of surface adsorbate. An appropriate fit of the adsorbate adsorption at low concentration is described by Henry's adsorption isotherm model in which all the adsorbate molecules are secluded from their closest neighbors. Consequently, the equilibrium concentrations of the adsorbate in the liquid phase and the adsorbed phases are described by g linear expression of Henry presented as [9]:

$$q_e = KC_e$$

II.6.1.2. Langmuir model

The simplest and still the most useful isotherm, for both physical and chemical adsorption, is the Langmuir isotherm. This model assumes that adsorption is limited to a monolayer: only a single layer of molecules on the adsorbent surface are absorbed, adsorbent surface is homogeneous and adsorption energy is uniform for all sites and there is no transmigration of adsorbate in the plane of the surface. Once a pollutant occupies a site, no further adsorption can take place in that site; the intermolecular attractive forces rapidly decrease as distance rises. There is no interaction between molecules adsorbed on neighboring sites; adsorption on surface is localized, which means that adsorbed atoms or molecules are adsorbed at definite and localized sites. Based on previous research studies, the Langmuir model has the best fitness quality with experimental data among two parameter monolayer adsorption isotherm models. The mathematical expression of Langmuir isotherm models are given as [10]:

$$qe = \frac{q_{max}K_L C_e}{1 + K_L C_e}$$

K_L is the equilibrium constant (L/mg), which is a criterion of the tendency of the adsorbate to adsorb onto the active sites of the adsorbent surface. A larger b value represents higher adsorption energy. The dimensionless constant of the separation factor or equilibrium parameter to predict the adsorption efficiency and usability of the Langmuir equation is determined as [11]:

$$R_L = \frac{1}{(1 + K_L C_0)}$$

where K_L (L/mg) refers to the Langmuir constant and C_0 is denoted to the adsorbate initial concentration (mg/L). In this context, lower R_L value reflects that adsorption is more favourable. In a deeper explanation, R_L value indicates the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

II.6.1.3. Freundlich model

Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. At present, Freundlich isotherm is widely applied in heterogeneous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves. The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. Whereas, a value

below unity implies chemisorptions process where $1/n$ above one is an indicative of cooperative adsorption. The equation of Freundlich isotherm models are given as [12]:

$$q_e = K_F C_e^{(\frac{1}{n_F})}$$

II.6.1.4. Temkin model

Temkin isotherm is the early model describing the adsorption of hydrogen onto platinum electrodes within the acidic solutions. The isotherm contains a factor that explicitly taking into the account of adsorbent–adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies. The Temkin isotherm model is given as [12]:

$$q_e = \frac{RT}{b_T} \ln A_T C_e$$

II.6.1.5. Elovich model

The Elovich is model based on a kinetic principle with the assumption of adsorption sites increasing exponentially with adsorption, which represents multilayer adsorption. The Elovich isotherm model is expressed as [13]:

$$C_e = \frac{q_e}{q_{mE} K_E \exp(\frac{-q_e}{q_m})}$$

II.6.1.6. Fowler-Guggenheim model

The Fowler-Guggenheim isotherm is the simplest equation developed by considering lateral interaction of the adsorbed molecules. The Fowler-Guggenheim model is defined as [11]:

$$K_{FG} C_e = \left(\frac{\emptyset}{1 - \emptyset} \right) - \exp\left(\frac{2W\emptyset}{RT} \right)$$

This isotherm model is predicated on the fact that the heat of adsorption varies linearly with loading. Therefore, if the interaction between adsorbed molecules is attractive, then the heat of adsorption will increase with loading because of increased interaction between adsorbed molecules as loading increases ($W =$ positive). However, if the interaction among adsorbed molecules is repulsive, then the heat of adsorption decreases with loading ($W =$ negative). But when then there is no interaction between adsorbed molecules, and the Fowler-Guggenheim isotherm reduces to the Langmuir equation [11].

II.6.1.7. Kiselev model

The Kiselev adsorption isotherm equation also known as localized monomolecular layer model is only valid for surface coverage $\theta < 0.68$ and its non-linearized expression is as follows [12]:

$$K_{K1}C_e = \left(\frac{\theta}{1 - \theta} \right) (1 + K_{K2}\theta)$$

Where K_{K1} is Kiselev equilibrium constant (L/mg) and K_{K2} is equilibrium constant of the formation of complex between adsorbed molecules.

II.6.1.8. Hill-de Boer model

Hill and De Boer represented an equation of the isotherm that takes account of lateral interactions among adsorbed molecules and the mobility of the adsorbed phase. The Hill-de Boer equation can be expressed as [11]:

$$K_H C_e = \left(\frac{\theta}{1 - \theta} \right) \exp \left(\frac{\theta}{1 - \theta} - K_n \frac{\theta}{RT} \right)$$

Where K_H and K_n represent, respectively, the adsorbate-adsorbent and the adsorbate-adsorbate interactions. A positive K_n value indicates attraction between adsorbed species and a negative value means repulsion. The apparent affinity rises with loading when there is attraction between adsorbed species, and it is reduced with loading when there is repulsion among the adsorbed species. When there is no interaction between adsorbed molecules ($K_n=0$)

II.6.1.9. Flory – Huggins model

Flory-Huggins isotherm model, which occasionally derives the degree of surface coverage characteristics of adsorbate onto adsorbent, can express the feasibility and spontaneous nature of the adsorption process. The equation of Flory-Huggins isotherm is presented as [12]:

$$\frac{\theta}{C_0} = K_{FH} (1 - \theta)^{n_{FH}}$$

The n_{FH} parameter is the number of adsorbate ions occupying sorption sites. The equilibrium constant, K_{FH} used for the calculation of spontaneity free Gibbs energy (ΔG^0) is related to the following equation [11]:

$$\Delta G^0 = -RT \ln K_{FH}$$

II.6.2. Three parameter isotherm models

II.6.2.1. Redlich–Peterson model

Redlich–Peterson isotherm [11] is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporate three parameters into an empirical equation. The model has a linear dependence on concentration in the numerator and an exponential function in the denominator to represent adsorption equilibria over a wide concentration range, that can be applied either in homogeneous or heterogeneous systems due to its versatility. Typically, a minimization procedure is adopted in solving the equations by maximizing the correlation coefficient between the experimental data points and theoretical model predictions with solver add-in function of the Microsoft excel. In the limit, it approaches Freundlich isotherm model at high concentration (as the exponent γ tends to zero) and is in accordance with the low concentration limit of the ideal Langmuir condition (as the γ values are all close to one). The mathematical expression of Redlich–Peterson isotherm models are given as [11]:

$$q_e = \frac{K_R C_e}{1 + a_R C_e b_R}$$

II.6.2.2. Sips model

Sips isotherm is a combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems and circumventing the limitation of the rising adsorbate concentration associated with Freundlich isotherm model. At low adsorbate concentrations, it reduces to Freundlich isotherm; while at high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. As a general rule, the equation parameters are governed mainly by the operating conditions such as the alteration of pH, temperature and concentration. The Sips isotherm model is given as [12]:

$$q_e = \frac{q_{ms} K_S C_e^{n_S}}{1 + K_S C_e^{n_S}}$$

II.6.2.3. Koble–Carrigan model

Similar to the Sips isotherm model, Koble–Carrigan isotherm is a three-parameter equation, which incorporated both Langmuir and Freundlich isotherm models for representing the equilibrium adsorption data. The isotherm constants, A, B and n are evaluated from the linear plot using a trial and error optimization. The Koble–Carrigan equation can be expressed as [13]:

$$q_e = \frac{A_K C_e^{n_K}}{1 + B_K C_e^{n_K}}$$

II.6.2.4. Toth model

Toth isotherm model, is another empirical equation developed to improve Langmuir isotherm fittings (experimental data), and useful in describing heterogeneous adsorption systems, which satisfying both low and high-end boundary of the concentration. Its correlation presupposes an asymmetrical quasi-Gaussian energy distribution, with most of its sites has an adsorption energy lower than the peak (maximum) or mean value. The equation of Toth isotherm is presented as [11]:

$$\theta = \frac{K_T C_e}{(1 + (K_T C_e)^{n_T})^{\frac{1}{n_T}}}$$

II.6.2.5. Khan model

Khan isotherm is a generalized model suggested for the pure solutions, with b_K and a_K are devoted to the model constant and model exponent. At relatively high correlation coefficients and minimum error function, its maximum uptake values can be well determined. The Khan model is defined as [12]:

$$q_e = \frac{q_{mKH} b_{KH} C_e}{(1 + b_{KH} C_e)^{a_{KH}}}$$

II.6.3. Four-five parameter isotherm models

II.6.3.1. Baudu model

The calculation of the Langmuir coefficients, q_{max} and K_L , carried out by the measurement of tangents at the different equilibrium concentrations indicates that they are not constants in a wide concentration range. Their variations with concentration are written as [12]:

$$b = b_0 C^x$$

Drawing plots of $\ln(q_{mL})$ and $\ln(b)$ versus $\ln C_e$ gives the parameters of model, b_0 , q_{mB} , x , and y . The Langmuir equation has been transformed to the flowing equation [11]:

$$q_e = \frac{q_{mb} b_0 C_e^{1+x+y}}{1 + b_0 C_e^{1+x}}$$

This equation is valid when $(1+x+y)$ and $(1+x) > 1$. For lower surface coverage, the model reduces to the Freundlich equation. From previous studies, Baudu provides the best agreement with experimental data regarding four parameter monolayer isotherm models.

II.6.4.2. Fritz-Schlünder (IV) model

Four-parameter isotherm model of another form of Langmuir Freundlich type was extended empirically by Fritz and Schlünder. The equation of this model is calculated as [11]:

$$q_e = \frac{C C_e^{M_1}}{1 + D C_e^{M_2}}$$

This equation is valid when M_1 and $M_2 \leq 1$. At high liquid-phase concentrations of the adsorbate, this model reduces to the Freundlich equation. For $M_1 = M_2 = 1$, the model reduces to the Langmuir equation.

II.6.4.3. Fritz-Schlünder (V) model

A broad field of experimental equilibrium data can be analyzed by using a five-parameter model, named Fritz-Schlünder isotherm model. This model requires nonlinear regression techniques with higher complexities for its solution. The Fritz-Schlünder equation is expressed as [12]:

$$q_e = \frac{q_{mFSS} K_{FS1} C_e^{M_1}}{1 + K_{FS2} C_e^{M_2}}$$

The isotherm model is valid when M_1 and $M_2 \leq 1$.

Tab. II.2 (a): Illustration of the linear forms, nonlinear forms and plot of various isotherm models analyzed for optimization studies.

	Non Linear form	Linear form	Plot
One parameter model			
Henry	$q_e = K C_e$ a	-	q_e Vs C_e
Two parameter models			
Freundlich	$q_e = K_F C_e^{\left(\frac{1}{n_F}\right)}$ b	$\log q_e = \log K_F + \frac{1}{n_F} \log C_e$	$\log q_e$ Vs $\log C_e$
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$ c $R_L = \frac{1}{(1 + K_L C_0)}$ d	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$	$\frac{C_e}{q_e}$ Vs C_e
Elovich	$C_e = \frac{q_e}{q_{mE} K_E \exp\left(\frac{-q_e}{q_m}\right)}$ e	$\ln \frac{q_e}{C_e} = \ln K_E q_{mE} - \frac{q_e}{q_{mE}}$	$\ln \frac{q_e}{C_e}$ Vs q_e
Temkin	$q_e = \frac{RT}{b_T} \ln A_T C_e$ f	$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$	q_e vs $\ln C_e$
Fowler–Guggenheim	$K_{FG} C_e = \left(\frac{\emptyset}{1 - \emptyset}\right) - \exp\left(\frac{2W\emptyset}{RT}\right)$ g	$\ln C_e \left(\frac{1 - \emptyset}{\emptyset}\right) = \ln K_{FG} + \left(\frac{2W\emptyset}{RT}\right)$	$\ln C_e \left(\frac{1 - \emptyset}{\emptyset}\right)$ Vs $\emptyset$
		K_1	

Chapter II: Adsorption

Tab. II.2 (b): Illustration of the linear forms, nonlinear forms and plot of various isotherm models analyzed for optimization studies.

	Non Linear form	Linear form	Plot
Kiselev	$K_{K1}C_e = \left(\frac{\emptyset}{1-\emptyset}\right)(1 + K_{K2}\emptyset) \mathbf{h}$	$\frac{1}{C_e(1-\emptyset)} = \left(\frac{K_1}{\emptyset}\right) + (K_2K_1)$	$\frac{1}{C_e(1-\emptyset)} V_S \left(\frac{1}{\emptyset}\right)$
Hill-de Boer	$K_H C_e = \left(\frac{\emptyset}{1-\emptyset}\right) \exp\left(\frac{\emptyset}{1-\emptyset} - K_n \frac{\emptyset}{RT}\right) \mathbf{i}$	$\ln\left(\frac{C_e(1-\emptyset)}{\emptyset}\right) - \left(\frac{\emptyset}{1-\emptyset}\right) = -\ln K_1 + K_n \left(\frac{\emptyset}{RT}\right)$	$\ln\left(\frac{C_e(1-\emptyset)}{\emptyset}\right) - \left(\frac{\emptyset}{1-\emptyset}\right) V_S \emptyset$
Flory-Huggins	$\frac{\emptyset}{C_0} = K_{FH}(1-\emptyset)^{n_{FH}} \mathbf{j}$	$\ln\left(\frac{\emptyset}{C_0}\right) = \ln K_{FH} + n_{FH}(1-\emptyset)$	$\ln\left(\frac{\emptyset}{C_0}\right) V_S (1-\emptyset)$
Three parameter models			
Redlich-Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e b_R} \mathbf{k}$	$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = b_R \ln C_e + \ln a_R$	$\ln\left(\frac{C_e}{q_e}\right) V_S \ln C_e$
Sips	$q_e = \frac{q_{ms} K_S C_e^{n_S}}{1 + K_S C_e^{n_S}} \mathbf{l}$	$\ln\left(\frac{q_e}{q_m - q_e}\right) = \frac{1}{n_S} \ln C_e + \ln k_S$	$\ln\left(\frac{q_e}{q_m - q_e}\right) V_S \ln C_e$
Koble-Carrigan	$q_e = \frac{A_K C_e^{n_K}}{1 + B_K C_e^{n_K}} \mathbf{m}$	$\frac{1}{q_e} = \frac{1}{A_K C_e^{n_K}} + \frac{B_K}{A_K}$	$\frac{1}{q_e} V_S \frac{1}{C_e^{n_K}}$
Radke-Prausnitz	$q_e = \frac{q_m K_{RP} C_e}{1 + K_{RP} C_e^{n_R}} \mathbf{n}$	$\frac{C_e}{q_e} = \frac{1}{K_{RP}} + \frac{1}{K_{RP}} C_e^{n_R}$	$\frac{C_e}{q_e} V_S C_e^p$
Toth	$\emptyset = \frac{K_T C_e}{(1 + (K_T C_e)^{n_T})^{1/n_T}} \mathbf{o}$	$\ln\left(\frac{q_e^{n_T}}{q_{m_K} - q_e^{n_T}}\right) = n_T \ln K_T + n_T \ln C_e$	$\ln\left(\frac{q_e^{n_T}}{q_{m_K} - q_e^{n_T}}\right) V_S \ln C_e$
Khan	$q_e = \frac{q_{mKH} b_{KH} C_e}{(1 + b_{KH} C_e)^{a_{KH}}} \mathbf{p}$	-	-
Four and five parameter models			-
Baudu	$q_e = \frac{q_{mb} b_0 C_e^{1+X+Y}}{1 + b_0 C_e^{1+X}} \mathbf{q}$	-	-
Fritz-Schlünder (IV)	$q_e = \frac{C C_e^{M1}}{1 + D C_e^{M2}} \mathbf{r}$	-	-
Fritz-Schlünder (V)	$q_e = \frac{q_{mFSS} K_{FS1} C_e^{M1}}{1 + K_{FS2} C_e^{M2}} \mathbf{s}$	-	-

- Henry's isotherm model adsorption constant.
- K_F : (mg/g)(L/mg)^{1/n} adsorption capacity, (1/n) :adsorption intensity.
- q_e and q_{max} (mg/g): equilibrium and the maximum adsorbate uptake, K_L (L/mg): the Langmuir isotherm constant, C_e (mg/L): the concentration of adsorbate at equilibrium .
- R_L : the separation (dimensionless) factor.
- K_E (L/mg): Elovich equilibrium constant, q_{mE} (mg/g) maximum adsorbate uptake from elovich model.
- A_T (L/g): equilibrium binding constant. b_T (Kj/mol):adsorption energy. R (J/mol· K) ideal gas constant. T (K) temperature.

- g.** K_{FG} (L/g): Fowler–Guggenheim equilibrium constant, W (KJ/mol): interaction energy between adsorbed molecules. θ : surface coverage of the adsorbent
- h.** K_{KI} (L/g): Kiselev equilibrium constant. K_{K2} : constant of complex formation between adsorbed molecules.
- i.** K_H (L/g): Hill–de Boer constant. K_n (kJ/mol): energetic constant of the interaction between adsorbed molecules.
- j.** K_{FH} (L/g): Flory–Huggins equilibrium constant. n_{FH} : number of adsorbates occupying adsorption sites.
- k.** a_R (L/g): constant in Redlich–Peterson isotherm, K_R (L/g): constant in Redlich–Peterson isotherm. b_R constant in Redlich–Peterson isotherm.
- l.** q_{mS} (mg/g): maximum adsorbate uptake from sips model. k_S (L/g): constant in Sips isotherm. n_S : coefficient in Sips isotherm.
- m.** A_k (mg/g): Koble-Carrigan isotherm constant. B_k (L/g): Koble-Carrigan isotherm constant, n_K : coefficient in Koble-Carrigan isotherm.
- n.** q_m (mg/g): maximum adsorbate uptake from Radke–Prausnitz model. K_{RP} (L/g): constant in Radke–Prausnitz isotherm n_R coefficient in Radke–Prausnitz isotherm.
- o.** q_{mk} (mg/g): maximum adsorbate uptake from Toth model. K_T (L/g): constant in Toth isotherm. n_T : coefficient in Toth isotherm.
- p.** q_{mkH} (mg/g): maximum adsorbate uptake from Khan model. b_{KH} (L/g): constant in Khan isotherm. a_{kh} : constant in Khan isotherm.
- q.** q_{mb} (mg/g): maximum adsorbate uptake from Baudu model. b_o (L/g): constant in Baudu isotherm, x and y are constant in Baudu isotherm.
- r.** C (L/g): Fritz-Schlünder (IV) constant. D (L/g): Fritz-Schlünder (IV) constant. M_1 and M_2 are constant in Fritz-Schlünder model.
- s.** q_{mFS} (mg/g) Fritz-Schlünder (v) maximum adsorption capacity. K_{FS1} and K_{FS2} (L/g) are Fritz-Schlünder (v) equilibrium constant.

II.7. Error functions

The goodness-of-fit measures were determined based on the error functions. The best-fit isotherm model was identified based on the lowest error distribution between the predicted and experimental values. The model with the minimum value of error functions is considered to be the most suitable isotherm model. In this regard, several mathematical error functions such as The coefficient of determination (R^2), Residual variance (S^2), The average relative error (ARE), The sum of the squares of the errors (ERSQ), the hybrid fractional error function (HYBRID) and the

Chapter II: Adsorption

Marquardt's percent standard deviation (MPSD), were examined in this work to make a comparison between experimental results and the predicted model, to select the most suitable fit isotherm to experimental data. The minimum value of error function assessments will indicate the similarity of isotherm to the experimental data. The mathematical expression of the error equations is illustrated in table II.3, where, n is the number of data points, p is the number of parameters in the model, q_{exp} and q_{cal} are respectively experimental and calculated values of sorption capacity of metal ions in the solid phase (mg/g) [14].

Tab. II.3: Error functions used in the study.

Error function	Equation
The coefficient of determination(R^2)	$\frac{(q_{exp} - \bar{q}_{cal})^2}{\sum (q_{exp} - \bar{q}_{cal})^2 + (q_{cal} - \bar{q}_{cal})^2}$
Residual variance (S^2)	$\sum_{n=1}^n \frac{(q_{exp} - q_{cal})_n^2}{n - p}$
The average relative error (ARE)	$\frac{100}{n} \sum_{n=1}^n \left \frac{q_{exp} - q_{cal}}{q_{cal}} \right _n$
The sum of the squares of the errors (ERSQ)	$\sum_{n=1}^n (q_{exp} - q_{cal})^2$
The hybrid fractional error function (HYBRID)	$\frac{100}{n - p} \sum_{n=1}^n \left(\frac{(q_{cal} - q_{exp})^2}{q_{cal}} \right)_n$
Marquardt's percent standard deviation (MPSD)	$100 \sqrt{\frac{1}{n - p} \sum_{i=1}^n \left(\frac{q_{cal} - q_{exp}}{q_{cal}} \right)_n^2}$

Bibliography

- [1] - Haloi N, Sarma HP. Chakravarty P, **2013**, *Appl Water Sci*, **3**: 559–565.
- [2] - Kuczajowska-Zadrozna M, Filipkowska U, Jóźwiak T, **2020**, *J. Environ. Chem. Eng*, 8: 103878. .
- [3] - Rangabhashiyam S, Anu N, Giri Nandagopal MS, Selvaraju N, **2014**, *J. Environ. Chem. Eng*, 2(1): 398–414.
- [4] - Ding TY, Hii SL, Ong L, **2012**, *Ong. Bioresources* 7(2): 1540–1547.
- [5] - Rescignano N, Fortunati E, Armentano I, Hernandez R, Mijangos C, Pasquino R, Kenny JM, **2015**, *J. Colloid Interf. Sci*, 445: 31–39.
- [6] - Mitra T, Sailakshmi G, Gnanamani A, Mandal AB, **2013**, *Mater Res*, 16: 755–765.
- [7] - Lim SH, Hudson SM, **2004**, *Carbohydr. Res*, 339: 313–319.

Chapter II: Adsorption

- [8] - Bhattacharya A, Mathur M, Kumar P, Malik A, 2019, *Biotechnol Biofuels*, 12: 178.
- [9] - Leal D, Matsuhira B, Rossi M, Caruso F, **2008**, *Carbohydr. Res*, 343(2): 308-316.
- [10] - Taşar Ş, Kaya F, Özer A, **2014**, *Journal of Environmental Chemical Engineering*. *J. Environ. Chem. Eng* 2(2): 1018-1026.
- [11] - Al-Ghouti MA, Da'ana DA, **2020**, *J. Hazard. Mater*, 393: 122383.
- [12] - Ozer A, **2007**, *J. Hazard. Mater*, 141(3): 753–761.
- [13] - Adewuyi A, Pereira FV, **2017**, *Beni Suef Univ J Basic Appl Sci*, 6(2):118–126. .
- [14] - Karnib M, Kabbani A, Holail H, Olama Z, 2014, *Energy Procedia*, 50: 113–120.
- [15] - Ajenifuja E, Ajao JA, Ajayi EOB, **2017**, *Appl Water Sci*, 7: 3793–3801.
- [16] - Awwad A M, Salem N M, **2014**, *J. Saudi Chem. Soc*, 18 (5): 486–493.
- [17] - Bhaumik R, Mondal NK, **2016**, *Appl Water Sci*, 6: 115–135.

Chapter III:

Methodology

III.1. Chemicals

All the chemical agents used in this study were of analytical grade. Stock solutions (1000) of heavy metal ions, such as Pb (II), Zn (II), Cu (II) and Cr (VI) were prepared by prepared by solubilizing a determined amount of their nitric salt in diluted heavy metal concentrations were obtained from the stock solution. Each metal ions solution diluted to the aqueous feed initial metal concentration for each experiment. The pH of solutions was adjusted adding diluted solutions to 0.1M HCl or NaOH prior commencing the biosorption experiments. Residual concentration of all heavy metal ions left in aqueous solution was determined using AAS-UNICAM-969 atomic absorption spectrophotometer, except for the measurement of the non-adsorbed Cr (VI) concentration was carried out according to the standard colorimetric method [1]. A sample of 1 ml of the solution is taken which is mixed in an acid medium with a complexion agent, 1, 5-diphenylcarbazide. Thus, a purple-violet complex is formed after 10 minutes and its intensity is measured spectro-photometrically at 540 nm.

III.2. Biosorbent and treatment of biosorbent

III.2.1. Native biosorbent

As a kind of abundant biological resources, luffa cylindrica biomaterials can be employed as biosorbent for the elimination of heavy metal ions from aqueous media, either used directly or after properly activation pre-treatment. Such LC biomaterials have intricate networks of stable, water-insoluble fibers with high surface areas and with functional groups (carboxyl, hydroxyl, amino and sulfonate groups) on their surface which give them such biosorbent characteristics [2]. In present study, the Algerian Luffa Cylindrica fibers were selected as biosorbents for the removal of heavy metals from aqueous solution. For this reason, the LC fibers were manually washed with distilled water and scrubbed with a brush to remove salts, lime scale and sediment from the surface. Subsequently, they were dried in the open air for 24 hours, then in an oven at 40 ° C for 48 hours. The dried leaves were then finely ground (the particle size between 0.5 and 2 mm), washed again with distilled water, and then placed in the oven at 80 ° C. for 48 hours until their weight become constant and then stored in desiccators.

III.2.2 Chemical treatment of biosorbents

Matured dried fruit of *L. cylindrica* was peeled to obtain the placental cushion of the ovary. The cushion was cut into longitudinal halves, which were then cut into rectangular discs (18x20 mm and 2-3 mm thick), soaked in boiling water for 30 min, washed thoroughly with tap water, and placed in

distilled water for 24 h, changed 3-4 times. The fibrous discs were dried at 70 °C and sterilized by autoclaving at 120 °C and 1.06 Kg/cm² pressure for 20 min. Each sponge disc was separately weighed and used for cell immobilization (Figure 2a). Discs thus prepared were suitable for immobilization of microalgal cells of *Chlorella pyrenoidosa*.

III.2.2.1 Organism and culture medium

The unicellular green microalgae, *C. Pyrenoidosa*, was maintained by sub-culturing on 1/5% YMG agar slants (yeast extract 4 gr, malt extract 10 gr, and D-glucose 6 gr per liter of distilled water). The growth medium (GM) consisted of (gr per liter of distilled water); KNO₃, 2; KH₂PO₄, 0.1; MgSO₄·7H₂O, 0.1; CaCl₂ ·H₂O, 0.05; H₃BO₃, 0.00286; MnCl₂·4H₂O, 0.00181, ZnSO₄·7H₂O, 0.00022; NaMoO₄ ·2H₂ O, 0.0004; CuSO₄ ·5H₂O, 0.00008; FeSO₄ ·7H₂O, 0.00557, Na₂ EDTA, 0.00745. The pH was adjusted to 7.5 and the temperature was fixed at 303 K under illumination (16:8 day-night cycle) at 20 μmol photons m⁻² s⁻¹ in 1-L Erlenmeyer flask. The microalgae were harvested by centrifugation at 5,000 rpm for 15 minutes and washed with distilled water and then used for sequester of Pb (II) from an aqueous solution [3].

II.2.2.2 Preparation of *C. Pyrenoidosa* -luffa cylindrica immobilized discs

A weighted portion of 1 g of luffa cylindrica discs was transferred to 100 ml of GM medium and inoculated with 5 ml, 30 days-old stationary phase cultures of *C. pyrenoidosa* and incubated for 14 days for developing inoculums biomass. The luffa discs were removed and washed thoroughly with fresh GM to remove any free microalgae cells. The *C. pyrenoidosa* -luffa sponge immobilized discs were harvested after 3 weeks, washed thoroughly with distilled water, and freeze-dried for further studies on metals biosorption.

III.3. Chemical analysis

The chemical composition of the Luffa Cylindrica (lignin, hemicelluloses, cellulose, and extractive components) was obtained following conventional analytical methods [4]. The biosorbent samples that have particle size ranging from 30 to 40 mesh were employed for this analysis method.

III.3.1. Analysis of extractives

A dried LC sample of 5 g (G₀) was leached with a mixture of benzene and ethanol (benzene: ethanol of 2:1) by stirring with a magnetic stirrer in a 250 mL flask at a constant temperature for 4 h. The residue was separated from the mixture by filtration and dried in an oven at 0 °C until the

weight was constant. The residue was cooled to ambient temperature in a desiccator and then weighed (G_1). The extractive materials wt% was determined by the following equations [4]:

$$W_1 = \frac{G_0 - G_1}{G_0} * 100$$

III.3.2. Analysis of hemicelluloses

After the each process as described above, the rest of the 6 g sample (G_1) was place in a 250 mL flask and a 150 mL of 0.5 M NaOH solution was added to the flask. The mixture was boiled for 3.5 h under reflux. The residue was separated from the mixture by filtration and washed until no Na^+ ions were detected in the supernatant. The dried residue was cooled to room temperature in a desiccator and weighed. The wt% of hemicellulosic material was calculated with the following equations. [5]:

$$W_2 = \frac{G_0 - G_1}{G_0} * 100$$

III.3. 3. Analysis of lignin and cellulose

About 1 g of the residue from the extractive analysis mentioned above was put into a 150 mL weighed flask and was dried in an oven at 100–110 °C until a constant weight was reached. Afterword, the sample was cooled in a desiccator and weighed (G_3). Thirty milliliters of sulfuric acid (75%) were poured slowly onto the sample. This mixture was kept at 15 °C for 1 day, after which it was transferred into a 250 mL flask and diluted with 300 mL of deionized water. The sample was boiled for 1 hour under reflux. After cooling and filtering, the residue was washed until no sulfate ions were present in the filtrate. Subsenqntly, the residue was dried in an oven at 70 °C, cooled to ambient temperature in a desiccator, and weighed (G_4). The percentage of lignin (wt%) was calculated with the following equations [6]:

$$W_3 = \frac{G_4 * (1 - W_1)}{G_1} * 100$$

The cellulose wt% was obtained with the following equations:

$$W_4 = 100 - (W_1 + W_2 + W_3 + ash)$$

III.4 Characterization

III.4.1 Equipment

- Atomic absorption spectroscopy (AAS-UNICAM-969 equipped with a graphite furnace GF95) was employed to determine the Residual concentration of lead ions left in aqueous solution.
- Fourier transform spectrometer (Prestige-21, Shimadzu spectrometer) was used for FTIR analysis.
- Scanning electron microscopy (HIT S2600 N), with energy dispersive X-Ray analyser (Bruker AXS Microanalysis GmbH, Germany) was used for SEM-EDX analysis. .
- X-Ray analysis (XRD) Shimadzu (Japan) 7000 X-ray diffractometer.
- Thermal gravimetric analyzer (Shimadzu DTG-60H), differential with temperature range (ambient to 1000 °C), ±500 mg measurable range (TG), ±1000 °C measurable range (DTA).
- VIS/UV spectrophotometer (Hitachi U-2000) was employed to determine hexavalent chromium left in aqueous solution.

III.4.2. Fourier Transform Infrared Ray (FTIR) analysis

FTIR analysis was employed to identify the functional groups on the surface of native and immobilized *Luffa cylindrica*. Spectra were recorded in KBr pellets using a FTIR spectrometer. To prepare the pellets, 1 mg of biosorbent was finely grinded for 1 to 2 min together with 200 mg of KBr. The FTIR spectra were recorded in the spectral range 400 to 600 cm^{-1} [7].

III.3.3. SEM – EDX analysis

Scanning Electron Microscopy (SEM) coupled to energy dispersive X-Ray (EDX) analysis was performed to obtain topographical and elemental information of biomass particles [7]. Samples were mounted on a stainless stub using a double-stick tape coated with a thin layer of carbon. Digital images were processed by using Quartz PCI program.

III.4.4. XRD analysis

Analysis of the crystalline structure present in lignocellulosic biomass and in the cellulose as derived from the biomass was carried out using a Shimadzu (Japan) 7000 X-ray diffractometer (XRD) instrument, with copper (Cu) as the radiant source. Analysis was performed at an energy of 40 kV, electric current of 30 mA, scanning speed of $2^\circ/\text{minute}$, recording every 0.02° , and scanning angle 10 to 80° . The observed parameters during the XRD analysis were comprised of the crystallinity degree, the value of Z (to determine which was the more dominant between cellulose I_α and cellulose I), and the comparison between cellulose I_α and I. The Z value was determined using the lateral distance between the cellulose polymer chains *i.e.*, d_1 (100 and 010) and d_2 (110 and 1-10)

III.4.5. TGA/DTG analysis

The main purpose of this study was to investigate the thermal behavior of the LC and CP-LC by a DTG analyzer. DTG analysis of the two biosorbents was carried out at the heating rate of 10 °C min⁻¹ in nitrogen atmosphere. The experiments were done with 0.1 g weight readability, sample quantity (1 g max. in gross weight) and inert gas atmosphere is used in this study. Nitrogen flow rate to the thermogravimetric analyzer was set at 20 ml/min with heating rate of 10 C/min.

III.4.6. pH of point zero charge (pH_{pzc})

The pH is a very important factor influencing on heavy metal ions sorption owing to its influence on chemical speciation of the metal in liquid phase and also on the ionization of chemically active sites on the biosorbent surface. Therefore, the net charge of biosorbent surface may play a crucial role in bioprocesses, and the propriety of protonation/deprotonation behavior of biosorbent material in aqueous solution could be useful elucidate biosorption mechanism [8]. The pH at which the biosorbent surface charge takes a zero value is known as point of zero charge (pH_{pzc}). At this pH point, the charge of the positive surface sites is equal to that of the negative ones. At solution pHs higher than pH_{pzc}, biosorbent surface is negatively charged and could interact with metal positive species while at pHs lower than pH_{pzc}, biomaterial surface is positively charged and could interact with negative species. Based on the protocol, mass titrations (MT) were performed to determine the pH_{pzc} of LC. By looking at the distribution of LC particle size, two kinds of particles which were the largest portions of LC were analyzed. Different masses of each particle size within the concentration range 0.2 -100 g/L were put into contact with a 50 mL 0.03 M KNO₃ solution. The aqueous suspensions were agitated for 1 day in an orbital shaker at a speed of 200 rpm until equilibrium pH was reached. The pH_{pzc} is the pH at which a plateau is attained when plotting equilibrium pH versus biosorbent mass. The same treatment and procedure was employed for blank solution (50 mL 0.03 M KNO₃).

III.5 Batch experiments

The experiments of biosorption were employed in 14 parallel erlenmeyer flasks by a mechanical shaker associated with a thermostatic water bath at an agitation speed of 150 rpm. The biosorbents was separated from the aqueous solution by centrifugation at 5000 rpm for 5 min. The pH of the solution was adjusted with 1.0 M HNO₃ or 1.0 M NaOH. The experiments in which the effect of temperature, pH, contact time, biosorbent concentration, and initial concentration of metal ions were investigated. The ranges of these considered parameters were “298–333 °C, 1–10.0, 5–120 min, 0.1–20 g/L, and 100– 300 mg/L, respectively.

The removal efficiency and the amount of adsorbed metal ions per unit mass of adsorbent of metal ions are calculated by the following equations [2]:

$$R(\%) = \frac{(C_o - C_e) * 100}{C_o}$$

$$q_e = \frac{(C_o - C_e)}{m} * v$$

Where C_o and C_e are the initial and final concentrations of metal ions in the solution (mg/L), m is the dose of biosorbent (g/L).

III.5.1 Influence of the initial pH

The effect of initial pH on the equilibrium was investigated in the pH range from 1.0 to 10.0 in a single and multiple heavy metal aqueous solution. The pH was adjusted using 0.1 mol/L NaOH and 0.1 mol/L HNO₃ solutions, alternatively. In this present study, each initial metal concentration is 10 mg/L in the multiple-metal aqueous solution. 10 mL of this solution, at each selected pH, was agitated by a rotary mixer with 1 g of each biosorbent sample (free and immobilized biomass). The temperature was kept constant at 298K.

III.5.2 Influence of the biosorbent dosage

Influence of the biosorbent dosage for each biomass (LC, CP and CP-LC) on the removal of metal ions was investigated in the range of 0.1 to 20 g/L of each biosorbent. Experiments are all conducted at optimum pH for each metal, and other conditions were kept equal as mentioned previously.

III.5.3 Desorption, regeneration and reuse

Desorption experiments were performed just for the case of Pb (II) onto LC-CP. To carry out the regeneration and desorption studies of immobilized *C.pyrenoidosa* biomass, five different desorption agents, tap H₂O, distilled water, 0.1 M HCl, 0.1 M H₂SO₄ and 0.1 M NaOH were utilized to desorb the lead (II) from the biosorbent. Exactly, 100 mL of the desorption agents was kept in 250 mL Erlenmeyer flasks with the recovered biosorbent and agitated for 30 min with continuous agitation at a 100 rpm at a temperature of 298 K. The regenerated biosorbent was used in five consecutive adsorption/desorption cycles to determine the reusability of the immobilized *C. pyrenoidosa* onto *luffa cylindrica*. The final metal ion concentrations in the aqueous solution were determined. Desorption and reloading ratio were calculated mathematically as follows[2] :

$$\text{Desorption ratio} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} * 100$$

$$\text{Reloading ratio} = \frac{\text{Amount of metal loaded in a higher cycle}}{\text{Amount of metal loaded in the first cycle}} * 100$$

III.5.4 Kinetic study

For the kinetic studies, 1 g of biosorbents (LC, CP and CP-LC) was contacted separately with 100mL of -metal aqueous solution by a rotary mixer during 5, 10, 20, 30 and 45 min and 1, 2 and 3h. At each predetermined interval of time, the aqueous and the solid phases were separated by filtration (with Millipore filters) and the concentration of metal ions in the final aqueous solution was analyzed by AAS all heavy metals except for hexavalent chromium we use the 1,5-diphenylcarbazide method.

III.5.5 Isotherm study

Biosorption isotherm studies were conducted as usual at 298K and the aqueous solution varying the initial metal concentration from 10 to 300 mg/L. So, 100 mL of metal aqueous solution at optimum was agitated by a rotary mixer with 1 g of each biosorbent (LC, CP and CP-LC). Meanwhile, this can be used to determine the effect of initial metal concentration onto the biosorbents efficacy and to evaluate the corresponding biosorption thermodynamic parameters (using different isotherm modeling systems).

Bibliograph

- [1] - Annija L, David R, Mark B, John C, **2019**, International Journal of Environmental Research and Public Health, 16(10): 1803-1818.
- [2] - Nouacer I., Benalia M., Henini G, Djedid M, Laidani Y, **2021**, Biomass Conv. Bioref.
- [3] - Dang VBH, Doan HD, Dang-Vu T, Lohi A, **2009**, Bioresource Technology, 100 (1): 211–219.
- [4] - Donmez G, Aksu Z, **2002**, Process Biochemistry, 38:751-762.
- [5] - Kalia S, Kumar A, Kaith B S, **2011**, Advanced Material Letters, 2(1):17-25.
- [6] - Sanghavi B J, Srivastava AK, **2013**, Analyst, 138 (5):1395–1404.
- [7] - Sanghavi BJ, Kalambate P K, Karna S P, Srivastava A K, **2014**, Talanta, 120: 1–9.

CHAPTER IV:

Results and discussion

IV.1. Biosorption of heavy metals by *Luffa Cylindrica*

The current section describes the biosorption of Pb (II), Zn (II), Cu (II) and Cr (VI) ions from aqueous solutions and waste petroleum water by using *Luffa Cylindrica* under different conditions. The parameters influencing the metal uptake including the contact time, the pH of aqueous solution, adsorbent dose, temperature and the initial metal concentration were analyzed. FT-IR, SEM-EDS, XRD and TGA-DTG analysis were followed to better characterize the biosorbent. The biosorption kinetics of heavy metals onto LC fiber was modeled by using the pseudo-first order and pseudo-second order kinetic model. The equilibrium data of each metal were modeled by several isotherm models of two parameters. Furthermore, the thermodynamic and the kinetic parameters for each system were determined. In addition, metal ions adsorbed by the LC are eluted with several desorption agents. The biosorption capacities of regenerated *Luffa Cylindrica* are examined.

IV.1.1. Characterization of *Luffa Cylindrica*

IV.1.1.1. Chemical analyses

The main components of the *Luffa Cylindrica* determined by chemical and proximate analysis are given in Table. IV.1. It is seen that cellulose is the dominant macromolecular component in the LC, and lignin is the second richest group. According to the results, it can be said that the *Luffa Cylindrica* possess typical lignocellulosic structure which contain –OH groups as main functional groups. According to the American Society for Testing and Materials (ASTM) standard [1], the average bulk density of *Luffa Cylindrica* was found to be 730 kg/m³.

Tab. IV.1: Chemical analyses used in this study.

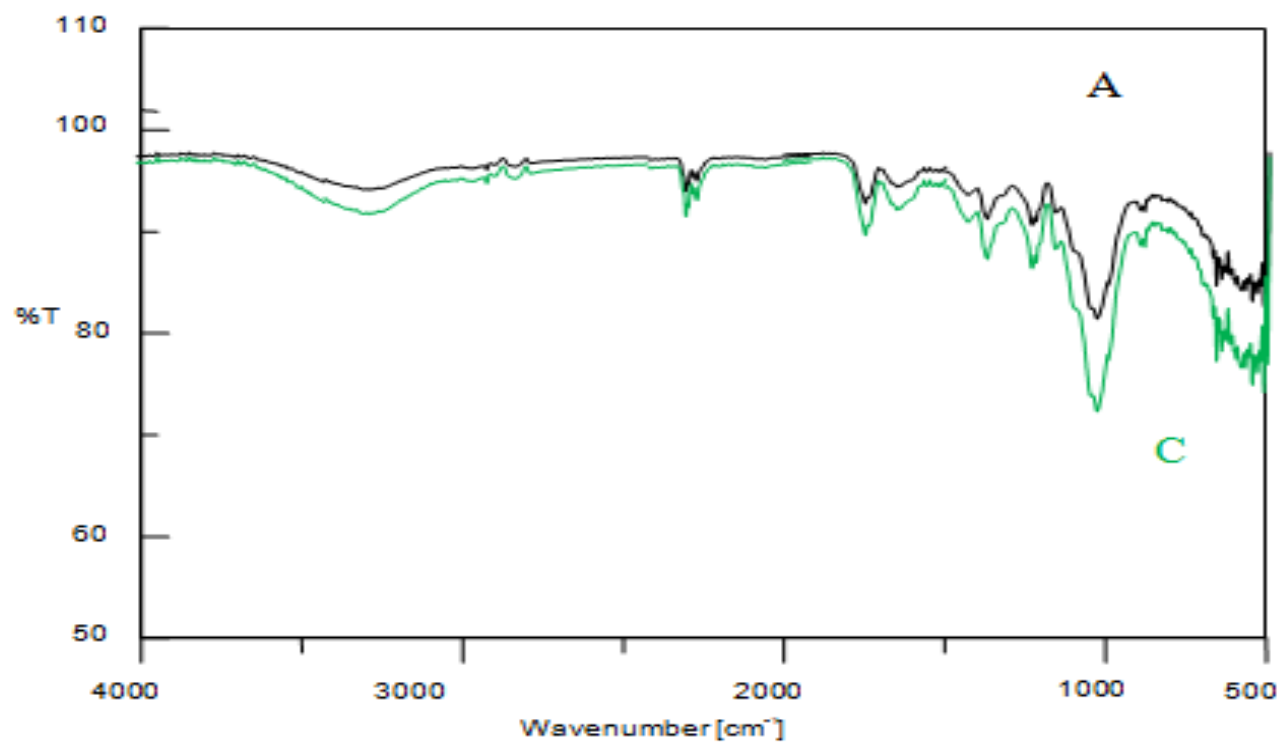
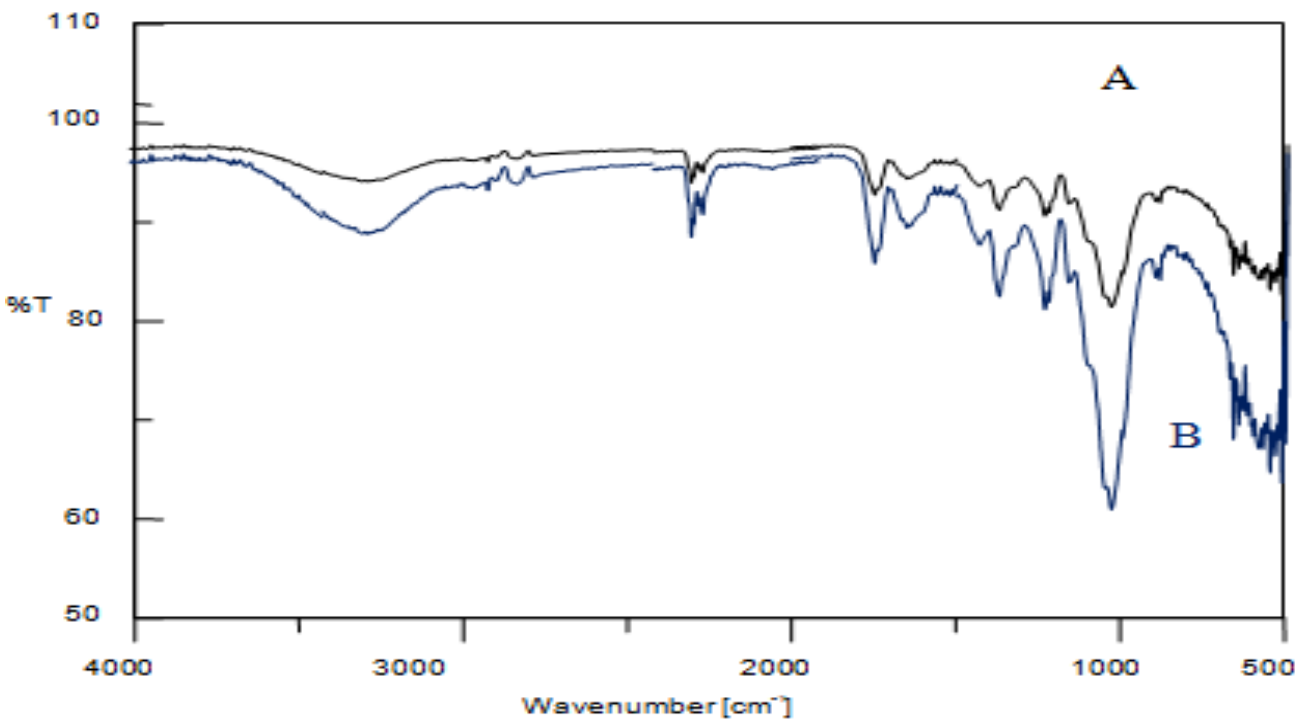
Chemical analyses	Extractives	Hemicelluloses	Lignin	(Cellulose + ash)
Wt%	13.76	8.95	31.6	40.2

IV.1.1.2. FTIR study

The identification and the existence of functional groups present in the fiber of *Luffa Cylindrica* before and after treatment with metal ions were studied by FTIR analysis at room temperature

Chapter IV: Results and discussion

(25±°C). For the comparative study, the spectra of untreated and treated biomass of LC with heavy metal ions (Pb (II), Zn (II), Cu (II) and Cr (VI) ions) were examined. The appended FTIR spectra are shown in Fig.IV.1 (A, B, C, D and E). In all the spectra, a broadband range of 3200-3550 cm⁻¹ corresponds to the presence of hydroxyl groups [2] associated with the N–H bond of amino groups [3]. The relative difference in band intensity to be similar to the difference in the concentration of respective functional groups associated with the bands. It was justified by the presence of broad band in the frequency range of 3200- 3550 cm⁻¹ corresponds to the existence of the hydroxyl group [4]. Two sharp peaks at 2925 and 2852 cm⁻¹ are attributed to the -CH asymmetric and symmetric stretching vibrations of methylene hydrogen [2]. Each spectra demonstrates a sharp, intense peak at 1752 cm⁻¹ attributed to the aromatic C=C, C=O and conjugated ketones or C=N amide stretching. The methyl asymmetric C-H bends at 1458, 1053 and 1034 cm⁻¹ ascribed to C-O stretching of alcohol, carbohydrates or polysaccharides-like substances. A medium intensity broad band in the range of 1050 cm⁻¹ is assigned to ν (C-O-C) asymmetrical stretching [3]. In comparison to the spectra of untreated biosorbent of *Luffa Cylindrica* with treated heavy metal ions (Pb (II), Cu (II), Zn (II) and Cr (VI)), a minute shift in peak position was observed (Fig.I.1 (A, B, D, C, and E). These changes were occurred owing to the binding of lead, copper, Zinc and chromium ions with amino and hydroxyl groups of *Luffa Cylindrica*. Thus, shifting of bands confirms the adsorption of metal ions on the surface of *Luffa Cylindrica*. The most remarkable difference amongst the four spectra is; at an intensity of 3000-3800 cm⁻¹ representing hydroxyl (-OH) stretching, and the medium intensity band in the range of 1600-1700 cm⁻¹ represents carbonyl (-C=O) stretching. These signify the involvement of hydroxyl groups in the binding of Pb (II), Zn (II), Cu (II) and Cr (VI) ions. A slight change in the frequency of peaks confirms the existence of biosorption.



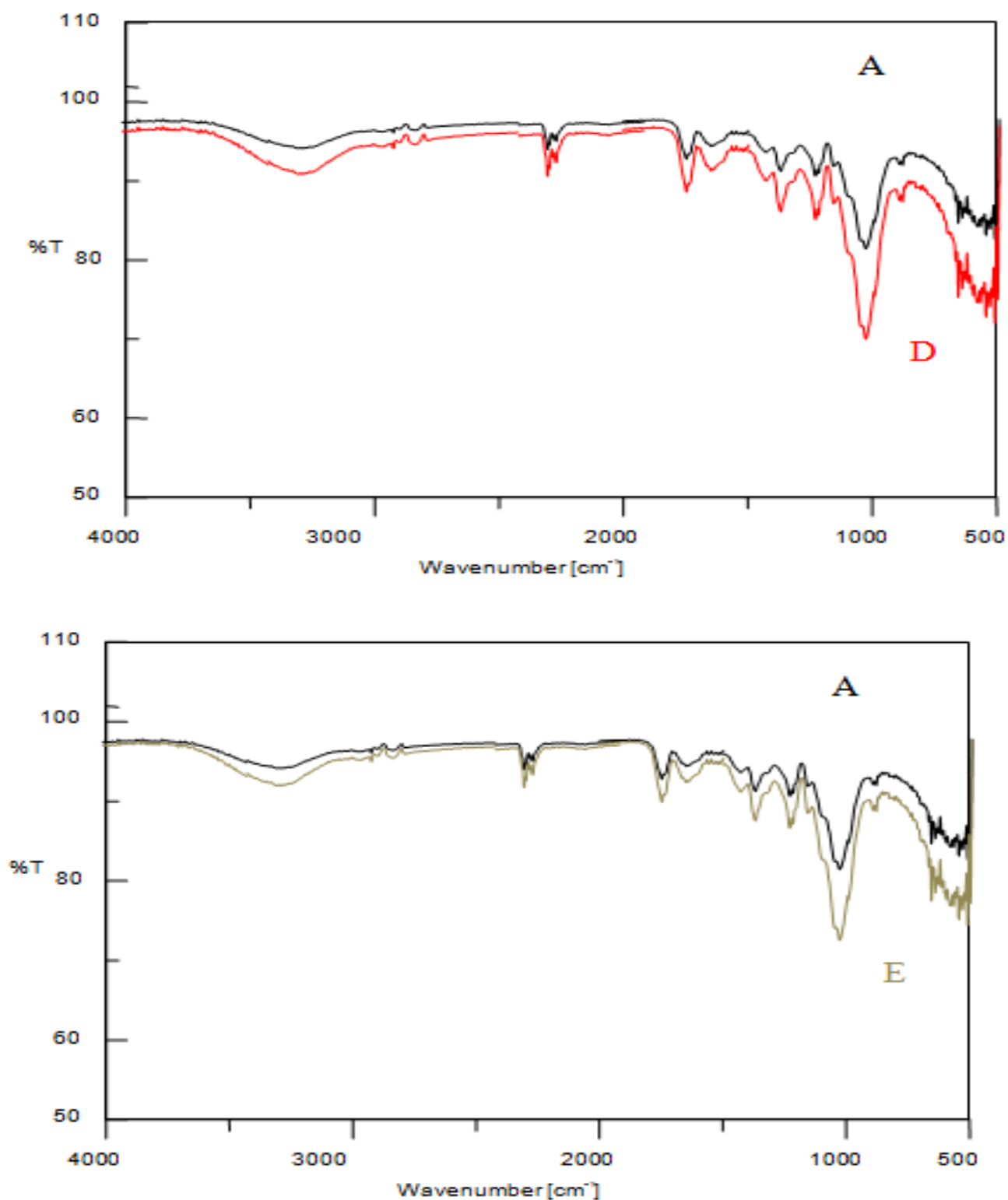


Fig. IV.1: FTIR spectrum. A: LC, B: LC-Pb (II), C: LC-Pb-Zn (II), D: LC-Cu (II), E: LC- Cr (VI).

IV.1.1.3. SEM-EDS study

The morphology of the *Luffa Cylindrica* was observed by SEM. The fibers, formed by fibrils glued, are disposed in a multi-directional array, forming a natural mat (Fig. IV. 2a); the

diameters of single fibers are in the range (63–125 μ m). To observe the inner fibrils and further investigate the complicated physical structures in the natural *Luffa Cylindrica*, a crude fiber was observed at high magnification (Fig.IV.2b). The SEM image shows that the fiber has a heterogeneous appearance with an outer rich lignin layer around the fibers. The internal fibrils cannot be seen due to the lignin layer. At higher magnification (Fig. IV. 2c, d), the SEM image displays a rougher surface with lots of waxy and gummy substances on the untreated *Luffa Cylindrica* fiber; the internal fibrils cannot be observed [5]. The EDS spectrum is shown in Fig.IV.3 and the contents of each element are listed in Table. IV. 2. The energy dispersive X-Ray microanalysis (SEM/EDS) of the *Luffa Cylindrica* fibers indicates mainly the presence of carbon (65.68 %) and oxygen (30.13 %). However, as the EDS analysis is less sensitive for light elements (Z B 10) [6], the carbon and oxygen content were quantified by ultimate analysis. Their concentrations suggest the presence of high amount of different oxygenated groups on the carbon surfaces, such as Cl, Ca, Na, Mg, K, Si and P whose contents are between 0.09 and 1.21%.

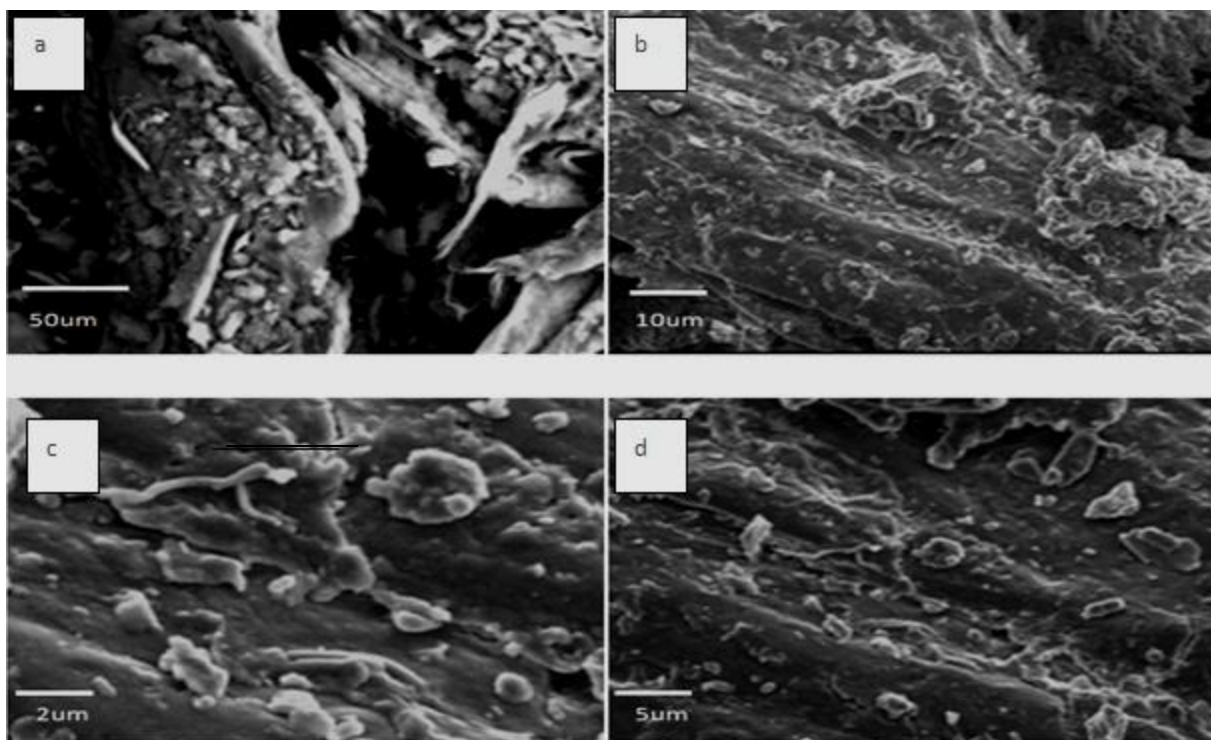


Fig. IV. 2 : SEM micrographs of *Luffa Cylindrica*.

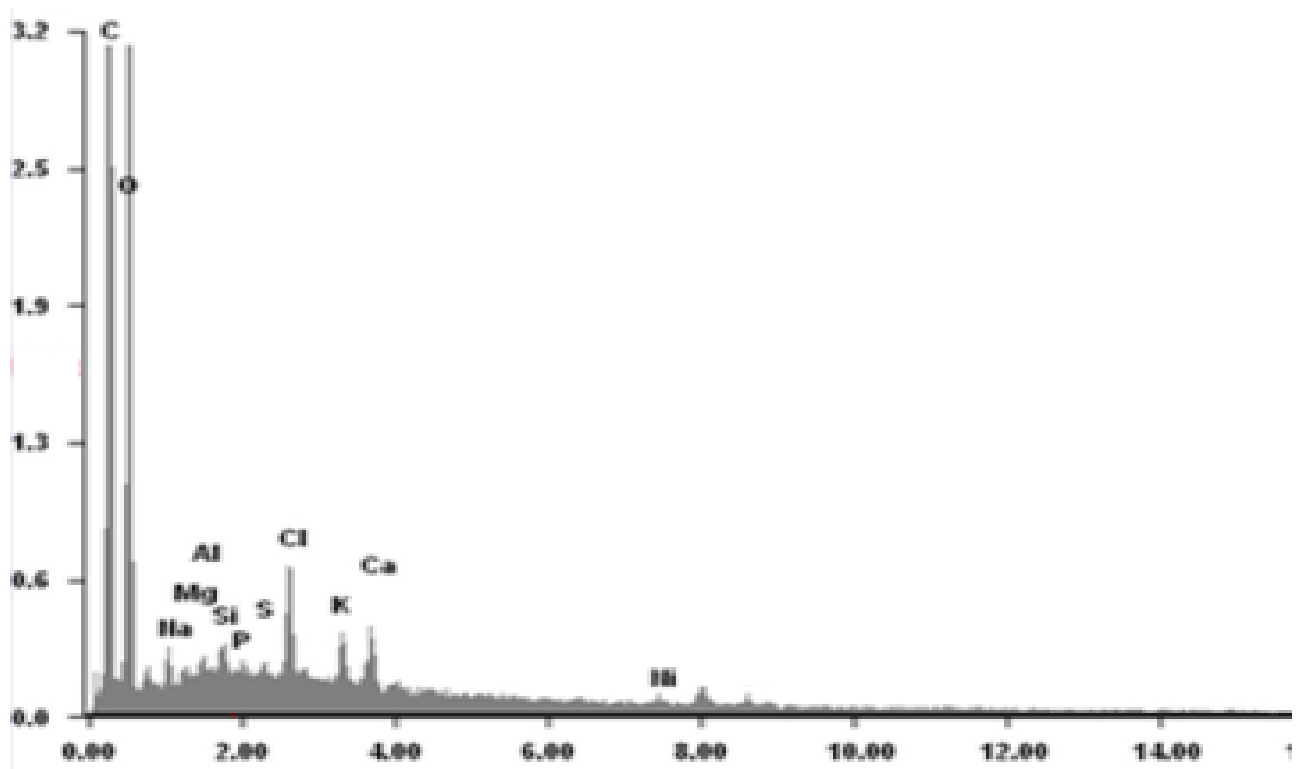


Fig. IV.3: EDS spectrum from the Luffa Cylindrica.

Tab. IV. 2: Principal elements identified on the biomass surface by SEM/EDS.

Element	C	O	Na	Mg	Si	P	Cl	K	Ca
Content (%)	65.68	30.13	0.71	0.59	0.27	0.09	1.21	0.36	0.77

IV.1.1.4. X-Ray Diffraction analysis

The crystallinity index of the tested LC was calculated from X- Ray Diffraction patterns recorded on an X'Pert pro MPD X-ray diffractometer. Diffractograms were obtained by varying angle (2θ) from 4° to 65° . The crystallinity index (I_{cr} %) of the LC was calculated using the following formula [7] :

$$I_{cr}\% = \left\{ \frac{I_a - I_{am}}{I_a} \right\} * 100$$

Where I_a is the maximum intensity of diffraction peak at 2θ angle between 20° and 25° and I_{am} is the intensity of diffraction of the amorphous material, which is taken at a 2θ angle between 13°

and 18° when the intensity is minimal.

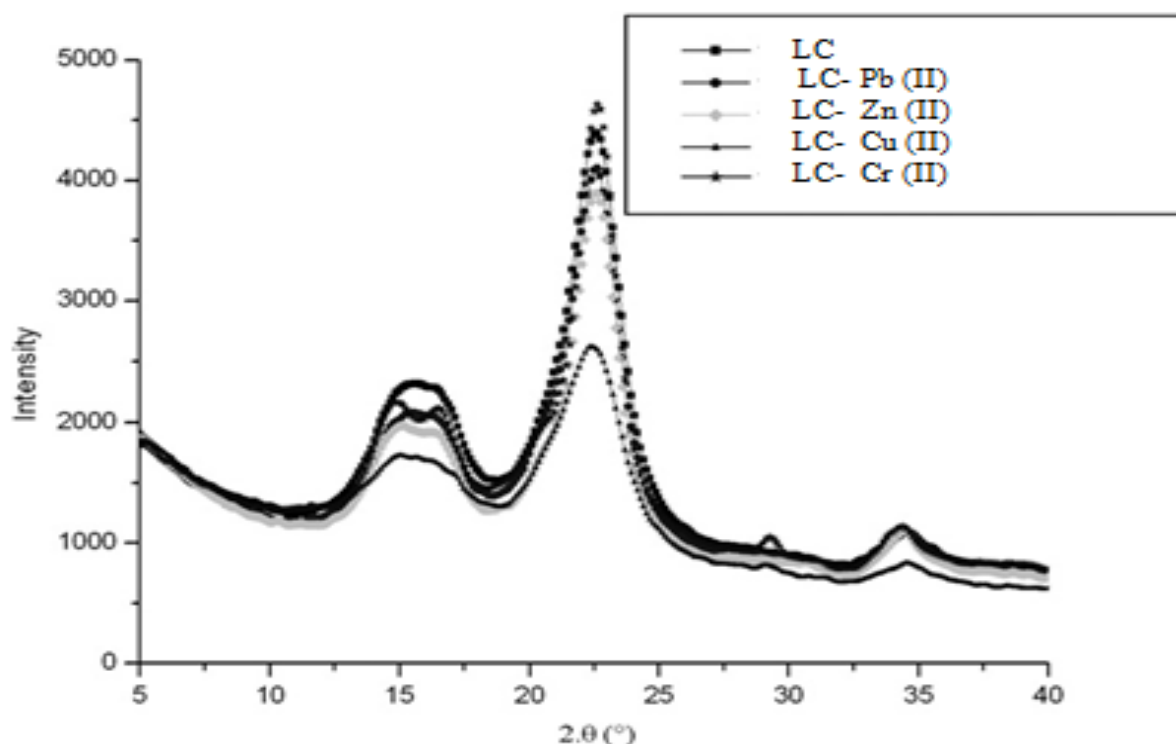


Fig. IV. 4: X-Ray Diffraction patterns of free and loaded *Luffa Cylindrica*.

The XRD examination of LC and LC-loaded metal ions shows that only the crystal polymorph I of cellulose is present. Fig. IV.4 shows the X-Ray Diffraction patterns of native LC and LC loaded with studied heavy metals. This figure shows many peaks at $2\theta = 15.1^\circ$, 16.4° , 22.4° and 34.4° . The peaks at $2\theta = 15.1^\circ$ and 16.4° correspond to respectively crystallographic planes (110) and (110). These two peaks will be confused in the case of the samples showing a high rate of amorphous products such as hemicelluloses, lignin and amorphous cellulose [8]. We can see in Fig. IV.4 that LC and LC-loaded metal ions, the peaks at $2\theta = 15.1^\circ$ and 16.4° are not confused indicating a low rate of amorphous products such as hemicelluloses, lignin and amorphous cellulose. The peaks at $2\theta = 22.4^\circ$ and 34.4° indicate respectively the (002) and (023) crystallographic planes. Table.IV.2 presents the data of crystallinity index for all metal studied. As shown in Table IV.2 the adsorption of heavy metals in *Luffa* fibres improves their crystalline structure. It was observed that the intensity of the peak in LC- M increased on adsorption. The increase in intensity of peak during adsorption indicated increased crystallinity of LC- M. However; the LC- M showed broadening of the peak after adsorption due to convergence of the fibers toward more disordered system [9, 10]. It has been observed that (Table IV.3) a slight increased in percentage crystallinity of the fiber on adsorption copolymerization resulted in increase

Chapter IV: Results and discussion

in randomness or disorder in the crystal lattice of cellulose fiber. This was due to incorporation of adsorbed metals on the active sites of backbone during adsorption and fibers became more amorphous and resulted in impaired crystalline structure [11] and [12].

Tab IV. 3: Crystallinity index LC and LC-Metals.

Sample	LC	LC- Pb (II)	LC- Cu (II)	LC- Zn (II)	LC- Cr (VI)
%Xc	50.00	66.32	70.56	70.84	68.18

IV.1.1.5. Thermogravimetric analysis

It is known that natural fibers contain cellulose, hemicellulose, and lignin, and these components contribute the thermal stability of natural fibers [13]. Therefore, the contents of these components affect the thermal stability of fibers. The thermal degradation of natural fibers is a two-stage process, one in the temperature range 220–280°C and another in the range 280–300 °C. The low-temperature degradation process is associated with degradation of hemicellulose, whereas the high-temperature process is due to lignin [14]. TG and derivative thermogravimetric analysis graphs of *Luffa Cylindrica* were presented in Fig. IV. 5. Weight loss values in the ranges 25–125 and 125–600°C are obtained to be about 8 and 71%, respectively. The weight loss versus temperature curve exhibits a first drop from 25 to 125°C, which could be due to the evaporation of water retained by the fibers. Weight loss values in the range 25–125°C and 125–600°C are 7.8 and 70.5%, respectively. Total weight loss value in the range 25–600 °C is 78.3%. The maximum degradation temperature of *Luffa Cylindrica* is obtained to be 381°C.

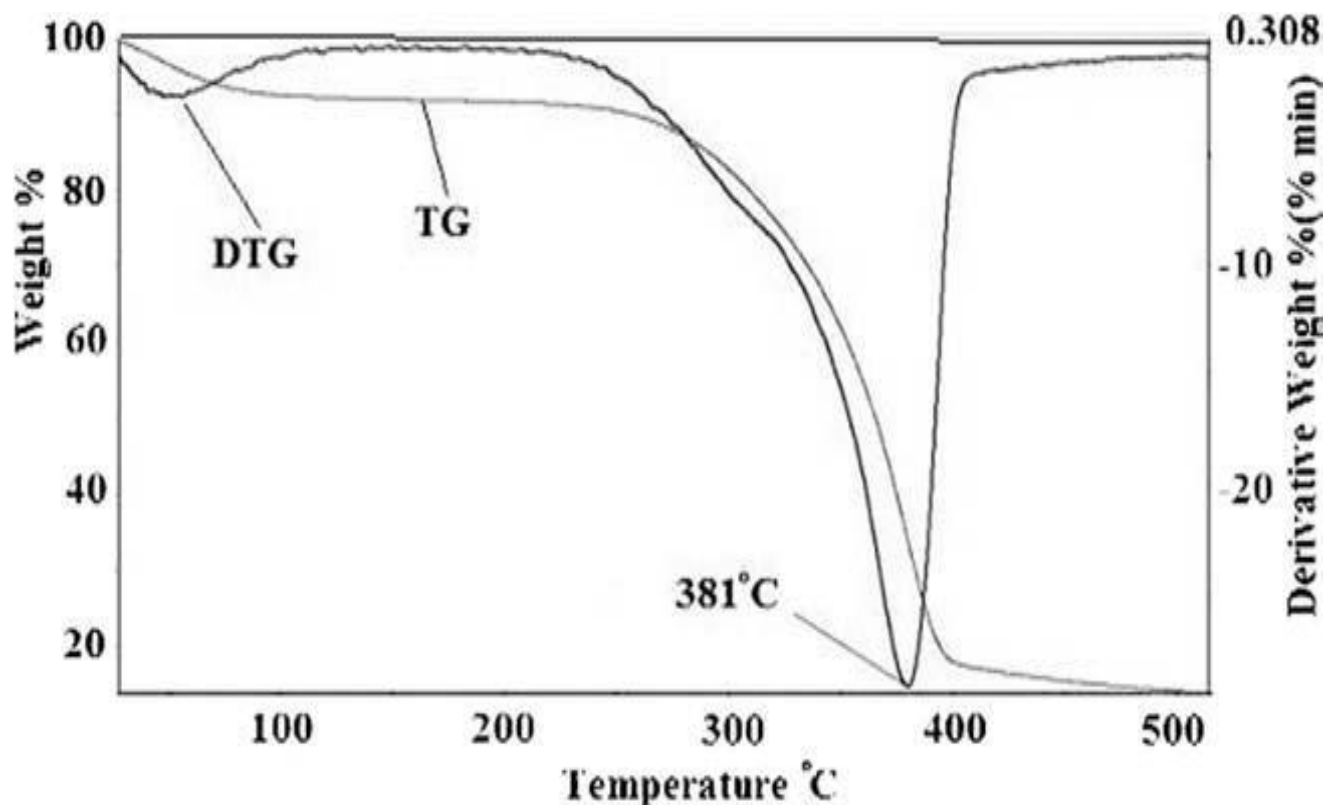


Fig. IV. 5: TGA/DTG analysis of Luffa Cylindrica.

IV.1.1.6. Point of zero charge (pH_{pzc})

The point of zero charge (pH_{pzc}) of the Luffa Cylindrica fiber was evaluated by the solid addition method using KNO₃ (0.01 M) solution [14]. The experiments were carried out in 100 mL Erlenmeyer flasks with stopper cork containing 50 mL of KNO₃ solution (10⁻² M). The initial pH (pH_i) in each flask was adjusted between 3 and 11 by adding NaOH or HCl solutions (0.1 M). Then, 0.5 g of the Luffa Cylindrica was added to each flask which is kept for 48 h with intermittent manual shaking to reach the equilibrium. The difference of the initial and final pH was plotted against the initial pH. The point of intersection of the resulting curve with the abscissa axis, for which $\Delta\text{pH} = 0$, gives pH_{pzc} (Fig. IV.6)

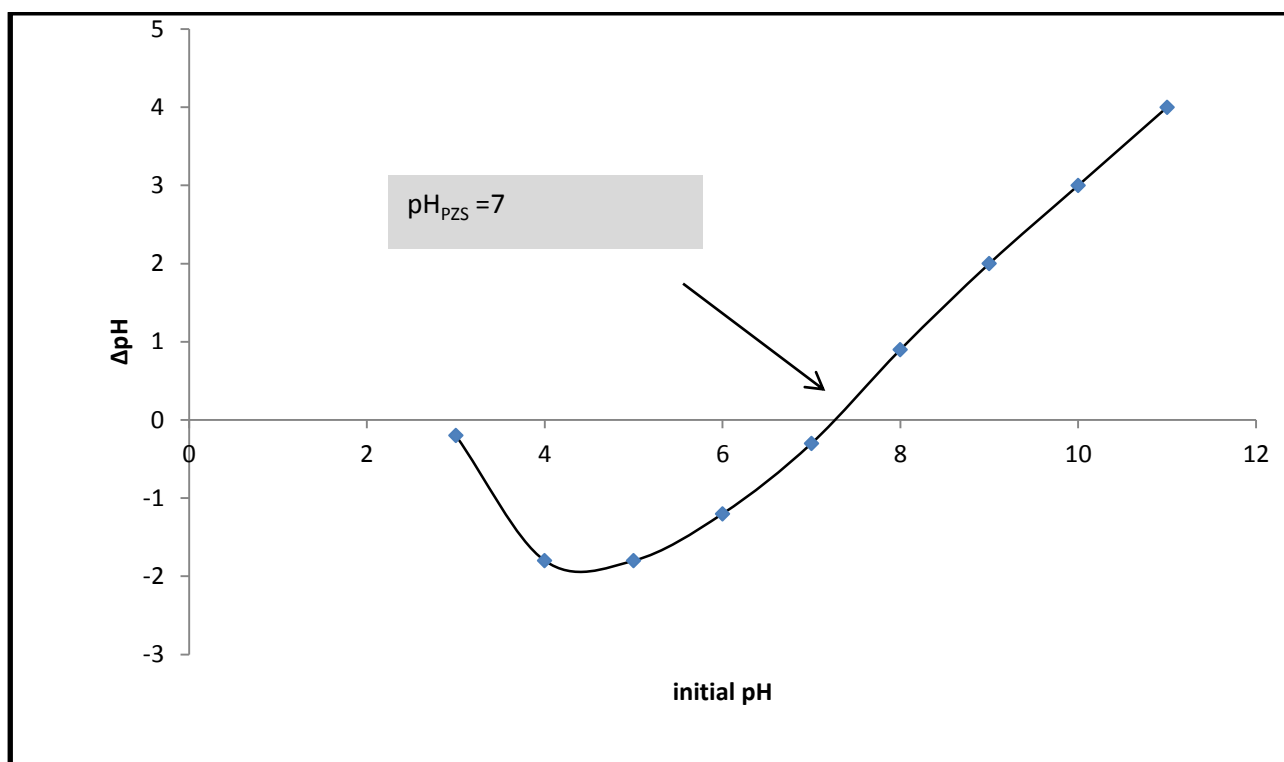


Fig. IV.6 : The determination of the point of zero charge (pH_{PZC}).

IV.1.2. Biosorption optimization

IV.1.2.1. Effect of contact time

The effect of contact time on the adsorbent and metal ions is shown in Fig. IV.7. the rate of adsorption with respect to residence time on the surface of *Luffa Cylindrica* shows that the percentage removal of the metal ions firstly increased with increasing contact time; that is, the adsorption processes is fast until they reached their optimum times. This is attributed to the availability of large surface areas of the adsorbent. At these points, the equilibrium times were attained. After the plateau, the surface pores of the adsorbent became enclosed and desorption began. The slow rate of adsorption at this stage also known as desorption process may be due to the agglomeration of metal ions on the surface of the adsorbent.

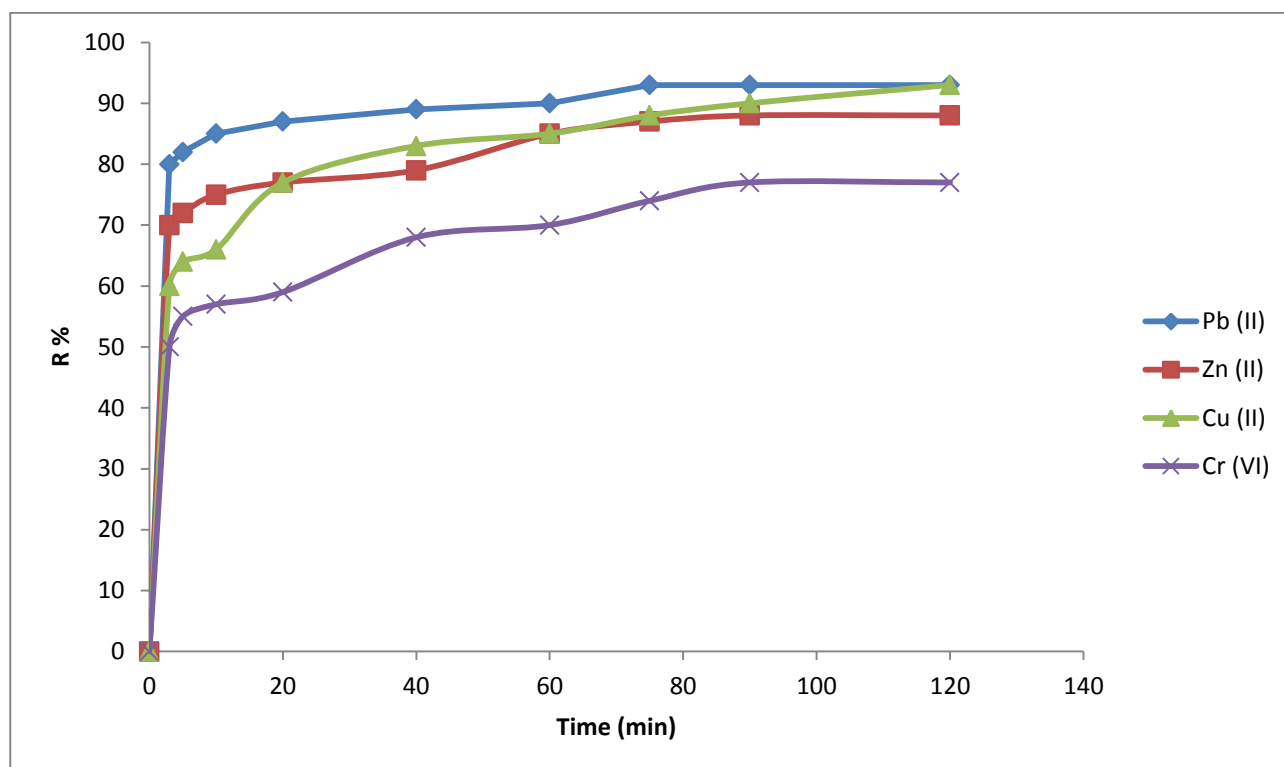


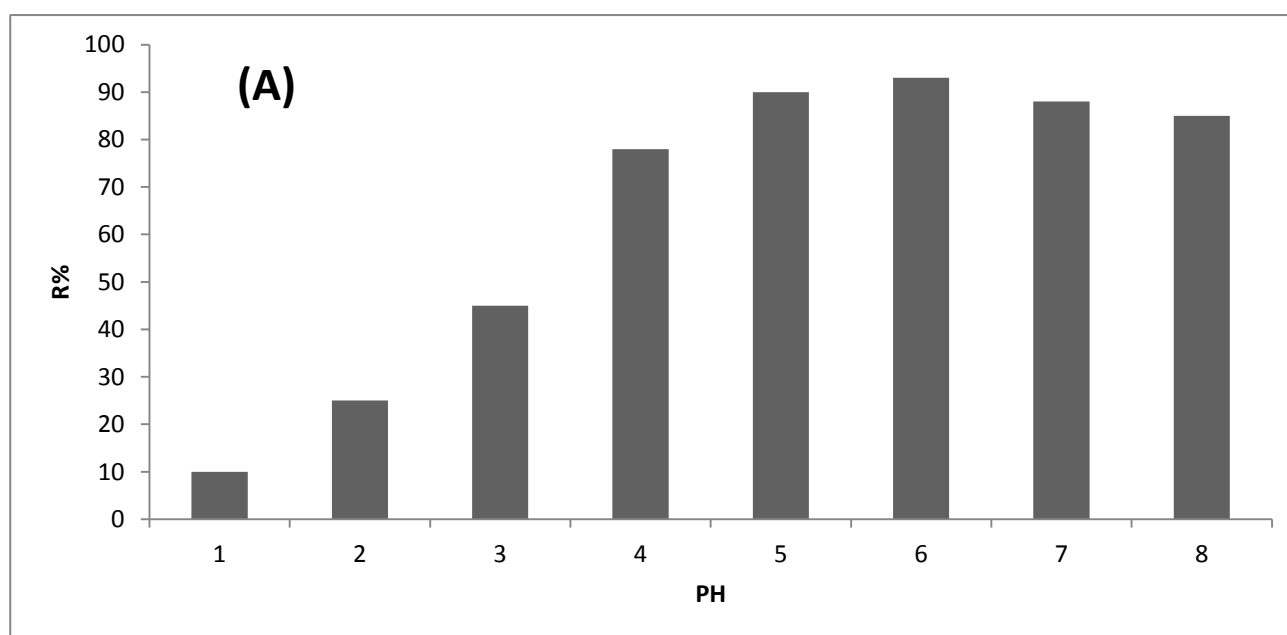
Fig. IV.7: Effect of contact time: initial concentration 10 mg/L; biosorbent dose: 1 g/100mL; temperature: 298K.

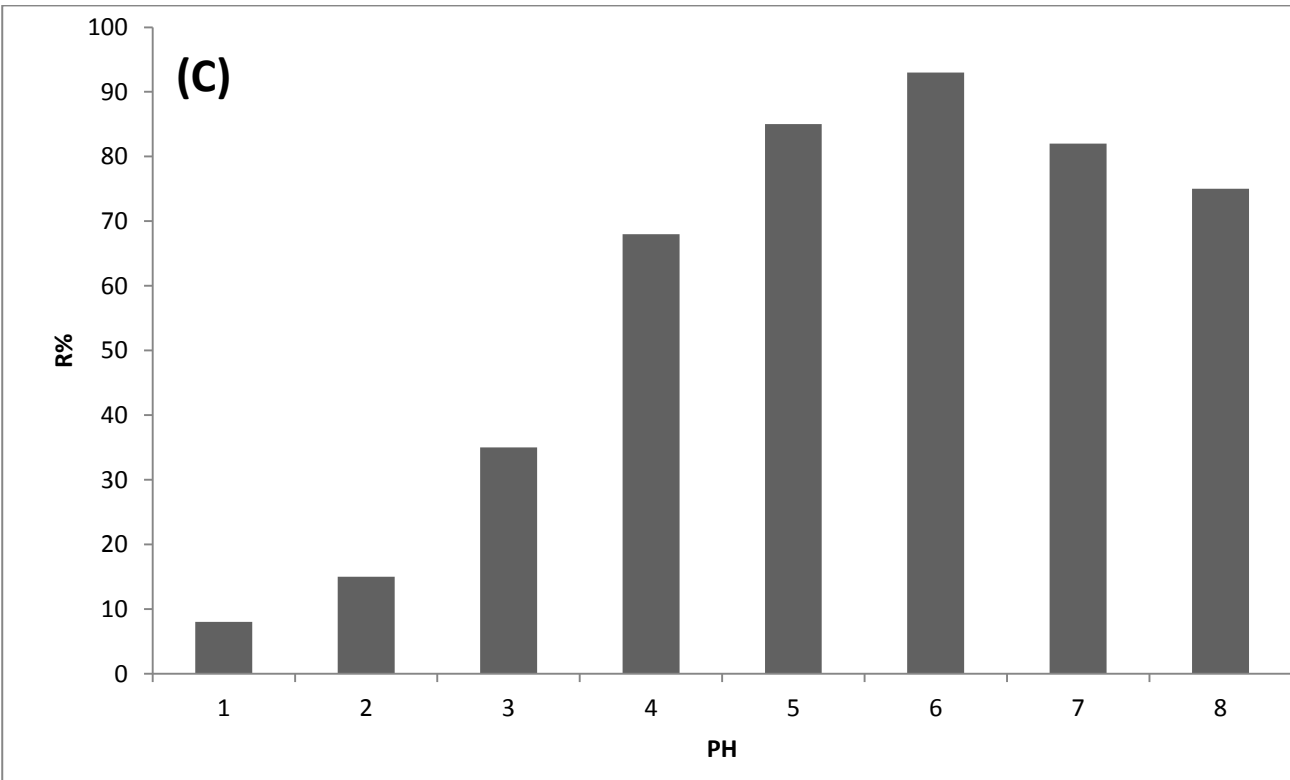
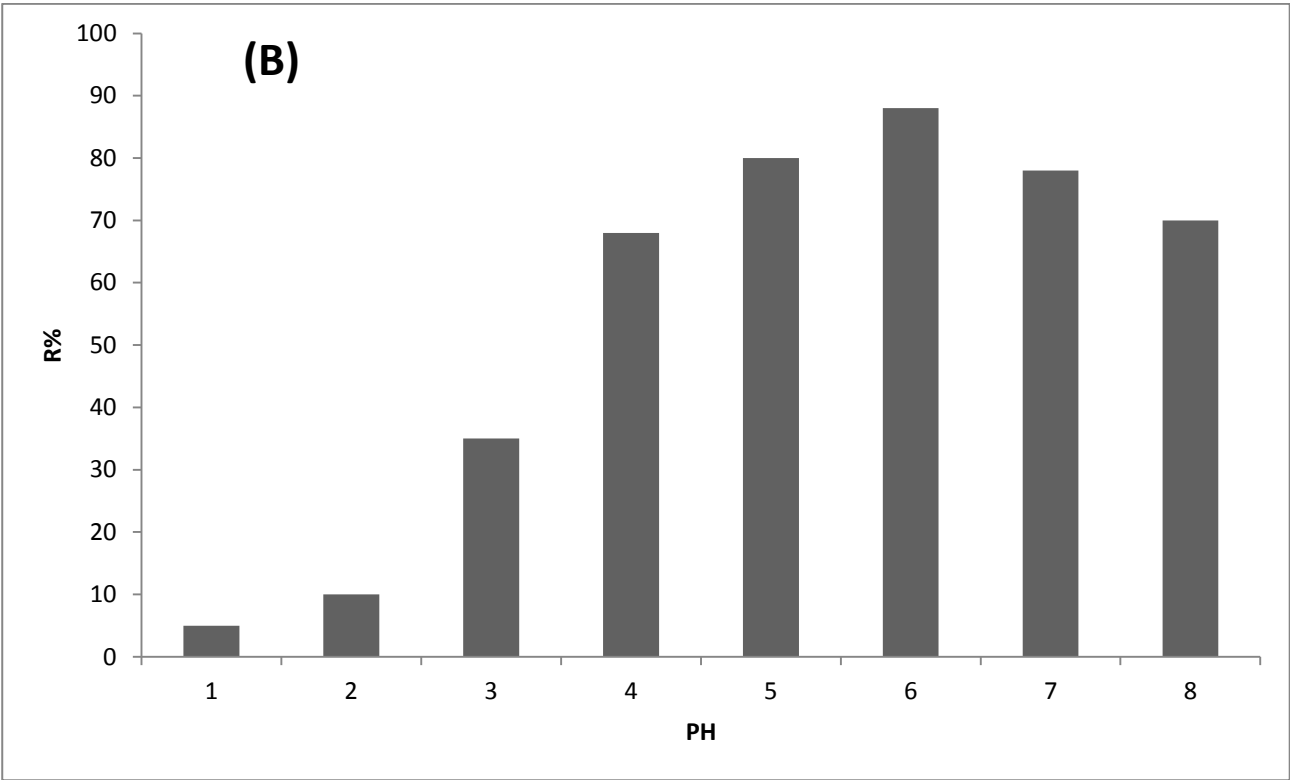
IV.1.2.2. Effect of pH solutions

The pH is an important process parameter on biosorption of metal ions from aqueous solutions since it is responsible for protonation of metal binding sites. The *Luffa Cylindrica* contain different groups of amino, hydroxyl and carboxyl on the surface, which are affected by changes in the solution pH [15]. The influence of solution pH on the metal ions adsorption capacity was examined at various pH values (2.0 to 8.0) as displayed in Fig.IV.8. (A, B, C, D). The maximum adsorption of Pb (II), Zn (II) and Cu (II) was obtained at pH5-6. At lower pH values Pb (II), Zn (II) and Cu (II) removal was inhibited, possibly as a result of the competition between hydrogen and Pb (II), Zn (II) and Cu (II) ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the active sites in *Luffa Cylindrica* (LC) would be exposed, increasing the negative charge density on the LC surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the LC surface. In this study, these Pb (II), Zn (II) and Cu (II) at around pH 5-6 would be expected to interact more strongly with the negatively charged binding sites in the biosorbent. As a result, the optimum pH for these metals biosorption was found as 5-6 and the other biosorption experiments were performed at this pH value. . In the case of Cr (VI), the

Chapter IV: Results and discussion

results showed that the maximum amount of Cr (VI) adsorbed occurs at pH 2. The adsorption capacity decreases sharply when the pH of the solution goes from 2 to 3. Beyond this value of pH, the adsorption capacity still decreases, but less significantly, to record its lowest value at pH7. This behavior is explained by the fact that at pH2, the functional groups present on the surface of the LC particles undergo a strong hydronation, which confers on the parietal bio polymers a positive overall charge. On the other hand, the ionic forms of hexavalent chromium which may be present in solution are anionic in nature such as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_3\text{O}_{10}^{2-}$ and $\text{Cr}_4\text{O}_{13}^{2-}$, and this for pH values ranging from 1.5 to 4 [14]. Thus, the biosorption involved in the present study seems to be mainly due to an electrostatic attraction phenomenon. In addition, the adsorption capacity recorded decreases with increasing pH. Indeed, the higher the pH, the more the solution is concentrated in free hydroxyl (OH^-) radicals which are likely to compete with the anionic species of Cr (VI) on the active adsorption sites available on the surface of LC fibers.





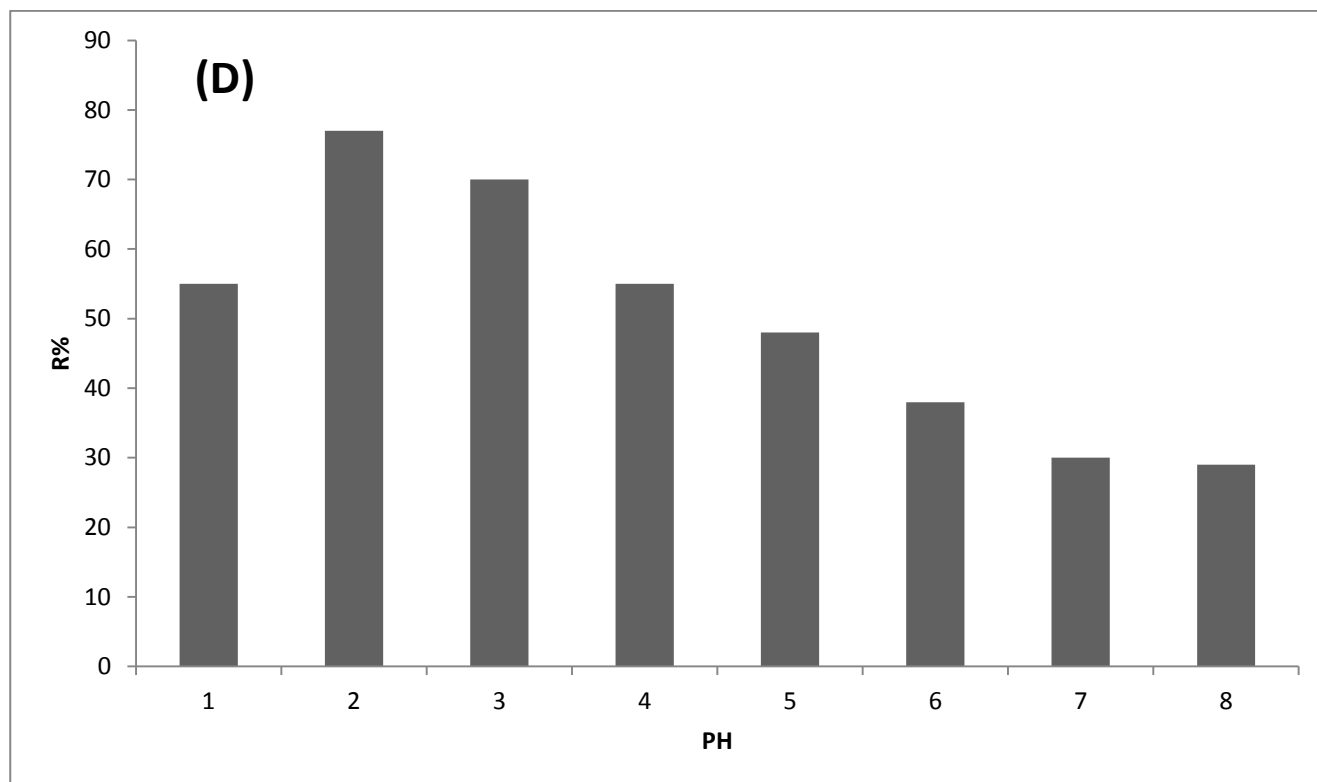


Fig. IV.8: Effect of pH solution: (A) LC-Pb (II), (B) LC-Zn (II), (C) LC-Cu (II), (D) LC-Cr (VI).
(Initial concentration 10 mg/L; contact time: 120 min; biosorbent dose: 1 g/100mL; T: 298 K).

IV.1.2.3. Effect initial concentrations of metal ions

These studies were carried out to determine the time required for biosorption of Pb (II), Zn (II), Cu (II) and Cr (VI) ions on *Luffa cylindrica* to reach equilibrium. These experiments were conducted using 1 g of LC with 100 mL of metal solution at different initial concentrations. As seen in Fig. IV.9 shows that as the initial heavy metal ion concentration increased, at 298K, constant pH and constant adsorbent mass for the respective optimum times, the percentage removal of the metal ions decreased. The higher initial metal ion concentrations provide a strong driving force between the liquid/solid phases [16]. At lower concentrations, the ratios of available binding sites to the initial metal ion concentrations were larger, while at higher concentrations, the saturation of the adsorption sites occurred. This behavior is attributed to less availability of surface-active sites.

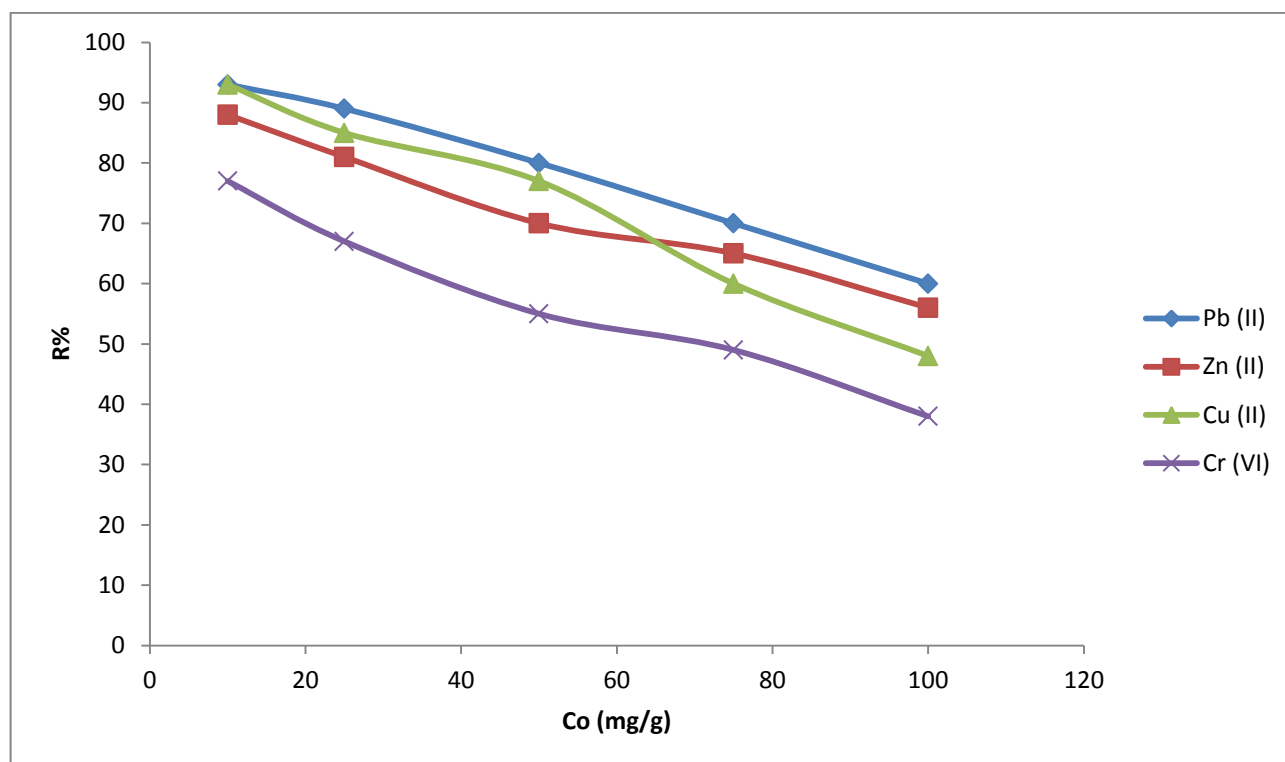


Fig.IV. 9: Effect of initial metal ion concentration onto LC .

IV.1.2.4. Effect of *Luffa Cylindrica* concentrations

The influence of adsorbent dose of *Luffa Cylindrica* powder was investigated in the range of 0.1–4g for 100 ml of initial metal ion concentrations. The plots of percentage removal of metal ions against dosage are presented in Fig.IV.10. It is worth noting that the percentage removals of the studied metal ions increased as the adsorbent dose increased. This could be due to the increased adsorbent surface area, pore size and volume, and the availability of vacant sites [17]. The higher adsorbent dosage gave rise to higher removal of metal ions, providing an important driving force to overcome all mass transfer resistances of the metal ions between the aqueous and solid phases.

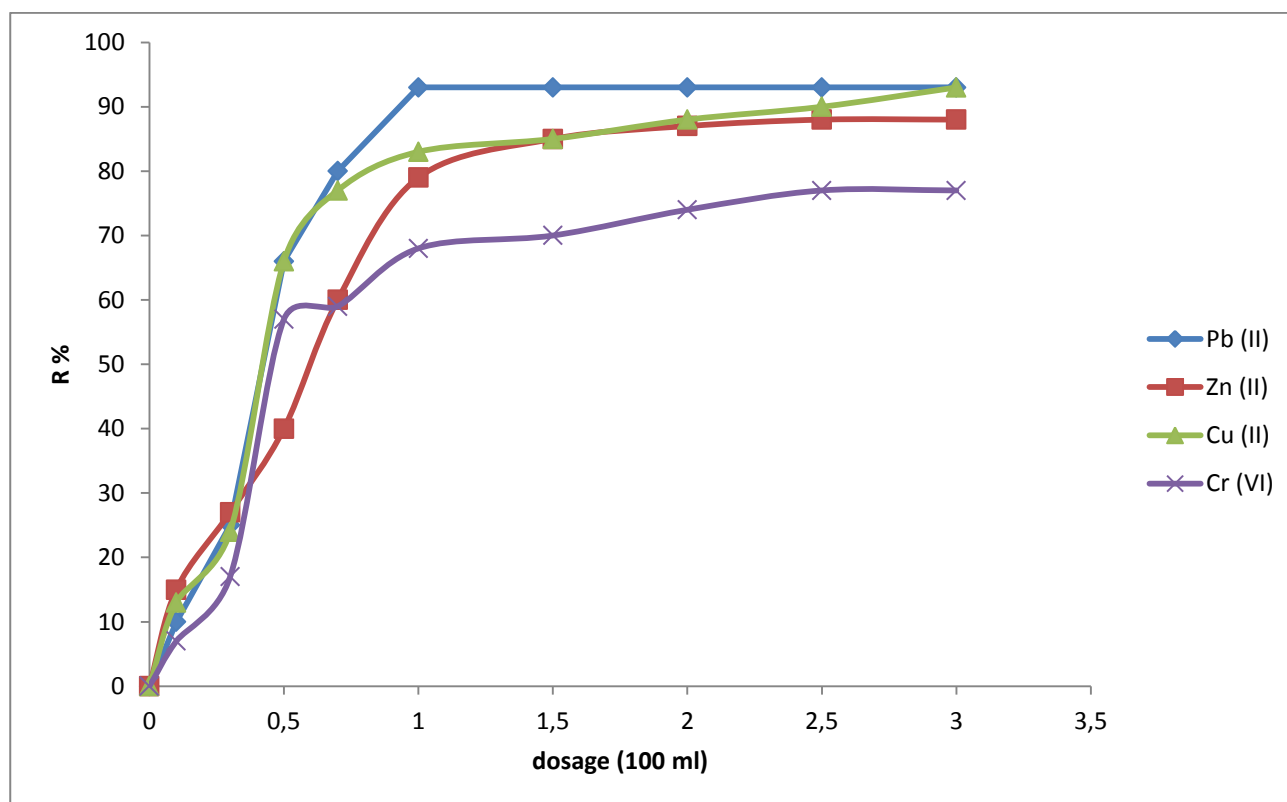


Fig. IV.10: Effect of adsorbent dosage on metal ion adsorption onto LC.

IV.1.2.5. Effect of temperature and thermodynamics of adsorption

The effect of temperature parameter on the uptake of metal ions by *Luffa Cylindrica* describes the relationship between temperature and the concentrations of the metal ions adsorbed onto the adsorbent at optimum contact time. As illustrated in Fig. IV.11, the adsorption of the metal ions on the adsorbent decreased as the temperature increased from 298 to 333 K. The decrease in adsorption of metal ions could be the result of a decrease in the mobility of the metal ions as a result of acquired energy in the system. This indicated that the interaction of metal ions with active sites at the surface of the adsorbent is an exothermic process, which could also be considered as a physical adsorption process. In order to describe the spontaneity of the adsorption process by thermodynamic parameters, temperature was varied from 298 to 333 K. The results are shown in Table.IV.4. The negative values of (ΔH°) obtained indicates that the adsorption processes of all metals studied are exothermic in nature [18]. This confirms the previously discussed results which showed a decreased retention by the elevation of the temperature of the solution. Also, the relative value of ΔH° confirms the idea that the binding of the metal molecules to the *Luffa Cylindrica* is likely of a physical type. On the other hand, the value of (ΔS°) indicates the good affinity of the

Chapter IV: Results and discussion

biosorbent with respect to the metals ions and reflects the increase of the "disorder" factor at the level of the solid interface / solution with some possible structural changes of the adsorbate and the biosorbent during the adsorption process. Moreover, the negative values of (ΔG°) show that the adsorption process studied is spontaneous [19]. The negative values of the standard enthalpy (ΔH°) (Table.IV.4) confirm that the adsorption at the sites of each adsorbent is of exothermic nature and which is also indicated by the increase of the adsorbed quantity with the decrease of the temperature, and that the molecule / particle interactions are of a physical nature.

Tab.IV.4: Thermodynamic parameters of Pb, Zn, Cu and Cr ions removal from aqueous solution by LC.

Metal ions	ΔH° (kJ/mol)	ΔS° (KJ/mol.K)	ΔG° (kJ/mol)				
			298K	303K	313K	323K	333K
Pb (II)	-5.8	-0.016	-1.032	-0.952	-0.792	-0.632	-0.472
Zn (II)	-7.11	-0.014	-2.93	-2.868	-2.728	-2.588	-2.448
Cu (II)	-10.77	-0.025	-3.32	-3.195	-2.945	-2.69	-2.450
Cr (VI)	-20.29	-0.05	-4.39	-5.140	-4.64	-4.14	-3.64

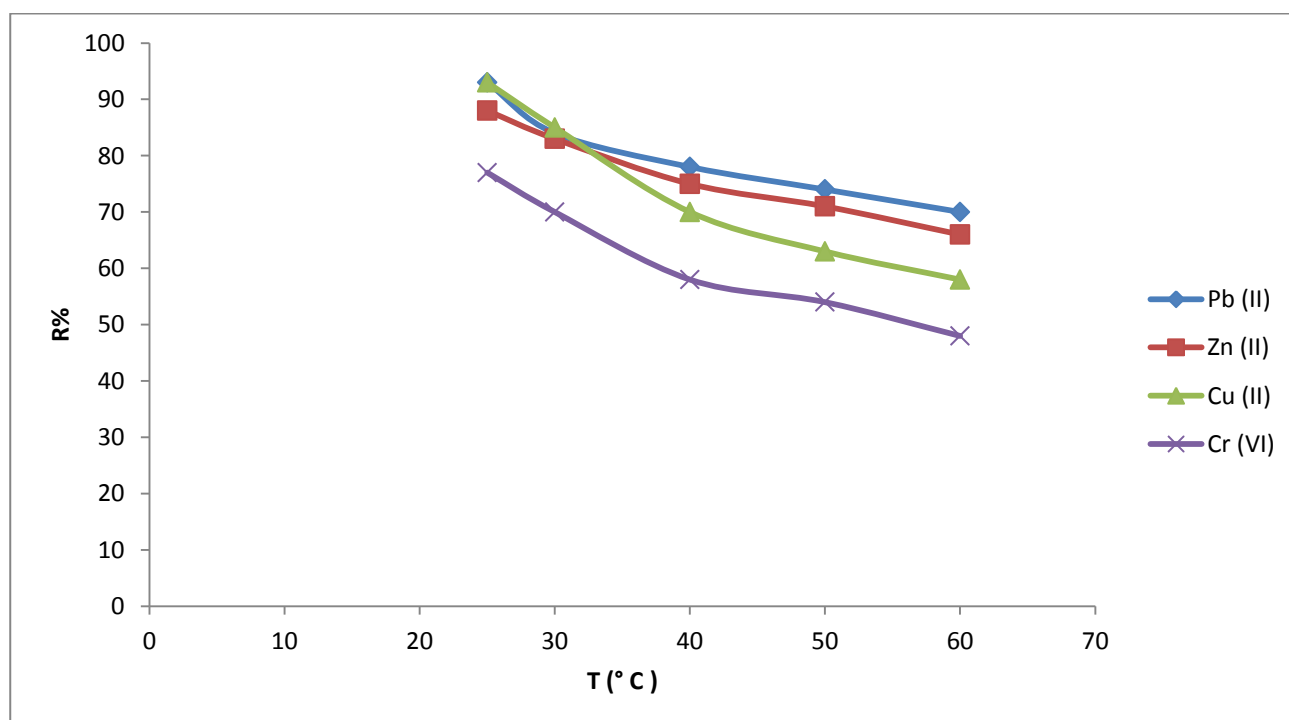
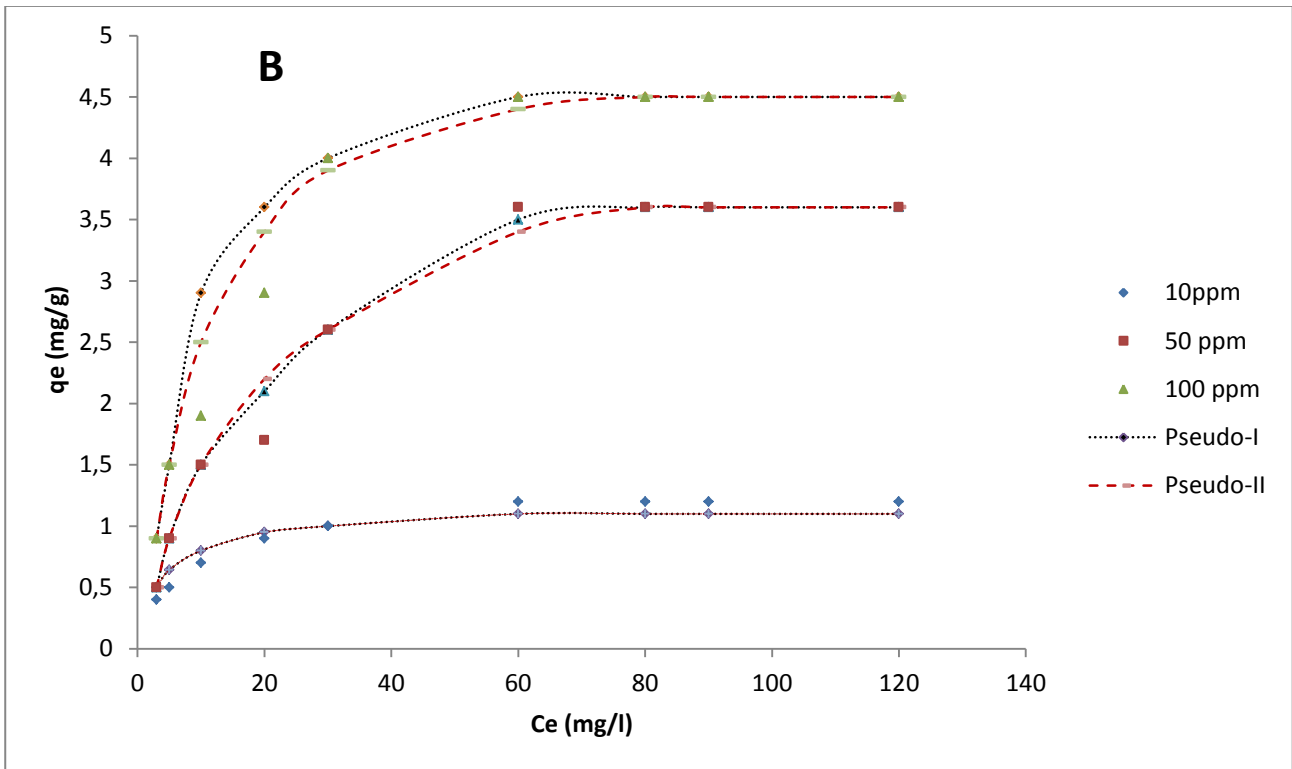
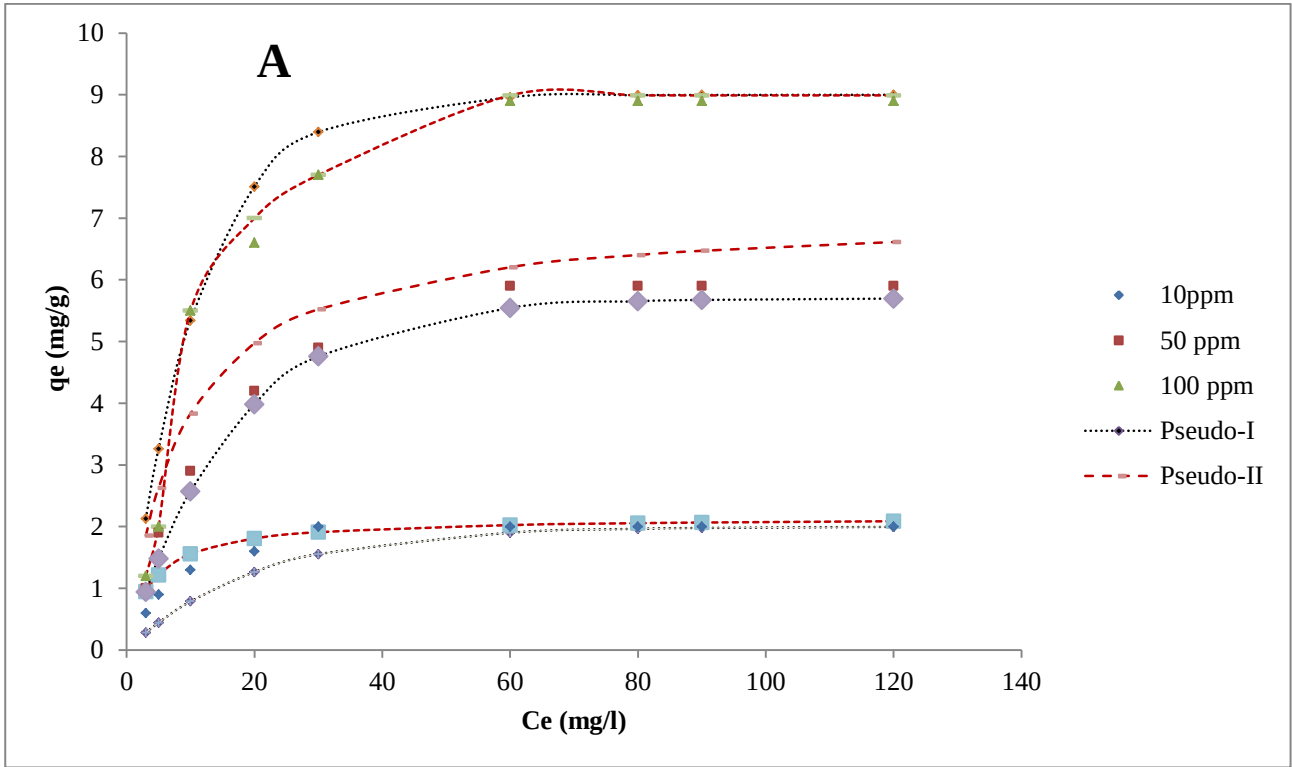


Fig. IV.11: Effect of temperature on the percentage removal of Pb (II), Zn (II), Cu (II) and Cr (VI) onto LC.

IV.1.3. Biosorption kinetics

The modeling of batch kinetics is important in explaining the mechanism of adsorption and to determine the potential controlling steps in mass transport. For all metal studied, the results fit the pseudo-second order (PSO) better than the pseudo first order model (Fig. IV.12 (A, B, C and D)) indicating the involvement of two species in the sorption process of metal ions. As agreed with the literature, a pseudo second order model best describes the adsorption of divalent metal ions [21]. The rate constant of a pseudo second order model (k_2) decreases as the concentration is increased till it reaches a peak. This shows that the uptake rate is decreased and resistance in the microspores is increased, till equilibrium is reached [22]. This may be attributed to a change in the ratio of binding interactions. The maximum adsorption capacity values of the experiments were very close in value to the model q_e values as shown in Table.IV.5. Also, the fastest exchange rate, shown to occur in less than 20 min in Fig. IV.12, may mean that exchange positions are initially on the surface. The increase in initial concentration results in a decrease in k_2 and then an increase in value had been reached, a further decrease in K_2 was seen as concentration further increased. This implies that other experimental factors, not solely diffusion, play an important role in the kinetic process of adsorption. Also, this further explains the relationship between the number of available binding sites and the rate of adsorption since availability of sites is related to the initial concentration of metal ions and the time at which equilibrium adsorption capacity is reached [21].

Model efficiency, which equates to the correlation coefficient R^2 value, is a good measure to avoid errors that occur as a result of experimental values and is the best indicator for model fitting data values [23].



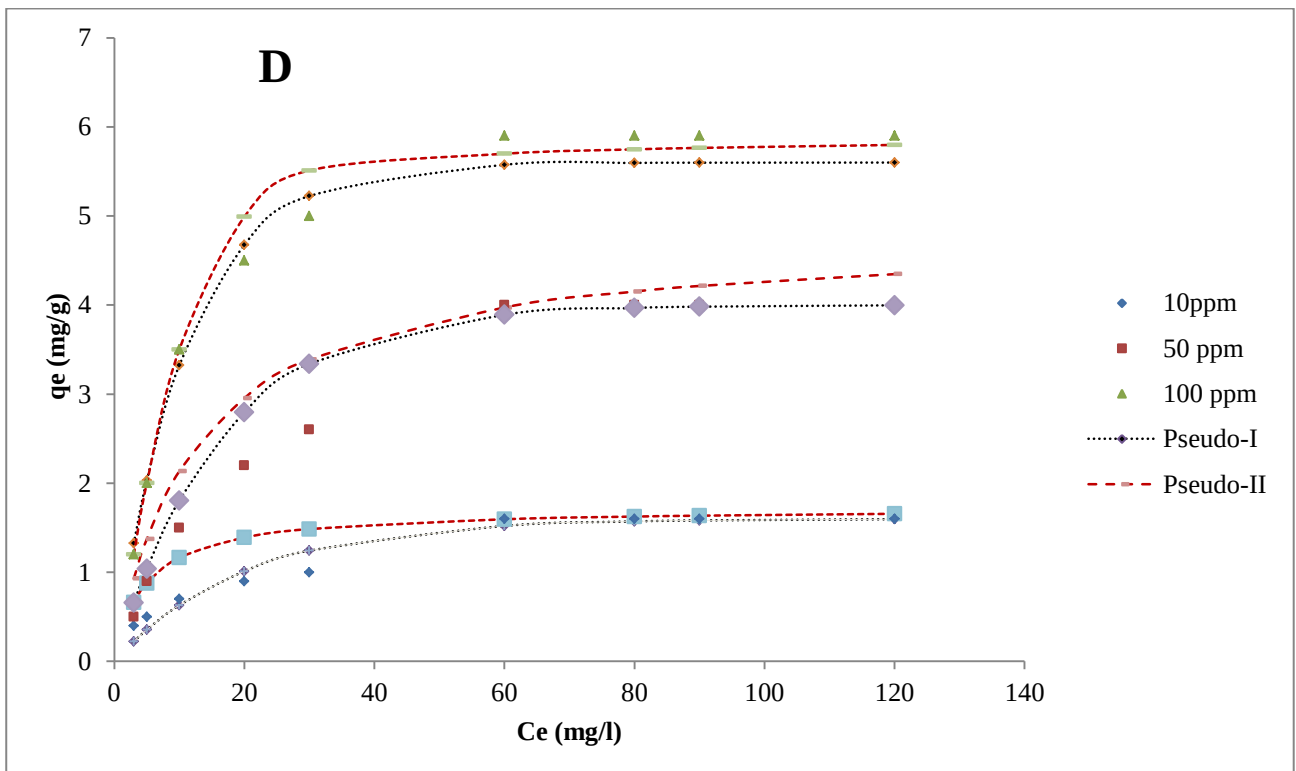
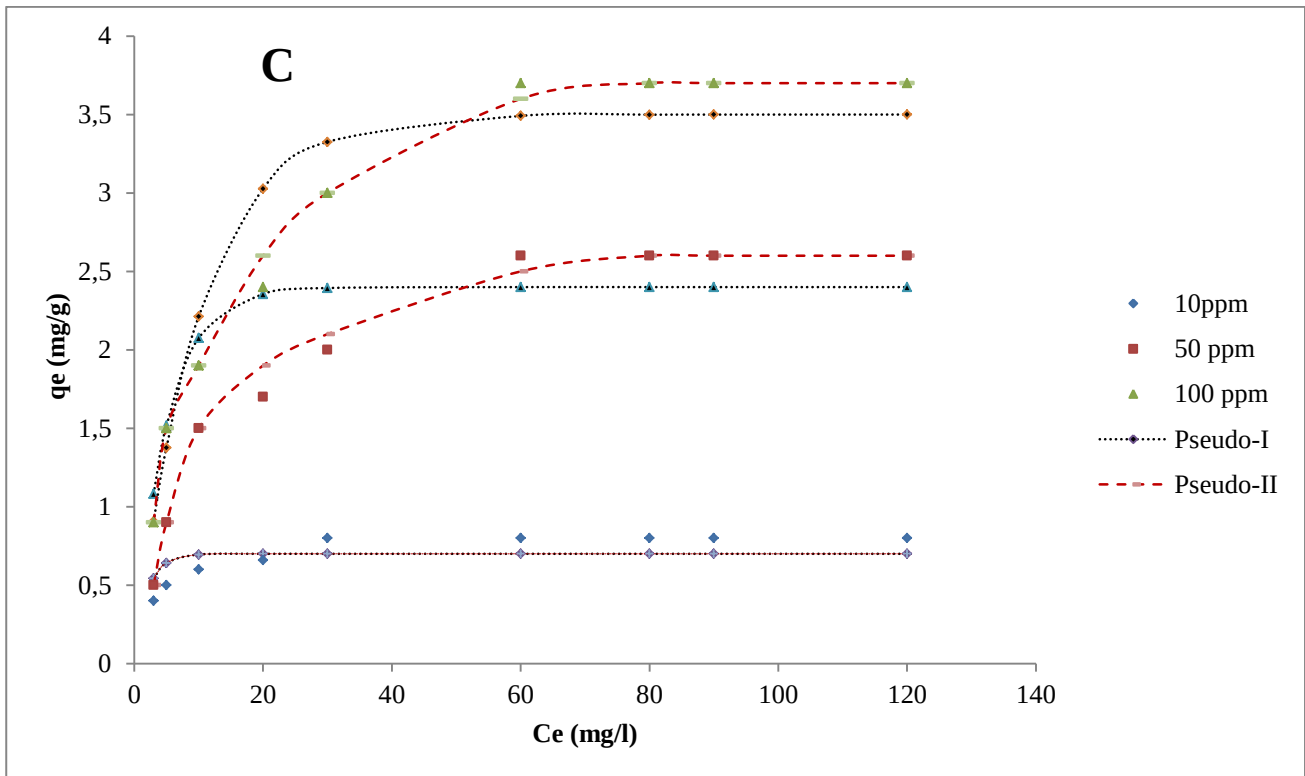


Fig. IV.12 : Adsorption kinetic models of Pb, Zn, Cu and Cr ions by LC.

Tab.IV.5: Kinetic parameters of Pb, Zn, Cu and Cr ions removal from aqueous solution by LC

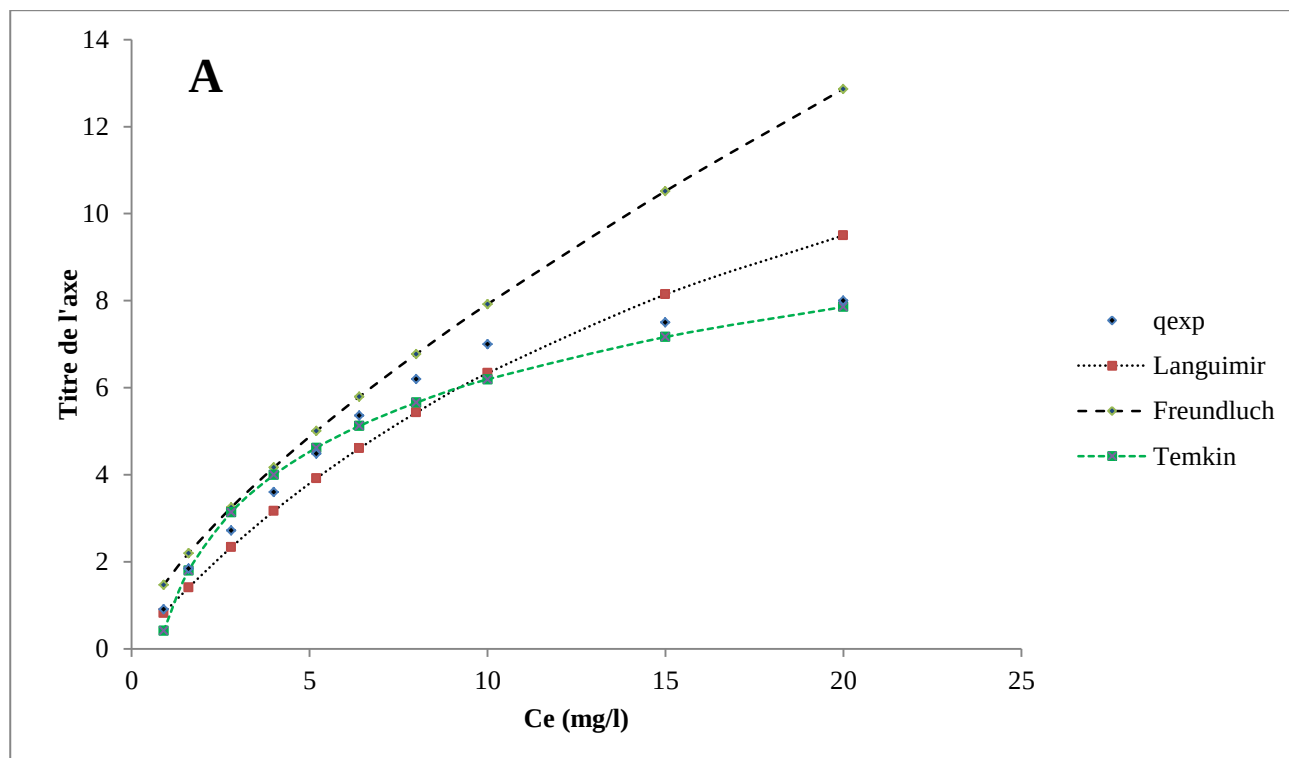
Metals	Initial metal concentration (mg/L)	Q Exp	Pseudo- first-order			Pseudo -second –order		
		q _{e,exp} (mg/g)	q _{e,cal} (mg/g)	k ₁ (min ⁻¹)	R ²	q _{e,cal} (mg/g)	k ₂ (g/mg. min)	R ²
Pb (II)	10	2.00	1.15	0.05	0.920	2.00	0.120	0.998
	25	5.9	4.99	0.069	0.930	5.9	0.05	0.999
	100	8.9	7.5	0.09	0.940	8.9	0.03	0.997
Zn (II)	10	1.07	0.96	0.16	0.920	1.07	0.15	0.999
	50	3.5	2.5	0.21	0.940	3.5	0.06	0.999
	100	4.6	3.26	0.30	0.940	4.6	0.014	0.998
Cu (II)	10	0.88	0.60	0.111	0.920	0.88	0.20	0.999
	50	2.5	2.11	0.19	0.940	2.5	0.14	0.998
	100	3.5	3.06	0.23	0.950	3.5	0.01	0.997
Cr (VI)	10	1.5	1.15	0.15	0.920	1.5	0.33	0.999
	50	3.6	2.29	0.29	0.940	3.6	0.45	0.998
	100	5.8	4.26	0.39	0.94°	5.8	0.09	0.998

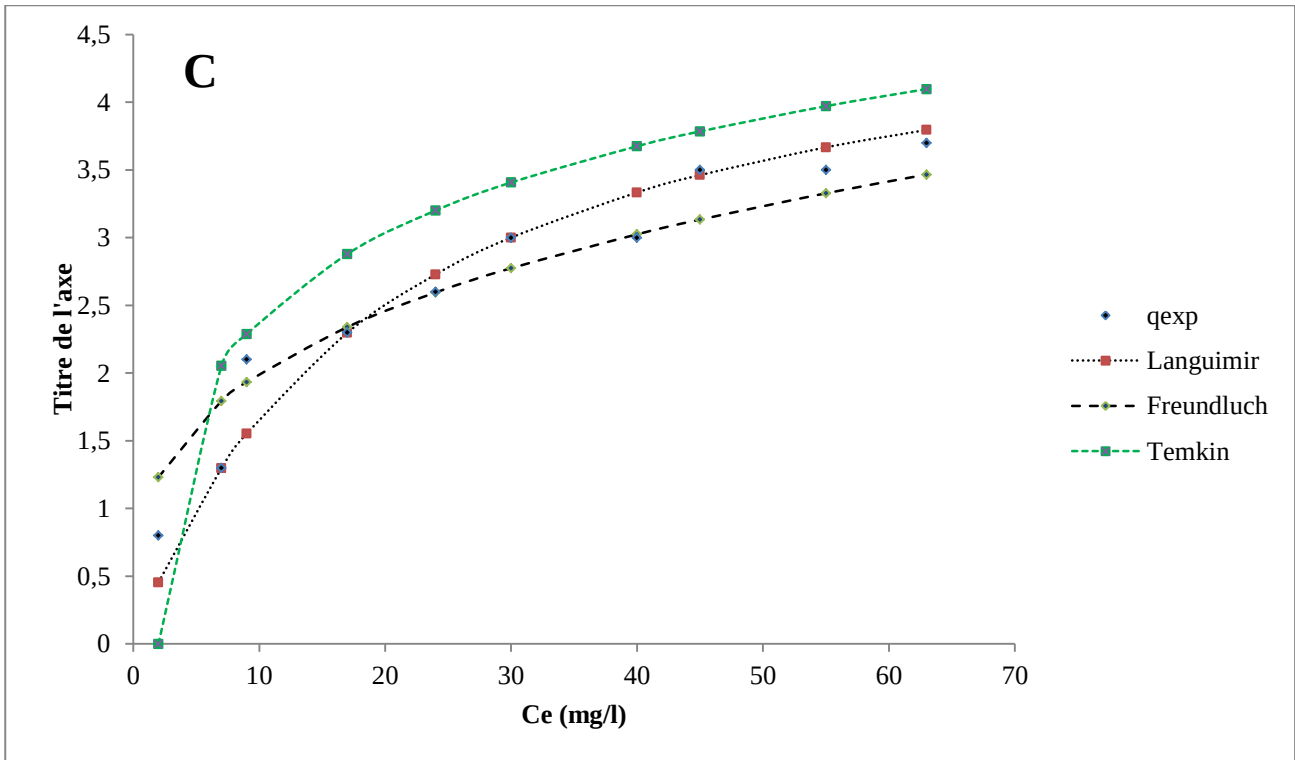
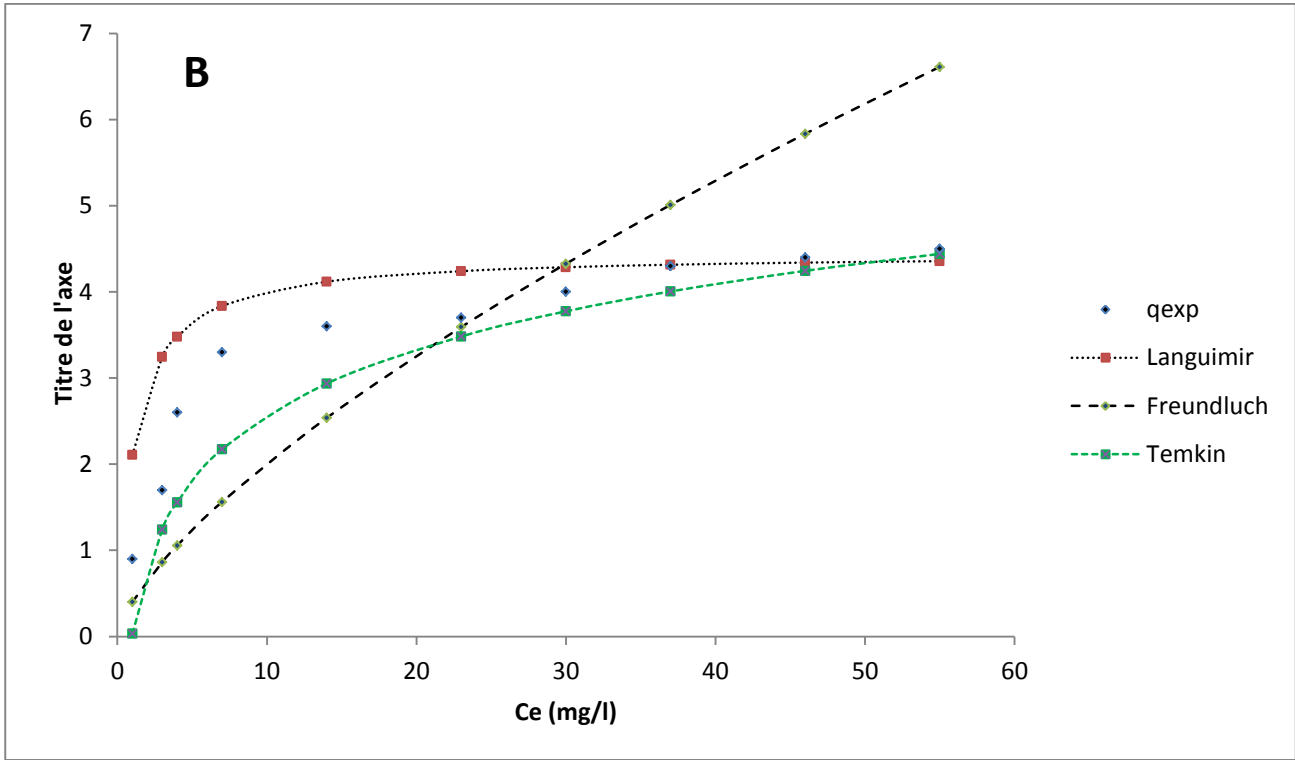
IV.1.4. Adsorption isotherms

Equilibrium data of the Pb (II), Zn (II), Cu (II) and Cr (VI) removal process were analyzed and modeled by Langmuir, Freundlich and Temkin isotherm models. These mathematical models are the most frequently employed for different adsorbent/adsorbate process. According to the theory of Langmuir, adsorption system onto adsorbent surface is limited to monolayer with definite and localized site; only a once layer of adsorbate on the solid surface are adsorbed. This empirical isotherm assumes that the adsorbent surface is homogenous and the energy of adsorption is identical for all sites and there is no interaction between adsorbed molecules on plan surface. Unlike Langmuir isotherm, Freundlich adsorption model [24] argues that adsorbent surface is heterogeneous active sites with multiple levels of adsorption temperatures and different affinity levels. The Temkin adsorption model [25] suggests the adsorption energy decreases linearly with the surface coverage owing to adsorbent/adsorbate interactions.

Chapter IV: Results and discussion

Equilibrium tests were studied under optimum conditions obtained from the isotherm model predicted by. Constants and parameters of each model were derived by coefficient of correlation (R^2). Isotherm model plots for removal of metal ions are shown in Fig. IV.13. the adsorption isotherm constants and R^2 values are presented in Table.IV.5. According to Fig. IV.13 and Table.IV.6, the equilibrium data are fitted better by the Langumuir model compared to other models for all metal studied with high error values (0.998, 0.999, 0.997 and 0.998 for Pb (II), Zn (II), Cu (II) and Cr (VI) respectively). This result shows that the adsorption phenomenon proceeds as a monolayer on uniform surfaces. The maximum sorption capacities are 8.9, 4.67, 3.9 and 5.91 mg/g for Pb (II), Zn (II), Cu (II) and Cr (VI) , respectively. The values of K_L which are attributed to the binding energy of the active site of LC are 0.05, 0.09, 0.05 and 0.06 L/g for Pb (II), Zn (II), Cu (II) and Cr (VI), respectively. The value of R_L vs initial lead ions concentrations between 10-120 mg/L are 0.66-0.14, 0.52-0.08, 0.66-0.14 and 0.625-0.12 for Pb (II), Zn (II), Cu (II) and Cr (VI) K , respectively .These results indicated that the bioprocess is favorable and reversible, because ($0 < R_L < 1$) [26]. Additionally, it was observed that the variation of adsorption energy ($b_T < 8$) in Temkin model, which validates the physical adsorption, was 2.4, 2.8, 2.98 and 2.71 kJ/mol for Pb (II), Zn (II), Cu (II) and Cr (VI), respectively.





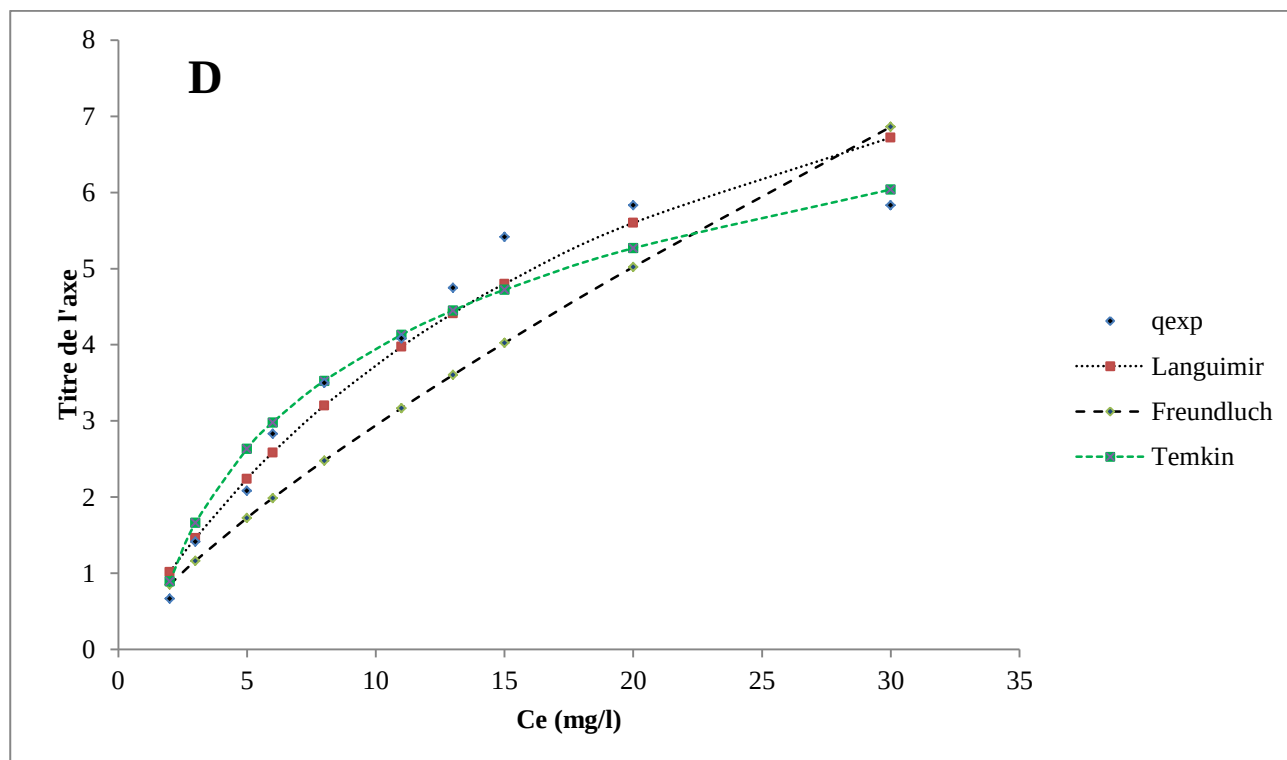


Fig. IV.13 : Adsorption isotherm models of Pb, Zn, Cu and Cr ions by LC.

Table.IV.6: Isotherm parameters of Pb, Zn, Cu and Cr ions removal from aqueous solution by LC.

Isotherm model	T (K)	isotherm parameters		R ²
		q _{max} (mg/g)	K _L (L/mg)	
Langmuir	Pb (II)	8.9	0.05	0.998
	Zn (II)	4.67	0.09	0.999
	Cu (II)	3.9	0.05	0.997
	Cr (VI)	5.91	0.06	0.998
Freundlich		K _F (mg/g)	1/n	
	Pb (II)	1.58	0.701	0.94
	Zn (II)	0,87	0.303	0.9
	Cu (II)	0,69	1.45	0.970
	Cr (VI)	0.427	0.713	0.981
Temkin		b _T (KJ/mole)	A _T (L/g)	
	Pb (II)	2.4	1.32	0.95
	Zn (II)	2.8	1.000	0.970
	Cu (II)	2.98	1.069	0.970
	Cr (VI)	2.77	0.999	0.964

IV.1.5. Recycling of *Luffa Cylindrica*

IV.1.5.1. Desorption of metals ions loaded on the *Luffa Cylindrica*

Desorption studies were conducted to select the optimum desorbing solution to be employed in successive regeneration cycles. The desorption experiments shown in Fig. IV.14 indicate that Pb (II), Zn (II), Cu (II) and Cr (VI) ions accumulated onto the *Luffa Cylindrica* could be desorbed and maximum percentage recovery of Pb (II), Zn (II), Cu (II) and Cr (VI) ions with 0.1 M HCl were 95.1%, 78.1%, 82.01 and 68.1, respectively. Therefore, 0.1 M HCl solution was selected as desorption reagents for removing Pb (II), Zn (II), Cu (II) and Cr (VI) ions from the *Luffa Cylindrica* surface. The resultant desorption phenomenon observed in Fig. IV.14 for Pb (II), Zn (II), Cu (II) and Cr (VI) ions might be attributed to ion exchange type interaction rather than chemical sorption [27]. Desorption is useful for the recovery and separation of metal ions in addition to the regeneration of the exhausted bisorbent [28]. The hydroxyl and carboxylic groups in the groundnut husk made it amenable to easy desorption and regeneration with the acid solutions [29]. The results of this study contradict the finding of Bhuvaneshwari et al [30]. Who studied on regeneration of chitosan after Cr (VI) sorption. In their study, 0.1 M H₂SO₄ was the best desorption agent and maximum desorption efficiency of Cr (VI) was found to be 88% under the following optimum conditions: agitation speed of 120 rpm, a contact time of 60 min and temperature of 40 °C. Furthermore, Wan et al. [31] investigated the desorption of Pb (II) and Cu (II) ions from chitosan-coated sand in a batch system using tap water and diluted HCl solutions. The results signified that more metal ions could be recovered by the HCl with desorption efficiency of 97.91% and 99.22% for Pb (II) and Cu (II), respectively.

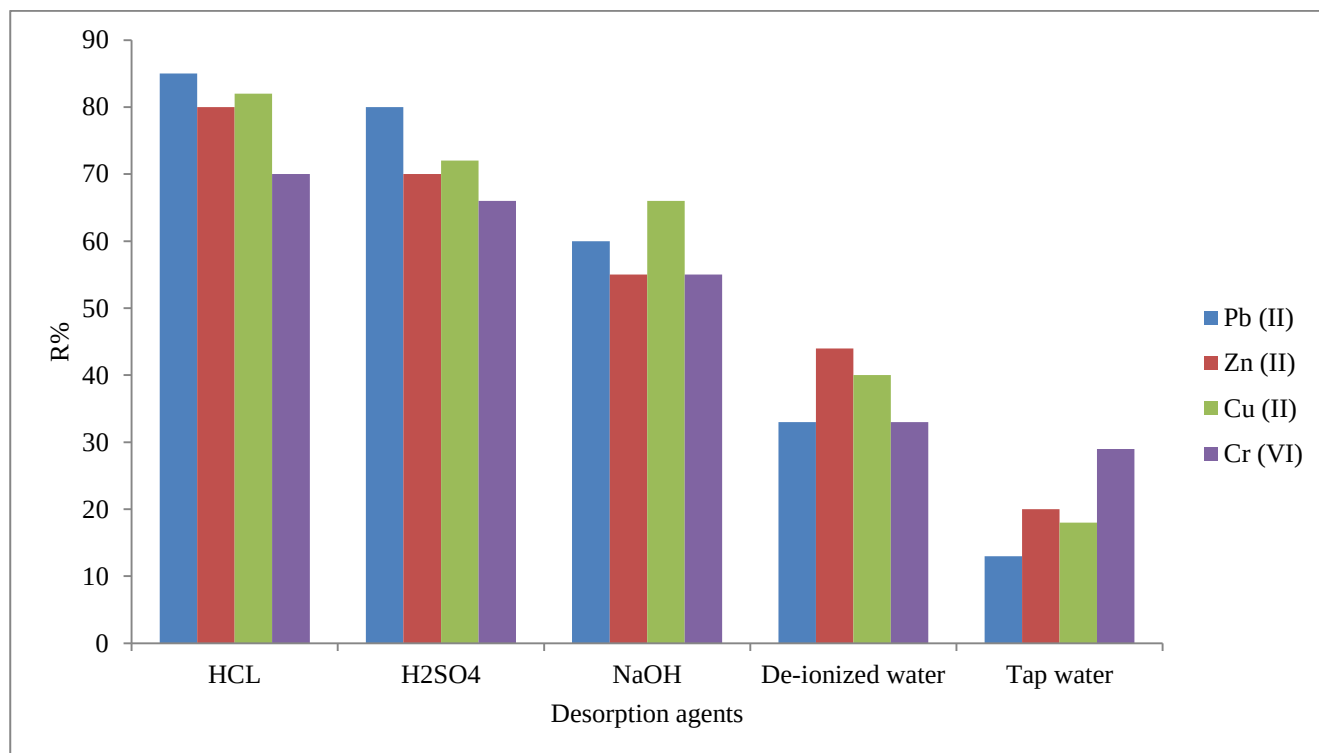


Fig. IV.14: Desorption of Pb (II), Zn (II), Cu (II) and Cr (VI) ions adsorbed on LC.

IV.1.5.2. Regeneration and reusability of the *Luffa Cylindrica*

Several adsorption-desorption cycles were conducted for Pb (II), Zn (II), Cu (II) and Cr (VI) ions to determine the adsorption-desorption potential of the *Luffa Cylindrica*, once it had been regenerated several times. The reusability of the used adsorbent was investigated by performing three successive Adsorption-desorption cycles Pb (II), Zn (II), Cu (II) and Cr (VI) ions on the adsorbent using 0.1 M HCl. There was a gradual decrease Pb (II), Zn (II), Cu (II) and Cr (VI) ions removal efficiencies with an increasing number of cycles as shown in Fig. IV.14. It was observed that the first cycles showed good retrieval of all metal ions accumulated on the adsorbent surface. For Pb (II), Zn (II), Cu (II) and Cr (VI) ions, the removal efficiencies of first cycles were found to be 80.4%, 68.3% 75.7and 68.5%, respectively, as presented in Fig. IV.14. the regeneration experiments showed that the LC could be reused repeatedly in the adsorption and recovery of Pb (II), Zn (II), Cu (II) and Cr (VI) ions ions without significantly losing its adsorption properties. Generally, regeneration is a key factor in improving the economy of the adsorption process and accessing the potential of the adsorbent for commercial applications. From the regeneration studies, Pb (II), Zn (II), Cu (II) and Cr (VI) ions uptake capacity on the LC was reduced after a sequence of three cycles. After this, no significant desorption was observed which indicated that a considerable part of the metal ions adsorbed was due to irreversible sorption. Hence, chemisorption has an important influence on metal ions removal [32]. The LC be reutilized repeatedly in Pb (II), Zn (II),

Cu (II) and Cr (VI) ions adsorption processes since the Pb (II), Zn (II), Cu (II) and Cr (VI) ions could be desorbed and adsorbent regenerated up to three cycles by 0.1 M HCl. This means that the adsorbent offered an economic benefit to be recycled repeatedly in Pb (II), Zn (II), Cu (II) and Cr (VI) ions adsorption process. It has been found that if the used adsorbent could be regenerated and used again at the end of the first cycle, then the adsorbent is said to be economical and could be used commercially [33]. The findings of this study could be compared to the findings of other studies on desorption and regeneration of exhausted biosorbents. Gupta and Rastogi [34] investigated sorption and desorption studies of chromium (VI) from the nonviable cyanobacterium *Nostoc muscorum* biomass. Sorption–desorption of chromium into inorganic solutions and distilled water were observed and the study indicated that the biosorbent could be regenerated using 0.1 M HNO₃ and EDTA with up to 80% recovery. The biosorbent was reused in five biosorption–desorption cycles without a significant loss in the biosorption capacity. Katsou et al [33] studied the regeneration of natural zeolite polluted by lead (II) and zinc (II) in wastewater treatment systems. Several desorbing solutions such as HNO₃, NaCl, KCl and NH₄Cl were examined for the removal of Pb (II) and Zn (II) from zeolite, and the highest desorption efficiency was obtained for 3 M KCl and 1 M KCl, respectively. KCl was the most effective solution for the desorption process exhibiting very high desorption efficiencies (>98.5%) for both metals. Kwon et al [35] conducted a study on the desorption and regeneration characteristics for previously adsorbed indium ions to phosphorylated sawdust. Various chemical reagents such as HCl, HNO₃, NaCl, ethylene diaminetetraacetic acid and nitrilotriacetic acid were tested on the desorption characteristics of indium ions adsorbed on phosphorylated sawdust. Among them, HCl was chosen as the best desorbing agent with a desorption efficiency of 97% at a concentration of 0.5 M. A study was conducted by Hossain et al.[36] on the adsorption and desorption of copper (II) ions onto garden grass. In their study, the desorption of adsorbed Cu (II) from exhausted garden grass was explored using eight types of desorption eluents including tap water, Milli-Q water, distilled water, 0.1 N H₂SO₄, 0.1 N HCl, 0.1 N HNO₃, 0.1 N NaOH and 0.1 N CH₃COOH. It was found that 0.1 N H₂SO₄ was a suitable eluent, which could be used up to five cycles of adsorption–desorption. In most studies, it is found that the desorption of metal ions in acidic media appeared to be rapid and higher than in basic and neutral media.

IV.1.6. Comparison of metals biosorption with different biosorbents

The biosorption capacity of *Luffa Cylindrica* biosorbent for the removal of Pb (II), Zn (II), and Cu (II) and Cr (VI) ions from aqueous solutions was compared with those of other biosorbents reported in literature. Table.IV.7 shows the biosorption capacity, $q_{\max}$ based on Langmuir adsorption

Chapter IV: Results and discussion

capacity. Maximum Pb (II), Zn (II), and Cu (II) and Cr (VI) ions biosorption onto LC at pH 6.0 and 25 °C obtained in this study were 8.9, 4.67, 3.9 and 5.91 mg/g for Pb (II), Zn (II), Cu (II) and Cr (VI) , respectively. These values found to be higher than many other biosorbents. The availability and cost effectiveness of LC are additional advantages to be used as an effective biosorbent for removal of Pb (II), Zn (II), and Cu (II) and Cr (VI) ions from industrial wastewaters.

Table.IV.7. Comparison of other biosorbents from selected literature with the present work.

Metals	Biosorbents	Qmax (mg g/g)	Pb ²⁺ concentration (mg/L)	pH	Biosorbent dosage (g/L)	Contact time (min)	References
Pb (II)	Penicillium sp.	4.6	10–200	-	10.0	120	[37]
	R. arrhizusBanana	5.2	10–200	5.0	10.0	60	[38]
	C. demersum	6.6	10–100	5.0	10.0	-	[39]
	Aspergillus niger	7.7	10–160	4.84	5.0	180	[40]
	Luffa Cylindrica	8.9	10–100	5.0	10	60	This study
Zn (II)	Neem bark	3.1	10–200	-	20.0	120	[41]
	Black gram husk	4.1	10–100	5.0	10.0	60	[42]
	Activated carbon	4.6	10–200	5.0	10.0	60	[43]
	Oxidised jute	5.02	10–150	4.84	5.0	180	[44]
	Luffa Cylindrica		10–100	5	10	60	This study
Cu (II)	Thyme leaves	0.04	10–100	5.0	5.0	120	[45]
	Sawdust	1.72	10–120	5.0	8.0	60	[46]
	Cotton ball	2.6	10–120	5.0	10.0	90	[47]
	Chlorella fusca	3.3	10–100	4.84	7.0	80	[48]
	Luffa Cylindrica		10–100	5	10	60	This study
Cr (VI)	A. sydoni	1.76	10–200	2.0	10.0	120	[49]
	Rhizopus	4.33	10–100	2.0	8.0	60	[50]
	Water lily	6.11	10–120	2.0	10.0	60-	[51]
	Green taro	6.06	10–100	2.0	20.0	180	[52]
	Luffa Cylindrica	5.4	10–100	2.0	10	60	This study

IV.1.7. Application the optimum conditions in industrial sample (Hassi R'mel)

The studied adsorbent was applied in the adsorption of Pb (II), Zn (II), Cu (II) and Cr (VI) ions from the sample of waste water of Hassi R'mel, Laghouat, Algeria. The sample was subsequently treated with the LC biosorbent materials to determine the percentage removal of the metal. The samples (500 mL) were then treated with 5 g of biosorbent at optimum condition of each metal. The two metal ions were quantified using spectrophotometer before and after the removal experiments Table.IV.8 shows the efficiency of *Luffa Cylindrica* of Pb (II), Zn (II), Cu (II) and Cr (VI) ions from industrial wastewater (wastewater composition is shown in chapter. I). Regardless of the type of used bacteria biomass, the efficiency of Zn (II), Cu (II) and Cr (VI) removal was over 75% because of the concentration in the wastewater did not exceed 12 mg/l. Only for lead ions did it remain lower than 25%, despite high concentrations of metal in the wastewater; 226.4 ppm. The descending order of selectivity of metal ions by the biomasses was Pb>Zn>Cu>Cr. This preferential type of adsorption may be ascribed to the difference in ionic radii and the electro-negativity of the metal ions. The ionic radius of Pb (II) is 1.20 Å°, while that of Zn (II) and Cu (II) is 0.9 Å°. The smaller the ionic radius, the greater its tendency to be hydrolyzed, leading to reduced biosorption. The electro-negativity of Pb (II) (2.33 Pauling) is greater than that of Cu (II) (1.91 Pauling) and Zn (II) (1.60 Pauling). Both the aforementioned factors contributed to the vegetal biomass had a greater affinity for lead than for nickel or zinc [53].

Thus, the results showed that LC is effective in removing Zn (II), Cu (II) and Cr (VI) ions from industrial waste water. Except for lead ions, this biosorbent is not sufficient for eliminate all heavy present in the industrial water. Thus, we propose to ameliorate the adsorbent capacity by immobilization of LC fiber with microalgal *chlorella pyrenoidosa*.

Tabl.IV.8. Adsorption of Pb (II), Zn (II), Cu (II) and Cr (VI) ions in the industrial waste water.

Metal ions	Time (min)	pH	T °C	C (mg/l)		Q _{max} (mg/g)	R%	
				before	after			
Pb (II)	60	5	25	226.4	183.1	2.6	11.03	0.005-0.015
Zn (II)	60	5	25	11.2	2.9	0.83	74.1	5
Cu (II)	60	5	25	7	1.01	0.599	84.2	1.0-1.3
Cr (VI)	60	2	25	5.3	0.01	0.538	100	0.05-0.25

IV.2. Biosorption of lead ions onto immobilized *Luffa Cylindrica*

In this section, an attempt was to explore the feasibility of an efficient biosorbent obtained by coating microalgal species (*Chlorella pyrenoidosa*) on the surface of lignocellulosic material (*Luffa Cylindrica* discs) for the removal of lead ions from aqueous solution and petroleum waste water.

IV.2.1. Characterization of *Luffa* immobilized

IV.2.1.1. FTIR study

The pattern of sorption of metal ions onto biomaterials is attributable to the functional groups present on active sites and characteristic bonds present on them. Fig. IV.15 depicts the FTIR spectrum determined for *Luffa Cylindrica* (LC) *Chlorella pyrenoidosa* (CP) and *C. pyrenoidosa* immobilized in *Luffa Cylindrica* (CP-LC). A broadband from 3600 to 3100 cm^{-1} may be observed in the *Luffa Cylindrica* spectrum, which is indicative of the elongation of -OH groups [54]. The bands located at 2810–2850 cm^{-1} correspond with the oscillation band of the group -CH [55, 56]. The intense peak near the 1500 cm^{-1} region is typical of *Luffa Cylindrica* and indicative to C=O vibrations. The weak band at 1450 cm^{-1} is ascribed to COO^- associations and indicates the presence of carboxyl groups in the *Luffa Cylindrica* molecules. The peak that appeared at 950 cm^{-1} is attributed to the oscillation of C-O , while the oscillation band at 930 cm^{-1} is assigned COC groups [54]. A wideband ranging between 3600–3000 cm^{-1} is the fingerprint of the oscillation of OH groups in the spectra of *C. pyrenoidosa* confirms the existence of a hydroxide group [56]. The absorption peak at 2800 cm^{-1} could be attributed to the presence of asymmetric and symmetric -CH groups [54]. Another peak at 1500 cm^{-1} is suggesting the oscillation of C=O (extension of amide I) indicates the presence of residual N-acetyl groups [57]. The intense bands at 1470 cm^{-1} and 1100 cm^{-1} relate to oscillations of the N-H with exists as amine groups in *Chlorella pyrenoidosa* [54]. One of the fundamental monosaccharide in *Chlorella pyrenoidosa* is glucosamine, an amino sugar, and thence the presence of the amide groups might represent this amino sugar [57]. Distinct bands at 960 cm^{-1} (extension of C-O group) and at 930 cm^{-1} (extension of COC- bond) confirms the $\alpha\text{-L-guluronic acid}$ of *C. pyrenoidosa* [58]. In turn, the spectra of *C. pyrenoidosa* immobilized in *Luffa Cylindrica* adsorption peaks typical of both compounds constituting the sorbent applied in the study. A new peak, which does not exist in pure *C. pyrenoidosa*, is an asymmetric peak of adsorption at 1350 cm^{-1} being typical of the COO^- bands. It indicates that the CP-LC occurs carboxyl groups origin native *Luffa Cylindrica*. The CP-LC spectrum depicts also a shift of the absorption peak from 1500 cm^{-1} to 1450 cm^{-1} and disappearance of the amine group band (1500 cm^{-1}), which elucidates the reaction proceeding between L.

Cylindrica and *C. pyrenoidosa* as a consequence of ionic interactions between the positively charged amine group of *C. pyrenoidosa* and negatively charged carbonyl group of *L. Cylindrica*. To control the functional groups involved in the biosorption of Pb (II) onto CP and CP-LC, a comparison between the FTIR spectrum before and after biosorption of Pb (II) was done (Fig. IV.16). FTIR spectra depict slight changes in functional groups and surface characteristics of the biosorbents, elucidated by the shift of some functional groups' peaks due to lead biosorption. Furthermore, the fact demonstrated that the lead ions were successfully adsorbed by the CP and CP-LC, probably via physical interactions between the lead ions and the functional groups present. These shifts could be attributed to the changes in lead (II) ions associated with carboxylate and hydroxylate anions, indicating that acidic groups, carboxyl, and hydroxyl, are predominant contributor in the complexation of lead ions and ion exchange processes [59].

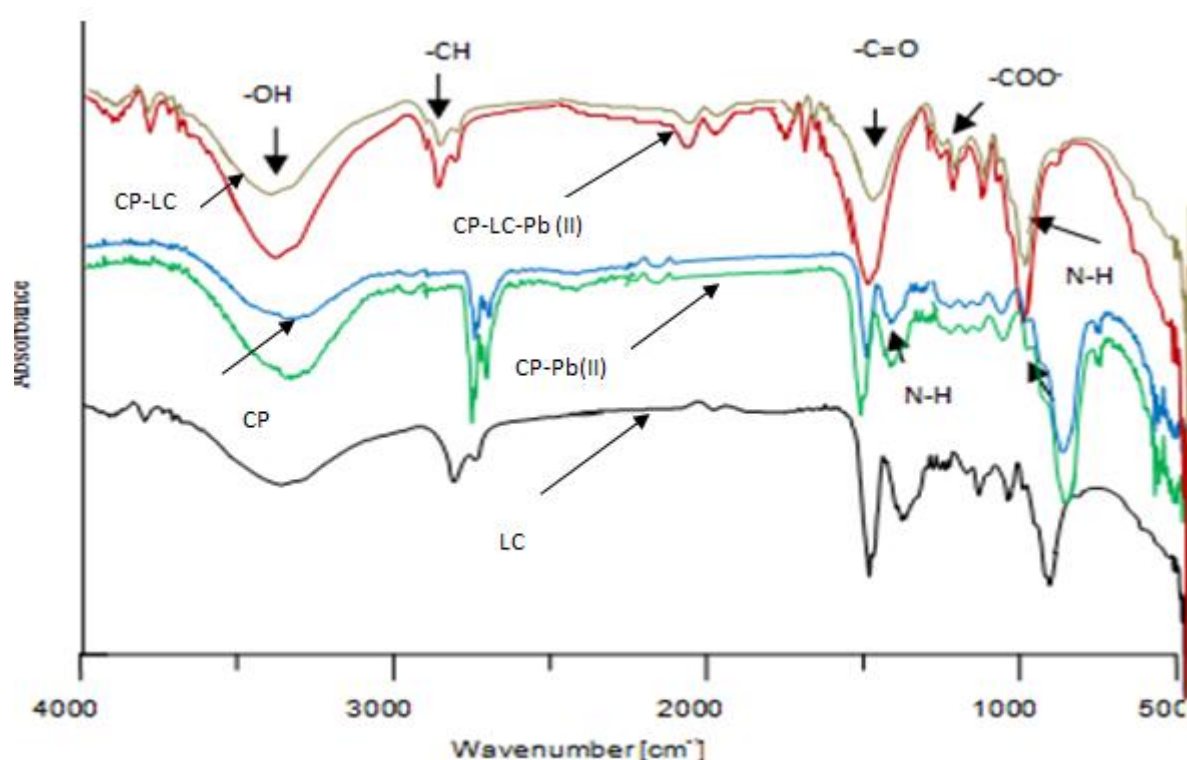


Fig. IV.15: FTIR spectrum of: L C, CP, CP-Pb (II), CP-LC, and CP-LC Pb (II).

IV.2.1.2. SEM-EDS study

SEM images showed a uniform spherical morphology for the sample (Fig. IV.17 (A)), with a particle diameter varying from 14.13 μm to 123.4 μm , with a median of 38.84 μm . It is possible to observe the presence of pores with an average diameter of $1.868 \pm 0.337 \mu\text{m}$, classified as macro-pores by the International Union of Pure and Applied Chemistry (IUPAC) [60]. Therefore, the selectivity of the biosorption process should be more associated with the interactions with the surface groups and not with the pore size itself [61]. Thus, the selectivity of the adsorption process should be more

Chapter IV: Results and discussion

related with the interactions with the surface function groups and not with the pore size [62]. The SEM micrograph of *C. pyrenoidosa* immobilized in *Luffa Cylindrica* thread showed a uniform microalgal growth along the surface of the LC fibers thread confirming that immobilized *C. pyrenoidosa* cells weren't fixed at single point. This uniform distribution in CP-LC is an important criterion for removal of metallic substances. Representative SEM of single LC before and after immobilization are depicted in Fig. IV.16 (B, C).

Results obtained through EDS (Fig. IV.17) confirmed the majority of carbon, 68.3%, followed by oxygen with 21.9%, copper 3.9% and other elements that added up to 5.8% of the material composition. Microalgae, when dry, can present 20% of triglycerides, 45% of proteins and 20% of carbohydrates [63], which justifies the predominant carbon composition found for the analyzed sample.

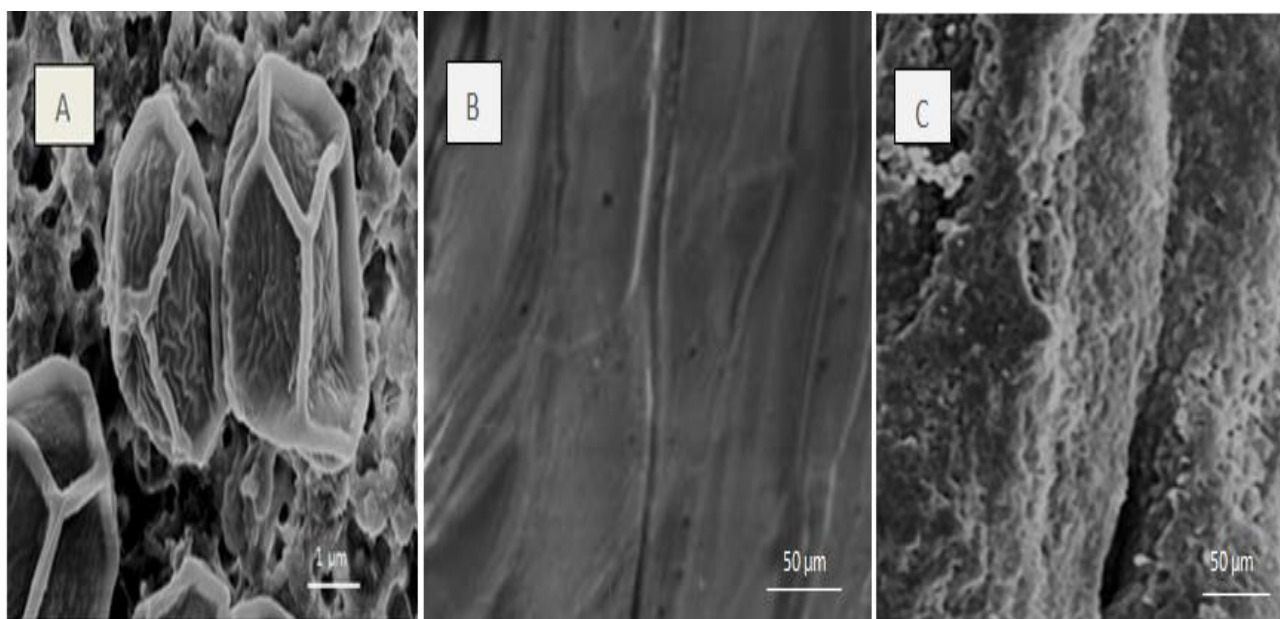


Fig. IV.16: (A) SEM of *C. pyrenoidosa* cells. (B) SEM of *Luffa Cylindrica* fiber. (C) SEM of *C. pyrenoidosa* immobilized in *Luffa Cylindrica*.

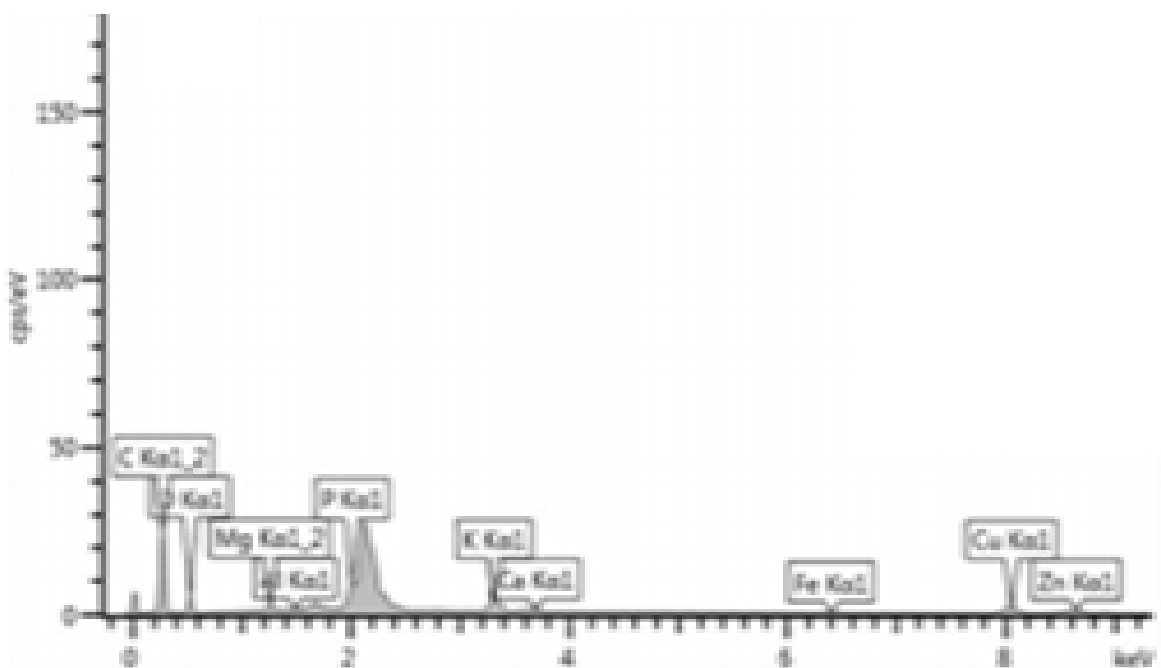


Fig. IV.17: EDS spectrum from the CP-LC.

IV.2.1.3. Thermogravimetric analysis

Like all vegetable biomass, CP-LC is composed of cellulose, hemi-cellulose, and lignin. Fig. IV.18 exhibits the curves for TGA and DTG for CP-LC in the temperature range of 30 to 600 °C in oxidizing atmosphere.

The overall mass loss during thermo-gravimetric analysis can be divided into steps related to moisture, hemi-cellulose, cellulose, and lignin. Thus, as one can see, the first stage of the weight loss (4.49%) can be attributed to the evaporation of physically absorbed water, structural water, and also perhaps due to the elimination of some side groups by heating the sesame leaf up to 180 °C. From 180 to 213 °C, mass loss was slight. Afterwards, the second stage of pyrolysis occurred when the temperature was varied from 213 to 430 °C. In this stage, almost all of the weight loss (53.33%) was observed with the maximum decomposition rate at 317 °C. The behavior of the pyrolysis curve at this temperature indicates hemi-cellulose and cellulose decomposition [64]. Lignin decomposition was evident in the 430 to 580 °C range (mass loss 36.50%), thus indicating that this structure was thermally more stable than hemi-cellulose and cellulose. Finally, no mass loss was detected when the temperature was increased further to 600 °C. This result indicates the presence of oxides (mainly those of aluminium and

silicon), which are stable at higher temperatures.

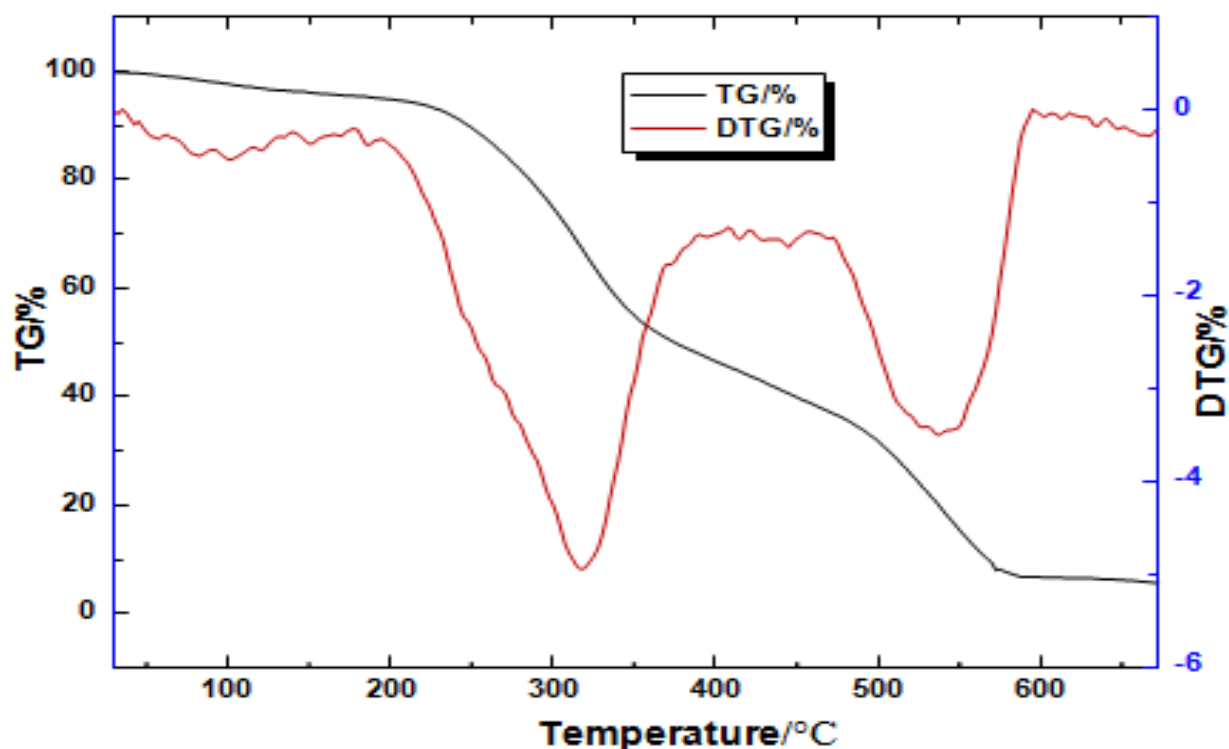


Fig. IV.18: Curves of thermo-gravimetric analysis (TG and DTG) of CP-LC.

IV.2.1.4. Point of zero charge (pH_{pzc})

The pH_{PZC} was defined by preparing a $0.5 \text{ g}\cdot\text{L}^{-1}$ solution of biosorbent in $0.03 \text{ mol}\cdot\text{L}^{-1}$ sodium chloride (NaCl) solution, adjusting the pH to different values (4–10). The mixture was placed in a shaker for 24 h at 250 rpm and 28°C and pH_{PZC} was obtained in the range where the buffer effect was observed [65]. For the adsorbent studied, the value of pH_{PZC} obtained was 5.95. In media with pH lower than pH_{PZC} , the surface charge of the adsorbent is positive and anions adsorption is favored. On the other hand, in media with pH above pH_{PZC} the surface charge of the adsorbent is negative and favors the biosorption of cations [66].

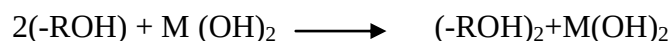
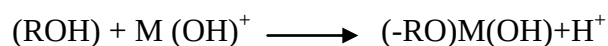
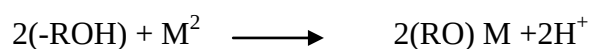
IV.2.2. Biosorption optimization

IV.2.2.1. Effect of pH

It is well documented that solution's pH is an important factor that has a significant influence on the metal solubility and the sorbate concentration of the counter ions on the functional group of

Chapter IV: Results and discussion

the biosorbent. Thus, the pH is considered as the most important factor that could affect the biosorption of metal ions from aqueous solutions [67]. Fig. IV.19 depicts the effect of pH variation on the biosorption of Pb (II) ions onto free and immobilized *C. pyrenoidosa*. The efficiency of Pb (II) biosorption in a pH in a range from 4.5 to 6 reached 91.36% for CP and 97% for CP-LC. Consequently, all the experiments were adjusted out at pH 5. The current outcome indicated that the biosorption of Pb (II) was increased with increment in pH value. Thus, at lower pH, Pb (II) would be present commonly as M (II) ions. The minimum biosorption showed at low pH of 2 could be, on one hand, due to the fact that the presence of higher proton concentration and its mobility favored hydronium ions biosorption parallel to M (II) ions and on the other hand, owing to the great solvability and ionizability of metals salt in the acidic solution. It would be credible to suggest that at a lower pH value, the adsorbent surface is surrounded by H_3O^+ ions, thereby preventing the positively charged metal ions from approaching the binding sites of the biomass surface. This condition suggests that the surface of biomass becomes more positively charged such that the attraction between active sites and metal cations is decreased. In contrast, when the pH level increased, the binding efficiency incremented because the functional groups of biomass surface were negatively charged thus facilitating biosorption of M (II), it could be deduced that the biosorption yield of Pb (II) increased with increasing pH as the metal species become less stable in the solution [68]. The optimum biosorption observed in the pH range from 4.5 to 6 could be due to partial hydrolysis of metal cations, which favors electrostatic attraction between the surface of biosorbents and Pb^{2+} ions. Resulting in the formation of soluble hydroxylated complexes of $M(OH)^+$ ions and $M(OH)_2$ (Fig. IV.20), which would be adsorbed to a considerable extent on a less-polar carbon surface of the biomass as regards M (II) ions [69]. The Pb (II) ions are presumably adsorbed at the surface of biomass by ion-exchange mechanism or via hydrogen bonding as previously mentioned as follows [69]:



In the overall equations, M represents the Pb (II) ions and R represents the matrix of CP or CP-LC. Attempt to elevate the pH above pH 6 resulted in the precipitation of lead (II) ions out of solution, thus, pH 5 was taken as the optimum pH for the biosorption of Pb (II) onto CP and CP-LC.

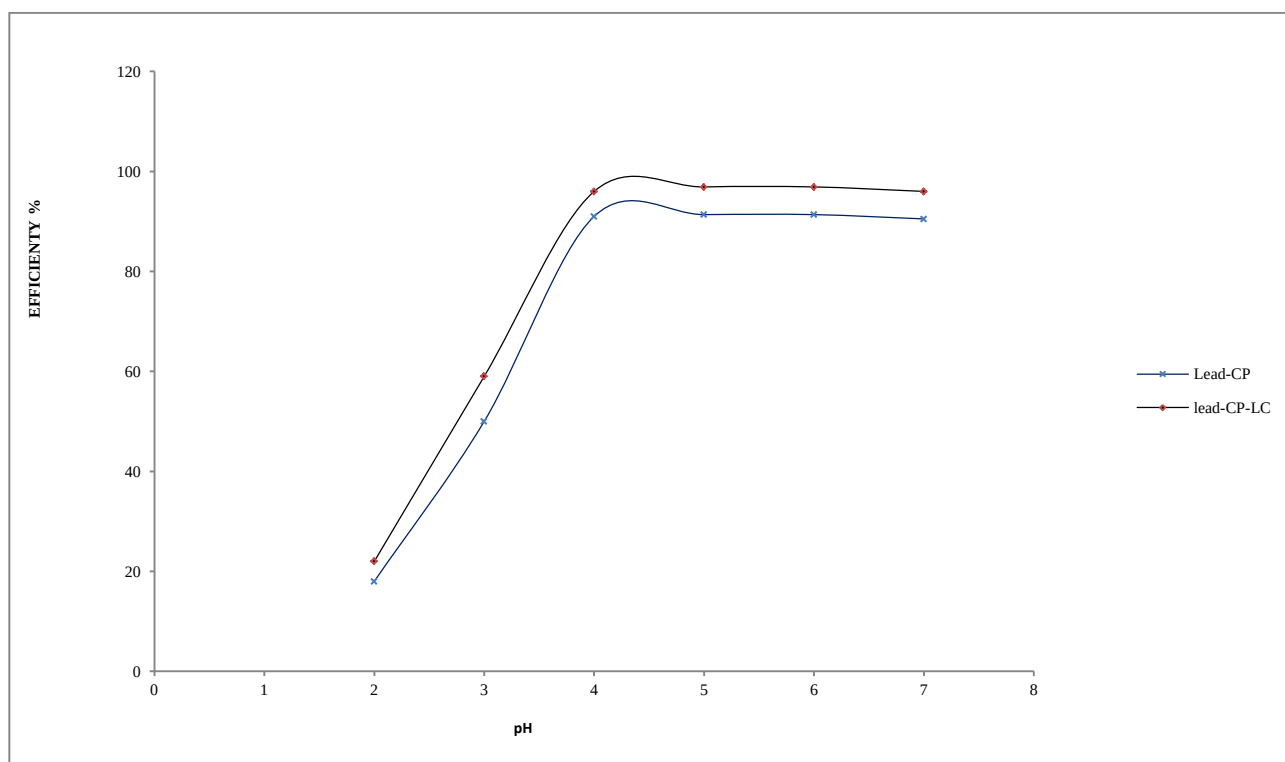


Fig. IV.19: Effect of initial pH of the solution on the biosorption of Pb (II) by CP and CP-LC. (initial concentration 10 mg/L; contact time: 40 min; biosorbent dose: 1 g/L; temperature: 298 K).

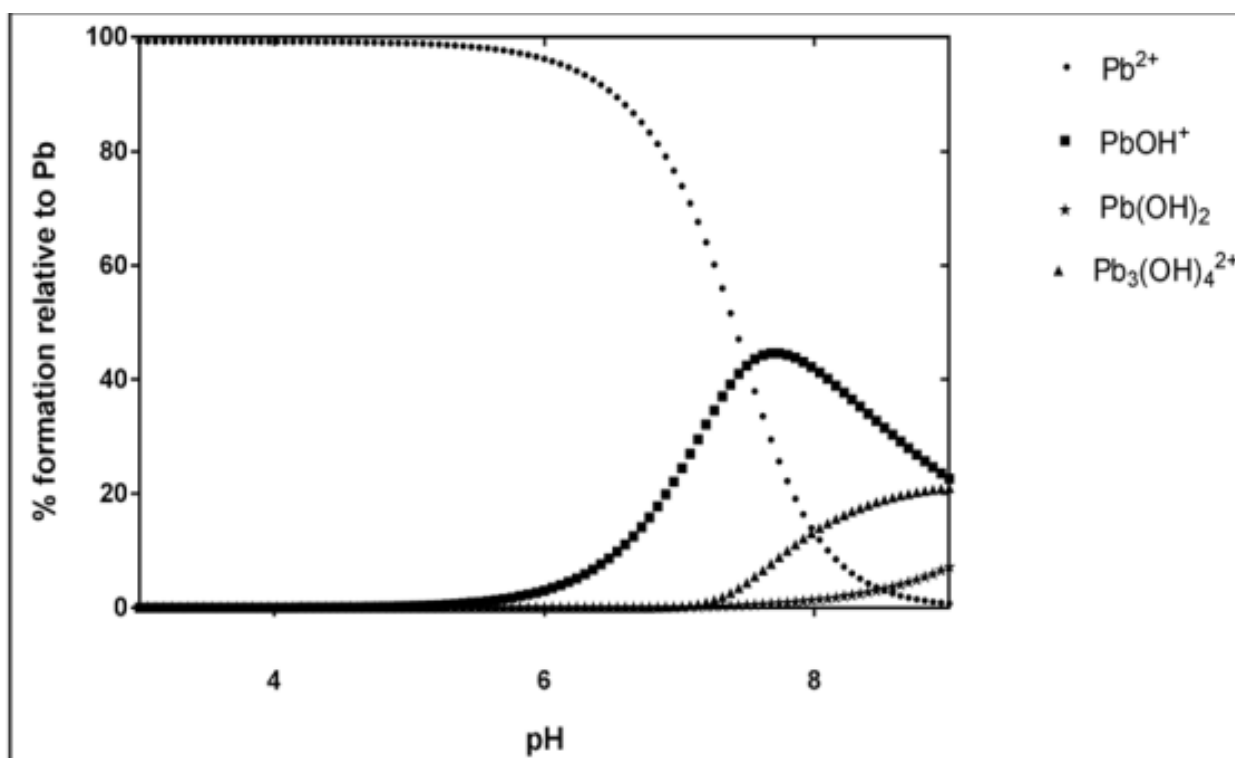


Fig. IV.20: Distribution of lead (II) species in aqueous solution as a function of pH.

IV.2.2.2. Effect of initial concentration

Lead solutions with deferent initial concentrations in the range of 10–300 mg/L at 298 K and optimal pH5 were equilibrated using 1 g biosorbent dose for both biomass CP and CP-LC. The analysis of the current results of metal ions biosorption demonstrated that the biosorption capability of sorbents was affected by the level of initial concentrations. Fig. IV.21 Shows that the Pb (II) ions equilibrium biosorption capacity onto free and immobilized *C. pyrenoidosa* increases from 9.2 to 108.04 mg/L, 9.8 to 123 mg/L, and elimination rate decreases from 91.36 to 35.86%, 96.9 to 41.36%, respectively when its initial concentration increases from 10 to 300mg/L. At higher initial concentrations, the active site's biomass surface would be surrounded with more metal ions in the solution, for that reason, the equilibrium adsorption capacity of the adsorbent increases with increasing the metal ions concentration which reinforces the adsorption process. In contrast, the removal efficiency decreases by an increase in metals' initial concentration. At low initial concentrations, the rate of the initial number of metal ions to the accessible active sites of sorbents is low; as-a-result, the removal efficiency of metal ions is higher and at higher initial concentrations [70].

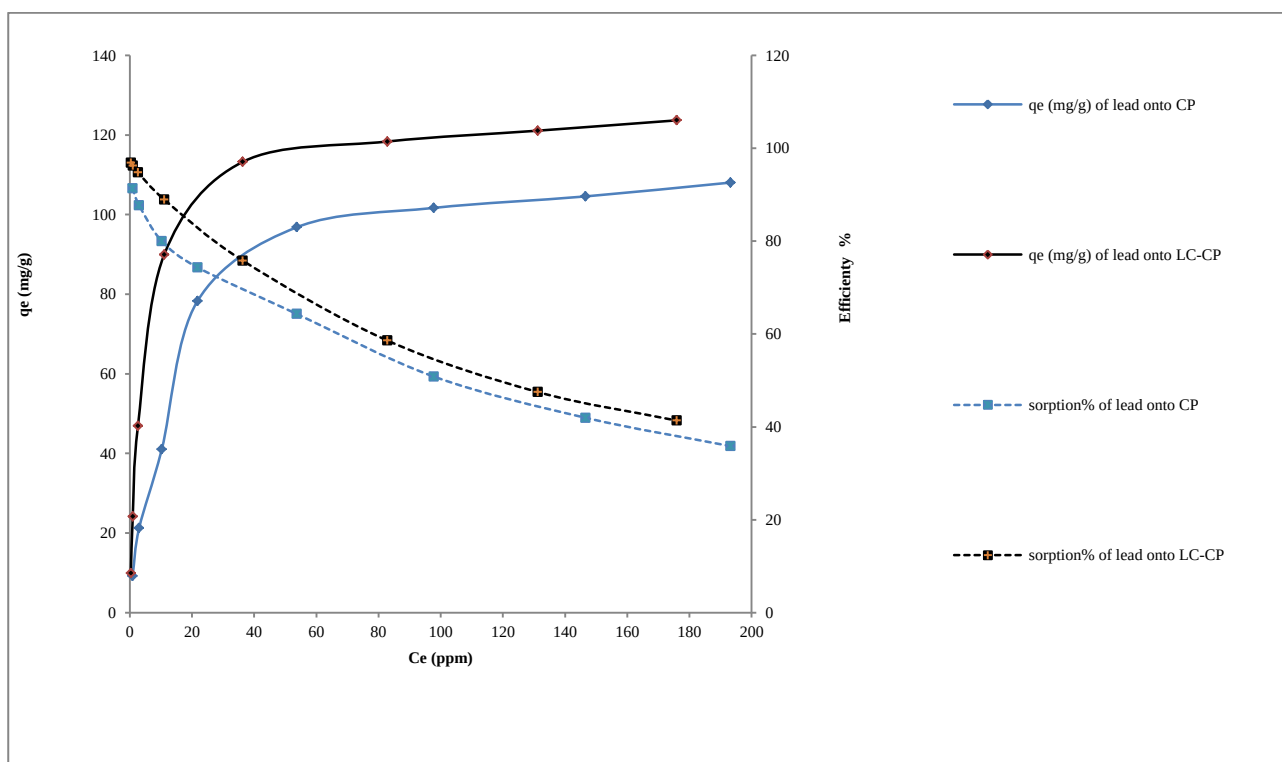


Fig. IV.21: Effect of the initial concentration of Pb (II) biosorption onto CP and CP-LC. (pH 5.0, time 40 min., temp. 298 K).

IV.2.2.3. Effect of temperature and thermodynamic parameters

In order to estimate the effect of temperature on the biosorption of Pb (II) onto CP-LC, the process was carried out at several temperatures ranging from 298 to 318 K with 100 mg/L of initial Pb (II) concentrations at pH 5.0. The equilibrium lead ions biosorption capacity of the CP-LC was better at lower temperatures as the adsorbed amount of lead ions decreased with the rise in temperature. It is important to mention that the bio-adsorption process is usually not functioned at high temperature [71]. Since bio-adsorption reactions are normally exothermic, the decrease in biosorption capacity between 298 and 343K may be due to the damage of active sites in the immobilized *C. pyrenoidosa* in *Luffa Cylindrica*. Temperature dependence of the bio-adsorption process is related with three thermodynamic parameters including enthalpy (ΔH°), entropy (ΔS°), and free energy change (ΔG°), which are used to determine whether the biosorption process is a spontaneous or not. Values of the standard Gibbs free energy change (ΔG°) for the biosorption process are listed in Table. IV.9. Gibbs free energy change (ΔG°) was found to be -10.64, -11.09, -11.24, -11.40 and -11.50 kJ/mol at 298, 303, 308, 313 and 318 K, respectively. The negative values of ΔG° indicated the spontaneous nature of the process and its feasibility for the temperature range evaluated. Moreover, the increase in temperature resulted in a decrease on Gibbs free energy, suggesting that a better adsorption is actually obtained at lower temperatures. The negative value observed for ΔH° (-1.70 kJ/mol) indicates an exothermic process and the positive values of ΔS° (0.031 kJ/mol.K) was not very large and indicated increased randomness at the solid/solution interface during the biosorption of lead ions and good affinity of Pb (II) towards CP-LC. Some researchers have indicated that the positive values of ΔS° reflected some structural changed in the sorbent [72].

Tab.IV.9: Thermodynamic parameters of Pb (II) biosorption onto CP-LC at different T.

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (K J/mol.K)
298	-10.64	-1.70	+0.031
303	-11.09		
308	-11.24		
313	-11.40		
318	-11.50		

IV.2.3. Biosorption kinetic

The effects of contact time and initial concentration of Pb (II) on the biosorption process were studied under the following conditions: time range from 5 to 120 min, pH 5.0, 298 K and using different initial Pb (II) concentrations, 10, 50 and 100 mg/L. For all Pb (II) concentrations studied it was possible to show that an increase in contact time corresponds to an increase in amount biosorption capacity. The biosorption increases quickly during the first 20 min and after 40 min the adsorption remains constant. According to the results presented in Fig. IV.23, it is possible to verify that the time necessary to reach the equilibrium was 40 min. The result obtained from the experiment data was used to study the kinetics of lead ion biosorption. The rate kinetics of Pb (II) biosorption on the CP-LC was analyzed using pseudo-first-order and pseudo-second-order models. The kinetic parameters for different Pb (II) initial concentrations are presented in Table. IV.10. Plots of pseudo-first-order and pseudo- second-order kinetic models are shown in Fig. IV.23. As shown in Table 4, the coefficients of determination (R^2) calculated from the plots of pseudo second-order kinetic models were higher ($R^2 > 0.999$) than those of the pseudo-first-order models for all studied initial Pb (II) concentration. However, the values of ARE determined from the pseudo-second-order kinetic model were much lower than that of the pseudo-first-order models. The value of ARE relates to the conformity between the model-predicted and the experimental data values. In general, the lower ARE values, the greater is the conformity effect. In contrast, the calculated values of $q_{e,cal}$ determined from the pseudo-second-order equation perfectly agreed with the experimental points of $q_{e,exp}$ at all initial concentrations. These results revealed that the pseudo-second-order fits the experimental data better than pseudo-first order model. It can also be seen in Table.IV.8 that, with an increase in initial Pb (II) concentration, the initial biosorption rate (h_0) increased from 3.5 to 36 mg/ g as the initial metal concentration increased from 10 to 100 mg/ L. This may be due to the increase of driving force between the solute sorbate and adsorbent molecules with the increasing lead (II) concentration. In contrast, the rate constant (k_2) of pseudo second-order model presented the opposite trend.

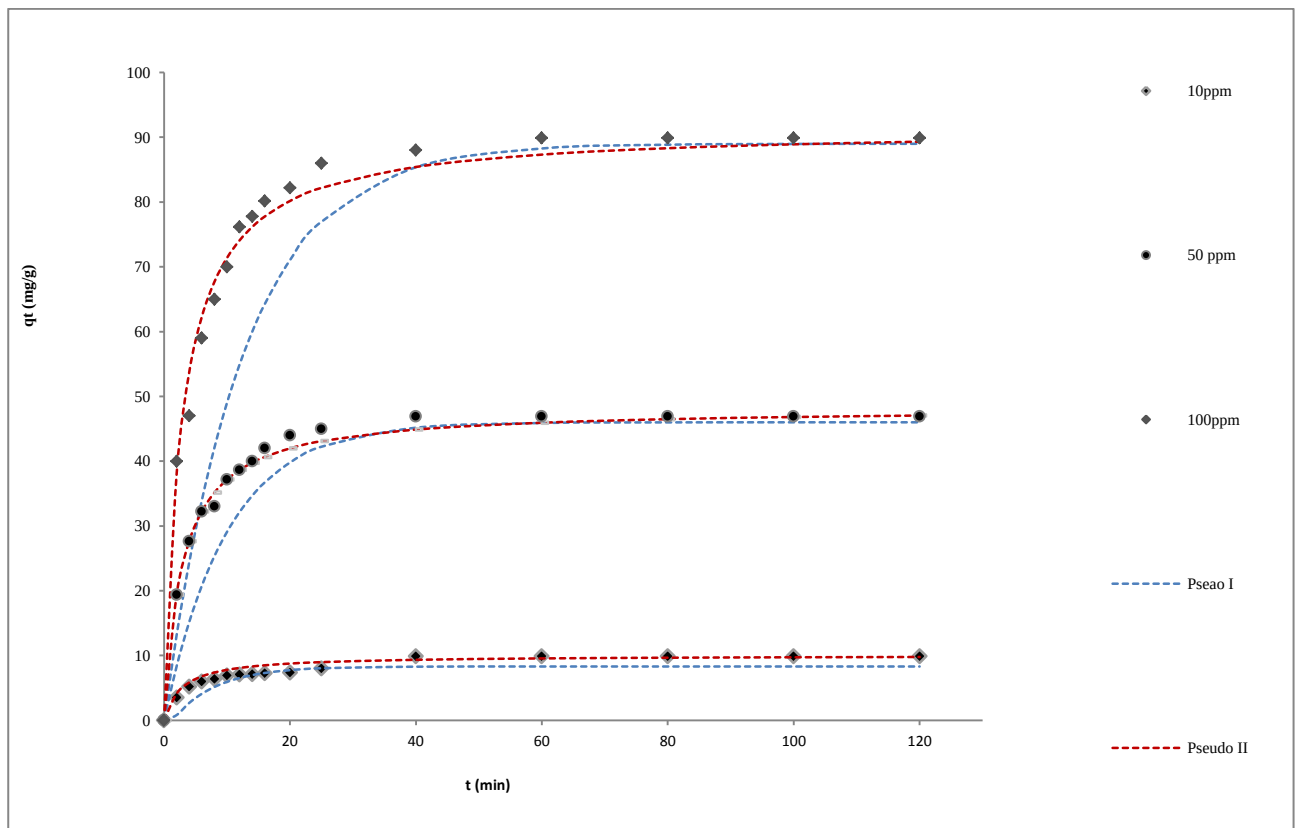


Fig. IV.22: Adsorption kinetic models of Pb (II) by CP-LC.

Table.IV.10: Kinetic parameters of Pb (II) biosorption by CP-LC.

Pb (II) concentration C (mg/L)	q _{e,exp} (mg/g)	Pseudo-first order				Pseudo-second order				
		q _{e,cal} (mg/g)	k ₁ (1/min)	R ²	ARE	q _{e,cal} (mg/g)	k ₂ (g/(mg/min))	h ₀	R ²	ARE
10	9.89	8.93	0.144	0.970	7.18	10.00	0.035	3.5	0.999	2.16
50	46.6	40.73	0.100	0.970	10.88	47.05	0.071	16	0.999	1.9
100	89.9	70.99	0.08	0.93	21.16	93.03	0.036	36	0.999	1.6

IV.2.4. Isotherm models

At explicit conditions, each adsorption system tends to control a dynamic equilibrium between the solute sorbate located on the internal surface of the biomass and the equilibrium concentration of sorbate in the solution. Adsorption isotherm models describe the relationship between the

sorption capabilities of molecules removed from the solution by a unit mass of adsorbent at a constant temperature ($T = \text{const}$). The parameters of isotherms often give useful information on the adsorption mechanism, surface characteristics affinity of the sorbent. It is necessary to emphasize the determination of the most suitable correlation of equilibrium curves for optimizing the conditions for designing the adsorption process. In this study, eighteen models of mono and multi-parameter are examined to analyze the experimental data.

IV.2.4.1. One- and two-parameter models

Henry's Isotherm model [73] is considered as the simplest adsorption isotherm model with one parametric linear regression model available at low concentration of sorbate without regard to the surface of coverage in which all the adsorbate molecules are secluded from their closest neighbors. The Langmuir model [74] is used to describe adsorption of dissolved molecules in solution. This empirical isotherm supposes that the sorption is limited to monolayer; once a molecule of adsorbate occupies a single layer, the theory of Langmuir assumes that the adsorbent surface is homogeneous and sorption activation energy is uniform for all sites of sorbent and there is no movement of adsorbates in the plane of the surface. There is no interaction between adsorbate molecules on neighboring sites. The Freundlich model [73] defines the reversible and non-ideal adsorption process and is not restricted to the monolayer sorption in which its application to the multilayer formation is possible with a non-uniform distribution for adsorption heat and affinity over a heterogeneous surface. The Elovich model [74] is based on the kinetic development and supposing that the multilayer formation increases exponentially with adsorption site. The Temkin model [73] takes into consideration the effects of indirect adsorbent-adsorbate interactive relation on adsorption and due to these interactions the heat of the adsorbent of all the molecules in the surface decreases linearly as a result of increase surface coverage. This model presumes that adsorption heat (ΔH_{ads}) as a function of temperature, of all adsorbed molecules existing in the layer declines linearly rather than logarithmically due to the surface coverage increase. The Fowler–Guggenheim model [73] is one of the simplest isotherms allowing for the lateral interaction of adsorbed molecules. If the interaction among adsorbate molecules is attractive, this means that the heat during adsorption will increase with loading this is due to the fact that the increased interaction between adsorbed molecules as the loading increases (that is W is positive), the heat. However the interaction between adsorbate molecules is repulsive and that is due the heat during adsorption shows a decrease with loading (that is W is negative). When there is no interaction between adsorbed molecules (that is $W = 0$), this Fowler–Guggenheim isotherm will reduce to the Langmuir equation. The Kiselev isotherm model [74] is used to explain the localized monomolecular

layer formation of adsorbate on adsorbents at equilibrium and This model is valid when surface coverage is greater than 0.68. The Hill-de Boer adsorption model [73] describes the mobile adsorption and lateral interaction among adsorbed molecules. The apparent affinity is increased with loading when there exist the attraction between adsorbed species (that is K_n is positive) and it is decreased with loading when there is repulsion among the adsorbed species (that is K_n is negative). The Flory-Huggins isotherm [74, 75] is used for understanding the nature of surface coverage degree of the adsorbate on the adsorbent. This model describes the nature of the adsorption process in regard to the feasibility and spontaneity of the process.

Equilibrium tests were performed under optimum conditions obtained from the model predicted. Constants and parameters of the adsorption isotherm models as well as their associated percentage error values are listed in Table.IV.10. As shown in Table.IV.11, Henry's isotherm model completely fails to predict the experimental data due to poor results showed in R^2 and error function values for both CP and CP-LC. This could be due to the unavailability of sorption data in the low sorbate concentrations. In a liquid-phase sorption system, the equilibrium data are commonly obtained at higher concentrations, where the sorbent surfaces are almost on the verge of saturation sites. Hence, this study supports the fact of the failure of Henry's model at the higher sorbate concentration range. Furthermore, high residual concentrations may suggest the applicability of an isotherm model with a linear regression between q_e and C_e at the final part of the experimental data. This requirement could be partly fulfilled by applying the Henry's Law model (Linear with intercept). The addition of a constant term in Henry's model reveals the model combines the basic characteristics of the experimental data at the high-level concentration. A comparison of regression constants provided the improvement in R^2 , S^2 , ARE, ERSQ, HYBRID, and MPSED values by Linear with intercept over Henry's model. The addition of the parameter in the model ameliorates the capability of modeling the equilibrium data. However, the applicability of the other two-parameter isotherm models were studied. Isotherm model plots for removal of Pb (II) onto CP and CP-LC shown in Fig. IV.23. According to Table.IV.10, experimental data are fitted better by the Langumir model compared to other isotherm models. Moreover, the accuracy analysis of the Langmuir, Freundlich, Temkin, Elovich, Fowler-Guggenheim, Kiselev, Hill de Boer and Flory-Huggins models was evaluated by the statistics of R^2 , S^2 , ARE, ERSQ, HYBRID, and MPSED. By comparisons with other isotherm models, the high R^2 (0.983 and 0.981 for CP and CP-LC, respectively) as well as the low S^2 (167.69 and 150.16 for CP and CP-LC, respectively), ARE (14.52 and 13.81 for CP and CP-LC, respectively), ERSQ (1183.18 and 1065.97 for CP and CP-LC, respectively), HYBRID and MPSED (1.86 and 1.90 for CP and CP-LC, respectively) values confirm that the Langmuir model is more fitted to the experimental data obtained (Table 4). This

Chapter IV: Results and discussion

result elucidates that the process of adsorption proceeds as a monolayer on uniform surfaces. The maximum biosorption capacities for Pb (II) onto CP and CP-LC are 114.94, 126.58 mg/g, respectively. The Langmuir constant value K_L which is attributed to the binding energy of the active site of biosorbents with lead ions onto CP and LC is 0.079, 0.324 L/g, respectively. The most important characteristics of the Langmuir isotherm parameter can be used to evaluate the affinity between the sorbate and sorbent using dimensionless equilibrium parameter or separation factor. The value of dimensionless equilibrium parameter R_L revealed important information about the nature of adsorption. The value of R_L vs initial Pb (II) concentrations between 10-300 mg/L are 0.55-0.04, 0.23-0.01 for CP and CP-LC, respectively. These results indicated that the sorption process is favorable and reversible, because ($0 < R_L < 1$) [73]. Unlike Langmuir model, the Elovich model exhibited lower coefficients of determination R^2 (0.826 and 0.783 for CP and CP-LC, respectively) as well as high S^2 (1343.81 and 3344.10 for CP and CP-LC, respectively), ARE (26.29 and 39.34 for CP and CP-LC, respectively), ERSQ (8063.28 and 20064.91 for CP and CP-LC, respectively), HYBRID (1739.56 and 2810.75 for CP and CP-LC, respectively) and MPSED (4.75 and 6.40 for CP and CP-LC, respectively) values. Furthermore, the values of maximum biosorption capacity obtained for CP and CP-LC were very lower than the experimental quantity of the sorbate on the biosorbent in the equilibrium state uptake corresponding to the plateaus of the adsorption isotherm. This is maybe due to the fact this isotherm model describes the multilayer sorption process indicating migration between layers. For this reason, the Elovich model is inefficacious to describe the biosorption isotherms of Pb (II) onto free and immobilized *C. pyrenoidosa*. The n value (Freundlich model constant) indicates the factor of non-linearity between sorbate concentration and adsorption as follows: if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process; if $n = 1$, then adsorption is linear [24, 25]. The n value in the Freundlich model was found to be 2.19, 2.69 for CP and CP-LC, respectively. Since n falling between 1 and 10, this is due to the physical biosorption of lead (II) onto CP and CP-LC. The variation of adsorption energy $b_T = (-\Delta H)$ in Temkin isotherm model was found 1.21, 0.78 KJ/mol for CP and CP-LC, respectively. Since the positive value of the variation indicates that the adsorption of Pb (II) onto the CP and CP-LC are exothermic in nature. Additionally, the low $b_T < 8$ values confirm that the interactions between the lead molecules and the biosorbents is weak and the adsorption mechanism of lead ions can be expressed as physiosorption [74]. Moreover, it was observed that the W values > 0 (Fowler–Guggenheim model constant) and the K_n values < 0 (Hill–de Boer model constant) for removal of Pb (II) on CP and CP-LC, which validate the repulsion between the adsorbed molecules, were w (68.210, 66.83 KJ/mol for CP and CP-LC, respectively) and K_n (-80.72, -88.66 KJ/mol for CP and CP-LC, respectively) [73]. On the other hand, the values

Chapter IV: Results and discussion

of K_{FH} (Flory-Huggins model constants) was found 0.00085, 0.00084 KJ/mol for CP and CP-LC, respectively. This positive values indicating negative Gibbs free energy ($\Delta G = -RT\ln K_{FH}$), for that reason spontaneity of the sorption process stemming from high Pb (II) occupancy of the CP and CP-LC surfaces. Results of the Flory model also reveal that the number of adsorbate molecules occupying adsorption sites ($n_{FH} < 1$) indicates grander than unity active zone of adsorbent materials would be occupied by adsorbate molecules [74]. In the case of Kisevel model, the equilibrium parameter of the formation of the complex between adsorbed compounds, k_n values, are negatives for both biosorbents, which is surprising because it is an equilibrium parameter and it should be positive. The fact of having negative values of k_n (L/mg) elucidates that there is no formation of the complex between the biosorbed molecules.

Tab.IV.1 (a)1: Isotherm constants of two-parameter models for Pb (II) biosorption onto CP and CP-LC

Isotherm model	parameters	CP	CP-LC
Henry model	K	0.745	0.933
	R^2	0.800	0.700
	S^2	1532.84	2624.21
	ARE	58.54	64.44
	ERSQ	10766.94	18579.49
	HYBRID	1086.40	37043.96
	MPSED	62.00	178.09
Henry's law(Linear with intercept)	A	0.446	0.529
	B	40.65	51.72
	R^2	0.808	0.764
	S^2	562.64	2228.89
	ARE	68.54	92.73
	ERSQ	3939.94	15602.24
	HYBRID	1055.40	1833.52
Langmuir	MPSED	4.62	4.71
	q_{mas} (mg/g)	114.94	126.58
	K_L (L/mg)	0.079	0.324
	R^2	0.983	0.981
	S^2	167.69	150.16
	ARE	14.52	13.81
	ERSQ	1183.18	1065.97
Freundlich	HYBRID	249.03	216.68
	MPSED	1.86	1.90
	K_F (mg/g)(L/mg) ^{1/n}	12.787	24.090
	n	2.19	2.69
	R^2	0.924	0.93
	S^2	422.69	400.05
	ARE	18.10	19.10
	ERSQ	2536.15	1999.38
	HYBRID	489.63	470.1
	MPSED	2.74	2.81

Chapter IV: Results and discussion

Tab.IV.11 (b): Isotherm constants of two-parameter models for Pb (II) biosorption onto CP and CP-LC

Isotherm model	parameters	CP	CP-LC
Elovich	q_{Me} (mg/g)	39,680	32.154
	K_E (L/mg)	0.341	1.896
	R^2	0.826	0.783
	S^2	1343.81	3344.10
	ARE	26.29	39.34
	ERSQ	8063.28	20064.91
	HYBRID	1739.56	2810.75
	MPSED	4.75	6.40
Temkin	A_T (L/g)	1.352	5.302
	b_T (Kj/mol)	1.21	0.78
	R^2	0.979	0.97
	S^2	77.44	170.3
	ARE	19.96	19.16
	ERSQ	464.69	722.25
	HYBRID	298.56	191.06
	MPSED	7.47	2.24
Fowler–Guggenheim	W (Kj/mol)	68.210	66.83
	K_{FG} (L/g)	1.720	$K_{FG}=3.67$
	R^2	0.894	0.971
	S^2	626.38	672.15
	ARE	28.309	74.10
	ERSQ	3.77	4032.90
	HYBRID	1234.74	1093.27
	MPSED	6.35	4.14
Kiselev	K_1 (L/g)		0.2834
	K_2	0.102	-0.4297
	R^2	-0.965	0.880
	S^2	0.864	1720.99
	ARE	1069.89	83.68
	ERSQ	32.46	10325.96
	HYBRID	6419.36	1828.66
	MPSED	2573.89	4.86
Hill–de Boer	K_H (L/g)		0.172
	K_H (Kj/mol)	0.054	-88.68
	R^2	-80.729	0.794
	S^2	0.828	1365.30
	ARE	774.08	37.23
	ERSQ	37.48	8191.81
	HYBRID	3639.67	4022.76
	MPSED	1449.43	12.43
Flory–Huggins	n_{FH}		0.220
	K_{FH} (L/g)	0.305	0.00084
	R^2	0.00085	0.98
	S^2	0.95	122.73
	ARE	119.37	14.26
	ERSQ	26.38	1136.42
	HYBRID	1219.23	136.21
	MPSED	127.52	1.83
		1.67	

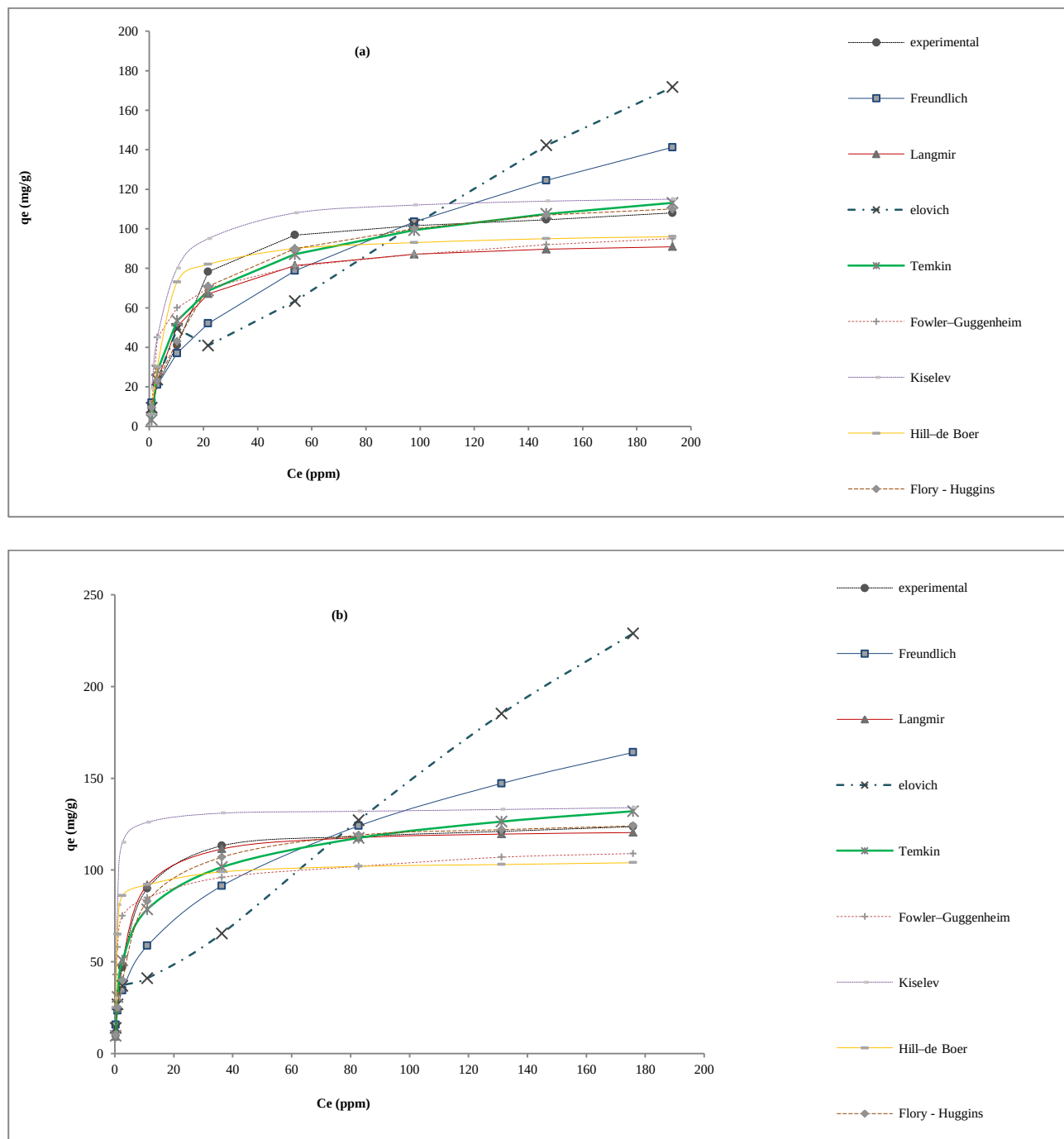


Fig. IV.23: Comparative non-linear plots for eight two-parameter isotherm models; (a) biosorption of Pb (II) onto CP, (b) biosorption of Pb (II) onto CP-LC.

IV.2.4.2. Three -parameter models

The abilities of the three parameter models, Redlich-Peterson, Sips, Koble-Carrigan, Radke-Prausnitz, Toth, and Khan models, to model the experimental biosorption data were tested. All These models have been derived from the Langmuir and Freundlich models. The Redlich-Peterson

Chapter IV: Results and discussion

isotherm [73] combines the features of these two models, and the mechanism of adsorption process is a hybrid and does not follow ideal monolayer adsorption. This isotherm can be applied for both homogeneous and heterogeneous systems. Sips isotherm [73, 74] proposed an expression that combines the Freundlich and Langmuir models. This produces an equation that exhibits a finite limit at sufficiently high concentration. This isotherm is available for predicting the heterogeneous adsorption process and localized adsorption without interaction between adsorbate/adsorbate. The Koble-Corrigan model [74] is generally applied for heterogeneous adsorbent surface. This model is valid only when $n_K > 1$ that is due the model which is able to describe the experimental data. Radke-Prausnitz isotherm [73] is simple yet powerful mathematical model for most adsorption systems at low adsorbate concentrations; this model reduces to a linear isotherm, while at high sorbate concentration it becomes the Freundlich model and when, it becomes the Langmuir isotherm. Another characteristic of this isotherm is that it gives a best fit over a wide range of sorbate concentration. Toth isotherm [73, 74] is an empirical modified form of the Langmuir expression; aiming to reduce the error between the value of both the experimental and predicted points. Mainly, this isotherm is used for the description of heterogeneous adsorption process; satisfying the low and high concentration of sorbate. Khan isotherm [75] is a generalized model suggested for the adsorbate adsorption from pure dilute equation solutions development of this model was made for both single and multicomponent adsorption.

The equilibrium data were examined according to the nonlinear regression of three parameter models. Table.IV.12 shows the isotherms parameters and worse fits of CP and CP-LC. The prediction of adsorption isotherms of Pb (II) onto CP and CP-LC show in Fig. IV.24. From the analysis of all tested isotherm models of three parameters and based on the error values, the isotherm model can be arranged according to their efficiency in predicting the equilibrium data. For Pb (II)-CP system: Sips > Radke-Prausnitz > Toth > Khan > Koble-Carrigan > Redlich-Peterson. In the case of Pb (II)-CP-LC system: Koble-Carrigan > Radke-Prausnitz > Khan > Sips > Redlich-Peterson > Toth. The values of g (Redlich-Peterson model constant), n_s (Sips model constant), n_R (Radke-Prausnitz model constant), n_T (Toth model constant) and a_K (Khan model constant) obtained using Redlich-Peterson, Sips, Toth, Radke-Prausnitz and Khan models are near than unity, which means that the adsorption processes reduce to the Langmuir isotherm. This implies that the adsorption already predicted to be on homogeneous surfaces is also confirmed by the Koble-Corrigan isotherm model. This model defines the validity or otherwise of a system. $n_K \geq 1$, imply a valid adsorption system, while $n_K \leq 1$ signifies the models' inefficiency in defining the experimental data, despite the results from other goodness-of-fit adjudging criteria (correlation coefficient or low error value). This is due to the fact this isotherm model describes the heterogeneous surface.

Tab.IV.12: Isotherm constants of three-parameter models for Pb (II) biosorption onto CP and CP-LC.

Isotherm model	Parameters	CP	CP-LC
Redlich–Peterson	K_R (L/g)	18	$K_R = 35$
	a_R (L/g)	0.682	$a_R = 0.4$
	b_R	0.690	$b_R = 0.9$
	R^2	0.955	0.990
	S^2	251.24	69.16
	ARE	16.93	6.51
	ERSQ	1256.12	334.83
	HYBRID	289.36	75.33
	MPSED	1.95	0.90
Sips	q_{ms} (mg/g)	117.1	123
	K_s (L/g)	0.086	0.2
	n_s	1.059	1.1
	R^2	0.992	0.980
	S^2	37.71	86.78
	ARE	7.16	11.96
	ERSQ	193.58	434.94
	HYBRID	61.878	135.28
	MPSED	1.13	1.95
Koble–Carrigan	A_K (L/g)	11.60	35
	B_K (L/g)	0.11	0.3
	n_K	1.02	1.1
	R^2	0.987	0.992
	S^2	82.82	42.33
	ARE	11.77	6.06
	ERSQ	414.14	211.66
	HYBRID	137.56	60.83
	MPSED	1.62	0.5
Radke-Prausnitz	q_m (mg/g)	333.33	308.33
	K_{RP} (L/g)	0.0187	0.93
	n_R	1.2	1.1
	R^2	0.994	0.992
	S^2	37.9	45.67
	ARE	7.52	6.12
	ERSQ	182.89	228.35
	HYBRID	64.39	67.48
	MPSED	1.13	0.51
Toth	q_{mK} (mg/g)	118	123
	k_L (L/g)	0.096	0.264
	n_T	0.90	0.95
	R^2	0.991	0.98
	S^2	38.435	324.49
	ARE	8.95	19.95
	ERSQ	269.04	1123.91
	HYBRID	65.63	412.45
	MPSED	1.13	3.34
Khan	q_{mKH} (mg/g)	107	121.84
	b_{KH} (L/g)	0.091	0.4
	a_{KH}	0.95	0.97
	R^2	0.991	0.993
	S^2	39.58	54.75
	ARE	9.97	6.36
	ERSQ	187.93	233.78
	HYBRID	68.066	69.75
	MPSED	1.50	0.57

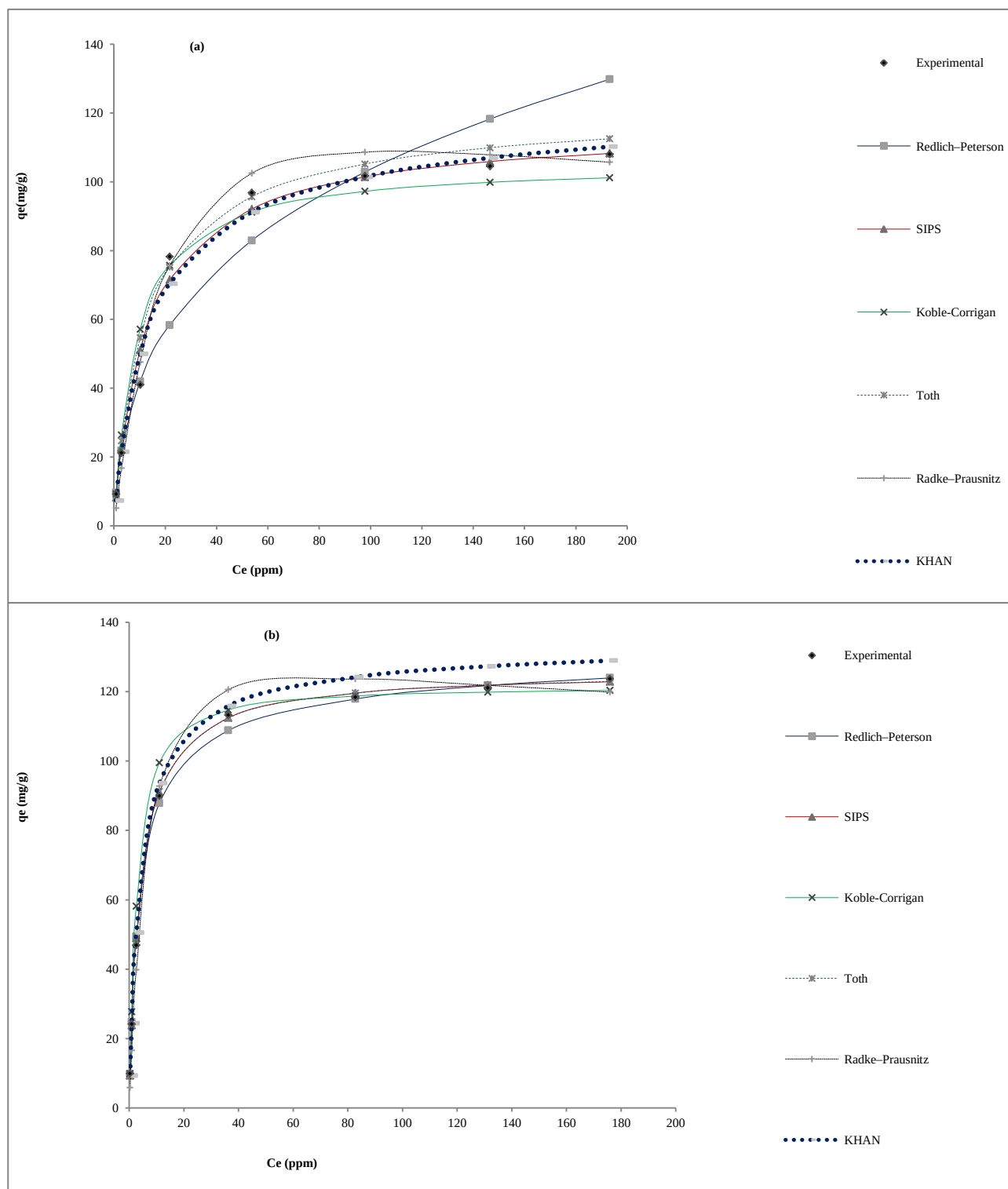


Fig. IV.24: Comparative non-linear plots for six three-parameter isotherm models; (a) biosorption of Pb (II) onto CP, (b) biosorption of Pb (II) onto CP-LC.

IV.2.4.3. Four- and five-parameter models

Among the four and five parameter models considered in the present study to modeled the experimental data, Baudu, Fritz-Schlünder model (IV), Fritz-Schlünder model (V). Baudu

model [73] has been developed mainly due to the arise of discrepancy in determining Langmuir parameters and coefficient from slope of tangent over a wide concentration range. This isotherm is valid in the range of $(1+x+y) < 1$ and $(1+x) < 1$. Fritz-Schlünder model (IV) Fritz-Schlünder model and (V) [73] are developed for the aim of simulating the model variations more accurately for application over a wide range of excremental data. The equilibrium data were modeled according to the nonlinear regression of the four and five parameter models. Fig. IV.25 depicts the predict curves of four and five parameter isotherm for CP and CP-LC.

Analyzing the results of four and five parameter model represented in Table.IV.13, it can be observe that the Fritz-Schlünder (V) isotherm model is the best to fit the experimental data of Pb (II) biosorption onto both CP and CP-LC. Indeed, this isotherm model shows a relatively high error values R^2 (0.996 and 0.997 for CP and CP-LC, respectively) and the lowest other error function values S^2 (27.40 and 10.40 for CP and CP-LC, respectively), ARE (5.00 and 2.53 for CP and CP-LC, respectively), ERSQ (137.02 and 50.02 for CP and CP-LC, respectively), HYBRID (47.71 and 11.68 for CP and CP-LC, respectively) and MPSED (0.75 and 0.44 for CP and CP-LC, respectively). This improvement is due to the increase in number of constants, which can perform a more accurate simulation of model variations for representation over a wide range of experimental results. Based on that and in order to give a goodness fit to the experimental data, we have modified the equation of Fritz-Schlünder (V) model. For this reason, we propose to introduce other constants which improved the fit of experimental data. The formula of the modified Fritz-Schlünder (V) model (seven parameters) that we have developed is expressed as follows:

$$q_e = \frac{q_{mFS} K_{FS1} C_e^{M1} + \alpha}{1 + (K_{FS2} C_e^{M2} + \beta)}$$

The constants α and β are considered as correction coefficients. These coefficients are added to the equation of the Fritz-Schlünder (V) that takes into consideration the experiment errors. K_{FS1} and K_{FS2} are the modified Schlünder (V) model parameters; M_1 and M_2 are the exponents of the modified First-Schlünder (V) equation. According to Table. IV.13, it is evident that the R^2 values have increased and error values decreased by using the modified First-Schlünder (V) equation, and the values of error functions are reduced compared to that of all other models studied for biosorption of Pb (II) onto CP and CP-LC. Fig. IV.26 shows the curves of the nonlinear regression of experimental data as well as the modified Schlünder (V) for CP and CP-LC. As observed, the curve of the nonlinear regression of the modified First-Schlünder (V) equation depicts a good

Chapter IV: Results and discussion

approximation between experimental and predicted data compared to the other model. Therefore, the m First-Schlünder (V) model shows a better representation of these experimental data.

Tab.IV.13: Isotherm constants of multi-parameter models for Pb (II) biosorption onto CP and CP-LC.

Isotherm model	parameters	CP	CP-LC
Baudu	q_{mb} (mg/g)	108	125
	b_0 (L/g)	0.09	0.32
	X	0.001	0.001
	Y	0.1	0.1
	R^2	0.992	0.994
	S^2	37.28	78.9
	ARE	8.00	9.08
	ERSQ	186	394.53
	HYBRID	71.5	108.27
	MPSED	1.37	1.33
Fritz–Schluender (IV)	C (L/g)	10	29.5
	D (L/g)	0.09	0.25
	M_1	0.95	0.9
	M_2	0.881	0.89
	R^2	0.995	0.996
	S^2	43.38	51.38
	ARE	6.89	6.77
	ERSQ	218	295.83
	HYBRID	68.67	71.77
	MPSED	1.10	1.12
Fritz–Schluender (V)	q_{MFS} (mg/g)	108	123
	K_{FS1} (L/g)	0.094	0.26
	K_{FS2} (L/g)	0.0881	0.25
	M_1	0.95	0.9
	M_2	0.881	0.89
	R^2	0.996	0.997
	S^2	27.40	10.40
	ARE	5.00	2.35
	ERSQ	137.02	50.02
	HYBRID	47.71	11.68
	MPSED	0.75	0.44
modified–Schluender (V)	q_{Mfs} (mg/g)	108	123
	K_{FS1} (L/g)	0.094	0.26
	K_{FS2} (L/g)	0.0881	0.25
	M_1	0.95	0.95
	M_2	0.881	0.881
	α	0.99	-1
	β	0.00	0.1
	R^2	0.999	0.999
	S^2	4.20	7.62
	ARE	2.50	2.26
	ERSQ	21.25	38.02
	HYBRID	9.5	8.61
	MPSED	0.49	0.3

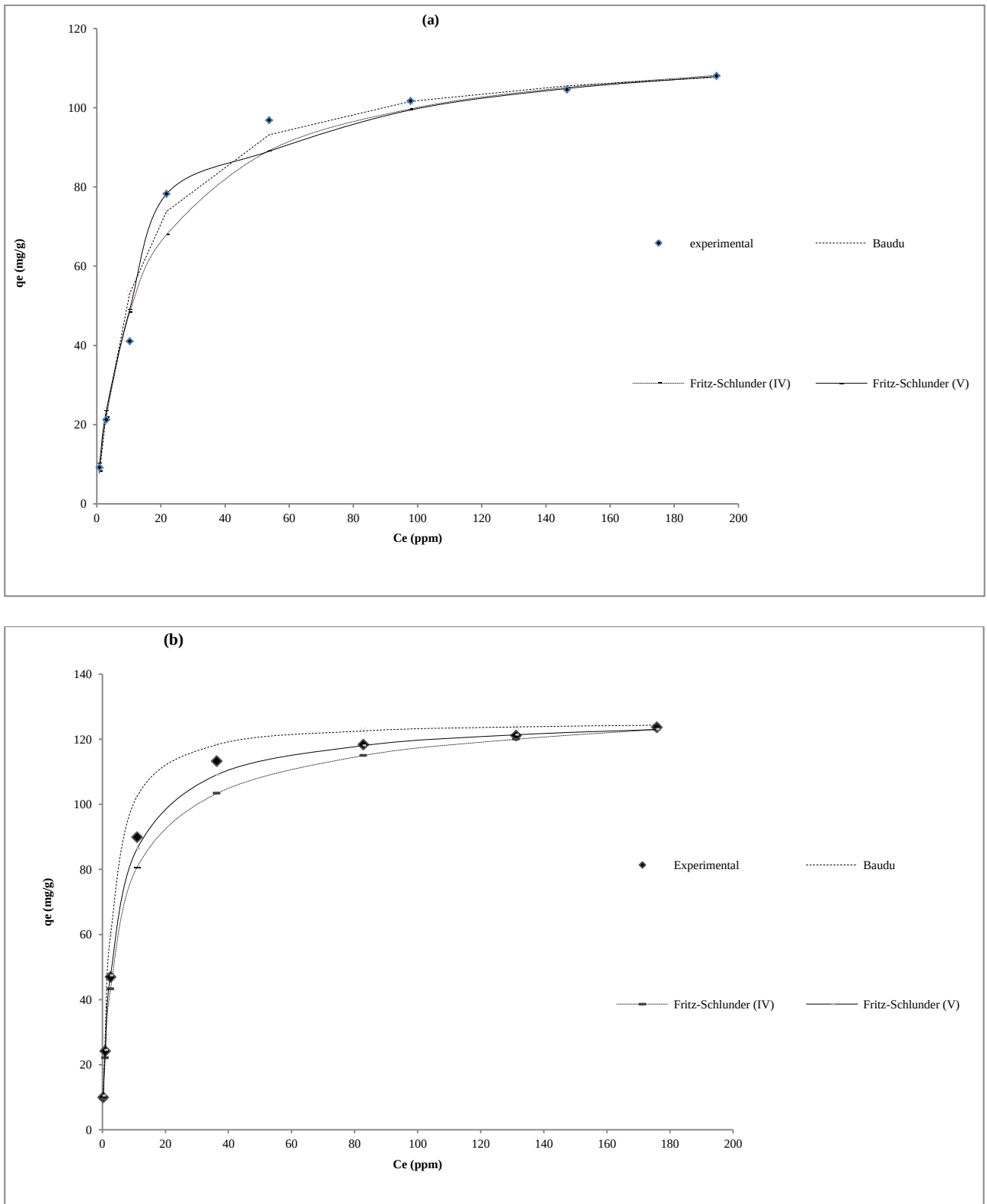


Fig. IV.25: Comparative non-linear plots of four and five parameter isotherm models; (a) biosorption of Pb (II) onto CP, (b) biosorption of Pb (II) onto CP-LC.

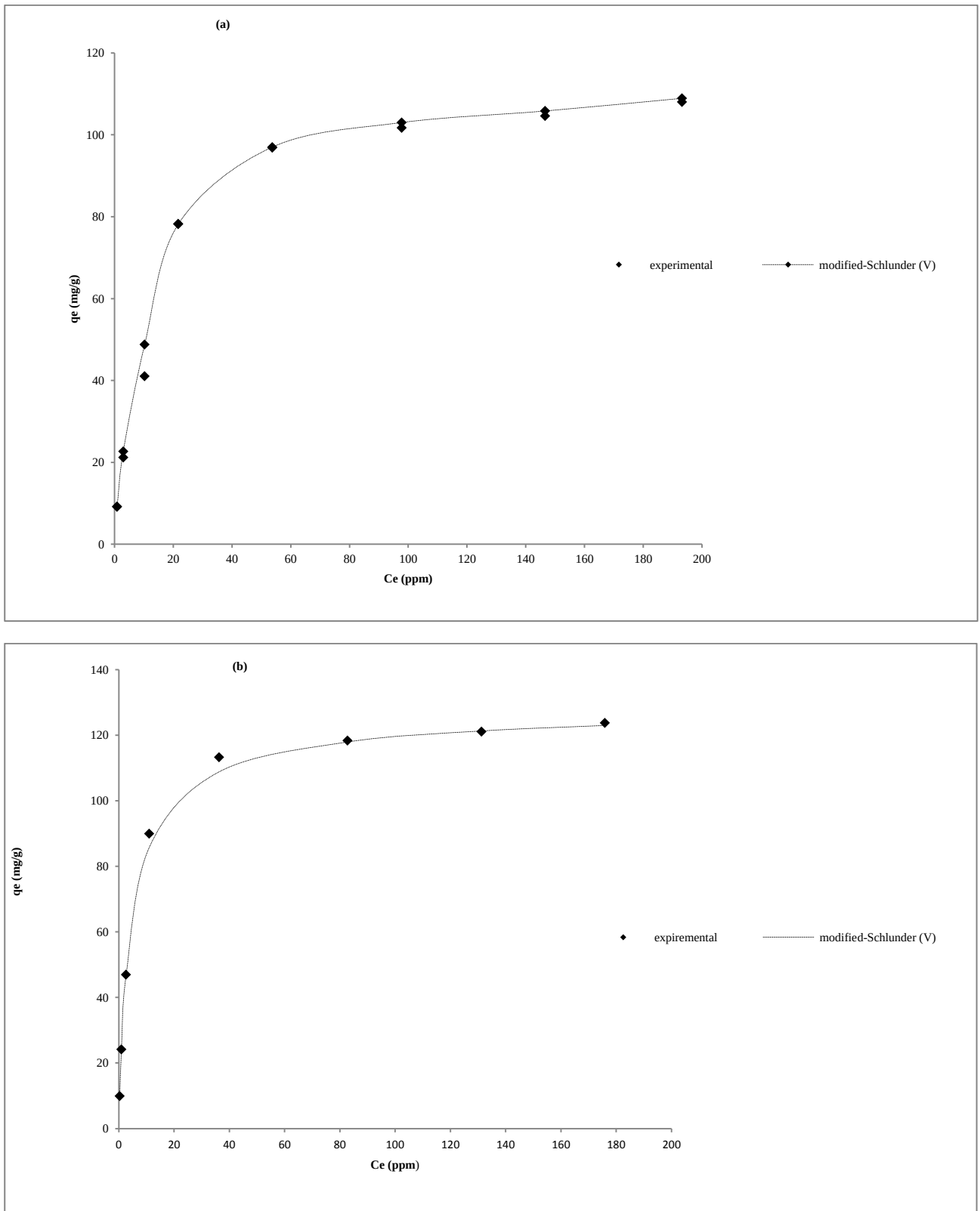


Fig.26: Non-linear isotherm representations of modified Schlunder (V); (a) biosorption of Pb (II) onto CP, (b) biosorption of Pb (II) onto CP-LC.

IV.2.5. Regeneration study

For wide-scale application, reusability and regeneration are the vital biosorbent proprieties, since the ability to reutilize a biosorbent is a crucial factor for the decontamination operation from the economic point of view. The desorption experiments present in Fig. IV.27 show that the H_2SO_4 and HCl recovered about 99% and 95% of Pb (II) adsorbed on the biosorbent surface, respectively. Tap water, de-ionized water and NaOH indicated low desorption ratio of 14.04%, 30.07% and 49.5% of Pb (II) adsorbed on the immobilized *C. pyrenoidosa* surface, respectively. The study indicated that Pb (II) ions accumulated onto the CP-LC could be desorbed and maximum ratio recovery of Pb (II) ions was 99% with 0.1 M H_2SO_4 . The hydroxyl and carboxylic groups in the CP-LC made it amenable to easy regeneration and desorption with the acid solutions [13]. Therefore, Sulfuric acid solutions were selected as desorption reagents for removing Pb (II) ions from the immobilized *C. pyrenoidosa* surface. According to Table.IV.1, the results for the adsorption/desorption cycle elucidated that CP-LC could be reused up to five times without significantly change. Therefore, the prospects of CP-LC are good for practical applications of removing lead ions from queues solutions.

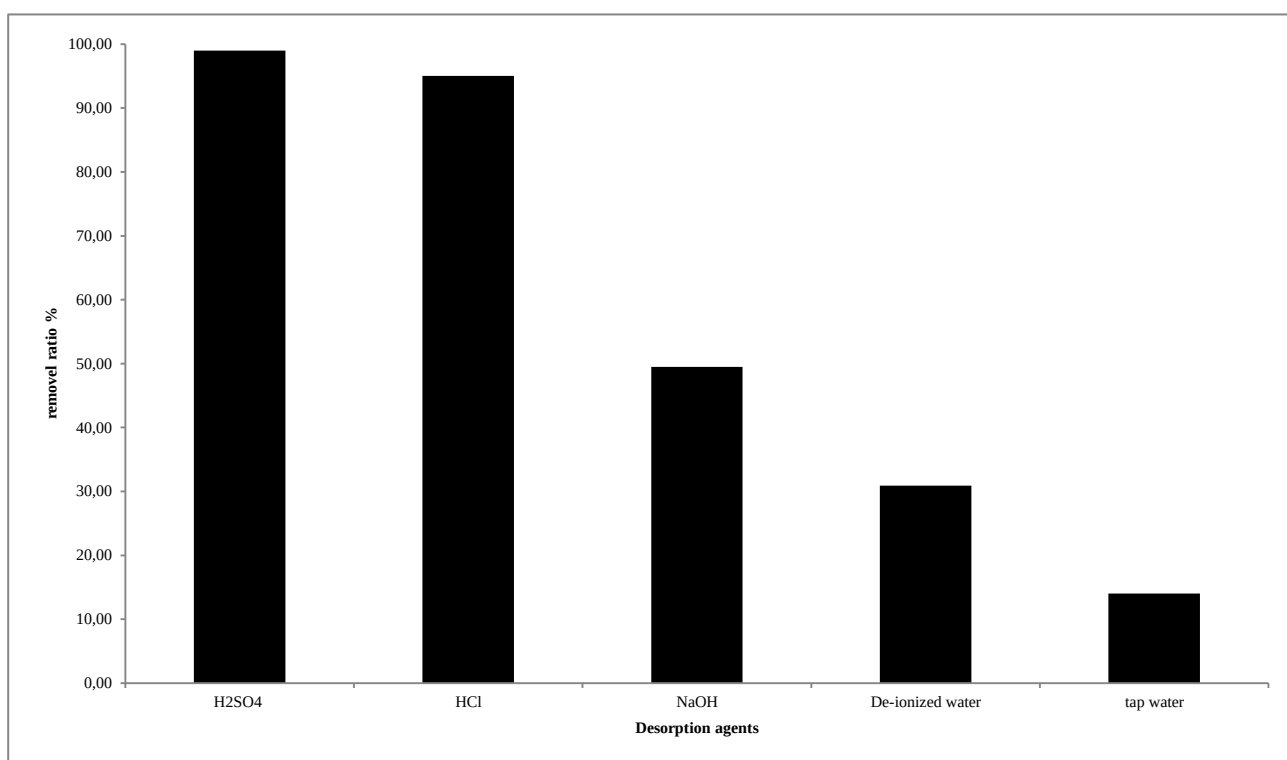


Fig. IV.27: Desorption of Pb (II) ions adsorbed on CP-LC.

Chapter IV: Results and discussion

Tab.IV.14: Adsorption, desorption and desorption/ reloading ratio of Pb (II) in five seductive cycles.

Number of cycles	Adsorption (mg/g)	Desorption (mg/g)	Desorption ratio %	Reloading ratio %
1	9.96	9.95	99.98	-
2	9.81	9.72	99.00	98.50
3	9.77	9.73	99.59	98.09
4	9.69	9.67	99.79	97.28
5	9.62	9.48	98.54	96.58

IV.2.6. Comparison of immobilized *C. pyrenoidosa* with other biosorbents

The biosorption removal capacities of different biosorbents towards lead ions as documented in literature have been mentioned in Table.IV.15. A comparison between this research and other documented data from the literature [76–37] elucidate that CP-LC a better biosorbent for Pb (II) compared to other biosorbents. Thus, it could be concluded that the CP-LC biomass has a significant potential for the removal of lead ions from an aqueous solution.

Tab. IV.15: Comparison of the maximum biosorption capacity of immobilized chlorella pyrenoidosa in *Luffa Cylindrica* for Pb (II) with other biosorbents.

Biosorbents	Qmax (mg Pb ²⁺ g/g)	pH concentration (mg/L)	Biosorbent dosage (g/L)	Contact time (min)	Temperature (C)	References
Oryza sativa L. husk	5.69	10–200	-	20.0	120	30.0 [76]
Cladonia furcata	12.30	10–400	5.0	8.0	60	20.0 [77]
Almond shell	13.7	10–300	5.0	10.0	-	25.0 [78]
Eichhornia crassipes	26.32	10–6	4.84	2.0	180	30.0 [79]
Pine bark	76.8	50-1000	5.0	5.0	240	40.0 [79]
Neem Bark	83.33	5-100	5.0	7.5	60	30 ± 2.0 [80]
Sawdust	88.49	5-100	5.0	7.5	60	30.0 ± 2.0 [80]
Ponkan peel	112.1	1-15 (mM)	5.0	-	60	25.0 [81]
CP	108	10–300	5.0	1.0	15	25.0 ± 0.5 Present study
CP-LC	123	10–300	5.0	1.0	15	25.0 ± 0.5 Present study

IV.2.7. Application the optimum conditions in industrial sample (Hassi R'mel)

Chapter IV: Results and discussion

The industrial sample has brought from the waste water of Hassi R'mel, laghouat, algeria. The optimum conditions (pH, time, temperature and adsorbent dose) which applied in the aqueous solutions have been applied in this experiment. The adsorption of lead was ($q_{\max}= 46$ mg/g, $R= 37\%$). The percentage of lead elimination in the real sample was lower than the aqueous solutions, maybe because of the real sample contained a crude oil, which led to the overlap of another factor to compete for binding to the active sites of the adsorbent surface with a lead [82]. also found that the wastewater produced by the petroleum industry and the processing of crude oil characterized by high levels of crude oil products and other product chemicals. The effect of a different pollutant concentration if the coexisting pollutant competes or forms a complex with a target contaminant for the binding sites, a higher concentration of another pollutant will reduce the biosorption removal of the target pollutant [83]. Most studies indicate that, because of their chemical structure, the removal potential of heavy metal ions from vegetal biomass residues is greater than other natural waste. Vegetal biomass Fibers are lignocellulose compounds made up of three essential components: cellulose (40-5%), hemicellulose (20-35%) and lignin (15-35%) [84]. Lignin is the most significant component and has complex chemical components within the CP-LC waste material, since it is a three-dimensional polymer of C-C or C-O-C bound phenyl propane units. The elementary composition therefore has a high carbon (62% by weight) and lower oxygen (32% by weight). A higher number of carbon atoms typically are related to a lower polarity and hence a greater absorption potential and lignin is very influential on the absorption process due to its large number of carbon atoms. For this reason, the ideal adsorbent for absorption techniques is a lignocellulosic material [85].

Bibliography

- [1] - ASTM International - Standards Worldwide, <https://www.astm.org/>
- [2] - Dang VBH, Doan HD, Dang-Vu T, Lohi A, **2009**, Bioresource Technology, 100 (1): 211–219.
- [3] - Annija L, David R, Mark B, John C, **2019**, International Journal of Environmental Research and Public Health, 16 (10): 1803-1818.
- [4] - Kalia S, Kumar A, Kaith B S, **2011**, Advanced Material Letters, 2(1): 17-25.
- [5] - Moreira VR, Lebron YAR, Freire SJ, Santos LVS, Palladino F, Jacob R S, **2019**, Microchemical Journal, 145: 119-129.
- [6] - Vidal CB, Melo DQ, Raulino GSC, da Luz AD, da Luz C, **2016**, Desalin. Water Treat.57 (19): 9001–9008.

- [7] – Tran HH, Roddick F A, O'donnell FA, **1999**, Water Research, 33: 2992-3000.
- [8] – Tobin JM, Cooper D G, Neufeld R J, **1984**, Applied Environmental Microbiology, 47: 821-824,
- [9] - Sharma S, Pathania D, Singh P. Preparation, **2013**, Advanced Materials Letters, 4 (4): 271-276.
- [10] - Witek-krowiak A, Szafran RG, Modelski S, **2011**, Desalination, 265: 126-134,
- [11] - Wei BG, Yang LS, **2010**, Microchem J, 94: 99–107.
- [12] - Wang J, Chen C, **2006**, Biotechnol Adv, 24 (5):427-51.
- [13] - Abhari PS, Manteghi F, Tehrani Z, **2020**, Nanomaterials, 10 (9):1647.
- [14] - Agarwal A, Upadhyay U, Sreedhar I, Singh SA, Patel, CM, **2020**, J. Water Process. Eng, 38: 101602.
- [15] - Rescignano N, Fortunati E, Armentano I, Hernandez R, Mijangos C, Pasquino R, Kenny JM, **2015**, J. Colloid Interf. Sci, 445: 31–39.
- [16] - Mitra T, Sailakshmi G, Gnanamani A, Mandal AB, **2013**, Mater Res, 16: 755–765.
- [17] - Lim SH, Hudson SM , **2004**, Carbohydr. Res, 339: 313–319.
- [18] - Bhattacharya A, Mathur M, Kumar P, Malik A, **2019**, Biotechnol Biofuels, 12: 178.
- [19] - Leal D, Matsuhira B, Rossi M, Caruso F, **2008**, Carbohydr. Res, 343 (2): 308-316.
- [20] - Taşar Ş, Kaya F, Özer A, **2014**, J. Environ. Chem. Eng, 2 (2): 1018-1026.
- [21] - Ozer A, **2007**, J. Hazard. Mater, 141 (3): 753–761.
- [22] - Adewuyi A, Pereira FV, **2017**, Beni Suef Univ J Basic Appl Sci, 6 (2):118–126.
- [23] - Karnib M, Kabbani A, Holail H, Olama, Z, **2014**, Energy Procedia, 50: 113–120.
- [24] - Ajenifuja E, Ajao JA, Ajayi EOB, **2017**, Appl Water Sci, 7: 3793–3801.
- [25] - Awwad AM, Salem NM, **2014**, J. Saudi Chem. Soc, 18 (5): 486–493.
- [26] - Bhaumik R, Mondal NK, **2016**, Appl Water Sci, 6: 115–135.
- [27] - Farhan S N, Khadom AA, **2015**, Int. J. Ind. Chem, 6(2):119–130.
- [28] - Wei W, Wang Q, Li A., Yang J, Ma F, Pi S, Wu D, **2016**, . Sci Rep, 6: 31575.
- [29] - Ngah, WSW, Hanafiah, MAK. **2008**, Bioresources Technolog, 99: 3935-3948,

Chapter IV: Results and discussion

- [30] – Bhuvaneshwari V, Goel N, Paul PK, **2015**, Plant Cell Rep, 34:1735–1745.
- [31] – Wan X, Wang W, Liu J, **2014**, BMC Med Res Methodol, 14: 135.
- [32] - Ding TY, Hii SL, Ong, L, **2012**, Bioresources, 7(2): 1540–1547.
- [33] – Kwon JY, Dahanukar A, Weiss LA, Carlson JR, **2011**, J. Neurosci. 31 (43): 15300-15309.
- [34] - Gupta VK, Rastogi A, **2008**, J Hazard Mater, 152 (1):407-14.
- [35] - Kwon OH, Kim JO, Cho DW, Kumar R, Baek SH, Kurade MB, Jeon BH, **2016**, Chemosphere, 160:126-133.
- [36] - Hossain MA, HaoNgo H, Guo WV, Nguyen TV, **2012**, Int. J.GEOMATE, 2: 227-234
- [37] – Ezzouhri L, Ruiz E, Castro E, **2010**, A finidad, 67 (545) :39–44,.
- [38] - Sag Y, Yalçuk A, Kutsal T, **2000**, Process Biochemistry, 35 (8): 787–799,
- [39] – Keskin O, Goksu MZL, Basibuyuk M, Forster CF, **2004**, Bioresource Technology, 92 (2): 197–200.
- [40] – Dursun AY, **2006**, Biochemical Engineering Journal, 28 (2): 187–195.
- [41] - Ferro-García MA, Rivera-Utrilla J, Rodríguez-Gordillo J, Bautista-Toledo I, **1988**, Carbon, 26 (3): 363–373,.
- [42] –Shukla SR, Pai RS, **2005**, Bioresource Technology, 96 (13): 1430–1438.
- [44] – Bhattacharya AK, Mandal SN, Das SK, **2006**, Chemical Engineering Journal, 123 (1): 43–51.
- [45] – Halawa R.A, Quora R, Salim, R, **2003**, Journal of Applied Sciences, 3 (2): 79-84.
- [46] – Low KS, Lee CK, Mak SM, **2004**, WoodScience and Technology, 38 (8): 629-640.
- [47] - Ozsoy H.D, Kumbur H, **2006**, Journal of Hazardous Materials, 136: 911–916.
- [48] - Febrianto J, Kosasih AN, Sunarso J, Ju N, **2009**, Journal of Hazardous Materials, 62 (2) 616–645.
- [49] - Canizares P, Carmona M, Baraza O, Delgado A, Rodrigo MA, **2006**, Journal of Hazardous Materials, 131: 243– 248.
- [50] - Kumar R, Bishnoi NR, Garima KB, **2008**, 135: 202-208.
- [51] - Zafar S, Aqil F, Ahmad, **2007**, Bioresource Technology, 98 (13): 2557–2561.

Chapter IV: Results and discussion

- [52] - Elangovan R, Philip L, Chandraraj K, **2008**, The Chemical Engineering Journal, 141(1-3): 99-111
- [53] - Barkat M, Chegrouche S, Mellah A, Bensmain B, Nibou D, Boufatit M, **2014**, Journal of Surface Engi-neered Materials and Advanced Technology, 4: 210-226 .
- [54] - Dakiky M, Khamis M, Manassra A , Mer'eb M, **2002**, Advances in Environmental Research, 6 (4): 533-540.
- [55] - Witek-krowiak A, Szaran RG, Modelski S, **2011**, Desalination, 265: 126-134,
- [56] - Kumar KV, **2006**, J. Hazard. Mater, 136 (21): 197-202.
- [57] - Kumar KV, Porkodi K, **2006**, J. Hazard. Mater, 138: 633-635.
- [58] - Haloi N, Sarma HP. Chakravarty P, **2013**, Appl Water Sci, 3: 559–565.
- [59] - Kuczajowska-Zadrozna M, Filipkowska U, Jóźwiak T, **2020**, J. Environ. Chem. Eng, 8: 103878.
- [60] - Rangabhashiyam S, Anu N, Giri Nandagopal MS, Selvaraju N, **2014**, J. Environ. Chem. Eng, 2(1): 398–414.
- [61] - Bayuo J, Abukari MA, Pelig-Ba KB, **2020**, Appl Water Sci, 10: 171.
- [62] - Zulkali MMD, Ahmad AI, Norulakmal NH, Sharifah NS, **2006**, J Chem Technol Biotechnol, 81: 1324–1327.
- [63] - Kumar U, **2006**, Scientific research and essays, 1 (2): 33-37.
- [64] - Tutic A , Novakovic S , Lutovac M, Biocanin R , Ketin S , Omerovic N, **2015**, Macedonian Journal of Medical Sciences, 3(2): 345–355.
- [65] - Anobe VOA, Sydenstricker THD, Munaro M, Amico SC, **2005**, Polym Test, 24(4): 474–482.
- [66] - Dang VBH, Doan HD, Dang-Vu T, Lohi A, **2009**, Bioresource Technology, 100 (1): 211–219.
- [67] - Annija L, David R, Mark B, John C, **2019**, International Journal of Environmental Research and Public Health, 16 (10): 1803-1818.
- [68] - Kalia S, Kumar A, Kaith B S, **2011**, Advanced Material Letters, 2(1):17-25.
- [69] - Sanghavi B J, Srivastava AK, **2013**, Analyst, 138 (5): 1395–1404.

Chapter IV: Results and discussion

- [70] - Sanghavi BJ, Kalambate P K, Karna S P, Srivastava A K, **2014**, Talanta, 120: 1–9.
- [71] – Prado A GS, **2003**, QuímicaNova, 26: 738-744,
- [72] - Lagergren S, **1898**, S. Handl, 24 (4), 1-39.
- [73] - Ho YS, Was DAJ, **1996**, Forster CF, 17 (1), 71-77.
- [74] - Al-Ghouti MA, Da'ana DA , **2020**, J. Hazard. Mater, 393: 122383.
- [75] - Sarı A, Tuzen M, Uluözlü ÖD, Soylak M, **2007**, Biochem. Eng. J, 37 (2): 151–158.
- [76] - Ronda A, Martín-Lara MA, Dionisio E, Blázquez G, Calero M, **2013**, J. Taiwan Inst. Chem. Engrs, 44 (3): 466–473.
- [78] - Mahamadi C, Nharingo T, **2010**, Bioresou.Technol, 101(3): 859–864.
- [79] - Gundogdu A, Ozdes D, Duran C, Bulut V N, Soylak M, Senturk HB, **2009**, Chem. Eng. Sci, 153 (1-3): 62–69.
- [80] - Naiya TK, Bhattacharya A. K, Das S K, **2008**, Environ. Prog, 27 (3): 313–328.
- [81] - Pavan FA, Mazzocato AC, Jacques RA, Dias SLP, **2008**, Biochem. Eng. J, 40 (2): 357–362.
- [82] - Boparai HK, Joseph M, O'Carroll DM, **2011**, Journal of Hazardous Materials, 186: 458–465.
- [83] - Al-Anbar ZA, Matouq MAD, **2008**, Journal of Hazardous Materials, 151:194–201.
- [84] – Sudha R, Kalpana K, Rajachandrasek T, Arivoli S, **2007**, E J Chem, 4 (2): 238-254.
- [85] - Riaz M, Nadeem R, Hanif MA, Khalilur-Rehman TM, **2009**, J. Hazard. Mater, 88: 161.

Conclusion

Biosorption is a relatively new process that has shown significant contribution for the removal of contaminants from aqueous effluents. *Luffa cylindrica* biomaterial has received increasing attention for the heavy metal removal due to their good performance, low cost and large available quantities. The functional groups present in the surface of the *Luffa cylindrica* biomaterial have some affinity in general for heavy metal ions. The potential of *luffa cylindrica* (LC) for the removal of Pb (II), Zn (II), Cu (II) and Cr (VI) ions from aqueous solutions was dependent on biosorption process such as pH, initial Pb (II), Zn (II), Cu (II) and Cr (VI) ions concentration, biosorbent dose, contact time, and temperature. The aqueous pH is found to be a critical parameter in the biosorption processes, with an optimum pH being 5.0 in all the cases except for hexavalent chromium the pH was found 2. The increase in the biosorbent dosage leads to an increase in the metal removal owing to the corresponding increase in the number of metal binding sites. In addition, the LC biomaterial exhibit good biosorption capacities in was in terms of total biosorption capabilities. The efficiency of Zn (II), Cu (II) and Cr (VI) removal was over 75% because of the concentration in the wastewater except for lead ions did it remain lower than 25%, despite high concentrations of this metal in the wastewater. For this reason, new biosorbent has been prepared by the immobilization of *chlorella pyrenoidosa* in *luffa cylindrica*. According to the experimental results, the optimum temperature of solution, pH, biosorbent concentration, contact time and initial lead ions concentration were determined as 298 K, 5.0, 1 g/L, 40 min and 300 mg/L, respectively. The maximum biosorbent capacity (q_e) and biosorption yield of Pb (II) were obtained found to be 123 mg/g and 41.36%, respectively, at the optimum conditions. The biosorption data were studied and modeled using eighteen well-known isotherm models. From the analysis of all tested models and the knowledge of the most principal parameters (q_m , R^2 , and error values), the isotherm model show that the goodness-of- fit was obtained using the five-parameter model of Fritz–Schluender (V) compared to the other model. Taking into account the outcome two coefficients added to equation Fritz–Schluender (V) for reducing the error between the experimental and predicts data. The results of the fulfillment of this new mathematical model have significantly improved an approximation of the experimental data than Fritz-Schlünder (V) isotherm. This study elucidates that the adjustment of more parameters provides a better fitting of the equilibrium isotherms.

Taking into consideration present findings, the *luffa cylindrica* and *chlorella pyrenoidosa* biomaterials, being cheap and easily available materials, could be an alternative to more costly adsorbents used really for heavy metals removal in wastewater treatment processes.

ANNEXES

Error values of some models studied

Annex 1: Error values of Hennery model of biosorption of lead onto CP.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,87	9,2	40,388803	31,188803	3,39008728	21,178803	24,0844333	0,59631461
25	2,97	21,22	41,327293	20,107293	0,94756329	10,117293	9,78295945	0,2367191
50	10,26	41,02	44,585194	3,565194	0,08691355	5,565794	0,28508586	0,00639418
100	21,73	78,25	49,711137	28,538863	0,3647139	38,539863	16,3839886	0,32958386
150	53,73	96,83	64,011937	32,818063	0,33892454	22,818063	16,8253815	0,26284756
200	97,81	101,68	83,711289	17,968711	0,17671824	27,9345711	3,85700159	0,04607505
250	146,6	104,57	105,51554	0,94554	0,00904217	1,55554	0,00847312	8,03020809
300	193,2	108,04	126,34108	18,30108	0,16939171	38,3018808	2,65099467	0,02098284

Annex 2: Error values of Hennery model of biosorption of lead onto CP-LC.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,31	9,89	0,11375	10,18625	0,98776882	9,18625	741,865398	8,7582418
25	0,93	24,15	0,40625	12,09376	0,98194444	22,09375	1201,5601	5,3846154
50	2,6	46,91	1,7875	27,2125	0,95416667	37,2125	774,696591	2,8181818
75	11,03	89,91	4,7125	31,5775	0,89755435	41,2875	361,731068	8,76127321
100	36,29	113,23	7,6375	36,3657	0,85589623	45,3625	269,428007	5,93944354
150	82,79	118,35	15,405	29,785	0,72092391	39,795	102,800521	2,58325219
200	131,23	121,08	23,075	14,125	0,60215517	34,925	52,8604821	1,5135428
300	175,9	123,67	38,8375	42,1725	0,36331967	22,1625	12,6469625	0,57064693

Annex 3: Error values of Languimir model of biosorption of lead onto CP.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,87	9,2	7,39191719	11,80808281	0,19653074	1,80808281	12,12308281	0,24460269
25	2,97	21,22	21,8436628	10,62366285	0,02939033	0,62366285	1,71266285	0,0285512
50	10,26	41,02	51,4570729	10,4370729	0,25443864	10,4370729	9,7854729	0,20283068
100	21,73	78,25	72,6321133	5,61788674	0,07179408	5,61788674	4,56788674	0,07734715
150	53,73	96,83	93,0260358	13,80396421	0,03928498	3,80396421	1,12396421	0,04089139
200	97,81	101,68	101,771136	10,09113582	0,0008963	0,09113582	3,098663582	0,0008955
250	146,6	104,57	105,806133	1,23613277	0,0118211	1,23613277	2,23613277	0,011683
300	193,2	108,04	107,874213	10,16578661	0,00153449	0,16578661	2,16578661	0,00153685

Annex 4: Error values of Languimir model of biosorption of lead onto CP-LC.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,31	9,89	5,49837659	13,80162341	0,40877671	1,88776882	1,86747411	0,47804549
25	0,93	24,15	16,0143176	16,48568241	0,28825255	2,98194444	1,6096431	0,16401912
50	2,6	46,91	37,6570077	11,34299229	0,0344357	5,95416667	4,2135452	0,00127191
75	11,03	89,91	49,9904928	13,99049277	0,08674984	2,89755435	5,343522	0,00637204
100	36,29	113,23	54,1405853	11,14058529	0,02152048	3,85589623	,5435483	0,00044382
150	82,79	118,35	58,0558526	12,85585262	0,05173646	4,72092391	6,53148358	0,0024198
200	131,23	121,08	59,46124	11,46124001	0,02519379	5,60215517	3,56645948	0,00060391
300	175,9	123,67	60,6582003	10,34179972	0,00560327	5,36331967	4,4566499	3,17520005

Annex 5: Error values of Freundlich model of biosorption of lead onto CP.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,87	9,2	12,0005698	12,40877671	0,30440976	3,34566978	6,8056978	0,23336973
25	2,97	21,22	21,0144485	11,28825255	0,00968669	2,2089949	4,9845149	0,00978144
50	10,26	41,02	36,9986406	13,0344357	0,09803412	3,0980594	2,9856594	0,10868938
100	21,73	78,25	52,107421	12,12674984	0,33409047	16,179879	21,172579	0,50170549
150	53,73	96,83	78,7584514	11,12152048	0,18663171	38,07178086	13,0968546	0,22945536
200	97,81	101,68	103,516863	11,1515946	0,01806514	1,98908701	1,09658321	0,01774458
250	146,6	104,57	124,51055	11,94951939	0,19069093	17,940792	18,565502	0,16015149
300	193,2	108,04	141,222622	11,5560327	0,30713275	36,0721	13,8695221	0,23496676

Annex 6: Error values of Freundlich model of biosorption of lead onto CP-LC.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,31	9,89	12,9726349	3,9866882	0,39490698	3,67263494	1,03974616	0,08014919
25	0,93	24,15	19,3473093	2,6985444	0,14011959	3,15269068	3,51373854	0,02655349
50	2,6	46,91	30,8080858	3,6916667	0,21004908	8,19191417	2,17824172	0,07070357
75	11,03	89,91	41,7696065	2,968635	0,09196508	4,23039351	4,42845099	0,01025748
100	36,29	113,23	48,6078195	1,6996623	0,08287133	4,39218046	5,39687543	0,00816485
150	82,79	118,35	60,5878066	2,7964391	0,09760519	-5,38780659	1,47911389	0,00790776
200	131,23	121,08	68,7837664	1,950917	0,18592701	-10,7837664	1,69065498	0,02457927
300	175,9	123,67	80,9998759	3,09671967	0,32786682	19,999875919	4,93821787	0,06096575

Annex 7: Error values of Sips model of biosorption of lead onto CP.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,87	9,2	8,20385776	5,8056978	0,10827633	0,99614224	3,40877671	0,12142364
25	2,97	21,22	22,6691101	3,9845149	0,06828982	1,44911006	2,28825255	0,06392444
50	10,26	41,02	51,0659432	1,9856594	0,24490354	10,0459432	3,0344357	0,19672491
100	21,73	78,25	71,5248511	21,172579	0,08594439	6,72514888	1,12674984	0,09402535
150	53,73	96,83	92,0892959	11,0968546	0,04895904	4,74070413	3,12152048	0,05147943
200	97,81	101,68	101,415773	13,09658321	0,00259861	0,26422675	8,1515946	0,00260538
250	146,6	104,57	105,894353	11,565502	0,01266475	1,32435261	3,94951939	0,01250636
300	193,2	108,04	111,251292	12,8695221	0,00195568	0,21129214	2,5560327	0,00195187

Annex 8: Error values of Sips model of biosorption of lead onto CP-LC.

C	Ce	Qe	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,31	9,89	9,3110077	5,6056978	0,05854321	1,5789923	2,03600385	0,06218363
25	0,93	24,15	23,8036305	2,9845149	0,01434242	8,14636952	2,00504007	0,01455112
50	2,6	46,91	48,9224654	1,8856594	0,04290056	1,11246543	3,0827844	0,04113581
100	11,03	89,91	90,9756679	11,172579	0,01185261	1,06566792	2,01248299	0,01171377
150	36,29	113,23	112,446327	11,1968546	0,00692107	1,17836727	1,00546165	0,0069693
200	82,79	118,35	119,5524	12,09658321	0,0101597	1,120240042	1,01209316	0,01005752
250	131,23	121,08	121,807809	10,125502	0,00601098	1,3278094	1,00434871	0,00597506
300	175,9	123,67	122,823258	12,8695221	0,00684678	1,184674157	1,00583742	0,00689398

Annex 9: Error values of Khan model of biosorption of lead onto CP.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,87	9,2	7,344808604	1,855191396	0,20165124	3,9866882	1,8056978	0,06379938
25	2,97	21,22	21,50724793	2,28724793	0,01353666	2,6985444	1,9845149	0,00017838
50	10,26	41,02	49,98562021	8,96562021	0,21856705	3,6916667	0,9856594	0,03217144
100	21,73	78,25	70,38761465	7,862385349	0,10047777	2,968635	1,172579	0,01247717
150	53,73	96,83	91,19948506	5,630514938	0,05814846	1,6996623	1,0968546	0,00381164
200	97,81	101,68	101,4285625	5,251437477	0,00247283	2,7964391	1,09658321	0,00145223
250	146,6	104,57	106,9543037	2,38430375	0,02280103	1,950917	0,565502	0,00049697
300	193,2	108,04	110,2207107	2,18071075	0,02018429	3,09671967	1,8695221	0,00039144

Annex 10: Error values of Khan model of biosorption of lead onto CP-LC.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,31	9,89	9,360931185	1,529068815	0,05349533	0,18056978	1,02990235	0,00319438
25	0,93	24,15	24,417133	3,267133	0,01106141	0,19845149	2,00292254	0,00011969
50	2,6	46,91	50,5661618	3,6561618	0,07793992	1,09856594	1,264357	0,00522794
100	11,03	89,91	93,58036529	3,67036529	0,04082266	0,1172579	1,14395735	0,00153833
150	36,29	113,23	115,8493833	2,61938333	0,0231333	0,1968546	2,05922491	0,00051122
200	82,79	118,35	124,1508452	5,80084518	0,04901432	1,19658321	1,27103968	0,00218315
250	131,23	121,08	127,2859624	6,20596244	0,05125506	0,1565502	2,3025783	0,00237715
300	175,9	123,67	128,9210846	5,25108458	0,04246046	1,08695221	1,21388192	0,00165901

Annex 11: Error values of Fritz–Schluender (IV) model of biosorption of lead onto CP.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,87	9,2	10,2816416	0,00816416	0,11756974	0,0816416	1,0816416	0,10520126
25	2,97	21,22	23,4941498	0,27414982	0,10717011	0,27414982	2,27414982	0,09679643
50	10,26	41,02	49,0455156	0,02551563	0,19564885	0,02551563	8,02551563	0,16363404
100	21,73	78,25	78,2052349	0,04476506	0,00057208	0,04476506	0,04476506	0,0005724
150	53,73	96,83	89,0131981	0,81680195	0,08072707	0,81680195	7,81680195	0,08781621
200	97,81	101,68	99,4288281	0,25117188	0,02213977	0,25117188	2,25117188	0,02264104
250	146,6	104,57	104,843679	0,27367857	0,00261718	0,27367857	0,27367857	0,00261035
300	193,2	108,04	107,871865	0,16813534	0,00155623	0,16813534	0,16813534	0,00155866

Annex 12: Error values of Fritz–Schluender (IV) model of biosorption of lead onto CP-LC.

C	Ce	Qex	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,31	9,89	9,2882171	0,6017829	0,06084761	0,6017829	0,03898947	0,006478993
25	0,93	24,15	22,0084576	0,1415424	0,0886767	2,1415424	0,2083837	0,09730543
50	2,6	46,91	43,2318665	0,67813352	0,0784083	3,67813352	0,31293273	0,08507922
100	11,03	89,91	80,7055725	0,2044275	0,10237379	9,2044275	1,04976005	0,11404947
150	36,29	113,23	103,333901	0,89609888	0,08739821	9,89609888	0,94773131	0,09576817
200	82,79	118,35	115,011698	0,351111	0,02830587	3,3587950	0,0975866	0,002913043
250	131,23	121,08	120,698096	0,08785	0,00891972	1,0889707	0,00972	0,009
300	175,9	123,67	123,8596	0,677854	0,00541764	0,6709658	0,00364959	0,00544715

Annex 13: Error values of Fritz–Schluender (V) model of biosorption of lead onto CP.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,87	9,2	8,23873034	0,96126966	0,10448583	0,096126966	0,96126966	0,0011667692
25	2,97	21,22	21,8669058	0,64690576	0,03048566	0,064690576	0,64690576	0,002958378
50	10,26	41,02	48,2146742	7,1946742	0,1753943	0,1946742	1,1946742	0,014922167
100	21,73	78,25	67,9642014	10,2857986	0,13144791	0,2857986	0,287986	0,015134142
150	53,73	96,83	89,4028144	7,42718555	0,07670335	0,42718555	0,942718555	0,008307552
200	97,81	101,68	100,12725	1,55274973	0,01527095	0,55274973	0,955274973	0,001550776
250	146,6	104,57	105,699153	1,1291532	0,01079806	0,1291532	0,1291532	0,001068271
300	193,2	108,04	108,813455	0,77345528	0,00715897	0,77345528	0,77345528	0,00710808

Annex 14: Error values of Fritz–Schluender (V) model of biosorption of lead onto CP-LC.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,31	9,89	10,411552	0,52155197	0,05273529	0,196126966	0,02612641	0,005009359
25	0,93	24,15	24,4585857	0,3085857	0,01277788	0,164690576	0,00389332	0,01261666
50	2,6	46,91	47,3754203	0,46542029	0,00992156	1,31946742	0,00457233	0,00982409
100	11,03	89,91	86,3598935	3,55010649	0,03948511	0,1287986	0,14593876	0,04110828
150	36,29	113,23	109,082523	4,14747697	0,03662878	0,1942718555	0,15769314	0,003802146
200	82,79	118,35	118,06403	0,28597043	0,00241631	0,1955274973	0,00069267	0,00242216
250	131,23	121,08	121,376421	0,29642094	0,00244814	0,12291532	0,00072391	0,00244216
300	175,9	123,67	123,032561	0,6374386	0,00515435	0,727345528	0,00330261	0,00518106

Annex 15: Error values of modified Fritz–Schluender (V) r model of biosorption of lead onto CP.

C	CE	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,87	9,2	9,15579632	0,0520368	0,00480475	0,02898947	0,04420368	0,000482794
25	2,97	21,22	22,6674588	1,00447458	0,06821201	0,02083837	0,44745881	0,006385625
50	10,26	41,02	45,00003	2,08885001	0,09702584	0,01293273	0,9899384	0,08844444
100	21,73	78,25	78,2000003	0,15006001	0,00063898	0,08976005	0,29356847	0,000063939
150	53,73	96,83	97,33333	0,24567704	0,00175565	0,94773131	0,1874398	0,00175258
200	97,81	101,68	100,685117	0,09488288	0,00978445	0,09758696	0,99488288	0,000988113
250	146,6	104,57	105,814933	1,08493346	0,01190526	0,00972	0,24493346	0,0117652
300	193,2	108,04	108,906429	0,58664289	0,00801952	0,00364959	0,8664289	0,007095572

Annex 14: Error values of modified Fritz–Schluender (V) model of biosorption of lead onto CP-LC.

C	Ce	Qexp	Qcal	S ²	ARE	ERRSQ	HYBRID	MPSD
10	0,31	9,89	9,2882171	0,6017829	0,06084761	0,0298947	0,03898947	0,00647899
25	0,93	24,15	22,0084576	0,1415424	0,0886767	0,0222837	0,2083837	0,00973054
50	2,6	46,91	43,2318665	0,67813352	0,0784083	0,0293273	0,31293273	0,00085079
100	11,03	89,91	80,7055725	0,2044275	0,10237379	0,02976005	1,04976005	0,00140497
150	36,29	113,23	103,333901	0,89609888	0,08739821	0,02773131	0,94773131	0,00576817
200	82,79	118,35	112,409699	0,94030097	0,05019266	0,067696	0,31391576	0,00284509
250	131,23	121,08	115,763791	0,31620858	0,04390658	0,00972	0,2441357	0,0959229
300	175,9	123,67	117,438713	0,23128704	0,05038641	0,00564959	0,3306315	0,005991

Abstract

In this study, *Luffa Cylindrica* (LC) fibers have been used as a new biological adsorbent for removal of Pb (II), Zn (II), Cu (II) and Cr (VI) ions from petroleum wastewater of Hassi R'mel, Laghouat, Algeria. This biosorbent was analyzed X-ray diffraction, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM / EDS) and infrared spectroscopy (IR) and thermogravimetric analysis (TG –DTG). At optimal condition, the maximum ions biosorption onto LC fibers were found to be 8.9, 4.67, 3.9 and 5.91 mg/g for Pb (II), Zn (II), Cu (II) and Cr (VI), respectively. This results showed that biomaterial is effective in removing Zn (II), Cu (II) and Cr (VI) ions from petroleum wastewater but it's not sufficient for eliminate all Pb (II) exist in the industrial wastewater of Hassi R'mel. For this reason, newly biosorbent was developed from unicellular green microalgal *Chlorella pyrenoidosa* immobilized in *Luffa Cylindrica* (CP-LC) for removal of lead ions. The maximum biosorbent capacity and biosorption yield of Pb (II) were obtained found to be 123 mg/g and 41.36%, respectively. In the experimental design of the Pb (II) removal process, new mathematical model was developed for predicting the equilibrium data. The results of the fulfillment of this model have significantly improved an approximation of experimental data with ($R^2=0.999$) and very low error values. The calculated thermodynamic factors (ΔG° , ΔH° , ΔS°) indicated that the all bioprocesses were spontaneous and exothermic. Finally, our results suggest that the native and immobilized *Luffa Cylindrica*-assisted adsorption method have a high capability to remove the heavy metals from industrial waste water.

Keywords: Algal, *Luffa Cylindrica*, biosorption, kinetics, mathematical model, industrial water.

Résumé

Dans cette étude, les fibres de *Luffa Cylindrica* (LC) ont été utilisées comme nouvel adsorbant biologique pour l'élimination des ions Pb (II), Zn (II), Cu (II) et Cr (VI) des eaux usées pétrolières de Hassi R'mel, Laghouat, Algérie. Ce biosorbant a été analysé par diffraction des rayons-X, microscopie électronique à balayage couplée à la spectroscopie des rayons X à dispersion d'énergie (MEB/EDS), spectroscopie infrarouge (IR) et l'analyse thermogravimétrique (TG -DTG). Dans des conditions optimales, la biosorption maximale des ions sur les fibres de LC s'est avérée être de 8,9, 4,67, 3,9 et 5,91 mg/g pour Pb (II), Zn (II), Cu (II) et Cr (VI), respectivement. Ces résultats ont montré que le biomatériau est efficace pour éliminer les ions Zn (II), Cu (II) et Cr (VI) des eaux usées pétrolières mais qu'il n'est pas suffisant pour éliminer tout le Pb (II) existant dans les eaux usées industrielles de Hassi R'mel. Ainsi, un nouveau biosorbant a été développé à partir de la microalgue verte unicellulaire *Chlorella pyrenoidosa* immobilisée dans le *Luffa Cylindrica* (CP-LC) pour l'élimination des ions plomb. La capacité de biosorption maximale et le rendement de biosorption de Pb (II) ont été obtenus à 123 mg/g et 41,36 %, respectivement. Dans la conception expérimentale du processus d'élimination du Pb (II), un nouveau modèle mathématique a été développé pour prédire les données d'équilibre. Les résultats de la réalisation de ce modèle ont considérablement amélioré une approximation des données expérimentales avec un ($R^2=0,999$) et des valeurs d'erreur très faibles. Les facteurs thermodynamiques calculés (ΔG° , ΔH° , ΔS°) ont indiqué que tous les bioprocédés étaient spontanés et exothermiques. Enfin, nos résultats suggèrent que la méthode d'adsorption assistée par *Luffa Cylindrica* native et immobilisée a une grande capacité à éliminer les métaux lourds à partir des eaux usées industrielles.

Mots clés : Algues, *Luffa Cylindrica*, biosorption, cinétique, modèle mathématique, eau industrielle.

المخلص

في هذه الدراسة ، تم استخدام ألياف الإسفنج الطبيعي كمتنص بيولوجي جديد لإزالة أيونات الرصاص (II) ، الزنك (II) ، النحاس (II) و الكروم (VI) من المياه الصناعية لحاسي الرمل ، الأغواط ، الجزائر. تم تحليل هذه المادة الحيوية عن طريق عن طريق حيود الأشعة السينية، المسح بالمجهر الإلكتروني المقرون بمطيافية تشتت الطاقة بالأشعة السينية (MEB/EDS) والتحليل الحراري الوزني (TG-DTG) في الحالة المثلى، يتم امتصاص الحد الأقصى من الأيونات على ألياف LC بمعدل 8.9 و 4.67 و 3.9 و 5.91 ملغ / غ ل - Pb (II) Zn (II) Cu (II) و Cr (VI) على التوالي. أظهرت هذه النتائج أن المادة الحيوية فعالة في إزالة أيونات الزنك (II) والنحاس (II) والكروم (VI) من مياه الصرف البترولية ولكنها غير كافية لإزالة كل الرصاص (II) الموجود في مياه الصرف الصناعي في حاسي الرمل. لهذا السبب، تم تطوير مادة الامتصاص الحيوي حديثاً من الطحالب الدقيقة الخضراء أحادية الخلية كلوريل بيرونويدوزا المثبتة في الإسفنج الطبيعي (CP-LC) لإزالة أيونات الرصاص. تم الحصول على أقصى سعة للامتصاص الحيوي للرصاص ب 123 ملغ / غ بنسبة 41.36%. في التصميم التجريبي لعملية إزالة الرصاص (II) تم تطوير نموذج رياضي جديد للتنبؤ ببيانات التوازن. أدت نتائج تطبيق هذا النموذج إلى تحسين تقريب البيانات التجريبية بدرجة عالية وقيم خطأ منخفضة جداً ($R^2=0.999$). أشارت العوامل الترموديناميكية (ΔG° , ΔH° , ΔS°) أن جميع العمليات الحيوية كانت عشوائية وطاردة للحرارة. وفي الأخير ، أكدت النتائج المحصل عليها إلى أن طريقة الامتزاز بمساعدة الإسفنج الطبيعي الحر والمجمد لديها قدرة عالية على إزالة المعادن الثقيلة من مياه الصرف الصناعي.

الكلمات المفتاحية: الطحالب ، الإسفنج الطبيعي ، الامتصاص الحيوي ، الخواص الحركية ، النموذج الرياضي ، المياه الصناعية.