PREPARATION OF LIGNOCELLULOSE BASED NANOMATERIAL AND ITS APPLICATION IN HEAVY METAL REMOVAL FROM WASTEWATER

Thesis Submitted for the Award of the Degree of

DOCTOR OF PHILOSOPHY

in
Biotechnology

By

AJAY KUMAR
41700217

Supervised By
Dr. Vineet Kumar
(UID: 21644)
Associate Professor
Department of Biotechnology
School of Bioengineering and Biosciences

LOVELY PROFESSIONAL UNIVERSITY

PUNJAB

2024

DECLARATION

I declare that the thesis entitled **"Preparation of Lignocellulose Based Nanomaterial and its Application in Heavy Metal Removal from Wastewater"** has been prepared by me under the guidance of Dr. Vineet Kumar, Associate Professor, Department of Biotechnology, School of Bioengineering and Biosciences, Lovely Professional University, Phagwara, Punjab, and as per the requirement for the award of the degree of Doctor of Philosophy (Ph.D.) in Biotechnology (specialization in Nanotechnology) is entirely an authentic record of my own research work and ideas and references are duly acknowledged. It is further certified that the results incorporated in this thesis have not been submitted, in part or full, to any other university or institution for the award of any degree or diploma.

Ajay Kumar
Ajay Kumar
Reg. No- 41700217
Department of Biotechnology
School of Bioengineering and Biosciences
Lovely Professional University
Phagwara, Punjab, India

Date: 04|05|2024

LOVELY
PROFESSIONAL
UNIVERSITY

Transforming Education Transforming India

CERTIFICATE

It is hereby certified that thesis entitled, **"Preparation of Lignocellulose Based Nanomaterial and its Application in Heavy Metal Removal from Wastewater"**, being submitted by **Mr. Ajay Kumar**, in Department of Biotechnology, School of Bioengineering and Biosciences, Lovely Professional University, Punjab, to award the degree of Doctor of Philosophy in Biotechnology is a record of bonafide research work carried out by **Mr. Ajay Kumar** under my supervision and guidance and has fulfilled all the requirements for the submission of the thesis. It is further certified that the results incorporated in this thesis have not been submitted, in part or full, to any other university or institution for the award of any degree or diploma.

Vineet
04/05/2024

Supervised By
Dr. Vineet Kumar
Associate Professor
Department of Biotechnology
School of Bioengineering and Biosciences
Lovely Professional University, Punjab

Abstract

Lignocellulosic-based nanomaterials such as nanolignin have the potential for decontamination of toxic heavy metals from industrial wastewater. Annually 181.5 billion tons of lignocellulose biomass are generated, primarily composed of cellulose, hemicellulose, and lignin. Pretreated cellulose and hemicellulose are widely used as substrates for the production of biofuels. Nanolignin is a phenolic compound that has been recognized as a potential candidate for the removal of heavy metals from wastewater. Due to the hazardous effects of heavy metals, remediation of heavy metals from wastewater is of great concern. The main heavy metals (HMs) sources are industrial wastewater effluents from tanning industries, electroplating industries, mining industries, etc. Several conventional techniques such as precipitation, coagulation, flocculation, membrane separation, oxidation, ion exchange, etc are intensively investigated for the remediation of heavy metals. Conventional chemical precipitation methods employed for the removal of harmful heavy metals (HMs) resulted in the generation of serious secondary pollutants. Similarly, the efficacy of remediation of heavy metals by ion exchange (cation and anion exchanger) using ion-exchange resin is highly dependent on resin structure and the concentration of the solution. It has been postulated that accumulations of heavy metals such as Cr (VI), Pb (II), Hg (II), Ni (II), etc disturb the metabolic pathways of humans which leads to the development of various metabolic diseases. In the present study, the role of nanolignin in the removal of Cr (VI) from aqueous solutions has been investigated. Hexavalent chromium is extremely harmful and can cause cancer, hence regulatory bodies are giving their attention to its removal from an aqueous solution. More than 0.05 mg/L of Cr (VI) in potable water is dangerous to human health as per the World Health Organization. The higher toxicity of Cr (VI) as compared to Cr (III) is due to chromate similarity in the structure with sulfate. Trivalent chromium cannot cross the membrane through the sulfate uptake pathway, whereas hexavalent chromium, a potent oxidizing agent, can. Thus, green materials such as nanolignin could be one of the promising techniques for the remediation of Cr (VI) through adsorption.

In this study, nanolignin was derived from coconut coir. Lignin was extracted through soda pulping methdod and subjected to size reduction through an ultrasonication process. The yield of nanolignin derived from coconut coir was determined and found to be 63.67±1.83. The size of the nanolignin particles obtained from coconut coir was observed in the range of 311.8-383.9 nm with zeta potential -29.9 to -32.3 mV at a nanolignin concentration of 1 mg/ml. By using scanning

electron microscopy (SEM) the topological morphology of nanolignin was investigated, and the results revealed spherical and irregularly shaped lignin nanoparticles particles (LNPs). The mixture of irregularly smaller and spherical structures of nanolignin particles was seen through Transmission electron microscopy (TEM) and analysis with a 122 nm diameter. The crystalline size of nanoparticles was determined by X-ray diffraction (XRD). The presence of a broad reflection peak around 22° indicates a semi-crystalline nature and weak intense reflections are observed at 12.8° and 26.7°. The functional groups on nanoliglin were determined using Fourier-Transform Infrared Spectroscopy (FTIR). Through the Brunauer-Emmett-Teller (BET) analysis, the surface area of the nano-lignin was observed as 4.130 m^2/g with a pore volume of 0.006 cc/g and pore radius of 24.393 Å. The thermal stability of the nanolignin was determined by TGA (Thermogravimetric analysis) and DSC (Differential scanning calorimetry).

The batch experiment of Cr (VI) elimination was carried out in a 250 ml conical flask using a magnetic stirrer bar at 400 rpm. The remediation of metal ions such as Cr (VI) from wastewater is affected by several factors like temperature, pressure, pH, biosorbent dose, initial metal ions concentration, contact time, and ionic strength. The removal efficiency of the nanoadsorbents is affected by their physical and chemical properties such as particle size, porosity, surface area, surface functional groups, etc. The chromium's maximum removal efficiency was 92.8% at acidic pH of 2, nanoadsorbent dosage (0.03 g), and contact time (80 min) as investigated in the batch study. The kinetic study of Cr (VI) was well represented by pseudo-second order and isotherm data were best fitted with the Langmuir model (R^2= 0.975). In this study, experimental data were analyzed for regression analysis using Microsoft Excel solver function (Microsoft Office 2019, USA) for various isotherm models and kinetics. On industrial wastewater, through the use of nanolignin, an adsorption study was conducted to remove Cr (VI) and 44.09 % of chromium (VI) removal from the tannery wastewater was observed at optimum removal conditions of pH 2, adsorbent dosage 0.03g/ 100 ml at 298 K and 400 rpm. Through the studies, it has been demonstrated that the process by which Cr (VI) ions are adsorbed by nanolignin was electrostatic attraction, reduction, or surface complexation.

Heavy metal pollution such as Cr (VI) is one of the major environmental pollutions that can be remediated by nano adsorbents. Thus, nanolignin particles showed good adsorption capacity for Cr (VI) at 30.94 mg/g at 298 K, in an aqueous solution and act as a potential adsorbent for the removal of heavy metals such as Cr (VI) from wastewater. In the future, surface modification of nanolignin will enhance its utility for the removal of hexavalent forms of chromium present in

alkaline water. As the practical method of wastewater treatment, the techniques such as adsorption, chemical, and membrane methods are addressed by most of the literature. Heavy metals remediation studies were performed using synthetic wastewater with one or a few metal types. Therefore, studies need to be performed on actual wastewater to fill the knowledge gap. Although a lot of improvement has been observed in the preparation of lignocellulosic-based nanomaterials and their composites, still the issues such as higher binding efficiencies of nanoadsorbents at a wide range of pH require further research and development. Thus, nanolignin can be used as an adsorbent for the removal of Cr (VI) from wastewater. As most of the nanomaterials are difficult to recycle and easy to agglomerate, how to solve these disadvantages will be a futuristic challenge for scientists. In the future, surface modification of nanolignin will enhance its utility for the remediation of hexavalent forms of chromium present in alkaline water.

Keywords: Nanolignin; Chromium (VI); Adsorption; Coconut coir; Kinetics

Contents

Acknowledgment

Foremost I am very grateful to God for sailing me through this journey and making this study possible.

I also take this opportunity to express my deep sense of gratitude and sincere thanks to my research supervisor, Dr. Vineet Kumar, Department of Biotechnology, Lovely Professional University for his invaluable guidance, support, and persistent encouragement. I am thankful to the Head of the School, Dr. Neeta Raj for her guidance and support. I also show my thanks to Dr. Himanshu Singh (HOD), and all the faculty members and staff of the Department of Biotechnology, Lovely Professional University for their unequivocal support throughout. I am also thankful to Dr Vishnu for his excellent guidance and critical suggestions throughout my research work.

I am grateful to Dr. Anand Mohan, Dr. Joginder Singh, Dr. Anupam Kumar, Dr Vijay Kumar, Dr. Arvind Kumar, Dr. Simranjeet Singh and Er. Shashank Garg for their constructive criticism and suggestions.

Any project cannot be done without the support of the head of the laboratory and the technical staff of the laboratory. So, I am very thankful to Dr. M. A . Khan, Mr. Chirag Chopra (HOL), and all the technical staff of the biotechnology department especially Mr. Kuldeep Singh, Mr. Baliram, and Mr. Sunney Gupta for their support during my laboratory work.

I especially want to thank my wife Priyanka Kumari for her support, advice, and patience. Thank you for always being there on this journey. I could not accomplish this feat without you by my side. Thank you to my little daughter Ananya Kumari and my little son Shivam Kumar for always cherishing me during this time.

I am also very much grateful to my father Bishnu Deo Rawat and mother Malti Devi for their moral encouragement and constant motivation. I would like to thank my sister Ms. Jayanti Kumari for encouraging me during this period. Lastly, I would like to thank my entire family for the care that they have shown me during the period of this work.

Ajay Kumar

Ajay Kumar

Date 4|5|2024

List of Figures

List of Tables

List of abbreviations

USEPA: United States Environment Protection Agency

WWF : Word Wide Life

LNPs: Lignin Nanoparticles

THF: Tetrahydrofuran

SEM: Scanning electron microscopy

EDS: Energy-Dispersive X-ray Spectroscopy

PSA : Particle Size Analyzer

TEM: Transmission Electron Microscopy

BET : Brunauer-Emmett-Teller

pH$_{PZC}$: Point of Zero charge

DPC: Diphenyl carbazide

DPCA: Diphenyl Carbazone

DLS: Dynamic Light Scattering

XRD: X-ray diffraction

FTIR: Fourier-Transform Infrared Spectroscopy
SSE : Sum of Square Error

SAE : Sum of Absolute Error

HYBRID : Hybrid fractional error function

TDS : Total dissolved solids

TGA: Thermogravimetric analysis

DSC: Differential scanning calorimetry

List of symbols:

C_0 : Initial concentration of metal (mg/L)

C_e : Equilibrium metal ions concentration (mg L^{-1})

K_f : Freundlich constant.

K_L : Langmuir biosorption constant (L mg^{-1})

m : Mass of adsorbent used (mg)

n : Freundlich constant.

Q_{DR} : Observed biosorption capacity,

q_e : Biosorption capacity at equilibrium (mg g^{-1})

q_m : Maximum uptake capacity of the biosorbent

r : Particle radius

R : Ideal gas constant (8.314 J/mol K)

T : Temperature in Kalvin (K)

V : Volume of solution used (mL)

ΔG_{ads}^0 : Gibb's energy (J/mol)

ΔH_{ads}^0 : Adsorption enthalpy (J/mol)

ΔS_{ads}^0 : Adsorption entropy (J/ mol K)

k_f **:** Diffusion co-efficient

J_f **:** Flux of heavy metal

Index

I would like to dedicate this thesis to my entire family and especially to my father Shri Bishnu Deo Rawat, my mother Smt. Malati Devi, my wife Priyanka Kumari, my daughter Ananya Kumari, and my son Shivam Kumar

CHAPTER-1

INTRODUCTION

1. Introduction

Water pollution by heavy metals (HMs) is an alarming situation due to the harmful effects of heavy metals at a higher concentration in human bodies (Kumar & Kumar, 2023; Ajiboye et al., 2020). The primary sources of heavy metals are industrial wastewater, sewage, mining waste, metal smelting, electroplating processes, leather tanning and textile, pharmaceuticals, pesticides, and organic chemicals. Adsorption is one of the techniques to remove toxic heavy metals from wastewater (Chai et al., 2021; Burakov et al., 2018; Chowdhury et al., 2016). Several heavy metals such as nickel (Ni^{2+}), zinc (Zn^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), cobalt (Co^{2+}), etc. are required in trace amounts for physiological and biochemical processes (Bhattacharya et al., 2016). It has been investigated that the metabolic process of humans is destroyed by the accumulation of heavy metals (Cr^{6+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ni^{2+}, etc.). Heavy metals accumulation results in the production of oxygen species, leading to the onset of various diseases (Tahoon et al., 2020; Muthusaravanan et al., 2018). Furthermore, the free radicals produced by a redox reaction in the biological system by carcinogenic metals such as nickel (Ni^{2+}) and arsenic (As^{3+}) cause oxidative damage to DNA and proteins (Fu & Xi., 2020). Metals with an atomic weight between 63.5 and 200.6 and a specific gravity higher than 5 are classified under the heavy metals group (Fu & Wang, 2011).

Directly or indirectly heavy metal contamination affects the economic status of the country along with human sustenance (Carolin et al., 2017). Many countries are facing challenges in the elimination of heavy metals due to the lack of advanced technologies for water purification (Thakur et al., 2024; Chowdhury et al., 2016). In the current scenario, heavy metal toxicity is a major concern due to its harmful effects on the cellular level. Heavy metal is also involved in oxidative stress resulting in macromolecular damage as well as activation of multiple pathways that control cell survival and death. Exposure to heavy metals has been associated with a high risk of thyroid cancer, kidney failure, infertility, etc. (Paithankar et al., 2021). The World Health Organization (WHO) and relevant government agencies have published practical manuals, handbooks, and training materials as a guideline for referring to optimum heavy metals concentration in drinking water (Ibrahim et al., 2021). Table 1 enlists heavy metal toxicity and its acceptable limits in drinking water.

Table 1: Heavy metal toxicity and its permittable limits in drinking water

Heavy metal	Toxicity	Permittable level (mg/L) in drinking water	Reference
Chromium	Lung carcinoma, Cancer, skin disease	0.05	Sall et al., 2020; Babel & Kurniawan, 2005
Lead	Nervous system disorder	0.006	Jia et al., 2018 ; Edition, 2011
Mercury	Pneumonitis and acute necrotizing bronchitis	0.00003	Rahman, & Singh, 2019
Arsenic	Cancer, Skin manifestations,	0.050	Sobhanardakani et al., 2018, Tabassum et al., 2019
Nickel	Skin irritation	0.20	Genchi et al., 2020
Cadmium	A respiratory disorder, Kidney damage	0.01	Ebrahimi et al., 2020
Copper	Liver disease, Gastrointestinal disease, pulmonary disease, Anaemia	0.25	Cheng et al., 2019
Zinc	Nausea, skin irritation, Dizziness	0.80	Chasapis et al., 2020

1.1 Remediation of heavy metals

Extensive investigations along with various conventional and emerging techniques have been employed by researchers for the remediation of heavy metal ions from wastewater. During the wastewater treatment process, treatment options such as coagulation and flocculation (Altaf et al., 2021), chemical precipitation operations (Azimi et al., 2017), ion exchange (Bashir et al., 2019), adsorption (Rashid et al., 2021), membrane filtration (Khulbe & Matsuura, 2018), photocatalysis (Sajjadi et al., 2021), electrodialysis advanced oxidation process, and biological treatment (Lu & Astruc, 2018) are widely used by industries.

Nanomaterials derived from lignocellulose such as lignin and its derivatives are potential solutions as suggested by many researchers for the bioremediation of heavy metals (Sajjadi et al., 2021; Pei et al., 2021). The adsorption capacity of adsorbent, recyclability, and production cost of adsorbent with high surface area determine the use of adsorbent at a large scale (Mu et al., 2020; Kumar et al., 2019). Different kinds of lignocellulosic biomass such as *Eucalyptus spp*., *Acacia confusa* wood chip, bamboo, etc have been investigated for the production of nano-lignin [Pavaneli et al., 2024; Khan et al., 2024; Zuo et al., 2024; Mili et al., 2023]. Table 2, shows the major benefits and drawbacks of the various wastewater technologies used for the treatment of heavy metals in wastewater. The lignocellulosic-based nanomaterials are eco-friendly and economically viable, hence used for the removal of heavy metal ions from wastewater.

Nanosorbent is made up of nanosized material that is used to remove hazardous materials like heavy metals, dyes, pesticides, pharmaceutical wastes, etc. due to high porosity, small size, high reactivity, more active sites, and large surface area to volume ratio. Nanoparticles are applied for the remediation of wastewater and due to their small size effect (1-100 nm), different physical and chemical properties such as thermal, mechanical, magnetic, optical, and catalytic. Thus, due to high surface area, nanoscale size and the presence or absence of function groups on nanosorbents increase its adsorption capacity in addition to shorten adsorption time and reusability (Janani et al.,2022; Deng et al.,2021; Schneider et al.,2021).

Table 2: The major benefits and drawbacks of wastewater technologies used for the treatment of heavy metals.

Treatment process	Advantages	Disadvantages	References
Advanced Oxidation processes	Highly oxidizing ability	Costly process, high energy requirement and formation of byproducts	Du et al.,2020
Chemical precipitation	Cost-effective method, matured process, and simple operation	High amount of precipitating agent required, High volume of sludge generation, pH adjustment requirement, sludge disposal cost	Fei, & Hu, 2023
Ion exchange	No sludge generation, wide range of heavy metals removal, Minimal amount of time-consuming	- Elevated capital expenses, -adsorbents require regeneration or disposal conditions such as pH, temperature, etc.,	Ali et al., 2023

Coagulation/flocculation	Less time is needed for suspended solids to settle, economically feasible, easy to operate	High sludge production, issues of binding of heavy metals with flocculants.	El Gaayda et al., 2023
Adsorption	Low-cost and regeneration of adsorbent, simple operating conditions, high adsorption efficiency at wide range of pH.	Low selectivity and high cost of regeneration of adsorbent at industrial scale	Wang et al., 2023
Membrane filtration	Simple operation, low energy consumption,	High investment cost, membrane fouling, concentrated sludge production and expensive low membrane life	Pezeshki et al., 2023
Electrodialysis	High selectivity for the separation of heavy metals and organic contaminants	High operating costs, Regular servicing required to prevent stack damage, membrane fouling	Ismanto et al., 2023

Photocatalysis	Removal by reducing high valence metal ions into low low valence metal ions. Removal of organic pollutants	UV-light requirement, long duration of time requirement,	Al-Nuaim et al., 2023
Biological treatment	Microbes involved in removing some of the metals	Technology at the nascent stage and future commercialization is yet to be done.	Sathya et al., 2023

Cr (VI) is a ubiquitous contaminant of wastewater due to its great mobility and high solubility [Hu et al., 2024]. Chromium which is a transition metal has seven oxidation states (0-VI), with metallic [Cr (0)], trivalent [Cr (III)], and hexavalent [Cr (VI)] states are most common. The International Agency for Research on Cancer [IARC] has classified Chromium (Cr) as a group 1 carcinogen [DesMarias, & Costa, 2019].

It persists in the soluble form of $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-} and is considered potentially carcinogenic, teratogenic, and mutagenic [Chang et al., 2023]. Cr (VI) can damage the cells and DNA. Chromium toxicity damages several organs like the liver, kidneys, and lungs by oxidative stress generation due to relative oxygen species (ROS), imbalance in antioxidant balance, and changes in the genome of the individuals [Chakraborty et al., 2022]. DNA methylation, acetylation, modification in the tail of histone protein, miRNA expression change, and alteration in the level of interleukins like IL-4, IL-8, and IL-1β have been observed due to exposure to high concentrations of Cr (VI) [Iyer et al., 2023]. As investigated by researchers, the toxicity of Cr (VI) is 10-100 times higher as compared to Cr (III) [Li et al., 2024].

Oxyanion (CrO_4^{2-}) form of Cr (VI) is more toxic because of its effect on renal damage, edema, lung congestion and chronic liver damage [Hu et al., 2024; Wu et al., 2023]. Chromite ore processing residue also contains huge amount of Cr (VI) which pose a great threat to human health and ecological safety [Li et al., 2024]. Hence suitable method must be adopted to treat it before its discharge. The reductive adsorption process is a promising approach for the remediation of Cr (VI) [Avola et al., 2023]. The conversion of Cr (VI) to Cr (III) by reduction is one of the suitable strategies for the elimination of Cr (VI) as Cr (III) is less toxic and has lower solubility. Cr (III) does not induce cancer [Bashir et al., 2022; Mushtaq et al., 2022].

As per the United States Environmental Protection Agency (USEPA), one of the leading causes of environmental pollution is the waste released by the leather tanning industry [Li et al.,2024]. It has been reported that worldwide, an estimated 7-9 billion tons of tannery waste from leather industries are disposed of annually without environmental treatment. Tannery waste contains Cr (VI), its removal from the effluent includes chemical precipitation, ion exchange, chlorine-based chemicals, ionic liquids (ILs), electrochemical, and membrane separations. But most of these processes generate secondary waste and are expensive and energy-intensive [Kabir et al., 2023; Zhao et al., 2024].

CHAPTER-2

REVIEW OF LITERATURE

2. Review of literature

Hexavalent chromium is highly toxic and carcinogenic, hence its removal from an aqueous solution has attracted regulatory bodies' attention [Ambika et al., 2023; Oladipo, 2018]. The maximum quantity of Cr (VI) that is permitted is 0.05 mg/L in drinking to adhere to the World Health Organization guideline while 0.1 mg/L is the permissible limit as defined by United States Environment Protection Agency (USEPA) [Masinga et al.,2022]. In India, Bureau of Indian Standards (BIS) (IS 10500:2012) is used to generate a quality index of water such as permissible and desirable limits of chromium in water (Ray et al., 2024; Robert et al., 2023; Vaiopoulou, & Gikas, 2020). The various anthropogenic activities like electroplating, tanning, corrosion prevention, and manufacturing of nuclear weapons, etc contribute to environmental contamination with hexavalent chromium [Mohanty et al.,2023]. In the present worldwide scenario, wastewater is a critical environmental issue [Oladipo et al., 2019]. To mitigate the wastewater problem and to meet the sustainable goals as per the UNs, nanoparticle-based wastewater treatment is of great concern among scientists. As per the report of WWF (Word Wide Life), two-thirds of the world's population might experience a shortage of water by 2025, and in the present scenario, there are about 1.1 billion individuals living in the glove are facing a water scarcity problem, and around 2.7 billion people worldwide experience a water shortage for at least one month out of the year [www.worldwildlife.org; Kumar et al.,2021].

Green nanomaterials whose dimension falls in the range of 1-100 nm are fabricated with the modification of the surfaces using -COOH (Carboxylic group), $-NH_2$ (Amino group), -SH (Thiol), and $-CH_3$ (Methyl group) in order to improve the removal efficiency of pollutants [Rani & Shanker 2022]. The high surface area to volume ratio of the green nanomaterials determines their adsorption effectiveness [Rajendran et al.,2022]. Contaminants such as pesticides, heavy metals ions, hormones, dyes, persistent organic pollutants (POPs), and inorganic anions and bacteria have been removed successfully by the applications of green nanomaterials [Roy et al.,2021]. Nanomaterials are produced either through the top-down (size reduction of bulk materials) or bottom-up approach (self-assembly of atoms and molecules via nucleation and crystal growth). Several methods such as physical (mechanical milling, laser ablation), chemical (sol-gel method, co-precipitation, pyrolysis, microemulsion, microwave, etc.), and biological methods (via bioreduction) are used for the synthesis of nanomaterials [Moreira et al., 2023; Kumar et al., 2023]. Uniform-shaped nanoparticles with controlled size, high purity, and controlled crystallinity can be achieved via physical methods of synthesis however, these techniques have high capital costs and are energy-intensive [Vijayaram et al., 2023].

Large-scale production of nanoparticles is possible with chemical methods but these methods use toxic solvents and stabilizing agents with non-eco-friendly delivery of products [Harish et al.,2023]. Biological methods of synthesis of nanoparticles are treated as green synthesis methods as these methods are simple, cost-effective and no toxic materials are used. However, the cost of these techniques is expensive and requires aseptic cultivation [Ying et al., 2022; Ahmed et al., 2022; Akintelu et al.,2020]. So, adsorption is a promising technique for the remediation of chromium from wastewater by agglomeration of substance at surface interphase through mass transfer [Irshad et al.,2023; Garg, et al.,2023]. Among the removal techniques of chromium from wastewater, adsorption is the most popular and economical approach due to its high removal rate, low initial cost, and high regeneration potential [Qi et al., 2023; Li et al., 2023]. Many methods have been investigated for the elimination of hexavalent chromium [Cr (VI)] from wastewater including advanced oxidation processes, chemical precipitation, electrocoagulation, photocatalysis, ion exchange, membrane filtration (ultrafiltration, nanofiltration), electrodialysis, reverse osmosis, etc. [Imdad et al.,2023; Bekchanov et al.,2023; Saravanan et al.,2023]. Figure 1, represents numerous approaches that have been explored for the efficient removal of chromium from wastewater (Irshad et al., 2023).

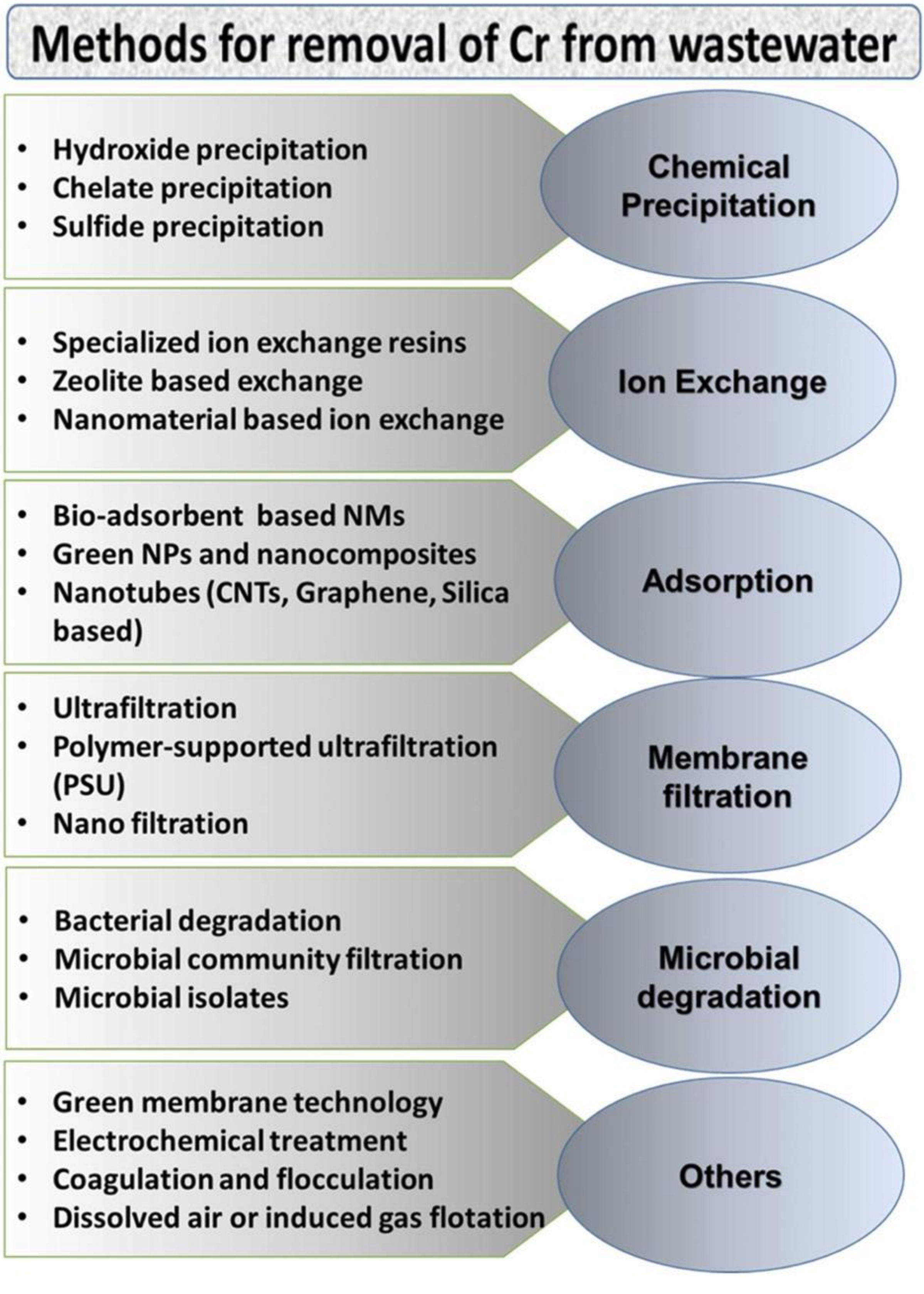


Figure 1: Numerous approaches have been explored for the efficient removal of chromium from wastewater (Irshad et al., 2023)

2.1 Production of lignocellulosic based nanoparticles

Lignocellulosic biomass contains cellulose (35-50 %), hemicellulose (20-35%) and lignin (5-10%) [Wijaya et al., 2021]. Thus, nanomaterials derived from lignocellulosic biomass have a great potential for the remediation of heavy metals from waste and real water as shown in Figure 2. About 70-80% of total plant biomass on the earth is contributed by lignocellulosic biomass only. The common lignocellulosic biomass used to form nanoparticles and its chemical composition is given in Table 3.

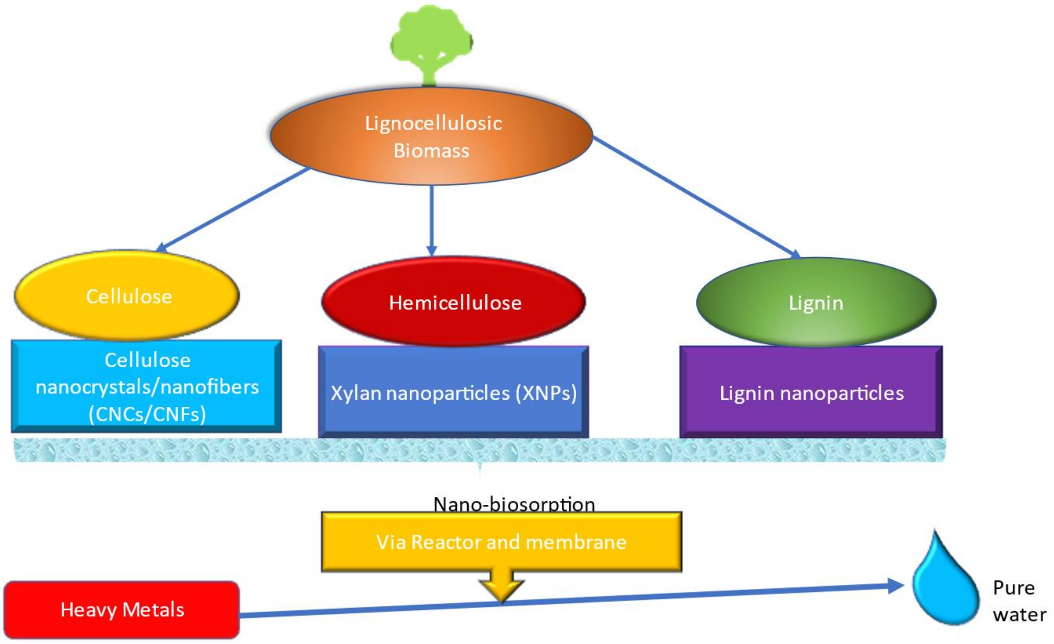


Figure 2: Lignocellulosic-based nanoparticles (Kumar & Kumar., 2022).

Table 3: The common lignocellulosic biomass used to form nanoparticles and its chemical composition (Manyatshe et al., 2022; Ee, & Li, 2021)

Source	Chemical composition		
	Cellulose	Hemicellulose	Lignin
Softwood	42.1± 7.1	25.1± 5.2	29.1± 1.7
Hardwood	50.8 ±6.3	29.7 ±4.3	19.5 ±4.1
Corn stover	34.3± 5.2	20.7 ±2.0	15.2 ±1.6
Bagasses	28.9± 2.9	16.7±3.9	15.7±1.7
Nutshell	25-30	25-30	30-40
Rice husk	35	25	20
Cocoa hulls	35	11	15
Peanut shell	45	6	36
Coconut coir	30	15-30	50

2.1.1 Lignin

Lignin (natural aromatic polymer) is the second most abundant industrial biopolymer next to cellulose on the earth (Deng et al., 2021). It contains crosslinked polymers of phenolic monomers primarily from the mixture of coniferyl (G), sinapyl (S), and p-coumaryl (H) alcohols (Lee et al., 2014) as shown in Figure 2. Functional groups containing oxygen such as carboxyl groups (-COOH) and phenolic units (Ar-OH) are present in lignin and capable of interacting with metal ions such as Cr^{6+}, Pb^{2+}, Ni^{2+}, Sn^{2+}, Cu^{2+}, etc. (Santander et al., 2021). The surface modification of the lignin is caused by many chemical processes, including esterification, carboxymethylation, epoxidation, hydroxymethylation, sulfonation, and oxidation (Parvathy et al.,2020). The three primary alcohols that make up the structure of lignin are shown in Figure 3.

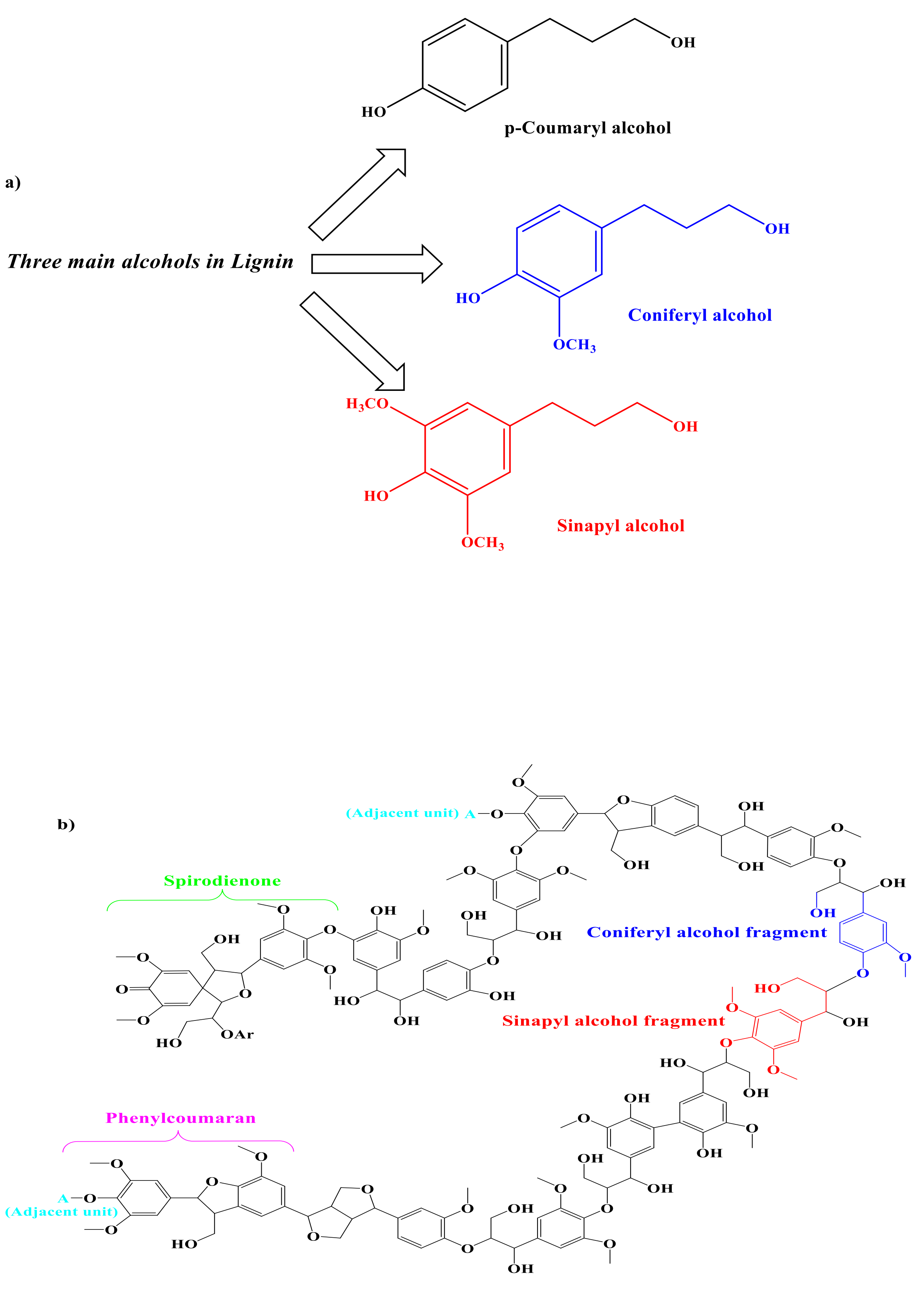


Figure 3. (a.) Diagram of the three major alcohol structures found in lignin (b.) Schematic representation of a lignin structure [Kumar & Kumar., 2023]

2.1.2 Cellulose

Cellulose is the most abundant carbohydrate polymer on earth. It is a linear polymer of β-D-glucose molecules with a molecular weight ranging from 50,000 to 10^6 Da, representing about 40% of the plant biomass. It has a β-1,4 glycosidic linkage between the glucose monomers (Menon et al.,2017). The plant cell walls have hemicelluloses which are heterogeneous polysaccharides, characterized by β-(1,4)-linked backbones. Figure 4, depicts the chemical structure of cellulose.

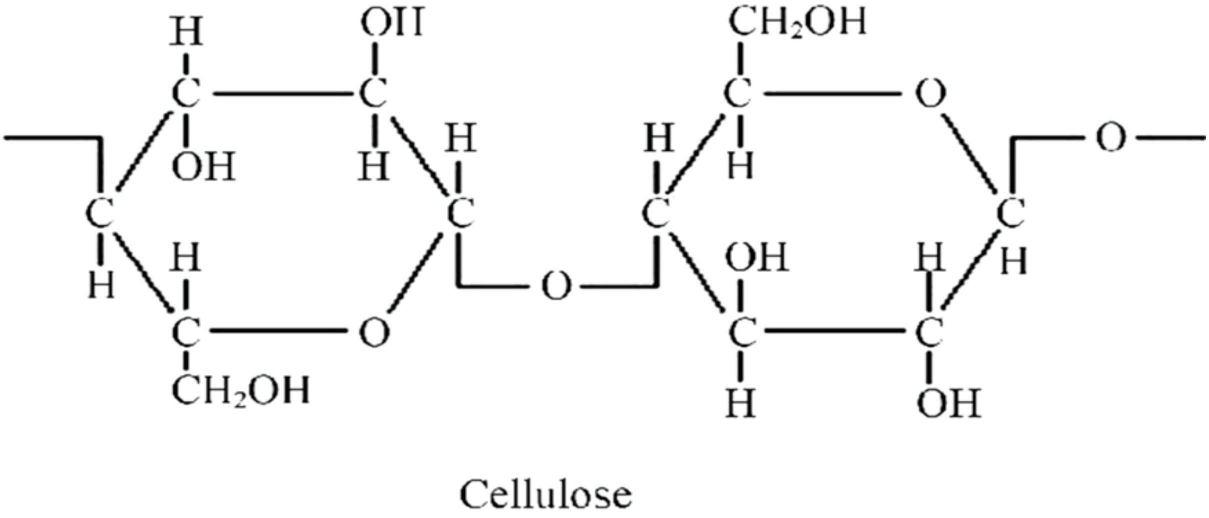


Figure 4: Chemical structure of cellulose [Kumar, & Kumar, 2022]

2.2 Nano-Lignin preparation methods

Several methods have been investigated for the preparation of lignocellulose-derived nanoparticles such as solvent shifting method, soda pulping method, acid precipitation method, ultrasonic method, cross-linking method, and CO_2 antisolvent method. (Iravani & Varma, 2020; Hoang et al., 2020; Peng et al., 2020; Chauhan, 2020). The size of nanolignin in terms of hydrodynamic diameter varies from ca. 80-230 nm which is stable at a wide range of pH (4-11) (Chen et al., 2018; Tian et al., 2017; Meng et al., 2021; Parvathy et al., 2020; Wu et al., 2021). Lignin nanoparticles (LNPs) have oxygen-containing groups such as the phenolic hydroxyl group which is higher than the aliphatic hydroxyl group, carboxylic and carbonyl groups may function as adsorptive sites for the removal of heavy metals (Gao & Fatehi ., 2019; Gao et al., 2019).

Different methods such as physical (mechanical), chemical, and biological methods are in practice for the preparation of lignin nanoparticles which vary in size, shape, and yield and have a diverse economic and environmental impact (Schneider et al., 2021; Low et al., 2020 ; Beisl et al., 2020 ; Sipponen et al., 2019; Zhang et al., 2021). Extraction of nanolignin requires harmful solvents, which can be replaced with ionic liquids (ILs), and supercritical fluids as an alternative to volatile organic solvents (Hussin et al., 2022). Most of the industrial lignin is extracted by soda pulping methods followed by size reduction either through ultrasonication or homogenization to get nanolignin (Kumar et al., 2020). Juikar & Vigneshwaran (2017a) proposed the extraction of nanolignin from coconut fibers by soda pulping process. They used a lignin-degrading fungal isolate, *Aspergillus* sp during the controlled hydrolysis to achieve 58.4% yield of nanolignin. The different methods of preparation of lignin nanoparticles (LNPs) are shown in Figure 5.

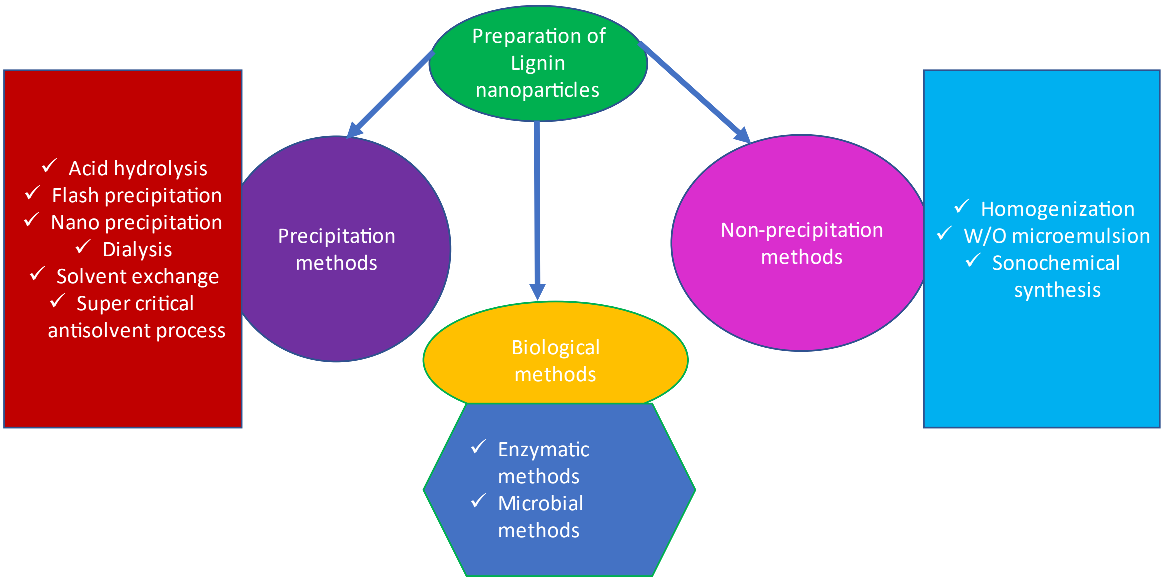


Figure 5: Methods of preparation of lignin nanoparticles (Kumar & kumar., 2022)

2.2.1 Antisolvent nanoprecipitation methods

The antisolvent method is used for the preparation of nanolignin as it is based on the dual solvent system. In this technique, lignin is dissolved in organic solvents such as tetrahydrofuran (THF), acetone, dimethylformamide (DMF), ethylene glycol, ethanol, dimethylsulfoxide (DMSO), and excess antisolvent is added as precipitating agent to promote the formation of lignin nanoparticles (Moreira et al., 2023; Gao & Fatehi, 2019). In many LNP studies, an adjustment in pH is used to precipitate nanoparticles, a process known as pH shifting (Tian et al., 2017).

2.2.2 The solvent exchange /shifting methods

The simple way of the production of high-quality LNPs can be achieved through the solvent exchange/shifting technique [Behera et al., 2023]. The solvent exchange /shifting methods of lignin nanoparticles use ethanol /H_2O and are produced via the dialysis process (Schneider et al., 2021).

2.2.3 Ultrasonication method

Ultrasonic waves of frequency 10-20 kHz are used for the preparation of lignin nanoparticles (LNPs**)** [Agustin et al., 2019]. Ultrasonic irradiation can be applied to the lignin suspension either directly or indirectly during the nanolignin preparation process. During indirect contact, the lignin suspension is immersed in an ultrasonic bath [Sabaruddin et al., 2023]. The schematic diagram of the ultrasonicator is given in the Figure 6.

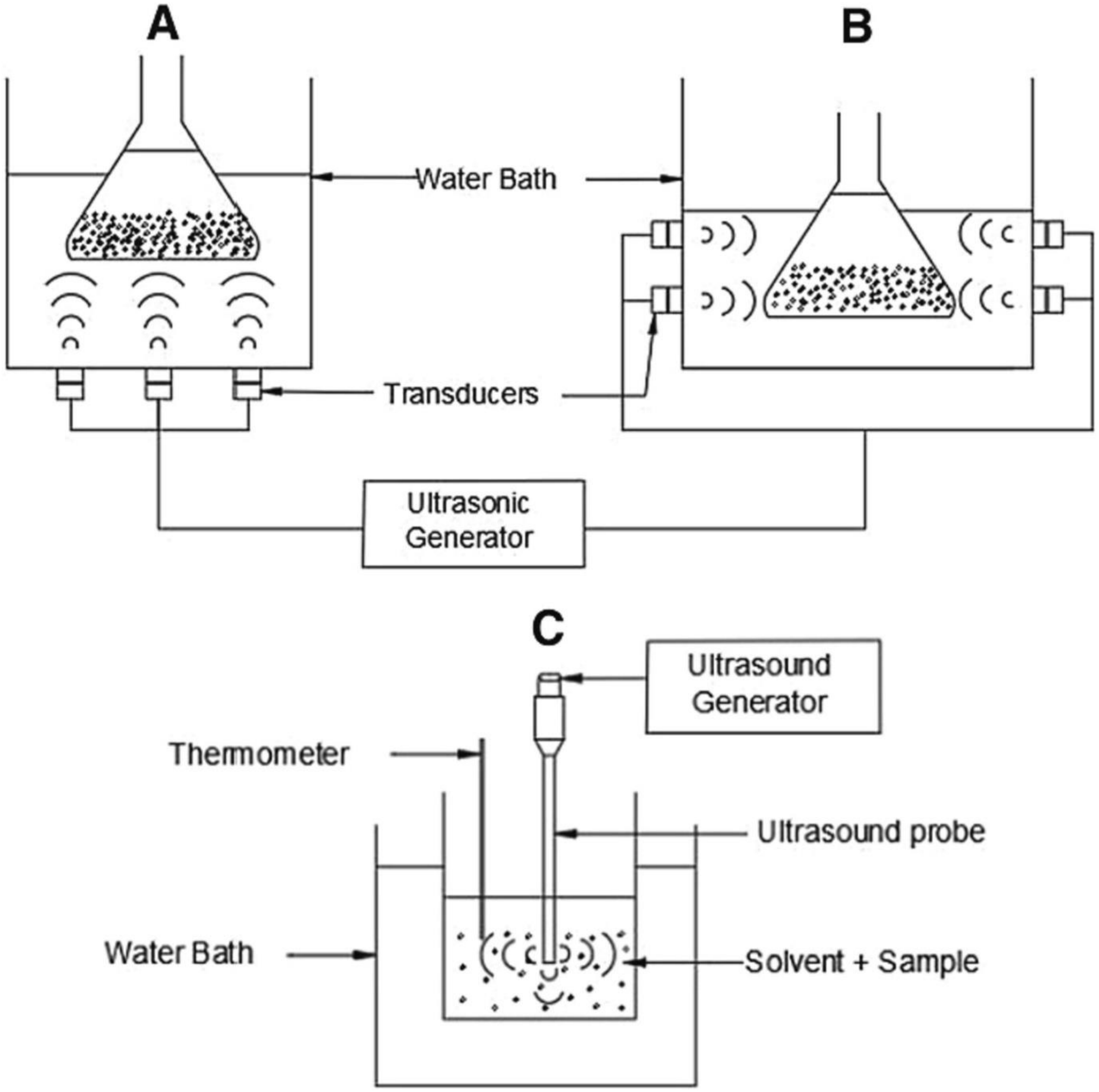


Figure 6: Ultrasonicator with transducer fixed (a) vertically (b) horizontally (c) with ultrasonic probe [Thilakarathna et al., 2023].

2.2.4 Biological methods

Biological methods usually use enzymes from bacteria and fungi for the synthesis of LNPs (Juikar & Nadanathangam, 2020). Juikar & Vigneshwaran, (2017 b) prepared coconut fiber nanolignin (size: 27.5 nm ± 2.7 nm) by using ligninase secreted from *Aspergillus nidulans* to hydrolyze bulk lignin derived from coconut fibers. Richter et al., (2016) reported the nanoparticle preparation by the process of supersaturation, nucleation, and crystal growth induced with flash precipitation methods. SEM analysis reveals that lignin nanoparticles (LNPs) have spherical-like shapes and an average size of roughly 10-20 nm (Ju et al., 2019). The schematic representation of nanolignin preparation and its application in wastewater is given in Figure 7.

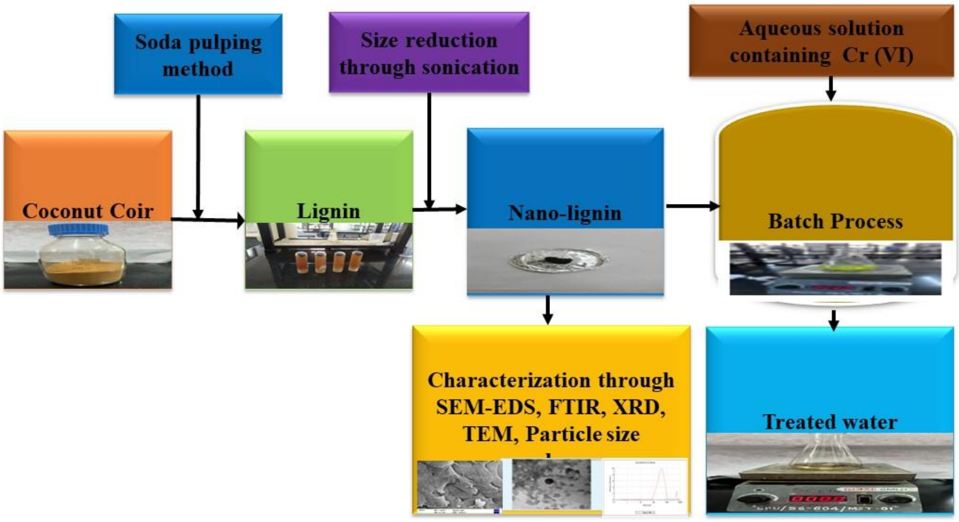


Figure 7: Preparation and application of nanolignin in wastewater treatment [Kumar & Kumar., 2023].

Studies using nanolignin derived from coconut coir for the removal of hexavalent chromium through adsorption are limited. The coconut is produced from the coconut palm (Cocos nucifera). In the agriculture sector, the estimated production of coconut is about 62.5 million tonnes globally. Coconut wastes contain cellulose (30 wt%), hemicellulose (15-30 wt%), and lignin (nearly 50 wt%) on a dry weight basis. For the generation of low-grade fuel, coconut wastes are used in many low-income countries [Anuchi et al., 2022]. Lignin is a phenolic compound that is more difficult to degrade than cellulose and hemicellulose. It is a mixture of three complex phenylpropanoid monolignols-p-coumaryl, coniferyl, and sinapyl alcohols and has -OH groups attached to an aromatic ring [Jiang et al., 2023; Karlsson et al., 2023; Wang & Ali, 2023].

2.3 Lignin nanoparticles (LNPs) modification

Lignin nanoparticles can be covalently modified by the addition of functional groups. The hydrophilicity and polyelectrolyte behavior of lignin can be improved by chemically modifying the lignin surface to have more oxygen-containing groups (Zou et al., 2021; Xiao et al., 2019).

Similarly, the introduction of nitrogen-containing functional groups (-NH_2 groups) could be achieved by amination. Heavy metal ions such as Cu^{2+}, Pb^{2+}, $Cd^{2+,}$ and Hg^{2+} can be adsorbed by modifying lignin with sulfur-containing functional groups such as mercaptan (thiol group), sulfonate (-SO^{3-}), xanthate (-OCS^{2-}), and dithiocarbamate (Ge & Li, 2018). To get rid of heavy metals, researchers are looking into a variety of chemical modifications, including changing the hydroxyl groups in lignin, creating new chemically active sites, and creating lignin graft copolymers (Li et al., 2020; Figueiredo et al., 2018).

2.4 Process variable for adsorption

The efficiency of the adsorption process is significantly affected by changes in pH, contact time, adsorbent dosage, temperature, Initial concentration of chromium, co-existing ions etc (Yadav et al., 2024; Sebabi et al., 2024). The adsorption capacity of chromium increases on biosorbent as the pH values decrease (Ramraj et al., 2023; Paul et al., 2023). The maximum adsorption capacity of biosorbents is significantly affected by contact time. With the increase in contact time, the biosorbents show a decline in maximum adsorption capacity (Anjum et al., 2023; Kumaraguru et al., 2023). The adsorption capacity of the adsorbent decreases as an increase in adsorbent dosage leads to the aggregation of particles hence a decrease in the availability of active sites for the binding of chromium (Garg et al., 2023; Padmavathy et al., 2016). An increase in temperature (10-30 °C) leads to an increase in biosorption of chromium

(Pagala, 2023). As the heavy metal ion concentration changes, the removal efficiency, as well as the adsorption capacity, gets changed. On increasing the initial concentration of heavy metal ions, the adsorption capacity of heavy metal ions increased and the removal efficiency decreased (Rekha, et al., 2023; Rai et al., 2023). Na$^+$, K$^+$, Ca^{2+}, Mg^{2+} are the most common ions present in the wastewater (Ponomarev et al.,2019). The adsorption capacity of the adsorbents for different ions is different due to the competition between metal ions and the difference in the affinity of the adsorbents for different metals. Thus, the competing ions may significantly affect the adsorption of heavy metals by lignocellulosic-based nanomaterials (Wang et al.,2021). It has been investigated that adsorbents with a negative charge on their surface will attract heavy metals with a positive charge. The various parameters affecting the process of adsorption by lignin nanoparticles (LNPs) are depicted in Figure 8.

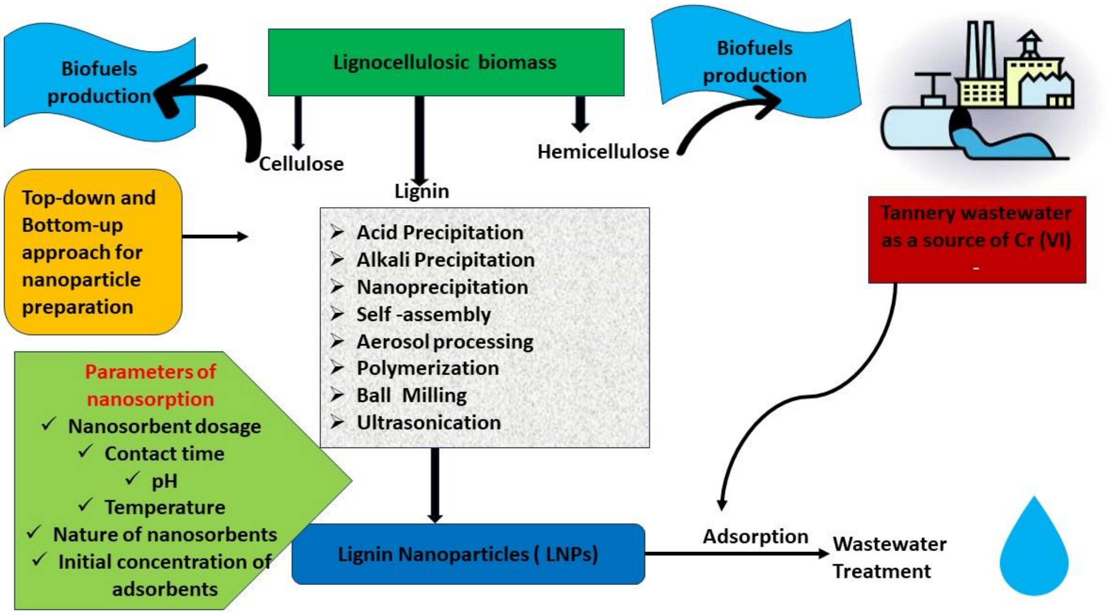


Figure 8: Parameters affecting the process of adsorption by lignin nanoparticles (LNPs)

.

2.5 Techno-economic analysis of nanolignin.

Lignocellulosic biomass-based waste (agriculture waste) such as rice husk, coconut shells, and sawdust are considered sustainable adsorbent sources for the removal of heavy metals and by repurposing waste materials, these adsorbents contribute to a circular economy (Thakur et al., 2024).

The lignocellulosic-derived nanoparticle toxicity is rarely described in the literature and should be investigated further. The precise mechanism of toxicity has not been fully defined depending on the size, dosage, and surface capping (Sakthivel et al., 2024). Nanoparticles produce reactive oxygen species (ROS) and have the potential to induce DNA damage. Lignin nanoparticles are non-toxic and biodegradable. To assess the impact on the environment associated with the production of nanolignin, global warming potential (GWP), human toxicity potential (HTP), and water depletion (WD) must be evaluated through life cycle assessment (LCA) analysis (Sakthivel et al., 2024; Moreira et al., 2023). By implementing global regulation for the disposal of nanoparticles, the environmental risk of health hazards can be minimized (Chavez-Hernandez et al., 2024). Current knowledge of nanomaterial combustion, waste incineration, and recycling strategies is useful for the disposal of nanomaterials to prevent their release into the environment (Song, et al., 2024; George,et al., 2023).

CHAPTER-3

3.1 Hypothesis for research

Wastewater can be treated using several techniques. Chemical methods have disadvantages as used chemicals are a threat to the environment. Biological methods have disadvantages in the form of converting toxic chemicals into more toxic waste. Further, the efficiency in terms of wastewater treatment efficiency of bulk material is less than nanomaterial of the same chemical composition. So, nanomaterials due to more surface area to volume ratio are more useful. But most of the nanomaterials used for wastewater treatment are synthesized through chemical routes involving chemicals that are harmful to the environment or themselves they are reactive causing toxicity to microorganisms, plants, or animals they come in contact with. So green chemistry approach is preferred over other traditional approaches using chemicals for the preparation of nanomaterials. The chemical precursor used for nanomaterial preparation also adds cost to the production process. So, the use of easily available cheap precursor is required. The structural arrangements of various functional groups collectively make lignocellulose a good biosorbent.

Converting lignocellulosic biomass from bulk to nanomaterial increases the surface area-to-volume ratio tremendously. Further, it is cheap and has good recyclability. Actually, the interaction of waste material with functional groups of lignocellulosic base materials affects the adsorption process. The chemical composition of lignocellulosic biomass differs from plant to plant source. So, the wastewater treatment ability of lignocellulosic biomass also depends upon the plant source selected.

In the proposed study, lignocellulosic nanomaterials from various plant sources will be explored for producing lignocellulosic nanomaterial for wastewater treatment. The lignocellulosic nanomaterials to be prepared in the proposed research will follow green chemistry principles and use cheap plant resources as a resource. Thus, lignocellulosic materials derived from various plant sources may be effective in wastewater treatment. Removal of chromium from wastewater using lignocellulosic-based nanomaterials is minimal to study by researchers.

3.2 Objectives of the research

i) Preparation and characterization of lignocellulose-based nanomaterial
ii) To study the heavy metal removal potential of lignocellulose-based nanomaterial using standard samples
iii) To evaluate the heavy metals removal capacity of lignocellulose-based nanomaterial using wastewater samples

CHAPTER-4

MATERIAL AND METHODS

4. Materials and Methodology

The present study contributes to the process of removing chromium in its hexavalent form from aqueous water using nanolignin as a biosorbent. The higher toxicity of Cr (VI) as compared to Cr (III) is due to chromate similarity in the structure with sulfate. Trivalent chromium cannot cross the membrane through the sulfate uptake pathway, whereas hexavalent chromium, a potent oxidizing agent, can. The precipitation of trivalent chromium occurs in biological conditions. [Saha et al., 2022; Kumar, & Kumar, 2023].

4.1 Materials

The coconut coir was purchased from the local market of Jalandhar, India. The coir samples of coconut were washed several times thoroughly with de-ionized (DI) water and then dried for 24 h in an oven at 60 °C to remove the moisture. Washing the samples with DI water promotes the removal of any dust and metals that could interact and interfere with the adsorption experiments. Figure 9, represents (A.) Cocunut coir fibre (B.) Fine particles of coconut coir for the extraction of lignin .

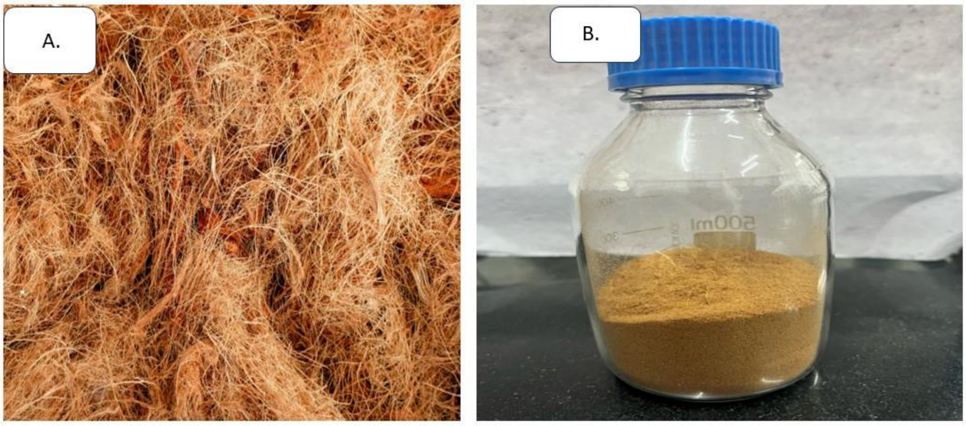


Figure 9: (A.) Cocunut coir fibre (B.) Fine particles of coconut coir

4.2 Lignin extraction

The Soda pulping method has been used to extract the lignin from coconut fiber. Fibers are cut into small pieces of fragments (1-2 cm), grounded in a high-speed grinder, and pass through a 63 µm size screen (BSS 240). To separate the solubilized hemicellulose, the dried powder of coconut coir was treated with hot water at a temperature of 70–80°C for two hours, with a solid–to–liquid ratio of 1:25 (W/V). NaOH, 15% (W/V) [CDH Pvt. Ltd. (India)] was used for pulping of separated solid at 90-98 °C with solid-to-liquid ratio of 1:25 W/V for 1.5- 4 hr under continuous stirring. Subsequently, black liquor was obtained by filtration using a Whatman filter grade 1 that was free of fibrous materials. In order to precipitate the lignin, the black liquor filtrate was acidified to pH 2 using (5N H_2SO_4) [Loba Chemie Pvt. Ltd. (India)]. It was then cleaned with deionized water (DI) water, separated by centrifugation, and allowed to dry by air [Moubarik et al.,2013]. A schematic representation of the preparation of lignin from coconut coir is depicted in Figure 10 and the lab scale prepared lignin from coconut coir is shown in Figure 11.

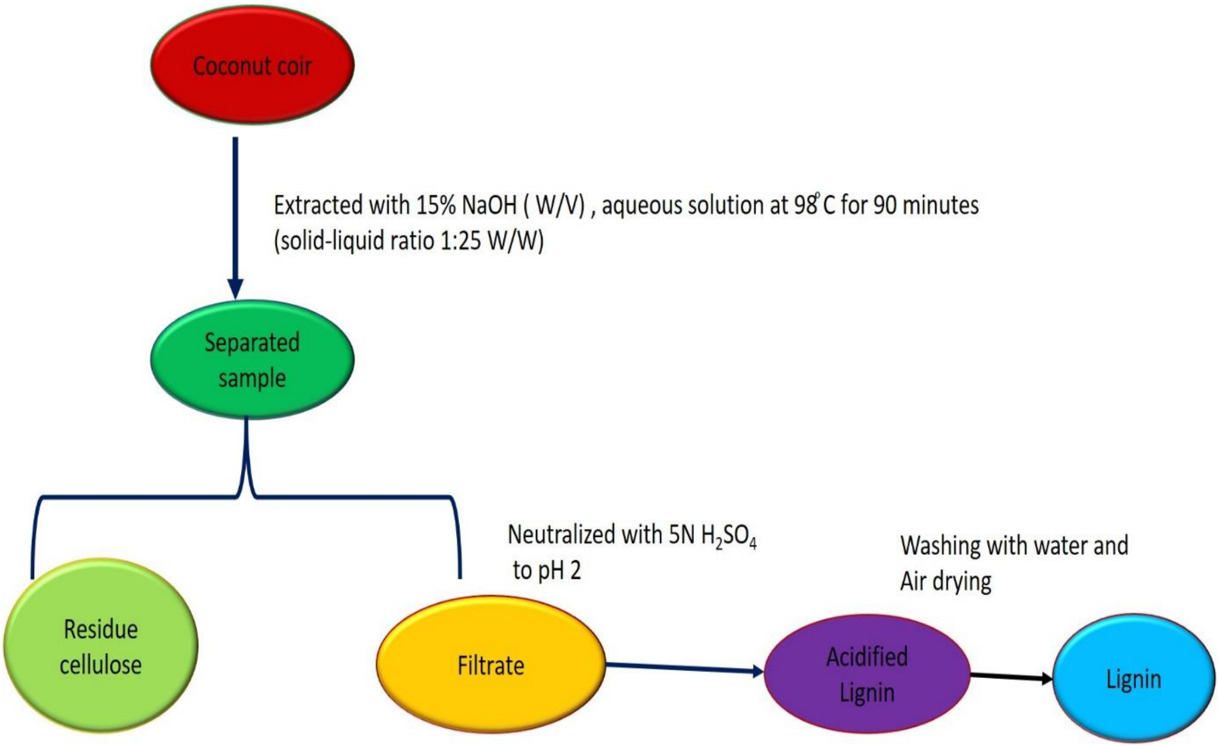


Figure 10: Preparation of lignin from coconut coir [Modified from Moubarik et al.,2013]

Figure 11: Lab scale prepared lignin from coconut coir

4.3 Lignin nanoparticle preparation

The ultrasonic-assisted alkali method which is a simple and environmentally friendly technique was used to generate lignin nanoparticles (LNPs). The longer chain of lignin was reduced to lignin nanoparticles (LNPs) by the impact of ultrasonic waves. The lignin suspension was prepared by adding 0.21g lignin in 30 ml DI water, after that, 900 µl 0.1M NaOH was added and was subjected to sonicate for 60 minutes at 400W at 20 KHz. Thereafter the suspension was centrifuged and finally, a stable nanodispersion was obtained. Then, the obtained LNPs were dried in mild conditions to be used for subsequent studies [Gilca et al. 2015; Yin et al., 2018].

The following equation was used to find out the yield of nanolignin [Worku et al., 2023]

$Y_{NP}(\%) = \frac{W_{NP}}{W_L} \times 100$………………………………………..[Eq.1]

Where, Y_{NP}= % Yield of nanolignin, W_L=Weight of lignin, W_{NP}=Weight of nanolignin particles obtained.

4.4. Characterization of adsorbent as nanolignin

In this study, nanolignin functional groups are determined by FTIR. The amorphous or crystalline structure of nanolignin was confirmed by XRD. SEM was used to scan the microstructure and surface topography of nanolignin. The elemental analysis of nanolignin was achieved through Energy-dispersive X-ray spectroscopy (EDS). The size of the nanolignin particles was analyzed by a particle size analyzer (PSA). The physical size of sonication-assisted nanolignin was determined by TEM. The surface area, pore volume, and pore radius of nanolignin were measure through Brunauer-Emmett-Teller (BET) method at 77K. A list of major instruments used during the study of nanolignin is enlisted in Table 4. The characterization of nanolignin was carried out in the Central Instrumental Facility (CIF), Lovely Professional University; Advanced Material Research Centre (AMRC), IIT Mandi; Icon Labs Pvt Ltd, Mumbai and Indian Institute of Science (IISC), Bangalore.

Table 4: List of major instruments used during the study of nanolignin

Instrument	**Model**
Transmission electron microscopy (TEM)	Tecnai 12 G2-TWIN
Particle Size analyser (PSA)	Malvern Nano-ZS Zetasizer
Brunauer-Emmett-Teller (BET)	Quanta chrome Autosorb iQ3
Sonicator	Citizen CD 4820
UV-vis spectrophotometer	Lasany L1- 2800 Ex
Fourier-Transform Infrared Spectroscopy (FTIR)	Thermo Scientific Nicolet Is50
Scanning Electron Microscopy paired with energy dispersive X-ray spectroscopy (SEM-EDS)	ThermoFisher® Sirion®
X-Ray Diffractometer (XRD)	Bruker D8 Advance

4.5 Point of Zero charge determination of nanolignin

The point of zero charge of nanoliglin at various pH values was found using the salt addition method [Bakatula et al., 2018]. A series of 50 ml falcon tubes were filled with 40 ml of 0.1 M $NaNO_3$ solution after the pH had been adjusted to 2-11 (± 0.1 pH units) using 0.1 M NaOH and 0.1 N HCl. The initial pH was denoted as pH_i. Each centrifuge tube received 40 mg of the sample, which was then incubated for 48 hours at 150 rpm in a rotating shaker. The final pH_f values of the supernatant were measured after it had settled. After conducting the experiment in triplicate and documenting the mean values, pH_{PZC} was derived from the plot of ΔpH ($=pH_f - pH_i$) against pH_i.

4.6 Reagent preparation

$K_2Cr_2O_7$ [Loba Chemie Pvt. Ltd. (India)], an analytical reagent, was dissolved in deionized water (DI) to make a stock solution of hexavalent chromium [Cr (VI)] at a concentration of 1000 mg/L [Dissolving 0.283g of potassium dichromate with 100 ml DI water in a volumetric flask] (Yoganand, & Umapathy, 2017). The initial pH of the solution was adjusted using reagents like 0.1 N HCl or 0.1 M NaOH.

4.7 Chromium [Cr (VI)] analysis

Diphenyl carbazide (DPC) was procured from Loba Chemie Pvt. Ltd. (India). 250 mg of diphenyl carbazide was dissolved in 50 ml of acetone to make the diphenyl carbazide solution, which was then placed in a brown bottle and covered with aluminium foil for storage [Mishra et al.,2021].

4.8 Sample preparation

Cr (VI) sample (1ml) was transferred to a glass test tube, sulphuric acid (6M, 330µl) and following the addition of 1,5-diphenyl carbazide (0.25% W/V, 400µl), the mixture was gently shaken and allowed to sit for five minutes. The formation of purple colour was observed and the absorbance was measured at 540 nm against the blank reagent using a UV-Visible spectrophotometer [Saran kumar, et al., 2020].

Diphenyl carbazide (DPC), under acidic conditions, reacts with a hexavalent form of chromium ions to form a purple colour complex as diphenyl carbazone (DPCA) as described by the following reaction (Ghosh et al., 2022):

$$2CrO_4^{2-} + 3C_{13}H_{14}N_4O + 8H^+ \rightarrow \left[Cr^{3+}(C_{13}H_{12}N_4O)_2\right]^+$$ ....[Eq.2]

Diphenyl carbazide (colourless)   Cr (III)-Diphenyl carbazone comlex (DPCA) Purple

4.9 Batch experiment

Adsorption occurs when adsorbate gets adsorbed on the adsorbent. The physisorption process involves weak vader Waal force of attraction and low enthalpy of adsorption ($\Delta H_{adsorption}$=20-40KJ/mol.) while the chemisorption process involves chemical forces/bond with a high enthalpy of adsorption ($\Delta H_{adsorption}$=200-400 KJ/mol.) (Burakov et al., 2018).

$$Adsorbate + Adsorbent \underset{Desorption}{\overset{Adsorption}{\rightleftharpoons}} Adsorbed.Species$$ .... [Eq.3]

The equilibrium and kinetics studies are the important aspects to analyze the adsorption (Silva, & Baltrusaitis, 2020 ; Tan & Hameed, 2017).

The mass transfer pathway for adsorbate is described by the following steps (Tan & Hameed, 2017):

i. Movement of the solute onto the adsorbent particle's surface from the bulk solution.
ii. Diffusion into the particle.
iii. Diffusion from the surface back into the bulk solution

250 ml conical flask was used for the batch experiment of Cr (VI) elimination, which was stirred at 400 rpm with a magnetic stirrer bar. 100 ml aqueous solution of Cr (VI) was diluted from a stock solution containing 1000 mg/L of Cr (VI) along with 0.01–0.05 g of nanolignin per flask. Following a reaction time of 20, 40, 60, 80, and 100 minutes, a sample of 2 ml was taken and filtered using a 0.22μm membrane filter. The concentration of hexavalent chromium [Cr (VI)] in the aqueous solution was determined by the Diphenyl carbazide (DPC) method.

Mean values were taken into account for the calculation, and each experiment was run in triplicate. The following equation was used to determine the removal efficiency of the Cr (VI).

Removal efficiency (%) $= \frac{(C_0 - Ct)}{C_0} \times 100$……………………………………..[Eq.4]

Where, C_0 is the initial Cr (VI) ions (mg/L) concentration

C_t represents the residual concentration of hexavalent chromium [Cr (VI)] ions (mg/L) after adsorption

The hexavalent metal ions (Cr (VI)) uptake q_t , at a particular time, was determined by the following equations [Ye et al.,2021]:

$q_t = \frac{(C_0 - C_t) \times V}{m}$……………………………………………….[Eq.5]

$q_e = \frac{(C_0 - C_e) \times V}{m}$ ……………………………………………[Eq.6]

Where, C_e is the equilibrium concentration of hexavalent chromium [Cr (VI)] ions (mg/L)]

V is the volume of a solution of $K_2Cr_2O_7$ used (mL),

m is the mass of nanolignin used as adsorbent (g)

q_e is the equilibrium adsorption capacity of nanolignin (mg/g).

CHAPTER-5

RESULT AND DISCUSSION

5. Result and discussion

5.1 Characterization of Nanolignin

The main parameters used to characterize the nanolignin are size and shape. To investigate the surface chemistry of nanolignin, surface charge, and specific surface area were also studied. The particle size of LNPs is ascertained by TEM and Dynamic Light Scattering (DLS) methods. Similar kinds of studies have been performed by Khan et al (2024) to characterize nanolignin derived from woody biomass. The morphology and size of LNPs were determined by transmission electron microscope (TEM). While surface charge properties of LNPs were studied from the zeta potential value of the particles. Cong et al., (2024) confirmed the structure of magnetic lignin-based palladium nanoparticles (Fe3O4-lignin@Pd-NPs) by SEM, TEM, XRD, EDS, and Zeta-potential.

5.1.1 Yield of Nanoliglin

The yield of nanolignin derived from coconut coir was determined and found to be 63.67±1.83. According to Wang et al. (2018), the yield of lignin nanoparticles reached 82.3% as the initial lignin concentration and the ultrasound intensity increased. Lignin nanoparticals prepared from coconut coir is shown in Figure 12. Juikar, & Vigneshwaran, (2017) extracted nanolignin from coconut fibers by controlled microbial hydrolysis using *Aspergillus* sp. yielded 58.4 % nanolignin while homogenization and ultrasonication processes yielded 81.4 % and 64.3% respectively. Fungal isolate consumes a significant amount of bulk lignin for its growth and metabolism which could be attributed to the comparatively low yield of nanolignin.

Figure 12 : Lignin nanoparticals prepared from coconut coir

5.1.2 Particle size analyzer

The particle size of nanolignin, in the aqueous phase is measured by dynamic light scattering analysis [DLS] (Luo et al.,2021). The DLS measures hydrodynamic diameter and is very sensitive to biological molecules (Tian et al.,2021; Mao et al.,2017). This size includes any stabilizer bound to the molecule and the scattering of light is due to the Brownian motion of the particles (Carvalho et al.,2018). Zeta potential, the overall charge that a particle accumulates in a specific medium, is necessary for stability and size distribution. Zeta potential value of +/-30 mV and above indicates good stability. It depends on pH and electrolyte solution (Chen et al., 2021; Sharma et al., 2022).

The particle size and zeta potential of lignin nanoparticles were measured using Malvern particle analyzer at 25 °C. The size of the nanolignin particles obtained from coconut coir was found in the range of 311.8-383.9 nm with zeta potential -29.9 to -32.3 mV at a nanolignin concentration of 1 mg/ml. Perera et al (2023) reported the average particle size of LNPs of about 220 nm obtained from oil palm empty fruit via ultrasonication. The lignin nanoparticles with negative zeta potential can be attributed to the presence of phenolic, hydroxyl, and carboxylic functional groups over their surfaces [Sharma et al.,2023; Pylypchuk et al.,2020]. The stabilization of lignin nanoparticles in water was determined by the zeta potential, which ranged from -29.9 to -32.3 mV. The size and zeta potential of lignin nanoparticles is depicted in Figure 13.

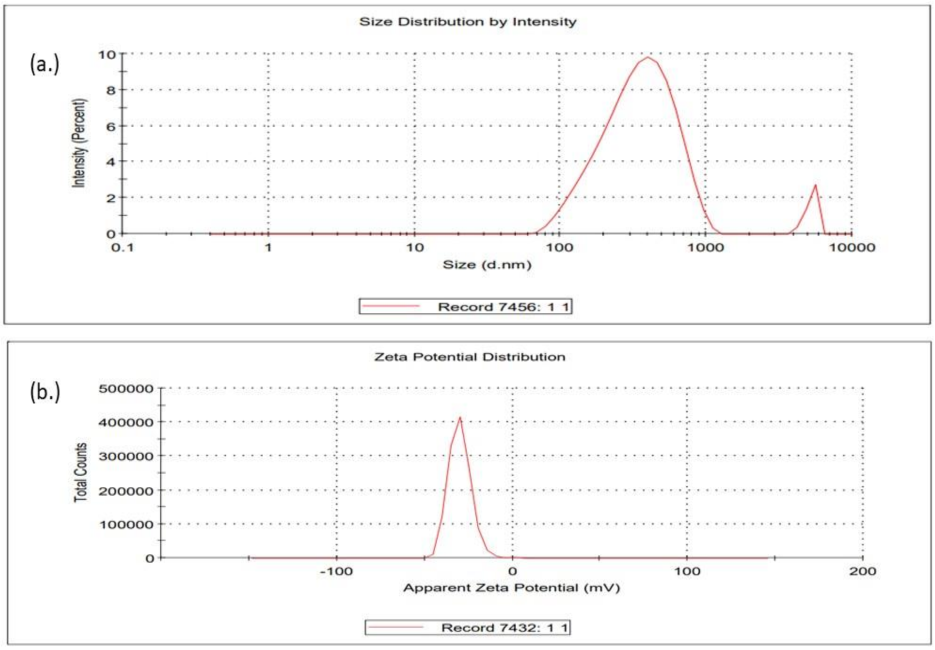


Figure 13: Particle size (a) and zeta potential (b) of lignin nanoparticles

Sharma et al (2024) reported the zeta potential of lignin nanoparticles in the range of -30 mV. In another study, Perera et al., (2023) showed that LNPs had a zeta potential of -40 mv, which was due to an electrical double layer formed by the surface of phenolic hydroxyl groups and carboxyl groups.

5.1.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) test was carried out to investigate the thermal behavior of the nanolignin using the thermogravimetric analyser. Approximately 2.8 mg of the sample was heated from 30-600 °C at a heating rate of 10 °C/min under nitrogen atmosphere (Yang et al., 2019; Qi et al., 2020). The TGA curve of nanolignin is shown in Figure 14. Three-stage nanolignin decomposition was observed as per the TGA peaks. In the first stage of decomposition (30-250 °C), the initial weight loss in the weight of nanolignin was due to the evaporation of water. In the second stage wide range of heat degradation between 250 -450 °C was observed for nanolignin. Decomposition of lignin backbone such as 4-O-5 and β-O-4 at 350–450 °C was noticed. In the last degradation step from 450 to 596 °C, shows constant decomposition of nanolignin where C-C single bond of nano lignin took place. Similar kinds of findings were reported by Worku et al (2023) during the characterization of lignin nanoparticles from *Oxytenanthera abyssinica.*

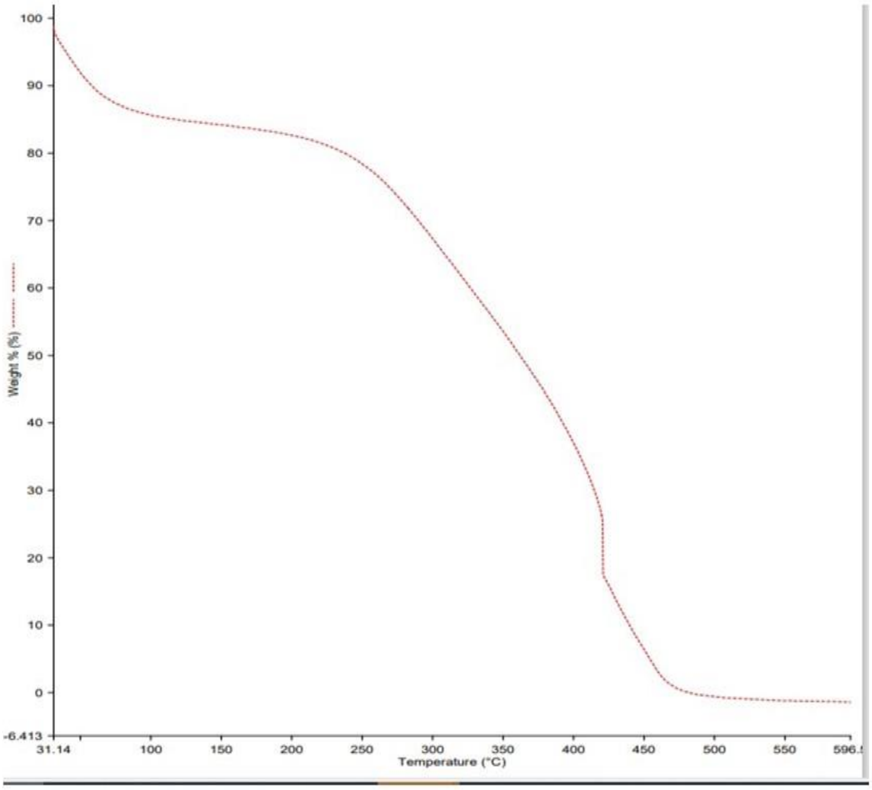


Figure 14: TGA curve of nanolignin

5.1.4 Differential scanning calorimetry

The curing behavior of nanolignin was tested using a differential scanning calorimeter (DSC). Measurement was carried out under nitrogen flow in the temperature range from 30-440 °C at a heating rate of 10 °C/min using DSC thermal analyzer into an aluminium pan (Tian, et al., 2017). The DSC curve of nanolignin is represented in Figure 15. The heat of the reaction was measured through DSC. Enthalpy of the reaction for nanolignin was measured as -362.1185 J/g, which suggests that more energy is required to break the bond of nanolignin. Watkins et al, (2015) investigated a similar kind of study and reported the enthalpy of flax fiber lignin as 190.57 J/g through DSC.

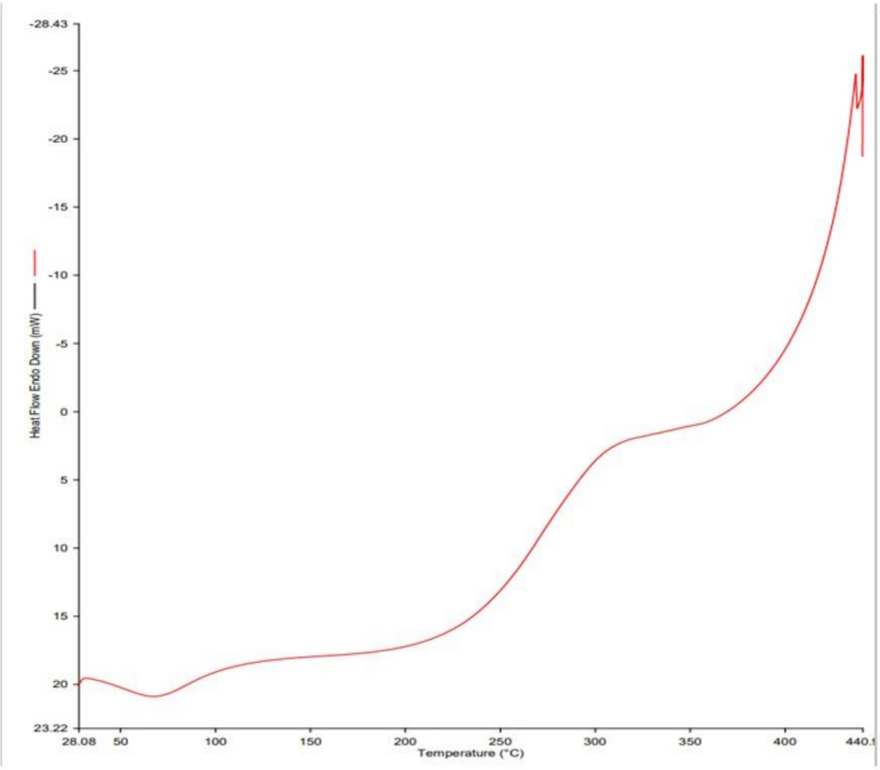
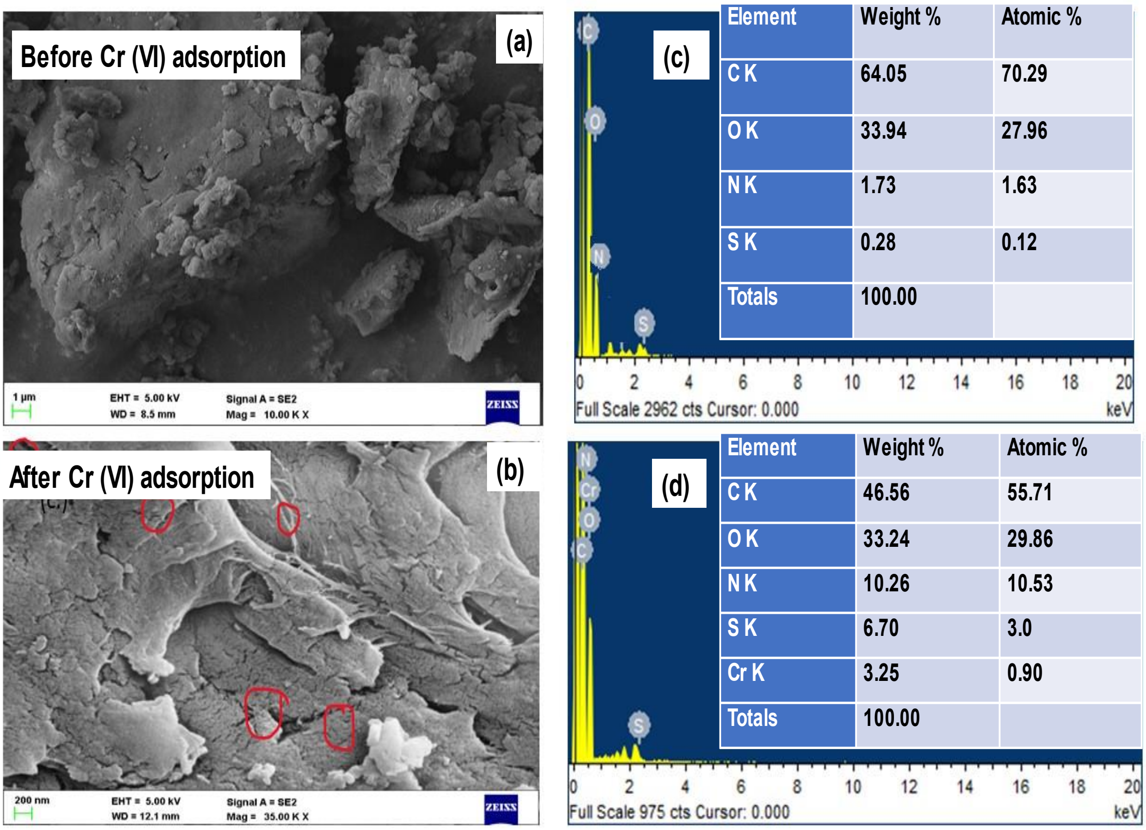


Figure 15: DSC thermogram of nanolignin

5.1.5 Scanning Electron Microscopy and energy dispersive X-ray spectroscopy (SEM-EDS)

By scanning the specimen's surface with an electron beam rather than a light source inside a vacuum chamber, SEM can be used to study topography and morphology, and grain orientation of nanolignin (Budnyak et al.,2018; Rismawati, et al.,2020). Elemental analysis is a classical method to obtain information about the elemental composition of nanomaterials (Daniel et al.,2021; Silva & Baltrusaitis. , 2020 ; Tran et al.,2017). Elemental analyzers are used to carry out the elemental analysis (C, H, N, S). The energy dispersive -x-ray spectroscopy (EDS) is a method of elemental analysis (Scimeca et al.,2018).

SEM was used to examine the lignin nanoparticles' size and surface morphology, and the results revealed spherical and irregularly shaped lignin nanoparticles particles (LNPs) [Behera, et al., 2023]. The EDS elemental maps confirm the presence of C, N, O, S, and Cr elements in the sample of nanolignin. The weight percentage of C, N, O, S and Cr are 46.56 %, 10.26 %, 33.24%, 6.70 %, and 3.24 % respectively demonstrating that Cr (VI) has been adsorbed on the surface of nano-lignin. Thus, the presence of Cr in the sample shows the adsorption of chromium by nanolignin. SEM-EDS analysis of nanolignin before and after adsorption of Cr (VI) is represented by Figure 16.



Element	Weight %	Atomic %
C K	64.05	70.29
O K	33.94	27.96
N K	1.73	1.63
S K	0.28	0.12
Totals	100.00	

Element	Weight %	Atomic %
C K	46.56	55.71
O K	33.24	29.86
N K	10.26	10.53
S K	6.70	3.0
Cr K	3.25	0.90
Totals	100.00	

Figure 16: SEM-EDS analysis of nanolignin to show the before (a, c) and after (b,d)adsorption of Cr (VI) ions

5.1.6 Transmission electron microscopy (TEM) analysis

TEM gives information about the size of the nanoparticles, morphology, crystallographic and compositional information (Onkarappa et al.,2020). The working principle of TEM is the same as an optical microscope but uses electrons instead of light. The morphology of nanolignin obtained from coconut coir was analyzed through TEM images. The mixture of irregularly smaller and spherical structures of nanolignin particles is seen through TEM analysis with a diameter of 122 nm. The successful preparation of nanoparticles is confirmed as a part of nanoparticle agglomerates observed through TEM. According to Assaf et al. [2023], alkali lignin nanoparticles can be prepared with the use of ultrasound in batch mode and confirmed the similar morphology of LNPs through TEM analysis with a diameter of 126.9 nm. TEM micrograph of lignin nanoparticles at (a.) 200 nm scale and (b.) 100 nm scale is given in Figure 17.

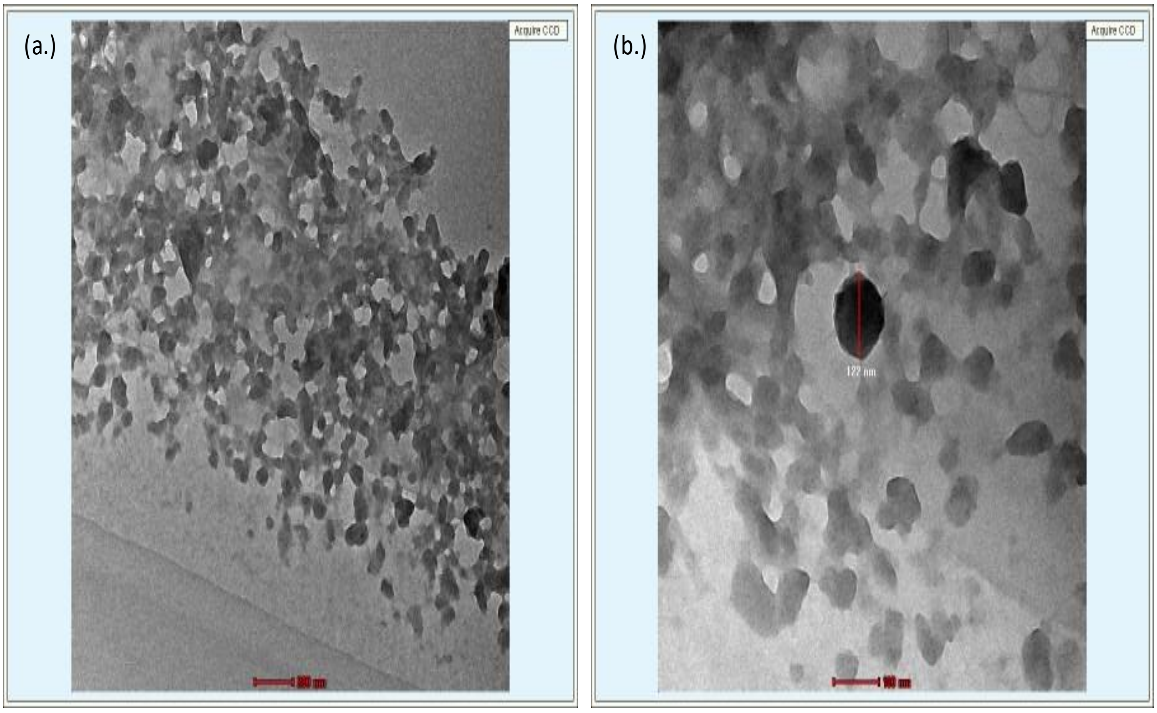


Figure 17 : TEM micrograph of lignin nanoparticles at (a.) 200 nm scale and (b.) 100 nm scale

5.1.7 X-ray diffraction (XRD)

The crystalline size of nanoparticles is determined by XRD (Juikar and Nadanathangam.,2020). It offers details about the phase, lattice parameters, crystalline grain size, and crystalline structure (Li et al., 2023; Mourdikoudis et al.,2018). To analyze the XRD of nanolignin, powder X-ray diffraction studies were conducted using CuKα1 radiation at 40 kV and 50 mA. Based on the XRD pattern depicted in Figure **18**, lignin appears to exhibit a mostly amorphous structure, with some level of crystallinity. The presence of a broad reflection peak around 22° indicates a semi-crystalline nature and weak intense reflections are observed at 12.8° and 26.7°.

Pinpointing individual planes may prove challenging, given the amorphous character of lignin. The Debye-Scherrer equation was used to determine the average size of the crystalline area.

$$C_D = \frac{0.94\lambda}{\beta \cos\theta} \quad \text{...[Eq.7]}$$

Where, λ is the wavelength of X-ray radiation (1.5406Å),

β is Full width at half maximum (FWHM) in radians of the XRD peak

θ is the angle of diffraction.

The reflection peaks at 2θ = 12.78° and 21.89° are used to evaluate the average crystallite size of Nano-Lignin, which were found to be 2 nm and 0.77 nm, respectively. After the adsorption process, the XRD reflection peak at 2θ = 21.89° is shifted to 20.42° while the other two peaks remained relatively unchanged. Worku et al., (2023) reported similar kinds of findings for the synthesis of lignin nanoparticles from Oxytenanthera abyssinica.

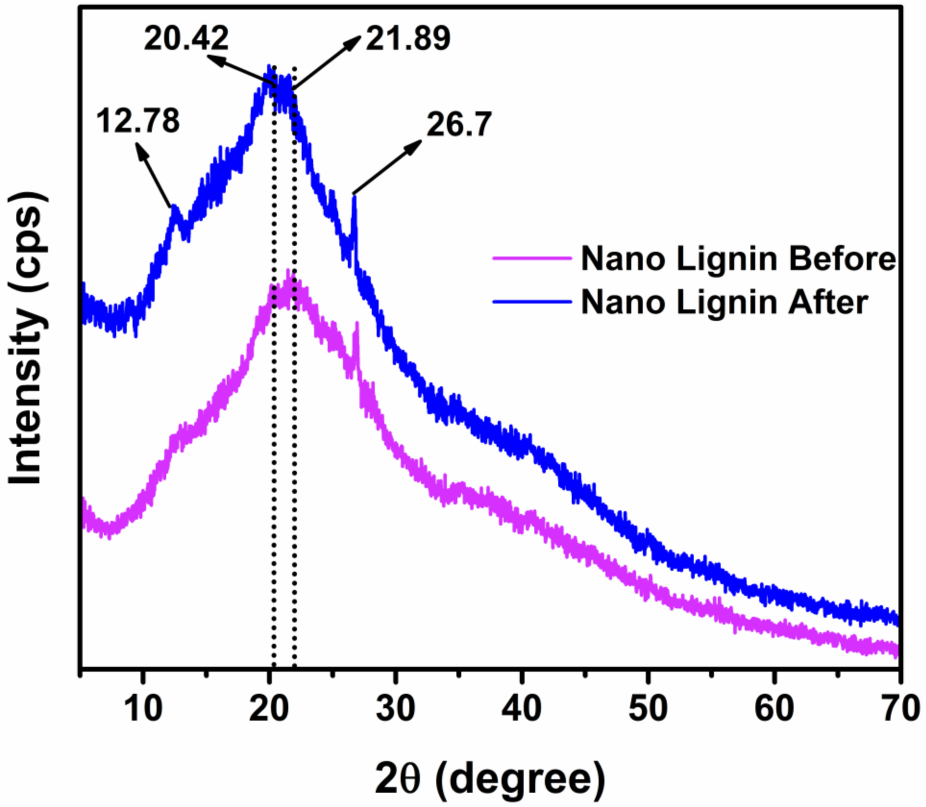


Figure 18: X-ray powder diffraction (XRD) spectra of nano-lignin before and after adsorption

5.1.8 Fourier-Transform Infrared Spectroscopy (FTIR)

The functional groups present in (nano)materials are identified using the FTIR (Ruthran et al., 2022; Theivasanthi, et al.,2018). In order to identify potential structural alterations in nanolignin following adsorption, the FTIR spectra of the material were recorded using KBr pellets method for the 4000- 500 cm^{-1} range both before and after Cr (VI) adsorption. The characteristic difference between lignin and nanolignin was found to be the shifting of the peak from 1425 to 1458 cm^{-1}, which is caused by the C-H deformation vibrations in the ethylene glycol found in LNPs. [Gupta et al., 2014; Juikar & Vigneshwaran ,2017a]. The presence of functional groups on nanolignin was verified through FTIR spectra analysis. As the stretching vibrations of hydroxyl groups present in nanolignin have been increased, the peak intensity in the range of 3000-3600 cm^{-1} was observed in FTIR spectra of nanolignin . LNPs displayed the peak characteristics of polar groups such as alcohols (3348, 1214, and 1039 cm^{-1}). The decrease in the intensity of absorption characteristics of hydroxyl groups and aromatic rings during adsorption is linked to the structural units of nanolignin's involvement in the reduction of Cr (VI). The FTIR spectra of nanolignin before and after adsorption of Cr (VI) are shown in Figure 19. The functional analysis of lignin nanoparticles based on FTIR is shown in Table 5.

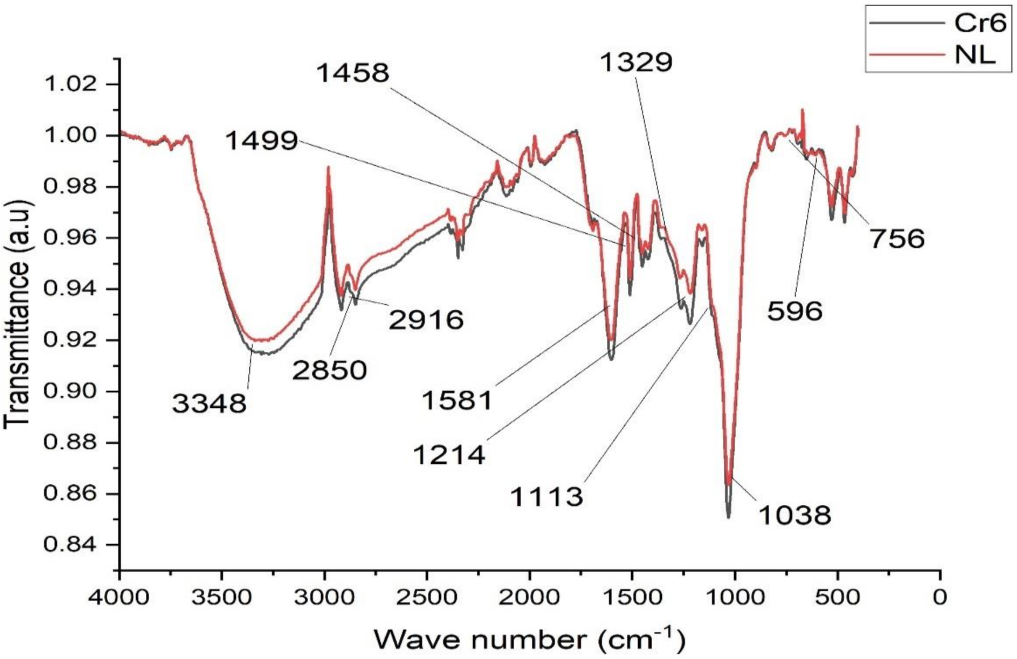


Figure 19: Fourier transform infrared spectroscopy (FTIR) spectra of nanolignin before and after adsorption of Cr (VI) ions [----- Before adsorption (Red colour); -----------After adsorption (Black colour)]

Table 5: Functional analysis of lignin nanoparticles based on FTIR

Characteristics peaks of Lignin NPs (LNPs)	Functional group
3348 cm^{-1}	OH
2916 cm^{-1} and 2850 cm^{-1}	C–H Stretching vibration
1581 cm^{-1}	Aromatic ring vibration
1499 cm^{-1}	Aromatic skeletal vibration
1458 cm^{-1}	Asymmetric deformation of C–H bond
1329 cm^{-1}	C–O stretching in syringyl (S- ring unit)
1214 cm^{-1}	C–O–C soft segment
1113 cm^{-1} and 1038 cm^{-1}	C–H stretching of polysaccharides
756 cm^{-1} and 596 cm^{-1}	Other C–H peaks

5.1.9 Ultraviolet-visible (UV-vis) spectroscopy

The UV-vis spectra of nanolignin, nanolignin bounded with chromium, and alone chromium were noted using a spectrophotometer in the 200-700 nm range as shown in Figure 20. As a reference sample, deionized water was utilised. In the organic phase, chromium gives a single peak around 364 nm [Ali et al., 2023]. Nanolignin bounded with chromium gives less absorbance with respect to nanolignin and chromium. This confirms the quantity of chromium bound to nanolignin during the process of adsorption.

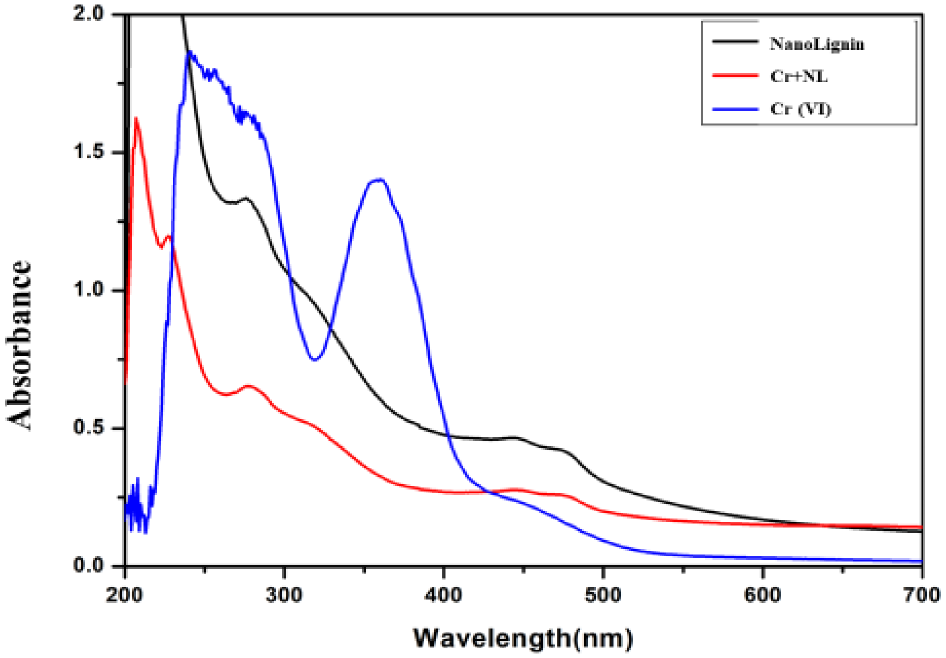


Figure 20 : Absorbance of Cr (VI), Nanolignin , and Chromium bounded with nanolignin.

5.1.10 Brunauer-Emmett-Teller (BET) analysis

Since the specific surface area of a nanoparticle is crucial for adsorption of metal ions from the aqueous solution, BET is used to analyze it (Hafidh et al., 2024). BET analysis was carried out to obtain the pore volume, pore size, and surface area of the nanolignin particles. The isotherm of the nano lignin exhibits a pronounced increase in N_2 adsorption at low pressures ($P/P0 < 0.01$), followed by a sustained high adsorption capacity with hysteresis observed at higher pressures. The presence of several pore architectures, including micropores, mesopores, and macro-pores, within the adsorbent material has been observed [Younesi-Kordkheili, & Pizzi, 2023; Singh et al 2022]. These pore structures offer advantages such as facilitating the adsorption process and providing a larger surface area for adsorption. The surface area of the nano-lignin was found to be 4.130 m^2/g with a pore volume of 0.006 cc/g and pore radius of 24.393 Å. Similar kinds of analysis was reported by Chen et al., (2019) for nanolignin with specific surface area 5.3765 m^2/g and average pore volume 0.0092 cm^3/g. In another study, Younesi-Kordkheili, & Pizzi, (2023) reported that the specific surface area of nanolignin was found to be 6.1766 m^2/g and average pore volume 0.0098 cm^3/g.

5.1.11 Calibration curve for Chromium (VI)

The Cr (VI) concentration standard curve was developed using the absorbance of the known concentration of Cr (VI) with 0-5.0 mg/L. To determine the linear equation of absorbance at 540 nm vs Cr (VI) concentration (mg/L), calculations were performed by the regression equation Y=0.3282X-0.0534 with correlation co-efficient (R^2) equal to 0.9913 (Liu et al., 2019) as shown in Figure 21.

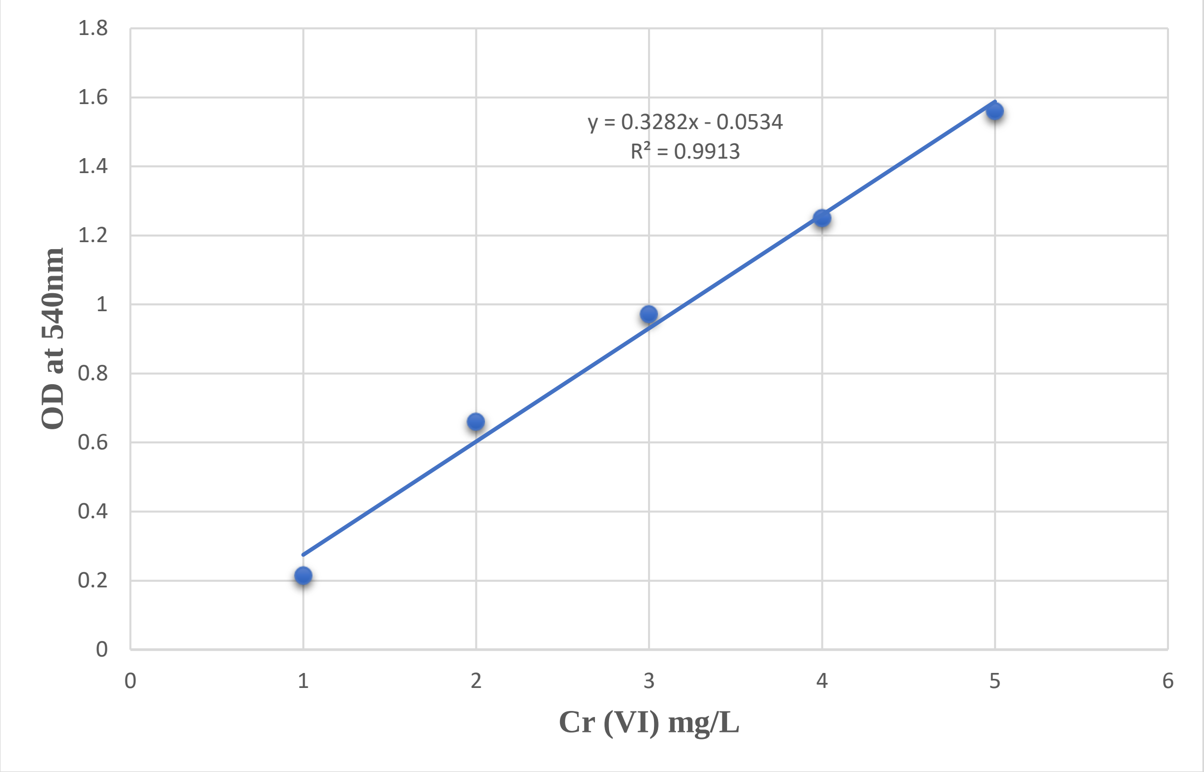


Figure 21: Calibration curve of Cr (VI)

Shakya, & Agarwal, (2019) demonstrated the Cr (VI) removal from water using pipeapple-derived biochar and estimated its concentration by making a calibration curve with high regression co-efficient (R^2=0.999). Similarly, the amount of Cr (VI) removed from date seed biochar modified with polyaniline was estimated using a colorimetric technique (Tripathy et al., 2021).

5.1.12 Error analysis

To find the best isotherm model for heavy metal adsorption, one can apply linear regression analysis. Researchers frequently use linear regression analysis to check the consistency of adsorption models and to perform mathematical analysis of experimental data. On the other hand, compared to linear regression, the model parameters derived from non-linear regression are more precise. In the case of heavy metal adsorption, non-linear regression is the better method for estimating isotherms parameters (Mouhamadou et al., 2023; Chen et al., 2022).

The Microsoft Excel solver function (Microsoft Office 2019, USA) was utilized in this study to perform regression analysis on experimental data for a variety of isotherm models and kinetics. To find the goodness of fit curve, different error functions were calculated for statistical analysis [Akdemir et al., 2022] as shown in Table 6.

Table 6: List of error functions for statistical analysis.

Error function	Equation
Sum of square error (SSE)	$\sum_{i=1}^{n}\left(q_{e,\exp}-q_{e,cal}\right)^2$ ....[Eq.8]
Sum of absolute error (SAE)	$\sum_{i=1}^{n}\left\|q_{e,\exp}-q_{e,cal}\right\|$ ....[Eq.9]
Hybrid fractional error function (HYBRID)	$\frac{100}{n-p}\sum_{i=1}^{n}\left\|\frac{\left(q_{e,\exp}-q_{e,cal}\right)^2}{q_{e,\exp}}\right\|$ ....[Eq.10]
Chi-square (χ^2) test	$\sum_{i=1}^{n}\frac{\left(q_{e,\exp}-q_{e,cal}\right)^2}{q_{e,\exp}}$ ....[Eq.11]

Where, $q_{e,exp}$, and $q_{e,cal}$ represent measured and calculated adsorption capacity; n is the number of data points ; p is the number of parameters

5.2 Factors affecting adsorption

The remediation of metal ions such as Cr (VI) from wastewater is affected by several factors like temperature, pressure, pH, biosorbent dose, initial metal ions concentration, contact time, and ionic strength. The removal efficiency of the nanoadsorbents is affected by their physical and chemical properties such as particle size, porosity, surface area, surface functional groups, etc. (Cheriyamundath & Vavilala, 2021).

5.2.1 Effect of pH on adsorption

At lower pH (2-3), Cr (VI) is reduced by the phenolic group of nano-lignin to form positively charged Cr (III) ions. Figure 22, illustrates the point of zero charges (PZC) for nano-lignin particles synthesized by a green method, with a measured value of 6.65. The results of this study provide compelling evidence that the surfaces of nano-lignin particles synthesized using green methods exhibit a positive charge when the pH values are below the point of zero charges (pHpzc). The Cr (VI) species, namely $HCrO_{4}^{-}$ and $Cr_2O_7^{2-}$, are expected to exhibit anionic properties. Nevertheless, when the pH drops below 4.0, there is a noticeable decline in the adsorption capacity of nanolignin. This can be attributed to the presence of chromium in the form of H_2CrO_4, which competes strongly with protons for adsorption sites. In the presence of an acidic solution, the functional groups have the ability to undergo protonation, leading to a robust electrostatic contact between the adsorbent nano-lignin particles and the $Cr_2O_7^{2-}$, ion (Singh, Anil, et al., 2022; Singh, Naik, et al., 2022). In the pH range of 5.0-7.0, the prevailing chemical species of chromium (Cr) is the chromate ion (CrO_4^{2-}). An excessive concentration of hydroxide ions (OH-) in the chromium solution leads to a competitive interaction with chromate ions (CrO_4^{2-}) for adsorption on the surface of the adsorbent material. In this competition, hydroxide ions tend to dominate the adsorption process. Hence, the adsorptive capacity of chromium (VI) diminishes when the pH level rises. The adsorption capacity of nano-lignin particles declined as the pH level increased. The highest adsorption concentration was observed at a pH of 2.0, while a near-complete decrease in adsorption was observed at a pH of 7. These findings align with various researchers' prior research on Cr (VI) adsorption (Singh et al., 2023). Thus, in acidic pH conditions, the oxygen-containing groups that are negatively charged in nanolignin attract positively charged Cr (III) for its removal during the process of adsorption. The highest removal efficiency was found to be 92.83 % at pH2 as shown in Figure 23. The removal of Cr (VI) from the aqueous synthetic solution after treatment with nanolignin is shown in Figure 24. Thus, pH is one of the important parameters for the adsorption of Cr (VI) as H^+ in the acidic medium is used to reduce Cr (VI) ions as represented in the Eq.**13** [Nagpal et al.,2023].

$HCrO_4^- + 12H^+ + 17e^-$ -------$Cr^{3+} + 12H_2O$………………………… [Eq.12]

With the increase in pH to a certain range, the adsorption of heavy metals on adsorbent increases but there is no obvious linear correlation between them (Huang et al., 2020). At lower pH, active sites on the adsorbent get protonated resulting in their electrostatic repulsion between metal ions, and that prevents more adsorption of ions. pH affects the chemistry of both the functional group of biosorbent and the chemistry of metal ions (Ali Radha, 2020). The process of adsorption is greatly affected by variations in pH as hydrogen ion itself is a tough competing adsorbate and as a general rule, the adsorption rate increases for heavy metals with an increase in pH value because it influences the surface properties of the adsorbents (Pang et al., 2022). Adsorption efficiency decreases at highly alkaline conditions (pH of 10 or higher). Hydroxide precipitation could be used for the retention of heavy metals which is also pH-dependent (Qasem et al.,2021). Metal ions could react with calcium hydroxide (lime) to produce metal hydroxide precipitates and calcium ions (Kumar & Kumar., 2023).

Du et al., (2023) demonstrated that pH 5 is the optimum condition for the adsorption of heavy metals such as Pb (II), Cu(II), and Ni(II) on lignin-based adsorbent. Their findings showed that raising the initial pH value (2-5) increased the adsorption capacities. The lower pH values are unfavorable due to the protonation of -OH, -COOH, and -NH on the surface of the adsorbent.

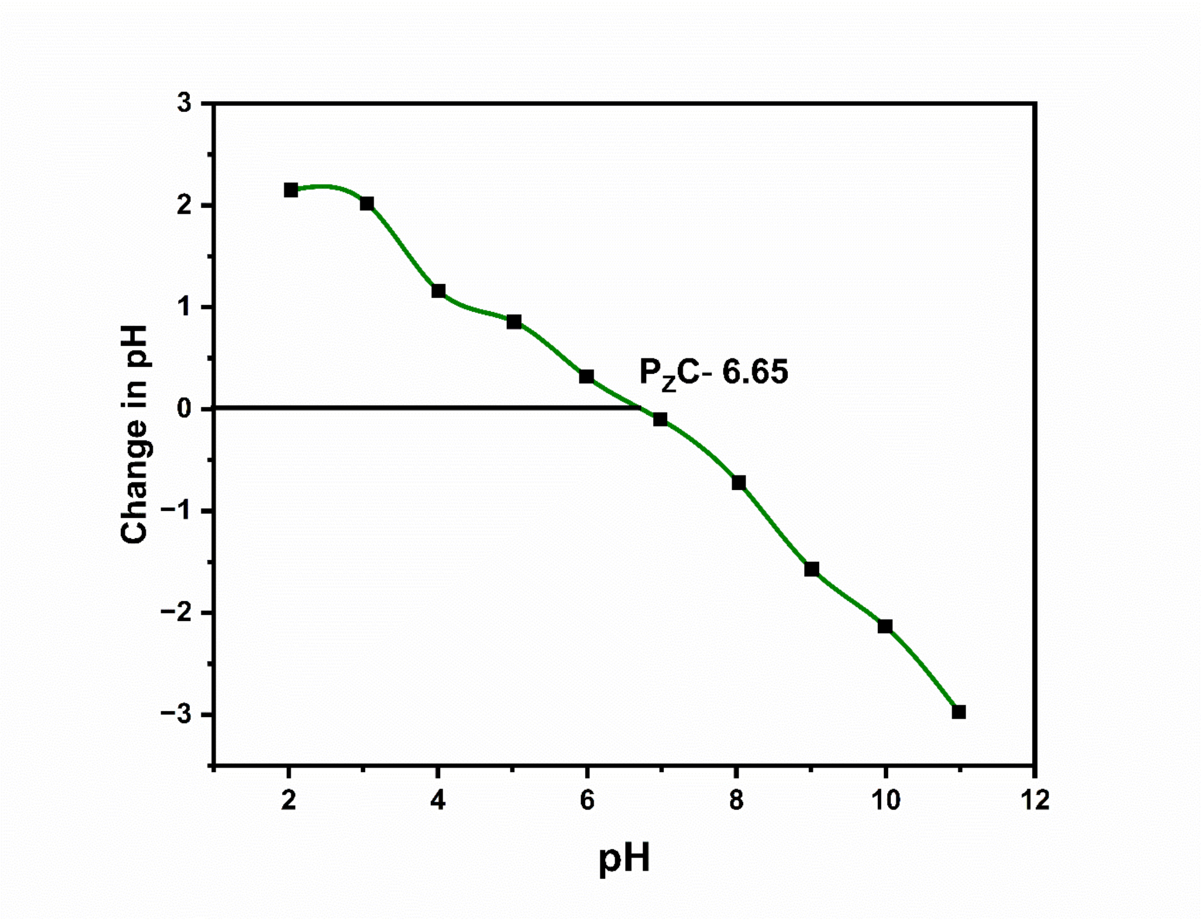


Figure 22: Determination of point of zero charge (pH_{pzc}) of nanolignin

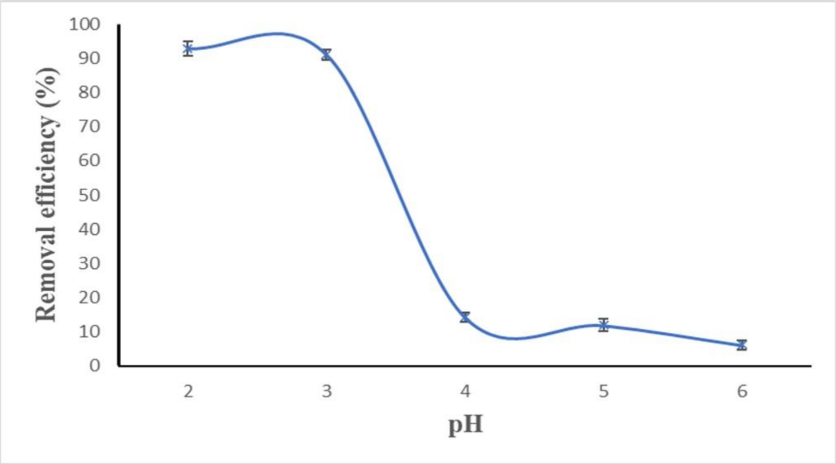


Figure 23: Effect of pH on adsorption at initial Cr (VI) ions concentration of 10 mg/L, 0.03 g adsorbent dosage, 400 rpm agitation, 80 minutes, and 298 K temperature

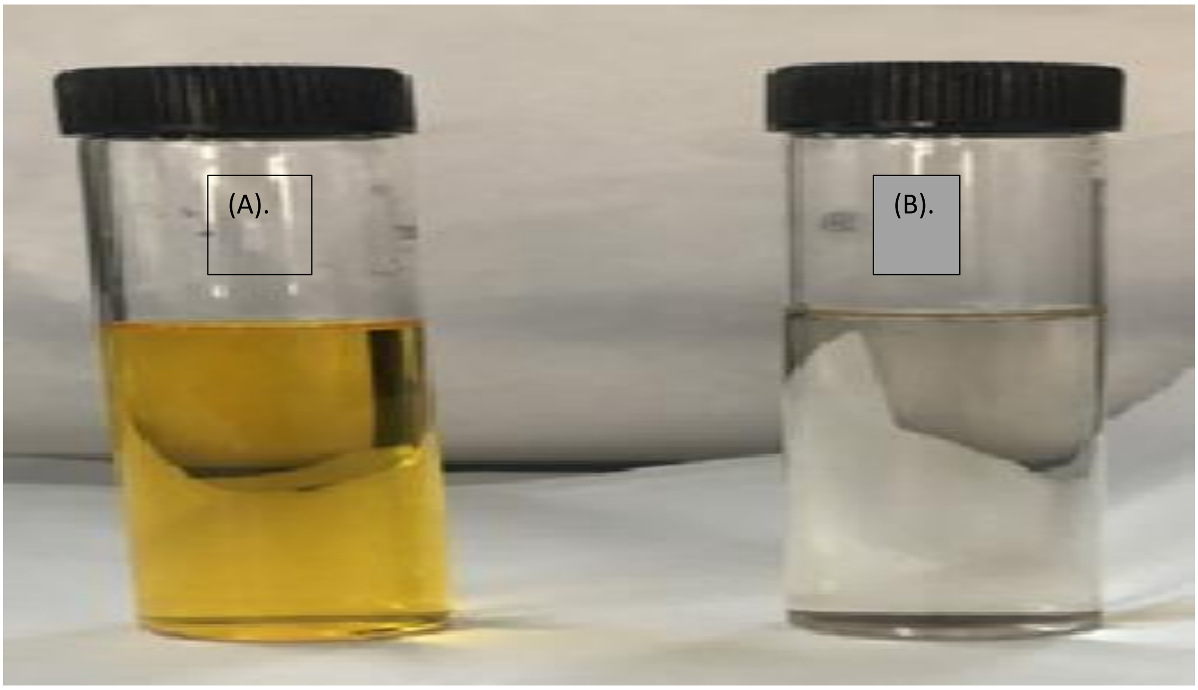


Figure 24 : Removal of Cr (VI) from the aqueous synthetic solution at the concentration of 10 mg/L (A) Before treatment (B) After treatment.

5.2.2 Effect of adsorbent dosage on adsorption

As the dose of nanolignin increases, the tendency of the removal of Cr (VI) is also enhanced due to the availability of more adsorption sites on nanolignin. The batch experiment was carried out at pH 2 with an initial concentration of Cr (VI) ions of 10 mg/L. Figure 25, shows that removal efficiency increased sharply up to a dosage of 0.02 g for the adsorbent and the maximum removal efficiency of 92.83 % was observed at the dosage of 0.03 g of nanolignin. Because nanoparticles tend to aggregate, adding more nanolignin to the dosage causes the active sites on the adsorbent to be hidden, which lowers removal efficiency (92.0 and 91.1% at the dosage of 0.04 g and 0.05 g of adsorbent, respectively) as shown in the graph. Similar kinds of findings have been investigated in different types of research [Daneshvar et al., 2019; Barad et al.,2022]. The adsorbent capacity of an adsorbent depends on the optimum quantity of the adsorbent used (Nguyen-Thi et al, 2024). As the heavy metal ion concentration changes, the removal efficiency, as well as the adsorption capacity, gets changed. On increasing the dose of adsorbent more active binding sites for heavy metal adsorption are available for effective removal of heavy metals (Hashem et al, 2024 a). Kumar et al., (2019) reported that at a constant dose of 0.015 g, Carboxymethyl nanocellulose stabilized nano zero-valent iron nanoparticles were able to reduce almost 100% of 15 mg/L of Cr (VI) in 90 minutes. Hashem et al., (2024b) reported the removal of chromium from tannery wastewater using Carica papaya tree as an adsorbent at the optimum dose of 3g/50ml, and 84.36% removal of chromium was achieved.

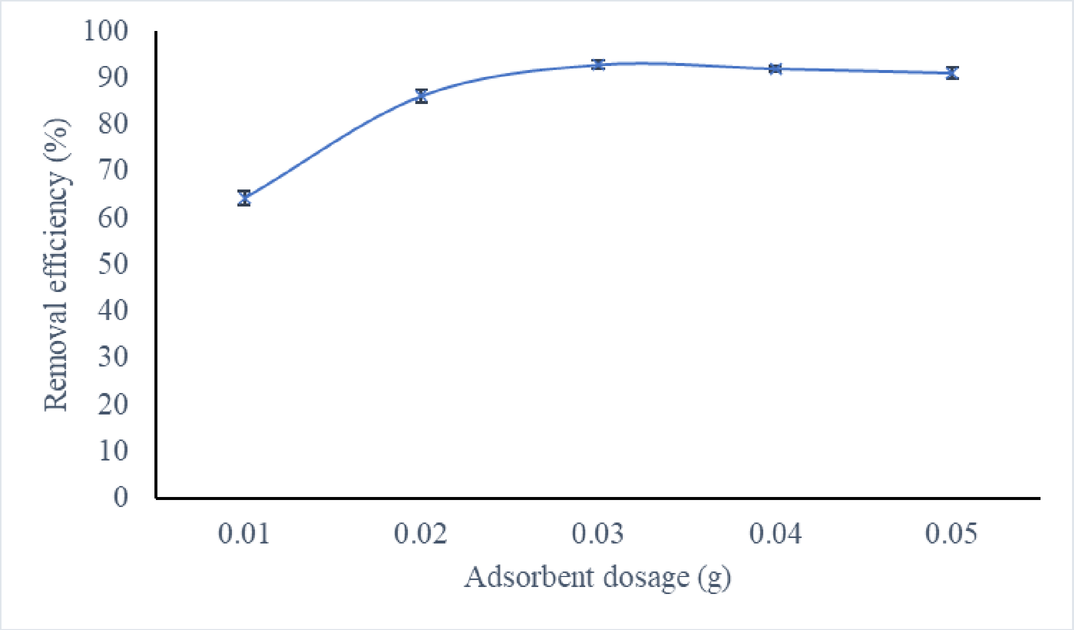


Figure 25: Effect of adsorbent dosage on adsorption at initial Cr (VI) ions concentration of 10 mg/L, pH 2, 400 rpm agitation, 80 minutes, and 298 K temperature

5.2.3 Effect of contact time on adsorption

The impact of contact duration on Cr (VI) adsorption was examined at study intervals ranging from 20 to 100 minutes. The equilibrium was reached after 80 min as in Figure 26. It was depicted that the percentage removal of Cr (VI) increases with time till it attained the equilibrium. At the beginning of the adsorption process, the percentage of removing Cr (VI) ions was higher due to the presence of more active sites on nanolignin. The percentage removal of 92.83 was achieved after 80 minutes of equilibrium time at an optimum adsorbent dosage of 0.03 g/ 100 ml at pH 2 at 298 K. Over the course of the adsorption process, the number of unoccupied adsorption sites on the surface of nanolignin gradually decreased. Hence until reaches equilibrium, the adsorption rate becomes slow. Similar kinds of studies were reported for the removal of Cr (VI) from wastewater by using olive leaves as adsorbent [Rzig et al., 2022]. The time required to attain equilibrium or contact time is one of the important factors for the adsorption process. The rate of adsorption increases during the initial period of time and decreases due to a limited number of active sites over the adsorption time. Finally, the adsorption equilibrium phase will be reached after a certain adsorption time (Huang et al.,2020; Kumar & Kumar ., 2022). Hokkanen et al., (2018) studied the effect of contact time for the removal of Ni (II), and Cd (II), from an aqueous solution by hydroxyapatite-bentonite clay-nanocellulose composite as adsorbent. Choudhury et al., (2024) reported the removal of Cr (VI) and showed that the adsorption capacity of nano zerovalent iron supported by sawdust remained nearly constant after 180 minutes, which signifying the establishment of equilibrium at 180 minutes.

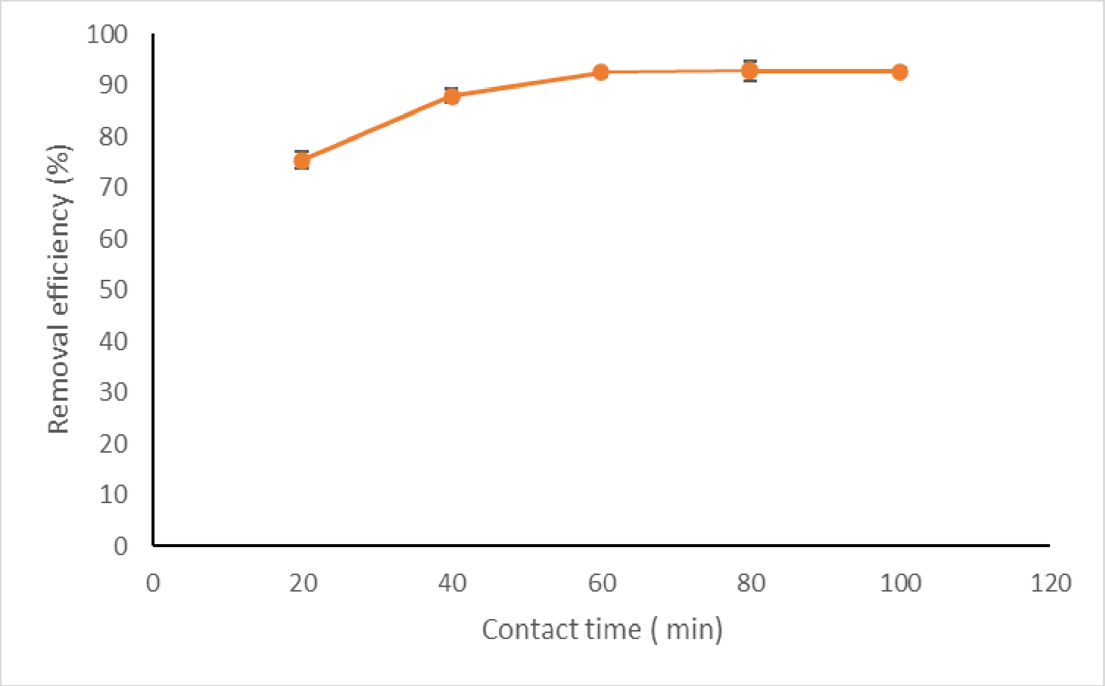


Figure 26: Effect of contact time on adsorption at initial Cr (VI) ions concentration of 10 mg/L, 0.03 g/100ml adsorbent dosage, pH 2, 400 rpm agitation, and 298 K temperature

5.2.4 Effect of temperature on adsorption capacity

The adsorption of Cr (VI) on nanolignin was studied at various temperatures. It was found that temperature has almost no significance on the adsorption of Cr (VI) on nanolignin and a slightly increased adsorption capacity from 30.94 mg/g to 31.14 mg/g at 298 K and 313K respectively was observed. The increase in the amount of Cr (VI) adsorption on nanolignin indicated the endothermic process. Similarly, when the temperature was raised to 328K, there was a small drop in the adsorption capacity (29.24 mg/g) of Cr (VI) (Figure 27). Similar kinds of studies were performed by El Malti et al. (2022) to show the impact of temperature on the adsorption of Cu (II) and Cd (II) on the activated carbon of citrus sinensis peel. Adsorption increases with increasing the temperature up to a certain temperature and then decreases at elevated temperature. The adsorption process of heavy metals is normally endothermic (Soliman & Moustafa, 2020). The capacity of adsorbent to bind more heavy metals as the temperature rises is due to an increase in the rate of adsorbate molecule diffusion across the interior pores and external boundary layer of adsorbent particles (Ajala et al., 2024) . Sbihi et al (2024) reported the removal of more hexavalent chromium by *Craticula subminuscula* from aqueous solution when the temperature was raised from 15-35 °C.

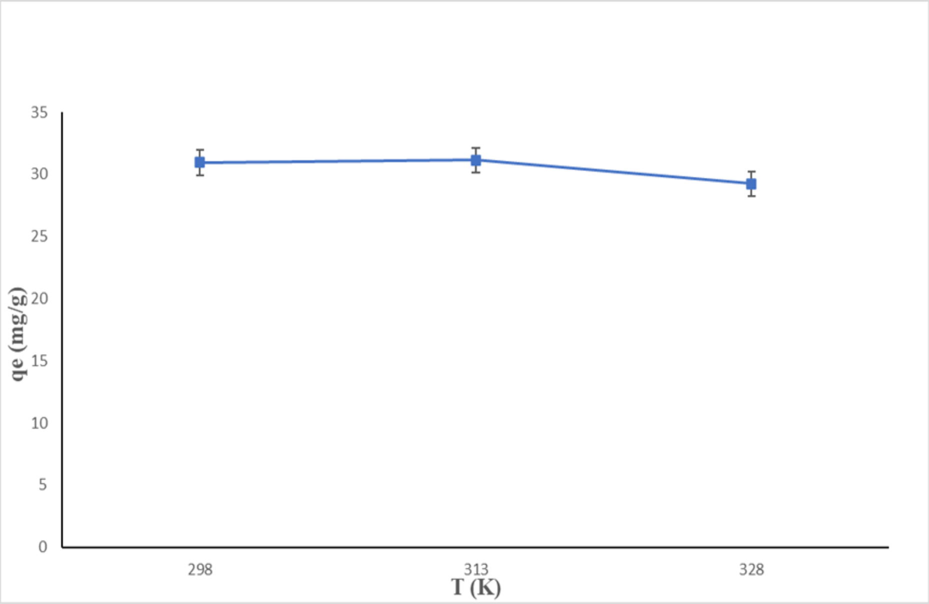


Figure 27: Effect of temperature on adsorption capacity of Cr (VI) on nanolignin at initial Cr (VI) ions concentration of 10 mg/L, 0.03 g /100 ml adsorbent dosage, pH 2 and 400 rpm agitation

5.2.5 Determination of adsorption capacity

In order to determine the maximum adsorption capacity ($q_{t,max}$) of nanolignin, batch experiments were conducted at 298 K. The batch study revealed that nanolignin had a maximum adsorption capacity of 30.94 mg/g at the equilibrium time exposure of 80 minutes and 0.03g /100ml as adsorbent dosage has been achieved as shown in Figure 28. Kumar and Chauhan (2019) reported the elimination of Cr (VI) from synthetic aqueous solution by using biomass from dried water hyacinth roots, which had a maximum adsorption capacity of 1.28

mg/g. Akar et al. (2019) investigated the removal of Cr (VI) from platting wastewater by means of *Platanus orientalis* bark, which had a maximum adsorption capacity of 13.42 mg/g.

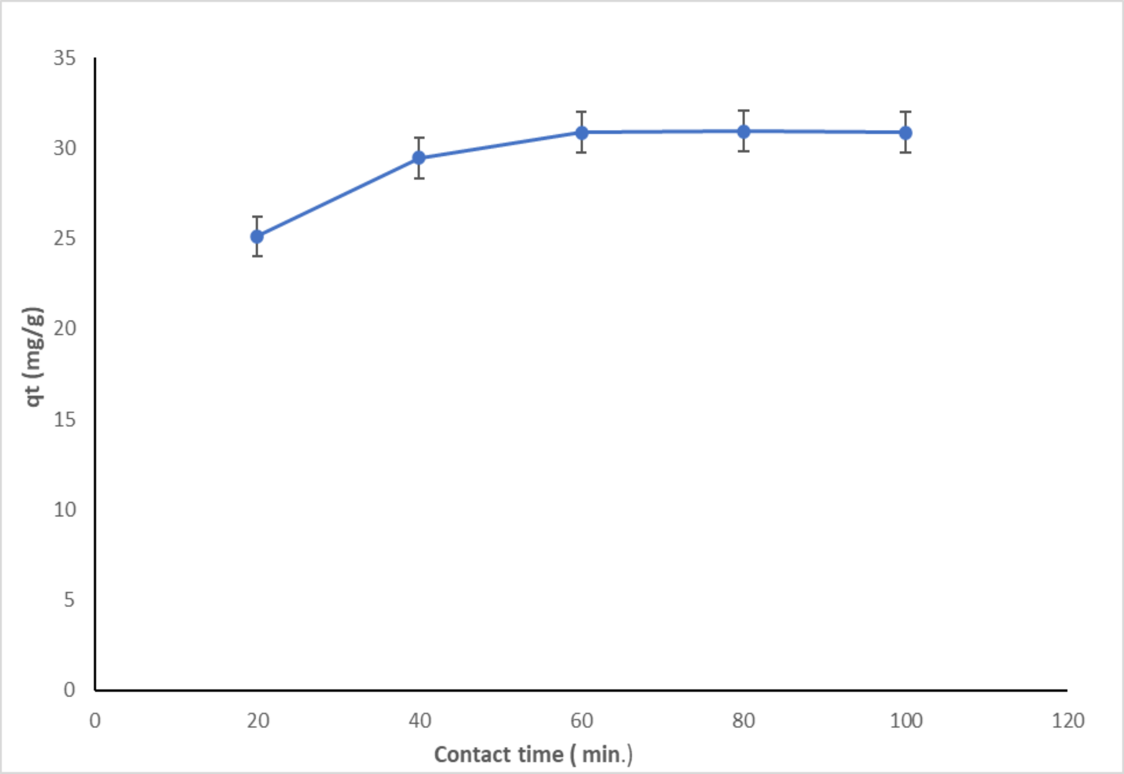


Figure 28: Kinetic of adsorption at the optimum condition at initial Cr (VI) ions concentration of 10 mg/L, pH 2, 0.03 g/100ml adsorbent dose, 400 rpm agitation, 80 minutes and 298 K temperature

5.3 Analytical method for the determination of chromium reduction

The UV-visible spectrum's time dependence in the Cr (VI) and nanolignin reaction mixture is displayed in Figure 29. The Cr (VI)] is reduced to Cr (III) is facilitated by the hydroxyl group of nanolignin. At 0 h, Chromium has a sharp peak at 230 nm, 290 nm, and 540 nm which decreased with time and disappeared at 540 nm when the reaction proceeded up to 60 minutes at pH 2 with 0.03 g dose of nanolignin. These results demonstrate that the reduction of Cr (VI). $K_2Cr_2O_7$ in an aqueous solution has been taken as control which shows characteristic maxima at 257 and 350 nm. Chen et al. (2015) used a UV-visible spectrum of the reaction mixture with time dependency to explain the mechanism of hexavalent chromium with sugarcane molasses.

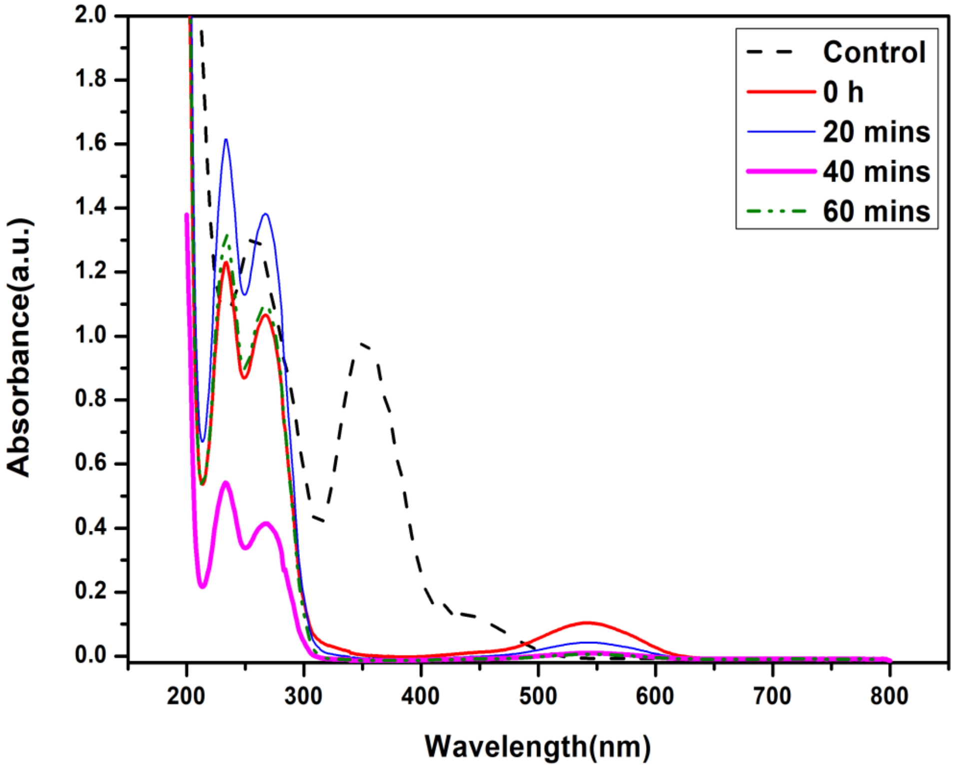


Figure 29: UV-visible spectrum of the reaction mixture at 10 mg/l of Cr (VI) at pH 2 with the adsorbent dosage of 0.03 g/100 ml of nanolignin.

5.4 Adsorption kinetic model

Adsorption kinetics modeling may be useful to comprehend the Cr (VI) ions adsorption mechanism on nanolignin. The adsorbed amount of Cr (VI) versus contact time was examined in the current work using pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models to identify the rate-limiting steps [Jimenez-Paz et al., 2023].

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{[Eq.13]}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{[Eq.14]}$$

Where, k_1 is the rate constant of pseudo-first-order kinetic model (PFO) in min^{-1} and

k_2 is the rate constant of the pseudo-second-order kinetic model (PSO) in (g mg^{-1} min^{-1}).

The adsorption of Cr (VI) on nanolignin by pseudo-first order (PFO) and pseudo-second-order (PSO) kinetic models are presented in Figure 30 and 31 respectively. Since the coefficient correlation values R^2 of the PSO model are higher and closer to unity than those of the PFO model, the kinetic study of Cr (VI) was well represented by pseudo-second-order kinetics as represented in Table 7. A good agreement for this adsorption was confirmed by the similarity in calculated q_e values and the experimental q_e values.

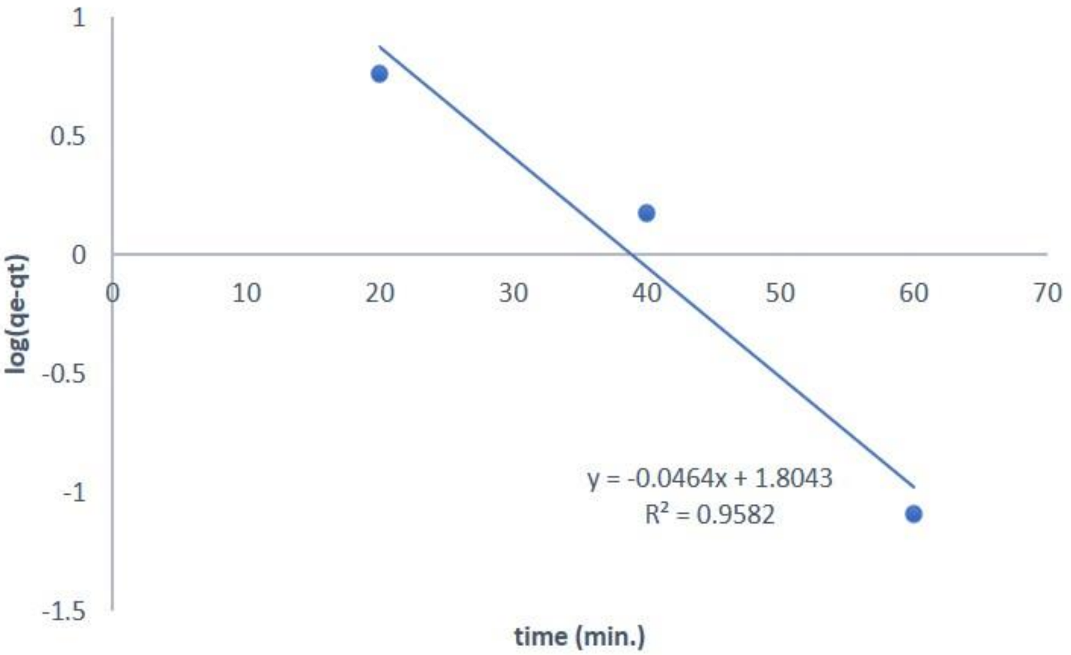


Figure 30: Pseudo-first order kinetic model for the adsorption of Cr (VI) ions on nanolignin at initial Cr (VI) ions concentration of 10 mg/L, 0.03 g/100ml adsorbent dosage, pH 2, 400 rpm agitation, and 298 K temperature

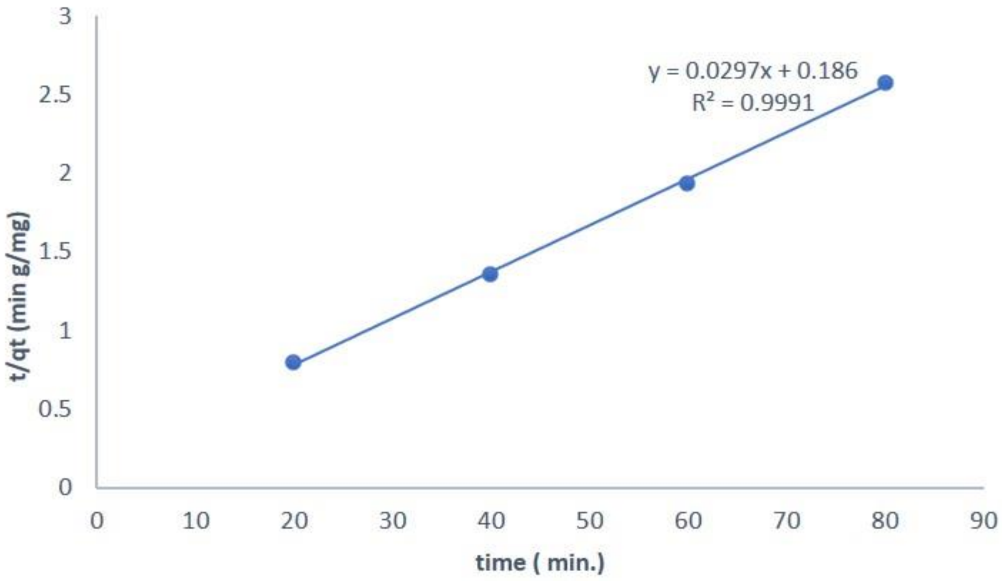


Figure 31 : Pseudo-second order kinetic model for the adsorption of Cr (VI) on nanolignin at initial Cr (VI) ions concentration of 10 mg/L, 0.03 g/100ml adsorbent dosage, pH 2, 400 rpm agitation, and 298 K temperature

Experimental data were analyzed by the Weber Morris intra-particle diffusion model to get information about the rate controlling the adsorption (Benmahdi et al., 2024; Saad et al., 2024)

$$q_t = K_{diff} t^{1/2} + C \quad \text{…………………………………………[Eq.15]}$$

Where q_t is the adsorption capacity at time t, $t^{1/2}$ is the half-life time in minutes, K_{diff} (mg/g min $^{1/2}$) is the rate constant of intraparticle diffusion and C represents the value of the thickness of the boundary layer (mg/g).

The movement of Cr (VI) from the fluid layer around the nanolignin surface to the interior adsorption sites utilizing pores is described by intra-particle diffusion model where they determine the rate of diffusion. The q_t vs $t^{½}$ is represented in Figure 32

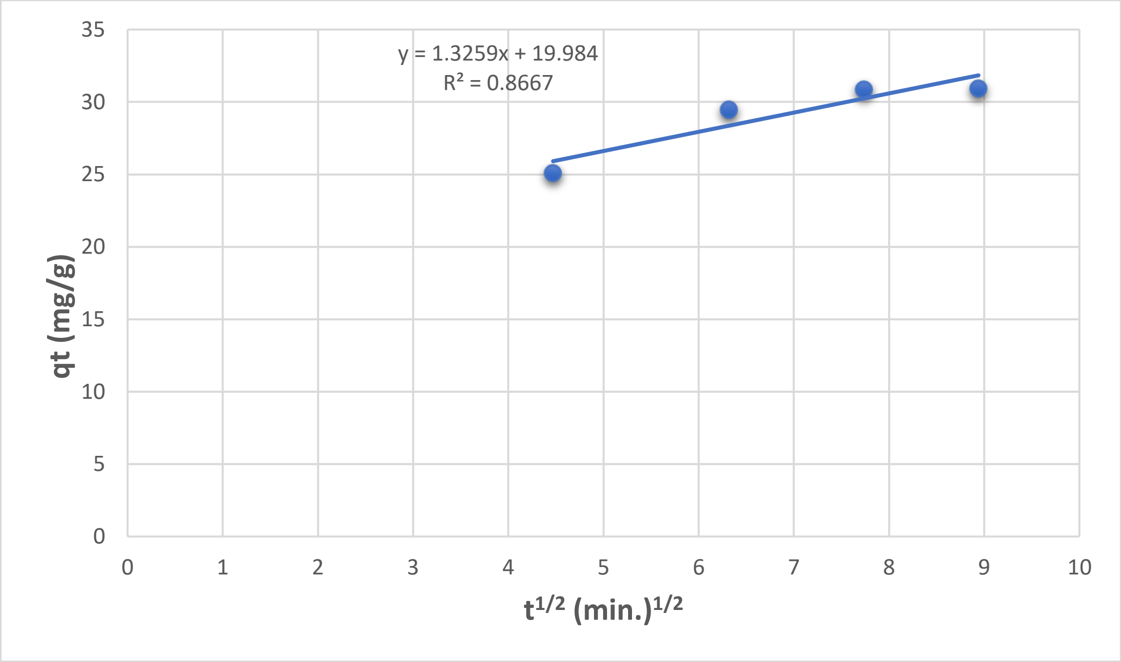


Figure 32: Intra-particle Diffusion Model for Cr (VI) adsorption onto nanolignin

Sohni et al., (2023) used an intra-particle diffusion model to show the adsorption of lead from aqueous solution on lignin nanoparticles reduced graphene oxide-based hydrogel to explore the kinetics of adsorption and K_{diff} was found as 0.92.

Table 7: Kinetics model constant for Cr (VI) adsorption on nanolignin

Kinetic model	qe (mg/g)	Rate constant	Error functions					Experimental value of qe (mg/g)
			R^2	SAE	SSE	HYBRID	χ^2	
Pseudo-first-order (PFO)	63.679	k_1=0.10685 (min^{-1})	0.958	0.4834	0.1446	1.729	0.00487	30.94
Pseudo-second-order (PSO)	33.67	k_2= 0.0047 (g mg^{-1} min^{-1})	0.999	0.0094	$4.27x10^{-5}$	0.592	$3.131x10^{-5}$	30.94
Intra-particle diffusion model	-	K_{diff}=1.3259	0.8667	2.4895	2.179	8.83	0.077	30.94

5.5 Adsorption isotherm model

Adsorption isotherms plot was used to determine Cr (VI) ion adsorption on nanolignin from an aqueous solution. In this batch study, two isotherms were taken into consideration i.e Langmuir and Freundlich isotherms. Langmuir and Freundlich isotherm models are expressed by the following equations [Singh et al., 2023].

$$\frac{1}{q_e} = \frac{1}{(K_L q_m) C_e} + \frac{1}{q_m} \text{ ....[Eq.16]}$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \text{ ---------------------------------------[Eq.17]}$$

Where, K_L is Langmuir adsorption constant (L/mg),

q_{max} is the maximum adsorption capacity of nanolignin (mg/g),

K_f is Freundlich constant related to adsorption capacity (mg/g) and

n is another Freundlich constant.

The multilayer adsorption process that takes place on heterogeneous surfaces is the basis of Freundlich isotherm whereas the Langmuir isotherm model postulates monolayer adsorption Cr (VI) metal ions onto a homogeneous surface with no interaction among adjacent adsorbed ions.

The isotherm was examined by plotting $1/q_e$ vs $1/C_e$ for Langmuir isotherm or ln q_e vs ln C_e for Freundlich isotherm for the best-fit curve using R-squared values. If the value of Freundlich constant (n) is greater than 1, adsorption will be favourable. The validation of Langmuir and Freundlich isotherm models for Cr (VI) adsorption on nanolignin is shown in Figures 33 and 34 respectively. Table 8, displays the experimental data that best fit the Langmuir isotherm for Cr (VI) adsorption on nanolignin.

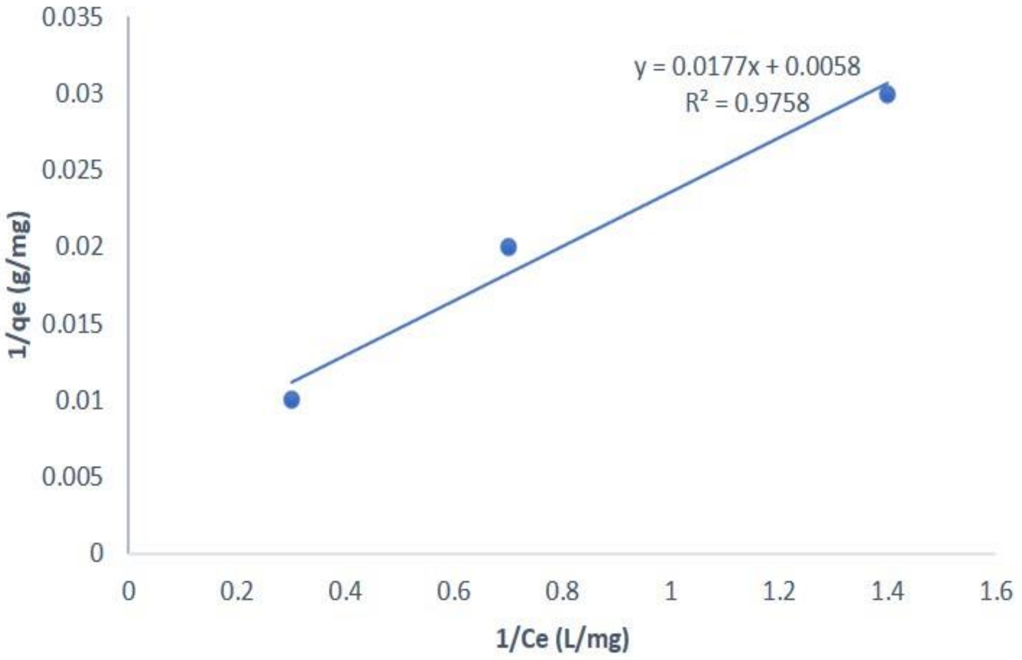


Figure 33: Validation of Langmuir isotherm model for Cr (VI) ions adsorption on nanolignin

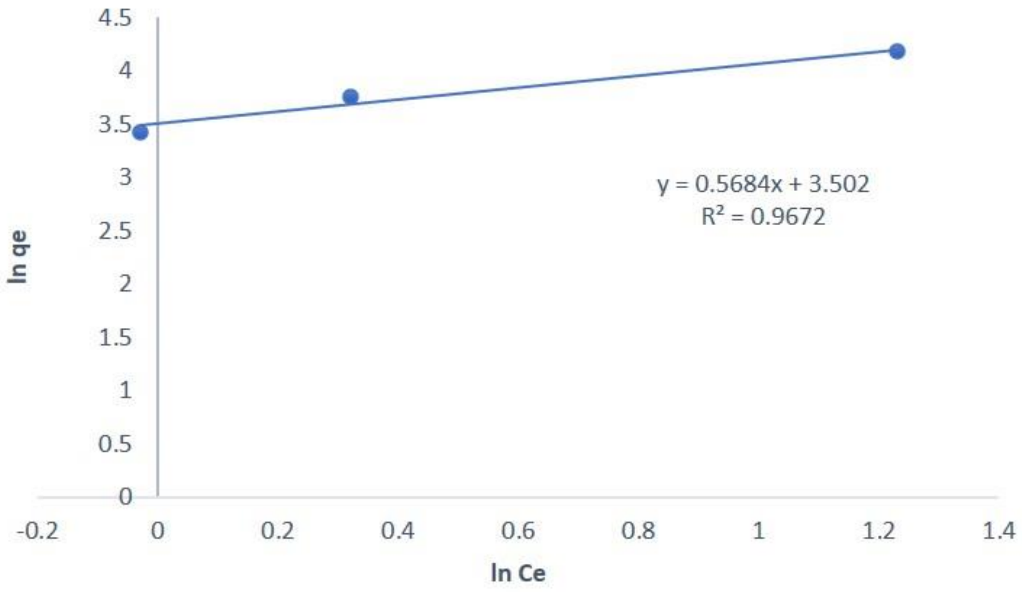


Figure 34 : Validation of Freundlich isotherm model for Cr (VI) ions adsorption on nanolignin

Redlich-Peterson's empirical adsorption model is the combination of Freundlich and Langmuir isotherm. Hence it does not follow the ideal monolayer adsorption (Yadav et al., 2024; Perera et al., 2023). The following equation represents the linear form of isotherm

$$\ln\left(\frac{C_e}{q_e}\right) = B\ln(C_e) - lnA \text{...[Eq.18]}$$

Where, A (L/mg) and B (L/mg) are the Redlich-Peterson isotherm constant.

This isotherm is evaluated by plotting ln (Ce/qe) vs ln (Ce) and represented in Figure 35.

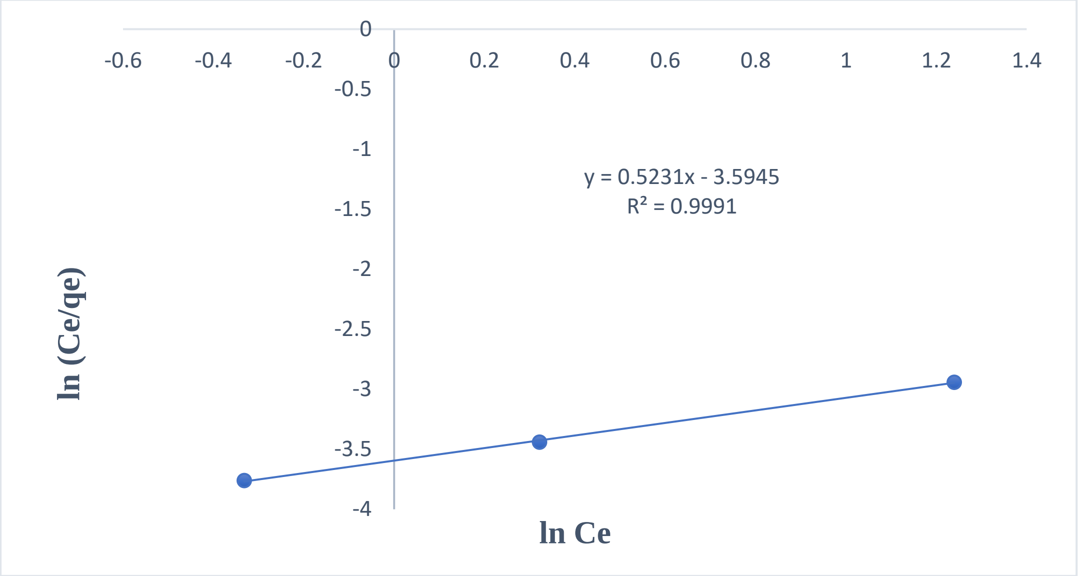


Figure 35 : Redlich-Petersons isotherm for adsorption of Cr (VI) onto nanolignin

Moon et al., (2023), exhibited Redlich-Peterson model to describe the adsorption isotherm. The adsorption equilibrium could be illustrated by Redlich-Peterson isotherm (Liu et al., 2023).

Table 8: Adsorption isotherm constant for Cr (VI) adsorption on nanolignin

Adsorption isotherm	Parameters	Values	Error functions				
			R^2	SAE	SSE	HYBRID	χ^2
Langmuir	q_{max} q_e K_L	200 mg/g 33.67 mg/g 0.282 L/mg	0.9758	0.003	4.84 $x10^{-6}$	13.636	0.00026
Freundlich	n K_f	1.759 33.18 mg/g	0.9672	0.122	0.0092	3.3003	0.00252
Redlich-Petersons	A B	3.5945 (L/g) 0.5231(L/mg)	0.9991	1.026	0.528	2.306	0.0119

5.6 Adsorption thermodynamics

The adsorption feasibility of Cr (VI) ions onto nanolignin was assessed using adsorption isotherms to calculate Gibb's free energy ($\Delta G^{\circ}{}_{ads}$) of adsorption. The constant of thermodynamic equilibrium (K_{eq}) has a relationship with the Gibb's free energy ($\Delta G^{\circ}{}_{ads}$) of adsorption as shown in the following equations [Sinha et al.,2022]:

$$K_{eq} = \frac{Q_e}{C_e} \text{---[Eq.19]}$$

$$\Delta G^{\circ}_{ads} = -RT \ln K_{eq} \text{--[Eq.20]}$$

Where, ΔG_{ads}^{0} is Gibb's free energy (J/mol) .

R is the ideal gas constant (8.314 J/mol K),

T is the absolute temperature (K),

The value of ΔG° was negative at room temperature (298 K), indicating spontaneous and endothermic adsorption. The value of Gibb's free energy (ΔG°) was found to be -9.327.65 KJ/mol at 298 K for the adsorption of Cr (VI) on nanolignin.

Dehghani et al., [2016] reported the ΔG_{ads}^{0}= -5.577 kJ/mole at 298 K during the elimination of Cr (VI) using waste newspaper as low-cost adsorbent. In another study, Giri et al., (2021) showed ΔG_{ads}^{0}= -5.23 kJ/mole at 313 K for the use of pomegranate peels as an adsorbent in the remediation of Cr (VI). Table 9, summarises the comparison of bioremediation of Cr (VI) ions using different adsorbents.

Table 9: Comparative analysis of the removal of Cr (VI) using various adsorbents

Adsorbent material	pH and Temperature	Initial Cr(VI) ions concentration (mg/L)	Maximum adsorption capacity (mg/g)	References
Microalgal based materials	pH 2, Temp. 22 ° C	10	25.19	Daneshvar et al., 2019
Maghemite nanoparticles	pH 2.5, Temp. 25, 30, 35 ° C	1-5	---	Barad et al.,2022
Micellar modified adsorbents	pH 2-12, Temp 25-30 °C	5-12	----	Sarfraz et al., 2022
Filamentous algae	pH 8, Temp 303K	5	0.77	Singh et al.,2021
Aegle-marmelos leaves	pH 2, Temp 30 °C	25	----	Mathai et al., 2022
Lagerstroemia speciosa seed hull biochar	pH 2, Temp 303 K	50	41.92	Nawaz et al., 2023

Corncob magnetic biochar	pH 3, Temp. 25 ° C	10	25.94	Van et al., 2019
Olive stones	pH 2, Temp 20 ° C	10	2.34	Amar et al., 2020
Pomegranate-peel-derived biochar	pH 4, Temp. 25 ° C	30	16.23	Chen et al., 2023
Pomegranate-peel	pH 2, Temp. 25 ° C	100	20.87	Giri et al., 2021
Nanolignin	pH 2, Temp. 25 ° C	10	30.94	Present study

5.7 Application of nanoliglin as adsorbent for the elimination of Cr (VI) from tannery wastewater

Tannery wastewater (TWW) sample was collected from the leather industry located in Bootan Mandi area of Jalandhar city, Punjab, India with latitude and longitude coordinates 31.306456 °N and 75.564067 °E, respectively. The removal capacity of nanolignin for Cr (VI) was tested at initial and optimum conditions. Tannery wastewater is basically dark brown-colored waste with a pungent odor and high content of TDS, chromium, phenolics, etc. The colour of the tannery effluent was similar as reported by Chowdhary et al (2015).

The chemical properties of wastewater from tannery are shown in Table 10., and the batch treatment of TWW is shown in Figure 36.

Table 10: Chemical characteristics of Tannery wastewater (TWW) of Jalandhar

Parameters	Values	unit
pH	4.6	
TDS (Total dissolved solids)	2650	mg/L
Electrical conductivity	54.8	mS/cm
Cr (VI)	2.143	mg/L

Table 10, shows that the pH of the TWW sample collected was 4.6, suggesting that the effluent was somewhat acidic in nature. The recommended range of pH of tannery effluent (TE) is 5.5 -9.5, however, TE's average pH can range from 6.0 to 9.0. [Shaibur et al., 2022; Ludvik, & Buljan, 2000]. Nigam et al (2019) reported the pH of the TWW sample as 3.9.

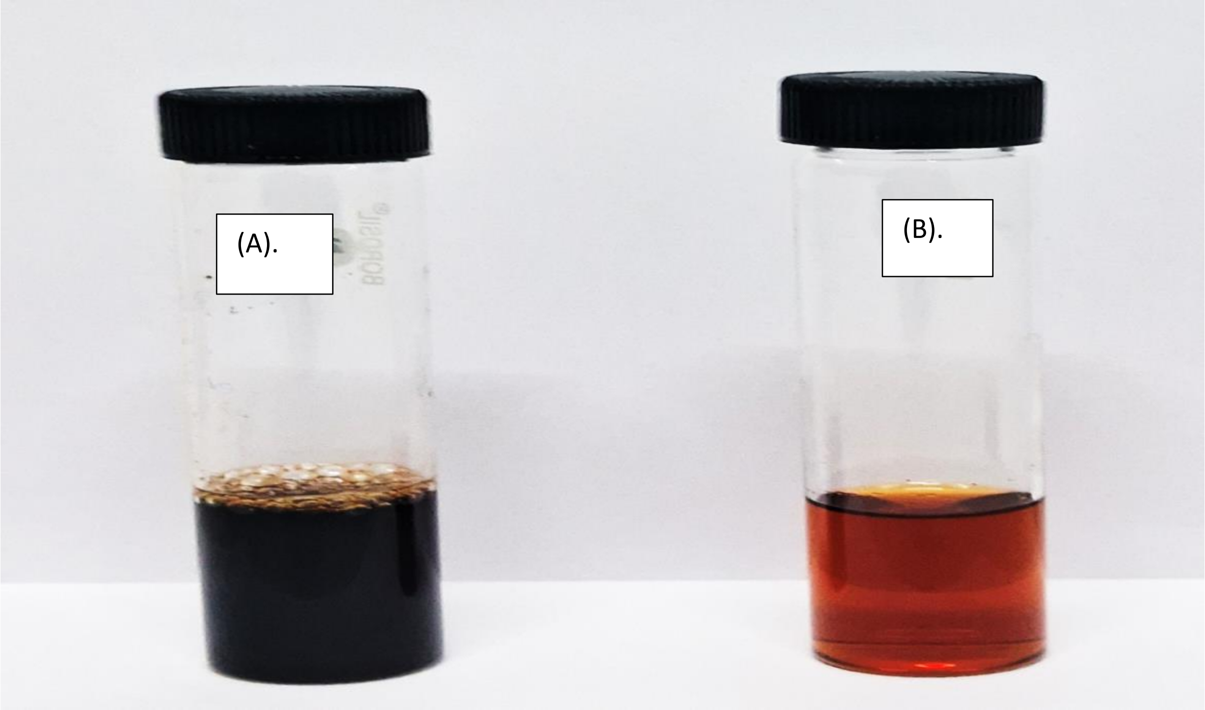


Figure 36 : Batch treatment of tannery wastewater from the leather industry (A) Before treatment (B) After treatment

Through the use of nanolignin, an adsorption study was conducted to remove Cr (VI) and 44.09 % of chromium (VI) removal from the tannery wastewater was observed at optimum removal conditions of pH 2, adsorbent dosage 0.03g/ 100 ml at 298 K and 400 rpm. The removal efficiency of Cr (VI) from tannery wastewater at both initial and optimum pH values is displayed in Table 11. The presence of other competing ions, such as phosphate, sulfate, etc., may be the reason for the decrease of nanolignin removal efficiency of Cr (VI) from TWW.

Table 11: Adsorption study of nanoliglin for Cr (VI) removal from tannery wastewater

Tannery wastewater	pH	C_0 (mg/L)	C_e(mg/L)	% Removal (R)
Initial condition	4.6	2.127	1.983	6.77
Optimum condition	2	2.143	1.198	44.09

In this study, TDS of tannery wastewater was increased from 2650 mg/L to 3300 mg/L after treatment with nanolignin. The electrical conductivity was decreased from 54.8 mS/cm to 39.5 mS/cm when exposed to nanolignin for wastewater treatment. Hashem et al (2020) reported that the TDS of tannery wastewater increased from 44.3 ± 0.6 mg/L to 48.9 ± 0.2 mg/L when treated with water hyacinth biochar. Similarly, Nigam et al (2019) investigated that the electrical conductivity of tannery wastewater decreased from 45.2 mS/cm to 21.5 mS/cm when treated with tea waste.

5.8 Mechanism of chromium adsorption on nanolignin

The remediation of Cr (VI) through nanolignin is governed by the adsorption sites, adsoption capacity, mechanical stability, regeneration and reusable potential (Dotto & McKay, 2020). Several functional groups have been demonstrated to be present in nanolignin, such as carboxylic (-COOH), carbonyl (C=O), phenolic and aliphatic hydroxyl (-OH), and others. The phenolic hydroxyl group of nanolignin is involved in the elimination of Cr (IV) ions by reducing it to Cr (III) [Li et al., 2023]. The uptake of Cr (VI) on nanolignin involves electrostatic interactions between the functional groups bound to the surface of nanolignin and reduced forms of Cr (VI) [Garg, et al.,2023; Zhang et al., 2021]. Hexavalent chromium can be found in nature as hydrogen chromate ($HCrO_4^{-1}$) and chromic acid (H_2CrO_4) which are the predominant form of Cr (VI) at lower pH (less than 3) in aqueous solution, while with the rise in pH from acidic to alkaline medium $HCrO_4^-$ is converted to chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) [Saouli et al.,2023]. At lower pH values, the best elimination of Cr (VI) ions was noted on oxygen-based functional groups of nanolignin due to an increase in electrostatic attraction at the acidic condition (Sinha et al., 2022). It has been reported that chromium in an aqueous solution possesses opposite net charges under different oxidative states as Cr (III) has a net positive charge while chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) have net negative charges (Ifthikar et al.,2021). Through the studies, it has been suggested that the process by which Cr (VI) ions are adsorbed by adsorbents is electrostatic attractions, adsorption, and reduction or simple adsorption [Narayanan et al., 2023; Kumar, & Kumar, 2023].

5.8.1. Electrostatic interaction

At acidic conditions ($pH<pH_{PZC}$), the OH atom of nanolignon get protonated to produce OH_2+. Then, the negatively charged Cr (VI) species such as $CrO_4^{2-}/Cr_2O_7^{2-}$ migrated toward the positively charged surface of nanolignin through electrostatic interaction.

$$Nanolignin.surface - OH + CrO_4^{2-} \rightarrow Surface - OH \equiv CrO_4^{2-} \text{......................................[Eq.21]}$$

$$-OH + CrO_4^{2-} / Cr_2O_7^{2-} \rightarrow Surface - OH \equiv CrO_4^{2-} / Cr_2O_7^{2-} \text{..[Eq.22]}$$

$$-COOH + CrO_4^{2-} / Cr_2O_7^{2-} \rightarrow Surface - COOH \equiv CrO_4^{2-} / Cr_2O_7^{2-} \text{....................................[Eq.23].}$$

.

5.8.2. Surface complexation

The Cr (VI) ions could form the inner sphere complexes with the function groups of nanolignin using the co-ordination chemisty principles.

$$C = O + Cr^{6+} \rightarrow \left[Cr(OH)_6\right] \text{..[Eq.24]}$$

5.8.3. Reduction

At the acidic conditions, -OH groups of nanolignin are involved in Cr (VI) reduction as these groups are the main electron donor for the reduction of Cr (VI). Dichromate gets ionized as chromate ions and hydrogen ions when dissolved in water (Bandara et al., 2022). At acidic pH, chromate in solution forms an equilibrium with $HCrO_4^-$. As $HCrO_4^-$ is highly reducible in the presence of an electron donor resulting in the transformation of Cr (VI) to Cr (III).

$HCrO_4^- + 7H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O$ ....[Eq.25]

$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^-$ ....[Eq.26]

$HCrO_4^- + 7H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O$ ....[Eq.27]

$Cr(VI) \xrightarrow{reduction} Cr(III)$ ....[Eq.28]

The schematic representation of the binding mechanism of hexavalent chromium [Cr (VI)] on nanolignin is shown in Figure 37.

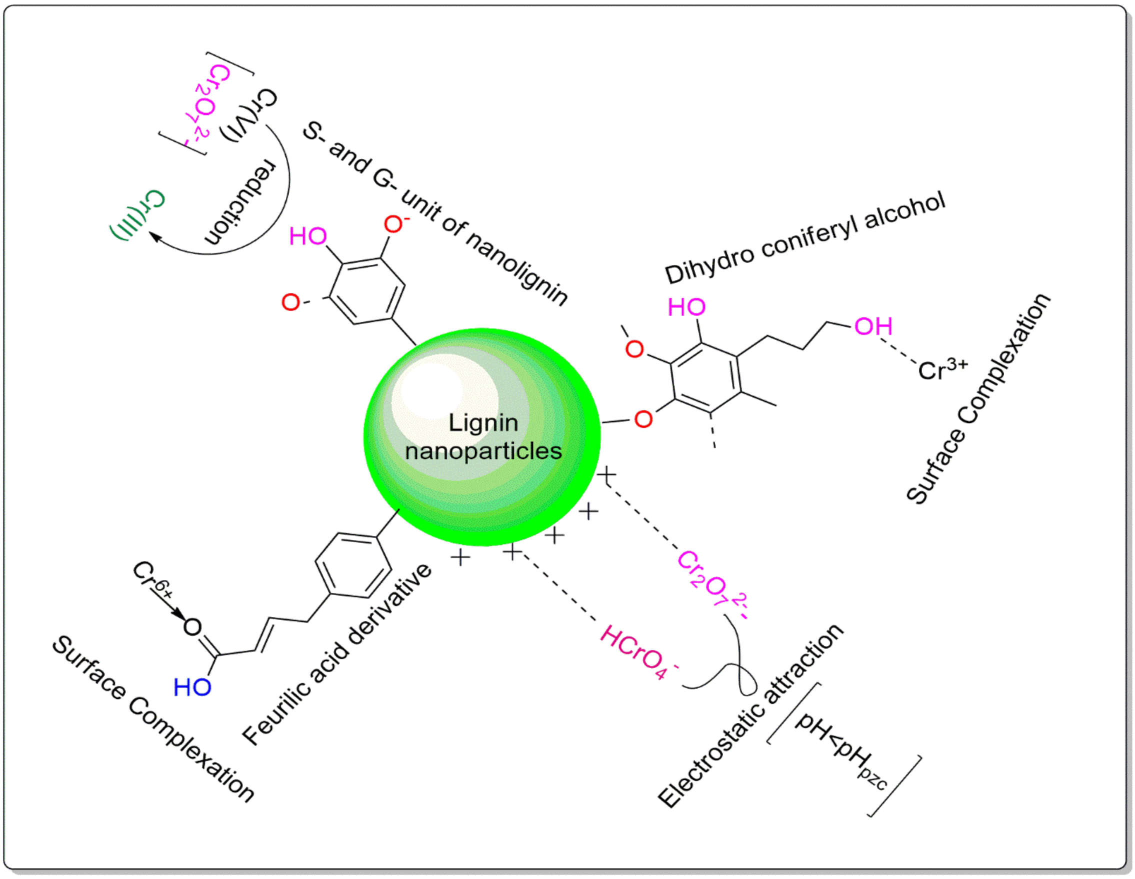


Figure 37: Diagrammatic illustration of the hexavalent chromium [Cr (VI)] binding on nanolignin.

6. Summary and Conclusions

One of the most serious environmental pollutants that nano adsorbents can mitigate is heavy metal pollution. Heavy metal removal from wastewater has been studied in relation to the function of nanoliglin, a lignocellulosic-based nanoparticle. Conventional methods of heavy metal removal from wastewater such as chemical precipitation resulted in the generation of secondary pollutants. Similarly, ion-exchange methods are highly dependent on the resin structure and solution of the environment. In the current study coconut coir-derived nanolignin was characterized by BET, XRD, FTIR, SEM-EDX, TEM, TGA, DSC, and particle size analyzer**.** The low initial concentration of Cr (VI) contributes to improved adsorption capacity at the active site of nano-lignin adsorbent.The adsorption of Cr (VI) on coconut coir-derived nanolignin is affected by the initial pH of the solution. The maximum Cr (VI) removal efficiency was observed to be 92.8% at acidic pH of 2, 0.03 g/ 100 ml of adsorbent dosage, and 80 minutes as equilibrium time has been investigated in batch studies by altering the pH, contact time, and dose of nanoadsorbent. Thus, nanolignin particles show good adsorption capacity for Cr (VI) in an aqueous solution. Thus, nanolignin has potential to remove heavy metals such as Cr (VI) from wastewater. The ability of nanolignin to eliminate Cr (VI) metal ions from alkaline water will be improved in the future by surface modification.

- The majority of the literature addresses methods like adsorption, chemical treatment, and membrane separation methods as the practical way of treating wastewater. Heavy metals remediation studies were performed using synthetic wastewater with one or a few metal types. Therefore, studies need to be performed on actual wastewater to fill the gap in knowledge. Although a lot of improvement has been observed in the preparation of lignocellulosic-based nanomaterials and their composites, still the issues such as higher binding efficiencies of nanoadsorbents at a wide range of pH require further research and development.
- Batch reactors were limited to most of the adsorption studies and it’s time to be transferred to adsorption columns filled with lignocellulosic-based nanomaterials as a porous structure for continuous filtration in wastewater treatment.
- The implementation of lignocellulose-based nanomaterial technologies on a large scale requires other reactors such as continuous reactors (CSTR), fixed bed reactors and fluidized bed reactors whose use is limited because still, the technologies are still at a nascent stage for the elimination of heavy metals ions from wastewater.

- In the future, optimization of adsorption conditions will help in the improvement in the performance of nanobiosorbent, and in combination with other treatment processes such as membrane technology will find ways for future research. Thus, hybrid adsorption membrane technologies are promising technologies for the elimination of heavy metal pollutants from wastewater.
- The commercialization of lignocellulosic-based nanoparticles depends on their price, greener method of synthesis, scale-up process, and regulatory hurdles. The better recycling performance of lignocellulosic-based nanomaterials helps in its commercialization.

Thus, the lignocellulosic-based nanomaterials show great potential as a component of new green material for wastewater treatment. As most of the nanomaterials are difficult to recycle and easy to agglomerate, how to solve these disadvantages will be a futuristic challenge for scientists. Hoverer, chemical modification of nanolignin such as the addition of functional groups, esterification, acetylation, grafting, etc, and physical dispersion techniques such as mechanical stirring, ultrasonication, and high shear homogenization are some of the strategies in practice to overcome the problem of agglomeration of nanolignin. In the future, surface modification of nanolignin will enhance its utility for the removal of hexavalent forms of chromium present in alkaline water.

BIBLIOGRAPHY

1. "www.worldwildlife.org", Water Scarcity | Threats | World Wildlife Fund (n.d.). [Online]. Available: https://www.worldwildlife.org/threats/water-scarcity. [Accessed on : July 20, 2023].
2. Agustin, M. B., Penttilä, P. A., Lahtinen, M., & Mikkonen, K. S. (2019). Rapid and direct preparation of lignin nanoparticles from alkaline pulping liquor by mild ultrasonication. *ACS Sustainable Chemistry & Engineering*, *7*(24), 19925-19934. https://doi.org/10.1021/acssuschemeng.9b05445
3. Ahmed, S. F., Mofijur, M., Rafa, N., Chowdhury, A. T., Chowdhury, S., Nahrin, M., ... & Ong, H. C. (2022). Green approaches in synthesising nanomaterials for environmental nanobioremediation: Technological advancements, applications, benefits and challenges. *Environmental Research*, *204*, 111967. https://doi.org/10.1016/j.envres.2021.111967
4. Ajala, E. O., Aliyu, M. O., Ajala, M. A., Mamba, G., Ndana, A. M., & Olatunde, T. S. (2024). Adsorption of lead and chromium ions from electroplating wastewater using plantain stalk modified by amorphous alumina developed from waste cans. *Scientific Reports*, *14*(1), 6055.
5. Ajiboye, T. O., Oyewo, O. A., & Onwudiwe, D. C. (2020). Simultaneous removal of organics and heavy metals from industrial wastewater: A review. *Chemosphere*, 128379. https://doi.org/10.1016/j.chemosphere.2020.128379
6. Akar, S., Lorestani, B., Sobhanardakani, S., Cheraghi, M., & Moradi, O. (2019). Surveying the efficiency of Platanus orientalis bark as biosorbent for Ni and Cr (VI) removal from plating wastewater as a real sample. *Environmental Monitoring and Assessment*, *191*, 1-19.
7. Akdemir, M., Isik, B., Cakar, F., & Cankurtaran, O. (2022). Comparison of the adsorption efficiency of cationic (Crystal Violet) and anionic (Congo Red) dyes on Valeriana officinalis roots: Isotherms, kinetics, thermodynamic studies, and error functions. *Materials Chemistry and Physics*, *291*, 126763. https://doi.org/10.1016/j.matchemphys.2022.126763

8. Akintelu, S. A., Folorunso, A. S., Folorunso, F. A., & Oyebamiji, A. K. (2020). Green synthesis of copper oxide nanoparticles for biomedical application and environmental remediation. *Heliyon*, *6*(7), e04508. https://doi.org/10.1016/j.heliyon.2020.e04508
9. Ali Redha, A. (2020). Removal of heavy metals from aqueous media by biosorption. *Arab Journal of Basic and Applied Sciences*, *27*(1), 183-193. https://doi.org/10.1080/25765299.2020.1756177
10. Ali, F., Saleem, A., Batool, N., Khan, H. A., Rehman, R., Mehboob, R., ... & Hussain, M. (2023). Adsorption and kinetic studies of chromium (VI) removal using Ag2Cu2O3 nanoparticles. *Zeitschrift für Physikalische Chemie*, *237*(4-5), 565-585. https://doi.org/10.1515/zpch-2022-0158
11. Ali, Q., Zia, M. A., Kamran, M., Shabaan, M., Zulfiqar, U., Ahmad, M., ... & Maqsood, M. F. (2023). Nanoremediation for heavy metal contamination: A review. *Hybrid Advances*, 100091.
12. Al-Nuaim, M. A., Alwasiti, A. A., & Shnain, Z. Y. (2023). The photocatalytic process in the treatment of polluted water. *Chemical Papers*, *77*(2), 677-701.
13. Altaf M., Yamin N., Muhammad G., Raza M.A., Shahid M., Ashraf R.S. (2021) Electroanalytical Techniques for the Remediation of Heavy Metals from Wastewater. In: Inamuddin, Ahamed M.I., Lichtfouse E. (eds) Water Pollution and Remediation: Heavy Metals. Environmental Chemistry for a Sustainable World, vol 53. Springer, Cham. https://doi.org/10.1007/978-3-030-52421-0_14
14. Amar, M. B., Walha, K., & Salvadó, V. (2020). Evaluation of olive stones for Cd (II), Cu (II), Pb (II) and Cr (VI) biosorption from aqueous solution: equilibrium and kinetics. *International Journal of Environmental Research*, *14*, 193-204.
15. Ambika, S., Kumar, M., Pisharody, L., Malhotra, M., Kumar, G., Sreedharan, V., ... & Bhatnagar, A. (2022). Modified biochar as a green adsorbent for removal of hexavalent chromium from various environmental matrices: Mechanisms, methods, and prospects. *Chemical Engineering Journal*, 135716. https://doi.org/10.1016/j.cej.2022.135716
16. Anjum, Amna, et al. "A review of novel green adsorbents as a sustainable alternative for the remediation of chromium (VI) from water environments." *Heliyon* (2023).

17. Anuchi, S. O., Campbell, K. L. S., & Hallett, J. P. (2022). Effective pretreatment of lignin-rich coconut wastes using a low-cost ionic liquid. *Scientific Reports*, *12*(1), 6108. https://doi.org/10.1038/s41598-022-09629-4
18. Assaf, I., Zhang, Z., Otaola, F., Leturia, M., Luart, D., Terrasson, V., & Guénin, E. (2023). A continuous flow mode with a scalable tubular reactor for the green preparation of stable alkali lignin nanoparticles assisted by ultrasound. *International Journal of Biological Macromolecules*, 125106. https://doi.org/10.1016/j.ijbiomac.2023.125106
19. Avola, T., Campisi, S., Polito, L., Arici, S., Ferruti, L., & Gervasini, A. (2023). Addressing the issue of surface mechanisms and competitive effects in Cr (VI) reductive-adsorption on tin-hydroxyapatite in the presence of co-ions. *Scientific Reports*, *13*(1), 18913.
20. Azimi, A., Azari, A., Rezakazemi, M., & Ansarpour, M. (2017). Removal of heavy metals from industrial wastewaters: a review. *ChemBioEng Reviews*, *4*(1), 37-59. **https://doi.org/10.1002/cben.201600010**
21. Babel, S., & Kurniawan, T. A. (2005). Various treatment technologies to remove arsenic and mercury from contaminated groundwater: an overview. *Proceedings of the Southeast Asian Water Environment*, *1*.
22. Bakatula, E. N., Richard, D., Neculita, C. M., & Zagury, G. J. (2018). Determination of point of zero charge of natural organic materials. *Environmental Science and Pollution Research*, *25*, 7823-7833. https://doi.org/10.1007/s11356-017-1115-7
23. Bandara, P.C., Peña-Bahamonde, J. & Rodrigues, D.F. Redox mechanisms of conversion of Cr(VI) to Cr(III) by graphene oxide-polymer composite. *Sci Rep* **10**, 9237 (2020). https://doi.org/10.1038/s41598-020-65534-8
24. Barad, Jaydeep M., Himanshu P. Kohli, and Mousumi Chakraborty. "Adsorption of hexavalent chromium from aqueous stream by maghemite nanoparticles synthesized by the microemulsion method." *Energy Nexus* 5 (2022): 100035. https://doi.org/10.1016/j.nexus.2021.100035
25. Bashir, A., Malik, L. A., Ahad, S., Manzoor, T., Bhat, M. A., Dar, G. N., & Pandith, A. H. (2019). Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods. *Environmental Chemistry Letters*, *17*(2), 729-754. https://doi.org/10.1007/s10311-018-00828-y

26. Bashir, M. S., Ramzan, N., Najam, T., Abbas, G., Gu, X., Arif, M., ... & Sillanpää, M. (2022). Metallic nanoparticles for catalytic reduction of toxic hexavalent chromium from aqueous medium: A state-of-the-art review. *Science of The Total Environment*, *829*, 154475.
27. Behera, S., Mohapatra, S., Behera, B. C., & Thatoi, H. (2023). Recent updates on green synthesis of lignin nanoparticle and its potential applications in modern biotechnology. *Critical Reviews in Biotechnology*, 1-21. https://doi.org/10.1080/07388551.2023.2229512
28. Beisl, S., Adamcyk, J., & Friedl, A. (2020). Direct Precipitation of Lignin Nanoparticles from Wheat Straw Organosolv Liquors Using a Static Mixer. *Molecules, 25*(6), 1388. **https://doi.org/10.3390/molecules25061388**
29. Bekchanov, D., Mukhamediev, M., Babojonova, G., Lieberzeit, P., & Su, X. (2023). Anion exchange material based on polyvinylchloride and urea for the removal of chromium (vi) ions from aqueous solutions. *CLEAN–Soil, Air, Water*, 2200411. https://doi.org/10.1002/clen.202200411
30. Benmahdi, F., Khettaf, S., & Kolli, M. (2024). Efficient removal of Cr (VI) from aqueous solution using activated carbon synthesized from silver berry seeds: modeling and optimization using central composite design. *Biomass Conversion and Biorefinery*, *14*(5), 7087-7101.
31. Bhattacharya, P. T., Misra, S. R., & Hussain, M. (2016). Nutritional aspects of essential trace elements in oral health and disease: an extensive review. *Scientifica*, *2016*. https://doi.org/10.1155/2016/5464373
32. Budnyak, T. M., Aminzadeh, S., Pylypchuk, I. V., Riazanova, A. V., Tertykh, V. A., Lindström, M. E., & Sevastyanova, O. (2018). Peculiarities of synthesis and properties of lignin–silica nanocomposites prepared by sol-gel method. Nanomaterials, 8(11), 950. https://doi.org/10.3390/nano8110950
33. Burakov, A. E., Galunin, E. V., Burakova, I. V., Kucherova, A. E., Agarwal, S., Tkachev, A. G., & Gupta, V. K. (2018). Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. *Ecotoxicology and environmental safety*, *148*, 702-712. https://doi.org/10.1016/j.ecoenv.2017.11.034

34. Carolin, C. F., Kumar, P. S., Saravanan, A., Joshiba, G. J., & Naushad, M. (2017). Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *Journal of environmental chemical engineering*, *5*(3), 2782-2799. https://doi.org/10.1016/j.jece.2017.05.029
35. Carvalho, P. M., Felício, M. R., Santos, N. C., Gonçalves, S., & Domingues, M. M. (2018). Application of light scattering techniques to nanoparticle characterization and development. Frontiers in chemistry, 6, 237. https://doi.org/10.3389/fchem.2018.00237
36. Chai, W. S., Cheun, J. Y., Kumar, P. S., Mubashir, M., Majeed, Z., Banat, F., ... & Show, P. L. (2021). A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application. *Journal of Cleaner Production*, 126589. https://doi.org/10.1016/j.jclepro.2021.126589
37. Chakraborty, R., Renu, K., Eladl, M. A., El-Sherbiny, M., Elsherbini, D. M. A., Mirza, A. K., ... & Gopalakrishnan, A. V. (2022). Mechanism of chromium-induced toxicity in lungs, liver, and kidney and their ameliorative agents. *Biomedicine & Pharmacotherapy*, *151*, 113119.
38. Chang, J., Zhang, J., Wang, H., Bai, Y., Liu, Y., Bi, Y., ... & Xie, H. (2023). Cr (VI) adsorption and reduction by magnetite-humic acid adsorption complexes under mildly acidic conditions: Synergistic/antagonistic mechanism and multi-step reaction model. *Chemical Engineering Journal*, *451*, 138648.
39. Chasapis, C. T., Ntoupa, P. S. A., Spiliopoulou, C. A., & Stefanidou, M. E. (2020). Recent aspects of the effects of zinc on human health. *Archives of toxicology*, *94,* 1443-1460. https://doi.org/10.1007/s00204-020-02702-9
40. Chauhan, P. S. (2020). Lignin nanoparticles: eco-friendly and versatile tool for new era. *Bioresource Technology Reports, 9,* 100374. https://doi.org/10.1016/j.biteb.2019.100374
41. Chavez-Hernandez, J. A., Velarde-Salcedo, A. J., Navarro-Tovar, G., & Gonzalez, C. (2024). Safe nanomaterials: from their use, application and disposal to regulations. *Nanoscale Advances*.

42. Chen, K., Wang, S., Qi, Y., Guo, H., Guo, Y., & Li, H. (2021). State-of-the-art: Applications and Industrialization of Lignin Micro/Nano Particles. *Chemsuschem*, *14*(5), 1284-1294. **https://doi.org/10.1002/cssc.202002441**
43. Chen, L., Zhou, X., Shi, Y., Gao, B., Wu, J., Kirk, T. B., ... & Xue, W. (2018). Green synthesis of lignin nanoparticle in aqueous hydrotropic solution toward broadening the window for its processing and application. *Chemical Engineering Journal*, *346*, 217-225. https://doi.org/10.1016/j.cej.2018.04.020
44. Chen, X., Hossain, M. F., Duan, C., Lu, J., Tsang, Y. F., Islam, M. S., & Zhou, Y. (2022). Isotherm models for adsorption of heavy metals from water-A review. *Chemosphere*, 135545. https://doi.org/10.1016/j.chemosphere.2022.135545.
45. Chen, Y., Gong, X., Yang, G., Li, Q., & Zhou, N. (2019). Preparation and characterization of a nanolignin phenol formaldehyde resin by replacing phenol partially with lignin nanoparticles. *RSC advances*, *9*(50), 29255-29262.
46. Chen, Y., Yang, J., & Abbas, A. (2023). Enhanced Chromium (VI) Adsorption onto Waste Pomegranate-Peel-Derived Biochar for Wastewater Treatment: Performance and Mechanism. *Toxics*, *11*(5), 440.
47. Chen, Z. F., Zhao, Y. S., Zhang, J. W., & Bai, J. (2015). Mechanism and kinetics of hexavalent chromium chemical reduction with sugarcane molasses. *Water, Air, & Soil Pollution*, *226*, 1-9. https://doi.org/10.1007/s11270-015-2629-6
48. Cheng, S. Y., Show, P. L., Lau, B. F., Chang, J. S., & Ling, T. C. (2019). New prospects for modified algae in heavy metal adsorption. *Trends in biotechnology*, *37*(11), 1255-1268. https://doi.org/10.1016/j.tibtech.2019.04.007
49. Cheriyamundath, S., & Vavilala, S. L. (2021). Nanotechnology-based wastewater treatment. Water and Environment Journal, 35(1), 123-132. doi:10.1111/wej.12610
50. Choudhury, T. R., Jahan, F. N., Bhowmik, S., Sowrav, S. F. F., & Nurnabi, M. (2024). Enhanced chromium (VI) removal: A remediation study employing nano zero-valent iron supported by sawdust. *Environmental Chemistry and Ecotoxicology*.
51. Chowdhury, M., Mostafa, M. G., Biswas, T. K., Mandal, A., & Saha, A. K. (2015). Characterization of the effluents from leather processing industries. *Environmental Processes*, *2*, 173-187.
52. Chowdhury, S., Mazumder, M. J., Al-Attas, O., & Husain, T. (2016). Heavy metals in drinking water: occurrences, implications, and future needs in developing

countries. *Science of the total Environment*, *569*, 476-488. https://doi.org/10.1016/j.scitotenv.2016.06.166

53. Cong, S. Q., Wang, B., Wang, H., Zheng, Q. C., Yang, Q. R., Yang, R. T., ... & Luo, F. X. (2024). Fe3O4-lignin@ Pd-NPs: A highly active, stable and broad-spectrum nanocomposite for water treatment. *International Journal of Biological Macromolecules*, *256*, 128233. https://doi.org/10.1016/j.ijbiomac.2023.128233
54. Daneshvar, E., Zarrinmehr, M. J., Kousha, M., Hashtjin, A. M., Saratale, G. D., Maiti, A., ... & Bhatnagar, A. (2019). Hexavalent chromium removal from water by microalgal-based materials: adsorption, desorption and recovery studies. *Bioresource technology*, *293*, 122064. https://doi.org/10.1016/j.biortech.2019.122064
55. Daniel, A. B., Zahir, E., & Asghar, M. A. (2021). Remediation of Vanadium (V) and Chromium (III) Ions from Aqueous Media by Modified Nanocellulose Obtained from Coconut Coir. *Journal of Macromolecular Science, Part B*, *60*(7), 500-520. https://doi.org/10.1080/00222348.2020.1870300
56. Dehghani, M. H., Sanaei, D., Ali, I., & Bhatnagar, A. (2016). Removal of chromium (VI) from aqueous solution using treated waste newspaper as a low-cost adsorbent: kinetic modeling and isotherm studies. *Journal of molecular liquids*, *215*, 671-679. https://doi.org/10.1016/j.molliq.2015.12.057
57. Deng, J., Sun, S. F., Zhu, E. Q., Yang, J., Yang, H. Y., Wang, D. W., ... & Shi, Z. J. (2021). Sub-micro and nano-lignin materials: Small size and rapid progress. *Industrial Crops and Products*, *164*, 113412. https://doi.org/10.1016/j.indcrop.2021.113412
58. DesMarias, T. L., & Costa, M. (2019). Mechanisms of chromium-induced toxicity. *Current opinion in toxicology*, *14*, 1-7.
59. Dotto, G. L., & McKay, G. (2020). Current scenario and challenges in adsorption for water treatment. *Journal of Environmental Chemical Engineering*, *8*(4), 103988. https://doi.org/10.1016/j.jece.2020.103988
60. Du, B., Chai, L., Zheng, Q., Liu, Y., Wang, X., Chen, X., ... & Sun, R. C. (2023). Designed synthesis of multifunctional lignin-based adsorbent for efficient heavy metal ions removal and electromagnetic wave absorption. *International Journal of Biological Macromolecules*, *234*, 123668
61. Du, J., Zhang, B., Li, J., & Lai, B. (2020). Decontamination of heavy metal complexes by advanced oxidation processes: A review. *Chinese Chemical Letters*, *31*(10), 2575-2582.

62. Ebrahimi, M., Khalili, N., Razi, S., Keshavarz-Fathi, M., Khalili, N., & Rezaei, N. (2020). Effects of lead and cadmium on the immune system and cancer progression. *Journal of Environmental Health Science and Engineering*, *18*(1), 335-343. https://doi.org/10.1007/s40201-020-00455-2
63. Edition, F. (2011). Guidelines for drinking-water quality. *WHO chronicle*, *38*(4), 104-108.
64. Ee, L. Y., & Li, S. F. Y. (2021). Recent advances in 3D printing of nanocellulose: Structure, preparation, and application prospects. *Nanoscale Advances*, *3*(5), 1167-1208.
65. El Gaayda, J., Rachid, Y., Titchou, F. E., Barra, I., Hsini, A., Yap, P. S., ... & Akbour, R. A. (2023). Optimizing removal of chromium (VI) ions from water by coagulation process using central composite design: Effectiveness of grape seed as a green coagulant. *Separation and Purification Technology*, *307*, 122805.
66. El Malti, W., Hijazi, A., Abou Khalil, Z., Yaghi, Z., Medlej, M. K., & Reda, M. (2022). Comparative study of the elimination of copper, cadmium, and methylene blue from water by adsorption on the citrus Sinensis peel and its activated carbon. *RSC advances*, *12*(17), 10186-10197. https://doi.org/10.1039/D1RA08997H
67. Fei, Y., & Hu, Y. H. (2023). Recent progress in removal of heavy metals from wastewater: A comprehensive review. *Chemosphere*, 139077.
68. Figueiredo, P., Lintinen, K., Hirvonen, J. T., Kostiainen, M. A., & Santos, H. A. (2018). Properties and chemical modifications of lignin: Towards lignin-based nanomaterials for biomedical applications. *Progress in Materials Science*, *93*, 233-269. https://doi.org/10.1016/j.pmatsci.2017.12.001
69. Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. *Journal of environmental management*, *92*(3), 407-418. https://doi.org/10.1016/j.jenvman.2010.11.011
70. Fu, Z., & Xi, S. (2020). The effects of heavy metals on human metabolism. *Toxicology mechanisms and methods*, *30*(3), 167-176. https://doi.org/10.1080/15376516.2019.1701594
71. Gao, B., Li, P., Yang, R., Li, A., & Yang, H. (2019). Investigation of multiple adsorption mechanisms for efficient removal of ofloxacin from water using lignin-based adsorbents. *Scientific reports*, *9*(1), 1-13. https://doi.org/10.1038/s41598-018-37206-1

72. Gao, W., & Fatehi, P. (2019). Lignin for polymer and nanoparticle production: Current status and challenges. *The Canadian Journal of Chemical Engineering*, *97*(11), 2827-2842. **https://doi.org/10.1002/cjce.23620**

73. Garg, R., Garg, R., Sillanpää, M., Alimuddin, Khan, M. A., Mubarak, N. M., & Tan, Y. H. (2023). Rapid adsorptive removal of chromium from wastewater using walnut-derived biosorbents. *Scientific Reports*, *13*(1), 6859. https://doi.org/10.1038/s41598-023-33843-3

74. Ge, Y., & Li, Z. (2018). Application of lignin and its derivatives in adsorption of heavy metal ions in water: a review. *ACS Sustainable Chemistry & Engineering*, *6*(5), 7181-7192.

75. Genchi, G., Carocci, A., Lauria, G., Sinicropi, M. S., & Catalano, A. (2020). Nickel: Human health and environmental toxicology. *International journal of environmental research and public health*, *17*(3), 679. **https://doi.org/10.3390/ijerph17030679**

76. George, B., John, A. B., Priyanila, M., & Suchithra, T. V. (2023). Two-faced nanomaterials: routes to resolve nanowaste. *International Journal of Environmental Science and Technology*, *20*(5), 5643-5658.

77. Ghosh, R., Gopalakrishnan, S., Renganathan, T. *et al.* Adsorptive colorimetric determination of chromium (VI) ions at ultratrace levels using amine functionalized mesoporous silica. *Sci Rep* **12**, 5673 (2022). https://doi.org/10.1038/s41598-022-09689-6

78. Gilca, I. A., Popa, V. I., & Crestini, C. (2015). Obtaining lignin nanoparticles by sonication. *Ultrasonics sonochemistry*, *23*, 369-375. https://doi.org/10.1016/j.ultsonch.2014.08.021

79. Giri, R., Kumari, N., Behera, M., Sharma, A., Kumar, S., Kumar, N., & Singh, R. (2021). Adsorption of hexavalent chromium from aqueous solution using pomegranate peel as low-cost biosorbent. *Environmental Sustainability, 4*(2), 401-417.

80. Gupta, A. K., Mohanty, S., & Nayak, S. K. (2014). Synthesis, characterization and application of lignin nanoparticles (LNPs). *Materials Focus, 3*(6), 444-454. https://doi.org/10.1166/mat.2014.1217

81. Hafidh, A., Chaabane, H., Touati, F., & Sediri, F. (2024). Design and synthesis of novel mesostructured nanohybrid materials as antimicrobials. *Journal of Molecular Structure*, *1295*, 136611. https://doi.org/10.1016/j.molstruc.2023.136611

82. Harish, V., Ansari, M. M., Tewari, D., Yadav, A. B., Sharma, N., Bawarig, S., ... & Barhoum, A. (2023). Cutting-edge advances in tailoring size, shape, and functionality of nanoparticles and nanostructures: A review. *Journal of the Taiwan Institute of Chemical Engineers, 149*, 105010. https://doi.org/10.1016/j.jtice.2023.105010
83. Hashem, M. A., Hasan, M., Momen, M. A., Payel, S., & Nur-A-Tomal, M. S. (2020). Water hyacinth biochar for trivalent chromium adsorption from tannery wastewater. Environmental and Sustainability Indicators, 5, 100022. https://doi.org/10.1016/j.indic.2020.100022
84. Hashem, M. A., Mim, M. W., Noshin, N., & Maoya, M. (2024a). Chromium adsorption capacity from tannery wastewater on thermally activated adsorbent derived from kitchen waste biomass. *Cleaner Water*, *1*, 100001.
85. Hashem, M. A., Mim, S., Payel, S., Sakib, M. S. R., Mizan, A., Basaran, B., ... & Sarker, M. I. (2024b). Thermally activated adsorbent over chemically modified Carica papaya tree adsorbents for removal of chromium from tannery wastewater. *Bioresource Technology Reports*, *25*, 101692.
86. Hoang, M. T., Pham, T. D., Verheyen, D., Nguyen, M. K., Pham, T. T., Zhu, J., & Van der Bruggen, B. (2020). Fabrication of thin film nanocomposite nanofiltration membrane incorporated with cellulose nanocrystals for removal of Cu (II) and Pb (II). *Chemical Engineering Science, 228,* 115998. https://doi.org/10.1016/j.ces.2020.115998
87. Hokkanen, S., Bhatnagar, A., Srivastava, V., Suorsa, V., & Sillanpää, M. (2018). Removal of Cd^{2+}, Ni^{2+} and PO_4^{3-} from aqueous solution by hydroxyapatite-bentonite clay-nanocellulose composite. *International journal of biological macromolecules*, *118*, 903-912. https://doi.org/10.1016/j.ijbiomac.2018.06.095
88. Hu, S., Liu, C., Bu, H., Chen, M., & Fei, Y. H. (2024). Efficient reduction and adsorption of Cr (VI) using FeCl3-modified biochar: Synergistic roles of persistent free radicals and Fe (II). *Journal of Environmental Sciences, 137*, 626-638.

89. Hu, Y., Xue, Q., Chen, H., Guo, H., Carroll, K. C., & Wang, S. (2024). Mechanistic insight into Cr (VI) retention by Si-containing ferrihydrite. *Journal of Environmental Sciences*, *139*, 217-225.
90. Huang, D., Li, B., Ou, J., Xue, W., Li, J., Li, Z., ... & Guo, X. (2020). Megamerger of biosorbents and catalytic technologies for the removal of heavy metals from wastewater: preparation, final disposal, mechanism and influencing factors. *Journal of environmental management*, *261*, 109879. https://doi.org/10.1016/j.jenvman.2019.109879
91. Hussin, M. H., Appaturi, J. N., Poh, N. E., Abd Latif, N. H., Brosse, N., Ziegler-Devin, I., ... & Ibrahim, M. N. M. (2022). A recent advancement on preparation, characterization and application of nanolignin. *International Journal of Biological Macromolecules*.
92. Ibrahim, H., Sazali, N., Salleh, W. N. W., & Ismail, A. F. (2021). Nanocellulose-Based Materials and Recent Application for Heavy Metal Removal. *Water, Air, & Soil Pollution*, *232*(7), 1-16. https://doi.org/10.1007/s11270-021-05245-6
93. Ifthikar, J., Shahib, I. I., Jawad, A., Gendy, E. A., Wang, S., Wu, B., ... & Chen, Z. (2021). The excursion covered for the elimination of chromate by exploring the coordination mechanisms between chromium species and various functional groups. *Coordination Chemistry Reviews*, *437,* 213868. https://doi.org/10.1016/j.ccr.2021.213868
94. Imdad, S., Dohare, R. K., Agarwal, M., & Srivastava, A. (2023). Efficient removal of Cr (VI) from wastewater using recycled polymer-based supported ionic liquid membrane technology. *Separation and Purification Technology,* 124908. https://doi.org/10.1016/j.seppur.2023.124908
95. Iravani, S., & Varma, R. S. (2020). Greener synthesis of lignin nanoparticles and their applications. *Green Chemistry*, *22*(3), 612-636. **https://doi.org/10.1039/C9GC02835H**

96. Irshad, M. A., Sattar, S., Nawaz, R., Al-Hussain, S. A., Rizwan, M., Bukhari, A., ... & Zaki, M. E. (2023). Enhancing chromium removal and recovery from industrial wastewater using sustainable and efficient nanomaterial: A review. *Ecotoxicology and environmental safety*, *263*, 115231. https://doi.org/10.1016/j.ecoenv.2023.115231

97. Ismanto, A., Hadibarata, T., Widada, S., Indrayanti, E., Ismunarti, D. H., Safinatunnajah, N., ... & Alkahtani, J. (2023). Groundwater contamination status in Malaysia: level of heavy metal, source, health impact, and remediation technologies. *Bioprocess and Biosystems Engineering*, *46*(3), 467-482.

98. Iyer, M., Anand, U., Thiruvenkataswamy, S., Babu, H. W. S., Narayanasamy, A., Prajapati, V. K., ... & Vellingiri, B. (2023). A review of chromium (Cr) epigenetic toxicity and health hazards. *Science of The Total Environment*, *882*, 163483.

99. Janani, R., Gurunathan, B., Sivakumar, K., Varjani, S., Ngo, H. H., & Gnansounou, E. (2022). Advancements in heavy metals removal from effluents employing nano-adsorbents: way towards cleaner production. *Environmental Research*, *203*, 111815.

100. Jia, Z., Li, S., & Wang, L. (2018). Assessment of soil heavy metals for eco-environment and human health in a rapidly urbanization area of the upper Yangtze Basin. *Scientific reports*, *8*(1), 1-14. https://doi.org/10.1038/s41598-018-21569-6

101. Jiang, B., Jiao, H., Guo, X., Chen, G., Guo, J., Wu, W., ... & Liang, Z. (2023). Lignin-Based Materials for Additive Manufacturing: Chemistry, Processing, Structures, Properties, and Applications. *Advanced Science*, *10*(9), 2206055. https://doi.org/10.1002/advs.202206055

102. Jimenez-Paz, J., Lozada-Castro, J. J., Lester, E., Williams, O., Stevens, L., & Barraza-Burgos, J. (2023). Solutions to hazardous wastes issues in the leather industry: adsorption of Chromium iii and vi from leather industry wastewaters using activated carbons produced from leather industry solid wastes. *Journal of Environmental Chemical Engineering*, *11*(3), 109715. https://doi.org/10.1016/j.jece.2023.109715

103. Ju, T., Zhang, Z., Li, Y., Miao, X., & Ji, J. (2019). Continuous production of lignin nanoparticles using a microchannel reactor and its application in UV-shielding films. *RSC advances*, *9*(43), 24915-24921. DOI: 10.1039/C9RA05064G

104. Juikar, S. J., & Nadanathangam, V. (2020). Microbial Production of Nanolignin from Cotton Stalks and Its Application onto Cotton and Linen Fabrics for Multifunctional Properties. *Waste and Biomass Valorization*, *11*(11), 6073-6083. https://doi.org/10.1007/s12649-019-00867-8

105. Juikar, S. J., & Vigneshwaran, N. (2017a). Extraction of nanolignin from coconut fibers by controlled microbial hydrolysis. *Industrial Crops and Products*, *109*, 420-425 https://doi.org/10.1016/j.indcrop.2017.08.067

106. Juikar, S. J., & Vigneshwaran, N. (2017b). Microbial production of coconut fiber nanolignin for application onto cotton and linen fabrics to impart multifunctional properties. *Surfaces and Interfaces*, *9,* 147-153. https://doi.org/10.1016/j.surfin.2017.09.006

107. Kabir, M. M., Nahar, N., Akter, M. M., Alam, F., Gilroyed, B. H., Misu, M. M., ... & Shon, H. K. (2023). Agro-waste-based functionalized and economic adsorbents for the effective treatment of toxic contaminants from tannery effluent. *Journal of Water Process Engineering*, *52*, 103578.

108. Karlsson, M., Romson, J., Elder, T., Emmer, Å., & Lawoko, M. (2023). Lignin Structure and Reactivity in the Organosolv Process Studied by NMR Spectroscopy, Mass Spectrometry, and Density Functional Theory. *Biomacromolecules*, *24*(5), 2314-2326. https://doi.org/10.1021/acs.biomac.3c00186

109. Khan, R. J., Lau, C. Y., Farid, M. U., Islam, M. K., An, A. K., Yi, J., & Leu, S. Y. (2024). Woody biomass derived nano lignin-enabled membrane with high structural stability for efficient wastewater treatment. *Process Safety and Environmental Protection*, *182,* 595-607. https://doi.org/10.1016/j.psep.2023.12.019

110. Khulbe, K. C., & Matsuura, T. (2018). Removal of heavy metals and pollutants by membrane adsorption techniques. *Applied water science*, *8*(1), 1-30. https://doi.org/10.1007/s13201-018-0661-6

111. Kumar, A., & Kumar, V. (2023). A comprehensive review on application of lignocellulose derived nanomaterial in heavy metals removal from wastewater. *Chemistry Africa*, *6*(1), 39-78.

112. Kumar, A., & Kumar, V. Coconut Coir Derived Nanolignin for the Removal of Chromium (VI) from Aqueous Solution: Adsorption Characteristic and Mechanism. *Chemistry Africa* (2023). https://doi.org/10.1007/s42250-023-00818-w

113. Kumar, A., Kumar, V., & Singh, J. (2019). Role of fungi in the removal of heavy metals and dyes from wastewater by biosorption processes. *Recent Advancement in White Biotechnology Through Fungi: Volume 3: Perspective for Sustainable Environments*, 397-418.

114. Kumar, M., Ambika, S., Hassani, A., & Nidheesh, P. V. (2023). Waste to catalyst: role of agricultural waste in water and wastewater treatment. *Science of The Total Environment*, *858*, 159762. https://doi.org/10.1016/j.scitotenv.2022.159762

115. Kumar, N., Kardam, A., Rajawat, D. S., & Jain, V. K. (2019). Carboxymethyl nanocellulose stabilized nano zero-valent iron: an effective method for reduction of hexavalent chromium in wastewater. *Materials Research Express*, *6*(11), 1150f3.

116. Kumar, P. M., Arunthathi, S., Prasanth, S. J., Aswin, T., Antony, A. A., Daniel, D., ... & Babu, P. N. (2021). Investigation on a desiccant based solar water recuperator for generating water from atmospheric air. *Materials Today: Proceedings, 45,* 7881-7884. https://doi.org/10.1016/j.matpr.2020.12.506

117. Kumar, P., & Chauhan, M. S. (2019). Adsorption of chromium (VI) from the synthetic aqueous solution using chemically modified dried water hyacinth roots. *Journal of Environmental Chemical Engineering*, *7*(4), 103218.

118. Kumar, S., Shahnaz, T., Selvaraju, N., & Rajaraman, P. V. (2020). Kinetic and thermodynamic studies on biosorption of Cr (VI) on raw and chemically modified Datura stramonium fruit. *Environmental monitoring and assessment*, *192*(4), 1-24. https://doi.org/10.1007/s10661-020-8181-x

119. Kumaraguru, K., Saravanan, P., Rajesh Kannan, R., & Saravanan, V. (2023). A systematic analysis of hexavalent chromium adsorption and elimination from aqueous environment using brown marine algae (Turbinaria ornata). *Biomass Conversion and Biorefinery*, *13*(9), 8223-8238.

120. Lee, H. V., Hamid, S. B. A., & Zain, S. K. (2014). Conversion of lignocellulosic biomass to nanocellulose: structure and chemical process. *The Scientific World Journal*, *2014*. https://doi.org/10.1155/2014/631013

121. Li, H., Liang, J., Chen, L., Ren, M., & Zhou, C. (2023). Utilization of walnut shell by deep eutectic solvents: enzymatic digestion of cellulose and preparation of lignin nanoparticles. *Industrial Crops and Products, 192*, 116034.

122. Li, H., Liang, Y., Li, P., & He, C. (2020). Conversion of biomass lignin to high-value polyurethane: A review. *Journal of Bioresources and Bioproducts*. https://doi.org/10.1016/j.jobab.2020.07.002

123. Li, L., Liao, Q., Hou, B., He, C., Liu, J., Li, B., ... & Yang, B. (2023). Synchronous reduction and removal of hexavalent chromium from wastewater by modified magnetic chitosan beads. *Separation and Purification Technology*, *304*, 122363. https://doi.org/10.1016/j.seppur.2022.122363

124. Li, Q., Zhang, X., Zheng, J., Qin, J., Ou, C., Liao, Q., ... & Yang, W. (2024). Phase transformation of Cr (VI) host-mineral driven by citric acid-aided mechanochemical approach for advanced remediation of chromium ore processing residue-contaminated soil. *Journal of Hazardous Materials*, *461*, 132530.

125. Li, W., Chai, L., Du, B., Chen, X., & Sun, R. C. (2023). Full-Lignin-Based adsorbent for removal of Cr (VI) from waste water. *Separation and Purification Technology*, *306,* 122644. https://doi.org/10.1016/j.seppur.2022.122644

126. Li, Z., Yu, D., Wang, X., Liu, X., Xu, Z., & Wang, Y. (2024). A novel strategy of tannery sludge disposal–converting into biochar and reusing for Cr (VI) removal from tannery wastewater. *Journal of Environmental Sciences, 138,* 637-649. https://doi.org/10.1016/j.jes.2023.04.014

127. Liu, B., Xin, Y. N., Zou, J., Khoso, F. M., Liu, Y. P., Jiang, X. Y., ... & Yu, J. G. (2023). Removal of chromium species by adsorption: fundamental principles, newly developed adsorbents and future perspectives. *Molecules*, *28*(2), 639.

128. Liu, H., Zhang, F., & Peng, Z. (2019). Adsorption mechanism of Cr (VI) onto GO/PAMAMs composites. *Scientific Reports, 9*(1), 3663. https://doi.org/10.1038/s41598-019-40344-9

129. Low, L. E., Teh, K. C., Siva, S. P., Chew, I. M. L., Mwangi, W. W., Chew, C. L., ... & Tey, B. T. (2020). Lignin nanoparticles: the next green nanoreinforcer with wide opportunity. *Environmental Nanotechnology, Monitoring & Management,* 100398. https://doi.org/10.1016/j.enmm.2020.100398

130. Lu, F., & Astruc, D. (2018). Nanomaterials for removal of toxic elements from water. *Coordination Chemistry Reviews, 356,* 147-164. DOI 10.1007/s10570-017-1194-0

131. Ludvik, J., & Buljan, J. (2000). *Chrome management in the Tanyard. United Nations Industrial Development Organization: Regional Programme for Pollution Control in the Tanning Industry in South Asia*. US/RAS/92/120/11–51.

132. Luo, T., Wang, C., Ji, X., Yang, G., Chen, J., Yoo, C. G., ... & Lyu, G. (2021). Innovative production of lignin nanoparticles using deep eutectic solvents for

multifunctional nanocomposites. International Journal of Biological Macromolecules, 183, 781-789. https://doi.org/10.1016/j.ijbiomac.2021.05.005

133. Manyatshe, A., Cele, Z. E., Balogun, M. O., Nkambule, T. T., & Msagati, T. A. (2022). Lignocellulosic derivative-chitosan biocomposite adsorbents for the removal of soluble contaminants in aqueous solutions–Preparation, characterization and applications. *Journal of Water Process Engineering, 47,* 102654.

134. Mao, Y., Liu, K., Zhan, C., Geng, L., Chu, B., & Hsiao, B. S. (2017). Characterization of nanocellulose using small-angle neutron, X-ray, and dynamic light scattering techniques. The Journal of Physical Chemistry B, 121(6), 1340-1351. https://doi.org/10.1021/acs.jpcb.6b11425

135. Masinga, T., Moyo, M., & Pakade, V. E. (2022). Removal of hexavalent chromium by polyethyleneimine impregnated activated carbon: Intra-particle diffusion, kinetics and isotherms. *Journal of materials research and technology, 18*, 1333-1344. https://doi.org/10.1016/j.jmrt.2022.03.062

136. Mathai, R. V., Mitra, J. C., Sar, S. K., & Jindal, M. K. (2022). Adsorption of Chromium (VI) from aqueous phase using Aegle marmelos leaves: Kinetics, isotherm and thermodynamic studies. *Chemical Data Collections, 39*, 100871.

137. Meng, X., Poonia, M., Yoo, C. G., & Ragauskas, A. J. (2021). Recent Advances in Synthesis and Application of Lignin Nanoparticles. *Lignin Utilization Strategies: From Processing to Applications*, 273-293. **DOI:** 10.1021/bk-2021-1377.ch011

138. Menon, M. P., Selvakumar, R., & Ramakrishna, S. (2017). Extraction and modification of cellulose nanofibers derived from biomass for environmental application. *RSC advances*, *7*(68), 42750-42773. DOI: 10.1039/C7RA06713E

139. Mili, M., Hashmi, S. A. R., Tilwari, A., Rathore, S. K. S., Naik, A., Srivastava, A. K., & Verma, S. (2023). Preparation of nanolignin rich fraction from bamboo stem via green technology: assessment of its antioxidant, antibacterial and UV blocking properties. *Environmental Technology*, *44*(3), 416-430.

140. Mishra, S., Chen, S., Saratale, G. D., Saratale, R. G., Ferreira, L. F. R., Bilal, M., & Bharagava, R. N. (2021). Reduction of hexavalent chromium by Microbacterium paraoxydans isolated from tannery wastewater and characterization of its reduced

products. *Journal of Water Process Engineering*, *39*, 101748. https://doi.org/10.1016/j.jwpe.2020.101748

141. Mohanty, S., Benya, A., Hota, S., Kumar, M. S., & Singh, S. (2023). Eco-toxicity of hexavalent chromium and its adverse impact on environment and human health in Sukinda Valley of India: A review on pollution and prevention strategies. *Environmental Chemistry and Ecotoxicology*. https://doi.org/10.1016/j.enceco.2023.01.002

142. Moon, S., Lee, C. G., Shin, G. A., & Park, S. J. (2023). Efficient removal of hexavalent chromium (Cr (VI)) from wastewater using FeCl3-modified Chlorella-based biochar. *Korean Journal of Chemical Engineering*, *40*(12), 2957-2964.

143. Moreira, W. M., Moreira, P. V. V., Dos Santos, D. F., Gimenes, M. L., & Vieira, M. G. A. (2023). Nanogreen is the new future: the conversion of lignin and lignocellulosic wastes into nanomaterials. *Environmental Science and Pollution Research*, *30*(8), 19564-19591. https://doi.org/10.1007/s11356-023-25150-1

144. Moreira, W. M., Moreira, P. V. V., Dos Santos, D. F., Gimenes, M. L., & Vieira, M. G. A. (2023). Nanogreen is the new future: the conversion of lignin and lignocellulosic wastes into nanomaterials. *Environmental Science and Pollution Research*, *30*(8), 19564-19591.

145. Moubarik, A., Grimi, N., Boussetta, N., & Pizzi, A. (2013). Isolation and characterization of lignin from Moroccan sugar cane bagasse: Production of lignin–phenol-formaldehyde wood adhesive. *Industrial crops and products*, *45*, 296-302. https://doi.org/10.1016/j.indcrop.2012.12.040

146. Mouhamadou, S., Dalhatou, S., Dobe, N., Djakba, R., Fasanya, O. O., Bansod, N. D., ... & Harouna, M. (2023). Linear and non-linear modelling of kinetics and equilibrium data for Cr (VI) adsorption by activated carbon prepared from Piliostigma reticulatum. *Chemistry Africa*, *6*(2), 719-731. https://doi.org/10.1007/s42250-022-00324-5

147. Mourdikoudis, S., Pallares, R. M., & Thanh, N. T. (2018). Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties. *Nanoscale*, *10*(27), 12871-12934. DOI: 10.1039/C8NR02278J

148. Mushtaq, F., Chen, X. Z., Veciana, A., Hoop, M., Nelson, B. J., & Pané, S. (2022). Magnetoelectric reduction of chromium (VI) to chromium (III). *Applied Materials Today, 26*, 101339.

149. Muthusaravanan, S., Sivarajasekar, N., Vivek, J. S., Paramasivan, T., Naushad, M., Prakashmaran, J., ... & Al-Duaij, O. K. (2018). Phytoremediation of heavy metals: mechanisms, methods and enhancements. *Environmental chemistry letters*, *16*(4), 1339-1359. https://doi.org/10.1007/s10311-018-0762-3

150. Nagpal, G., Kaushik, A., Gupta, P., Masri, M. N., Yahya, M. Z. A., & Diantoro, M. (2023). Effective removal of Cr (VI) ions from aqueous solution using low-cost adsorbents (orange mesocarp, Bengal gram husk, and Khangar): equilibrium, kinetic, and thermodynamic study. *Biomass Conversion and Biorefinery*, 1-14. https://doi.org/10.1007/s13399-023-04473-6

151. Narayanan, I., Kumar, P. S., Franco, D. S., Georgin, J., Meili, L., & Selvasembian, R. (2023). Insight into the biosorptive removal mechanisms of hexavalent chromium using the red macroalgae Gelidium sp. *Biomass Conversion and Biorefinery*, 1-15. https://doi.org/10.1007/s13399-023-04390-8

152. Nawaz, A., Singh, B., & Kumar, P. (2023). H3PO4-modified Lagerstroemia speciosa seed hull biochar for toxic Cr (VI) removal: isotherm, kinetics, and thermodynamic study. *Biomass Conversion and Biorefinery*, *13*(8), 7027-7041.

153. Nguyen-Thi, N. Y., Nguyen, C. Q., Le Dang, Q., De Tran, Q., Do-Thi, T. N., & Thanh, L. H. V. (2024). Extracting lignin from sugarcane bagasse for methylene blue and hexavalent chromium adsorption in textile wastewater: a facile, green, and sustainable approach. *RSC advances*, *14*(7), 4533-4542.

154. Nigam, M., Rajoriya, S., Singh, S. R., & Kumar, P. (2019). Adsorption of Cr (VI) ion from tannery wastewater on tea waste: kinetics, equilibrium and thermodynamics studies. *Journal of Environmental Chemical Engineering*, *7*(3), 103188. https://doi.org/10.1016/j.jece.2019.103188

155. Oladipo, A. A. (2018). MIL-53 (Fe)-based photo-sensitive composite for degradation of organochlorinated herbicide and enhanced reduction of Cr (VI). *Process Safety and Environmental Protection*, *116*, 413-423. https://doi.org/10.1016/j.psep.2018.03.011

156. Oladipo, A. A., Ahaka, E. O., & Gazi, M. (2019). High adsorptive potential of calcined magnetic biochar derived from banana peels for Cu2+, Hg2+, and Zn2+ ions removal in single and ternary systems. *Environmental Science and Pollution Research*, *26*(31), 31887-31899. https://doi.org/10.1007/s11356-019-06321-5

157. Onkarappa, H. S., Prakash, G. K., Pujar, G. H., Rajith Kumar, C. R., & Betageri, V. S. (2020). Facile synthesis and characterization of nanocellulose from Zea mays husk. *Polymer Composites*, *41*(8), 3153-3159. **https://doi.org/10.1002/pc.25606**

158. Padmavathy, K. S., Madhu, G., & Haseena, P. V. (2016). A study on effects of pH, adsorbent dosage, time, initial concentration and adsorption isotherm study for the removal of hexavalent chromium (Cr (VI)) from wastewater by magnetite nanoparticles. *Procedia Technology*, *24*, 585-594.

159. Pagala, B. (2023). Biosorption of Chromium and Lead from Electroplating Industry Effluent Using Modified Cane Bagasse. *Journal of The Institution of Engineers (India): Series D*, 1-12.

160. Paithankar, J. G., Saini, S., Dwivedi, S., Sharma, A., & Chowdhuri, D. K. (2021). Heavy metal associated health hazards: An interplay of oxidative stress and signal transduction. *Chemosphere*, *262*, 128350. https://doi.org/10.1016/j.chemosphere.2020.128350

161. Pang, Y., Zhao, C., Li, Y. *et al.* Cadmium adsorption performance and mechanism from aqueous solution using red mud modified with amorphous MnO_2. *Sci Rep* **12,** 4424 (2022). https://doi.org/10.1038/s41598-022-08451-2

162. Parvathy, G., Sethulekshmi, A. S., Jayan, J. S., Raman, A., & Saritha, A. (2020). Lignin based Nanocomposites: Synthesis and Applications. *Process Safety and Environmental Protection*. https://doi.org/10.1016/j.psep.2020.11.017

163. Paul, A., Dey, S., Ram, D. K., & Das, A. P. (2023). Hexavalent chromium pollution and its sustainable management through bioremediation. *Geomicrobiology Journal*, 1-11.

164. Pavaneli, G., da Silva, T. A., Zawadzki, S. F., Sassaki, G. L., de Freitas, R. A., & Ramos, L. P. (2024). Production of highly antioxidant lignin nanoparticles from a hardwood technical lignin. *International Journal of Biological Macromolecules*, *257*, 128612.

165. Pei, X., Gan, L., Tong, Z., Gao, H., Meng, S., Zhang, W., ... & Chen, Y. (2021). Robust cellulose-based composite adsorption membrane for heavy metal removal. *Journal of Hazardous Materials, 406,* 124746. https://doi.org/10.1016/j.jhazmat.2020.124746

166. Peng, B., Zhou, R., Chen, Y., Tu, S., Yin, Y., & Ye, L. (2020). Immobilization of nano-zero-valent irons by carboxylated cellulose nanocrystals for wastewater remediation. *Frontiers of Chemical Science and Engineering*, *14*(6), 1006-1017. https://doi.org/10.1007/s11705-020-1924-y

167. Perera, H. M., Rajapaksha, A. U., Liyanage, S., Ekanayake, A., Selvasembian, R., Daverey, A., & Vithanage, M. (2023). Enhanced adsorptive removal of hexavalent chromium in aqueous media using chitosan-modified biochar: Synthesis, sorption mechanism, and reusability. *Environmental Research*, *231*, 115982.

168. Perera, U. P., Foo, M. L., & Chew, I. M. L. (2023). Synthesis and characterization of lignin nanoparticles isolated from oil palm empty fruit bunch and application in biocomposites. *Sustainable Chemistry for Climate Action, 2,* 100011. https://doi.org/10.1016/j.scca.2022.100011

169. Pezeshki, H., Hashemi, M., & Rajabi, S. (2023). Removal of arsenic as a potentially toxic element from drinking water by filtration: A mini review of nanofiltration and reverse osmosis techniques. *Heliyon*.

170. Ponomarev, N., Pastushok, O., Repo, E., Doshi, B., & Sillanpää, M. (2019). Lignin-Based Magnesium Hydroxide Nanocomposite. Synthesis and Application for

the Removal of Potentially Toxic Metals from Aqueous Solution. *ACS Applied Nano Materials*, *2*(9), 5492-5503. https://doi.org/10.1021/acsanm.9b01083

171. Pylypchuk, I. V., Lindén, P. A., Lindström, M. E., & Sevastyanova, O. (2020). New insight into the surface structure of lignin nanoparticles revealed by 1H liquid-state NMR spectroscopy. *ACS Sustainable Chemistry & Engineering*, *8*(36), 13805-13812. https://doi.org/10.1021/acssuschemeng.0c05119

172. Qasem, N.A.A., Mohammed, R.H. & Lawal, D.U. Removal of heavy metal ions from wastewater: a comprehensive and critical review. *npj Clean Water* **4,** 36 (2021). https://doi.org/10.1038/s41545-021-00127-0

173. Qi, G., Yang, W., Puglia, D., Wang, H., Xu, P., Dong, W., ... & Ma, P. (2020). Hydrophobic, UV resistant and dielectric polyurethane-nanolignin composites with good reprocessability. Materials & Design, 196, 109150.

174. Qi, J., Li, B., Zhou, P., Su, X., Yang, D., Wu, J., ... & Liang, X. (2023). Study on adsorption of hexavalent chromium by composite material prepared from iron-based solid wastes. *Scientific Reports*, *13*(1), 135. https://doi.org/10.1038/s41598-023-27414-9

175. Rahman, Z., & Singh, V. P. (2019). The relative impact of toxic heavy metals (THMs)(arsenic (As), cadmium (Cd), chromium (Cr)(VI), mercury (Hg), and lead (Pb)) on the total environment: an overview. *Environmental monitoring and assessment*, *191*(7), 1-21. https://doi.org/10.1007/s10661-019-7528-7

176. Rai, R., Aryal, R. L., Paudyal, H., Gautam, S. K., Ghimire, K. N., Pokhrel, M. R., & Poudel, B. R. (2023). Acid-treated pomegranate peel; An efficient biosorbent for the excision of hexavalent chromium from wastewater. *Heliyon*, *9*(5).

177. Rajendran, S., Priya, A. K., Kumar, P. S., Hoang, T. K., Sekar, K., Chong, K. Y., ... & Show, P. L. (2022). A critical and recent developments on adsorption technique for removal of heavy metals from wastewater-A review. *Chemosphere*, 135146. https://doi.org/10.1016/j.chemosphere.2022.135146

178. Ramraj, S. M., Kubaib, A., Imran, P. M., & Thirupathy, M. K. (2023). Utilizing Sida Acuta leaves for low-cost adsorption of chromium (VI) heavy metal with activated charcoal. *Journal of Hazardous Materials Advances*, *11*, 100338.

179. Rani, M., & Shanker, U. (2022). Remediation of Chromium Heavy Metal Ion by Green Synthesized Nanocomposites. In *Handbook of Green and Sustainable Nanotechnology: Fundamentals, Developments and Applications* (pp. 1-30). Cham: Springer International Publishing. https://doi.org/10.1007/978-3-030-69023-6_49-2

180. Rashid, R., Shafiq, I., Akhter, P., Iqbal, M. J., & Hussain, M. (2021). A state-of-the-art review on wastewater treatment techniques: the effectiveness of adsorption method. *Environmental Science and Pollution Research*, 1-17. https://doi.org/10.1007/s11356-021-12395-x

181. Rekha, A., Srinivasan, L., Pavithra, S., Gomathi, T., Sudha, P. N., Lavanya, G., ... & Vidhya, A. (2023). Biosorption efficacy studies of Sargassum wightii and its biochar on the removal of chromium from aqueous solution. *Journal of the Taiwan Institute of Chemical Engineers*, 105241.

182. Richter, A. P., Bharti, B., Armstrong, H. B., Brown, J. S., Plemmons, D., Paunov, V. N., ... & Velev, O. D. (2016). Synthesis and characterization of biodegradable lignin nanoparticles with tunable surface properties. *Langmuir*, *32*(25), 6468-6477. https://doi.org/10.1021/acs.langmuir.6b01088

183. Rismawati, R., Nurdin, I. A., Pradiptha, M. N., Maulidiyah, A., & Mubarakati, N. J. (2020,). Preparation and characterization of lignin nanoparticles from rice straw after biosynthesis using Lactobacillus bulgaricus. In *Journal of Physics: Conference Series* (Vol. 1524, No. 1, p. 012070). IOP Publishing. doi:10.1088/1742-6596/1524/1/012070

184. Roy, A., Sharma, A., Yadav, S., Jule, L. T., & Krishnaraj, R. (2021). Nanomaterials for remediation of environmental pollutants. *Bioinorganic Chemistry and Applications*, *2021*. https://doi.org/10.1155/2021/1764647

185. Ruthran, V. B.; Barman, P.; Kadam, R.; Kumar, A. Lignin-based adsorbent for effective removal of toxic heavy metals from wastewater. *Emergent Mater.* **2022**, *5*, 923– 943, DOI: 10.1007/s42247-021-00311-5

186. Rzig, B., Guesmi, F., Sillanpää, M., & Hamrouni, B. (2022). Biosorption potential of olive leaves as a novel low-cost adsorbent for the removal of hexavalent chromium from wastewater. *Biomass Conversion and Biorefinery*, 1-19. https://doi.org/10.1007/s13399-022-03356-6

187. Saad, E. M., Abd-Elhafiz, M. F., Ahmed, E. M., & Markeb, A. A. (2024). Hexavalent chromium ion removal from wastewater using novel nanocomposite based on the impregnation of zero-valent iron nanoparticles into polyurethane foam. *Scientific Reports*, *14*(1), 5387.

188. Sabaruddin, F. A., Megashah, L. N., Shazleen, S. S., & Ariffin, H. (2023). Emerging trends in the appliance of ultrasonic technology for valorization of agricultural residue into versatile products. *Ultrasonics Sonochemistry,* 106572.

189. Saha, B., Amine, A., & Verpoort, F. (2022). Hexavalent Chromium: Sources, Toxicity, and Remediation. *Chemistry Africa*, *5*(6), 1779-1780. **https://doi.org/10.1007/s42250-022-00443-z**

190. Sajjadi, M., Ahmadpoor, F., Nasrollahzadeh, M., & Ghafuri, H. (2021). Lignin-derived (nano) materials for environmental pollution remediation: Current challenges and future perspectives. *International Journal of Biological Macromolecules*. https://doi.org/10.1016/j.ijbiomac.2021.02.165

191. Sakthivel, S., Muthusamy, K., Thangarajan, A. P., Thiruvengadam, M., & Venkidasamy, B. (2024). Nano-based biofuel production from low-cost lignocellulose biomass: environmental sustainability and economic approach. *Bioprocess and Biosystems Engineering*, 1-20.

192. Sall, M. L., Diaw, A. K. D., Gningue-Sall, D., Efremova Aaron, S., & Aaron, J. J. (2020). Toxic heavy metals: impact on the environment and human health, and treatment with conducting organic polymers, a review. *Environmental Science and Pollution Research*, *27,* 29927-29942. https://doi.org/10.1007/s11356-020-09354-3

193. Santander, P., Butter, B., Oyarce, E., Yáñez, M., Xiao, L. P., & Sánchez, J. (2021). Lignin-based adsorbent materials for metal ion removal from wastewater: A review. *Industrial Crops and Products*, *167*, 113510. https://doi.org/10.1016/j.indcrop.2021.113510

194. Saouli, A., Adjroud, O., Ncir, M., Bachir, A., & El Feki, A. (2023). Attenuating effects of selenium and zinc against hexavalent chromium-induced oxidative stress, hormonal instability, and placenta damage in preimplanted rats. *Environmental Science and Pollution Research*, *30*(21), 60050-60079. https://doi.org/10.1007/s11356-023-26700-3

195. Saran Kumar, R. K., Selvi, A., Murugan, K., & Rajasekar, A. (2020). Electrokinetic (EK) and bio-electrokinetic (BEK) remediation of hexavalent chromium in contaminated soil using alkalophilic bio-anolyte. *Indian Geotechnical Journal*, *50*, 330-338. https://doi.org/10.1007/s40098-019-00366-6

196. Saravanan, R., Sathish, T., Sharma, K., Rao, A. V., Sathyamurthy, R., Panchal, H., & Zahra, M. M. A. (2023). Sustainable wastewater treatment by RO and hybrid organic polyamide membrane nanofiltration system for clean environment. *Chemosphere*, 139336. https://doi.org/10.1016/j.chemosphere.2023.139336

197. Sarfraz, S., Ameer, S., Javed, M., Iqbal, S., Aljazzar, S. O., Zahra, M., ... & Ibrahium, H. A. (2022). Removal of hexavalent chromium ions using micellar modified adsorbent: isothermal and kinetic investigations. *RSC advances*, *12*(37), 23898-23911 DOI: 10.1039/D2RA03906K

198. Sathya, R., Arasu, M. V., Al-Dhabi, N. A., Vijayaraghavan, P., Ilavenil, S., & Rejiniemon, T. S. (2023). Towards sustainable wastewater treatment by biological methods–A challenges and advantages of recent technologies. *Urban Climate*, *47*, 101378.

199. Sbihi, K., Elhamji, S., Lghoul, S., Aziz, K., El Maallem, A., Mabrouki, J., ... & Aziz, F. (2024). Biosorption of Hexavalent Chromium by Freshwater Microalgae Craticula subminuscula from Aqueous Solutions. *Sustainability*, *16*(2), 918.

200. Schneider, W. D. H., Dillon, A. J. P., & Camassola, M. (2021). Lignin nanoparticles enter the scene: A promising versatile green tool for multiple

applications. *Biotechnology Advances*, *47,* 107685. https://doi.org/10.1016/j.biotechadv.2020.107685

201. Scimeca, M., Bischetti, S., Lamsira, H. K., Bonfiglio, R., & Bonanno, E. (2018). Energy Dispersive X-ray (EDX) microanalysis: A powerful tool in biomedical research and diagnosis. *European journal of histochemistry: EJH*, *62*(1). doi: 10.4081/ejh.2018.2841

202. Sebabi, M. O., Mabuba, N., Pillay, K., & Malinga, S. P. (2024). Hyperbranched-Polyethylenimine-Functionalized Coal Fly Ash as an Adsorbent for the Removal of Hexavalent Chromium and Reuse as a Dye Photocatalyst. *ACS omega*.

203. Shaibur, M. R., Tanzia, F. S., Nishi, S., Nahar, N., Parvin, S., & Adjadeh, T. A. (2022). Removal of Cr (VI) and Cu (II) from tannery effluent with water hyacinth and arum shoot powders: A study from Jashore, Bangladesh. *Journal of Hazardous Materials Advances*, *7*, 100102.

204. Shakya, A., & Agarwal, T. (2019). Removal of Cr (VI) from water using pineapple peel derived biochars: Adsorption potential and re-usability assessment. *Journal of molecular liquids*, *293*, 111497.

205. Sharma, M., Marques, J., Simões, A., Donato, M. M., Cardoso, O., & Gando-Ferreira, L. M. (2024). Optimization of lignin precipitation from black liquor using organic acids and its valorization by preparing lignin nanoparticles. *International Journal of Biological Macromolecules*, 131881.

206. Sharma, S., Kachhia, P., Shukla, V., Patel, A., Rathod, V., & Narra, M. (2022). Valorization of lignin into nanoparticles and nanogel: Characterization and application. *Bioresource Technology Reports*, *18,* 101041. https://doi.org/10.1016/j.biteb.2022.101041

207. Sharma, S., Kaur, A., Kumar, S., Pathania, K., Kumar, K., Arora, A., ... & Pawar, S. V. (2023). Lignin nanoparticles as a novel carrier for efficacious delivery of toll like receptor 7/8 agonist: Physicochemical and in-vitro evaluation. *Journal of the Indian Chemical Society*, *100*(5), 101008. https://doi.org/10.1016/j.jics.2023.101008

208. Silva, M., & Baltrusaitis, J. (2020). A review of phosphate adsorption on Mg-containing materials: kinetics, equilibrium, and mechanistic insights. *Environmental Science: Water Research & Technology* **https://doi.org/10.1039/D0EW00679C**

209. Singh, A., Pal, D. B., Kumar, S., Srivastva, N., Syed, A., Elgorban, A. M., ... & Gupta, V. K. (2021). Studies on Zero-cost algae based phytoremediation of dye and heavy metal from simulated wastewater. *Bioresource technology*, *342*, 125971.https://doi.org/10.1016/j.biortech.2021.125971

210. Singh, K., Azad, S. K., Dave, H., Prasad, B., Maurya, D. M., Kumari, M., ... & Prasad, K. S. (2023). Effective removal of Cr (VI) ions from the aqueous solution by agro-waste-based biochar: an exploration of batch and column studies. *Biomass Conversion and Biorefinery*, 1-15. https://doi.org/10.1007/s13399-023-04268-9

211. Singh, S., Anil, A. G., Naik, T. S. S. K., U., B., Khasnabis, S., Nath, B., Kumar, V., Subramanian, S., Singh, J., & Ramamurthy, P. C. (2022). Mechanism and kinetics of Cr(VI) adsorption on biochar derived from Citrobacter freundii under different pyrolysis temperatures. *Journal of Water Process Engineering*, *47*, 102723. https://doi.org/10.1016/J.JWPE.2022.102723

212. Singh, S., Naik, T. S. S. K., Anil, A. G., Khasnabis, S., Nath, B., U, B., Kumar, V., Garg, V. K., Subramanian, S., Singh, J., & Ramamurthy, P. C. (2022). A novel CaO nanocomposite cross linked graphene oxide for Cr(VI) removal and sensing from wastewater. *Chemosphere*, *301*, 134714. https://doi.org/10.1016/J.CHEMOSPHERE.2022.134714

213. Singh, S., Naik, T. S. S. K., Thamaraiselvan, C., Behera, S. K., N, P., Nath, B., Dwivedi, P., Singh, J., & Ramamurthy, P. C. (2023). Applicability of new sustainable and efficient green metal-based nanoparticles for removal of Cr(VI): Adsorption anti-microbial, and DFT studies. *Environmental Pollution*, *320*, 121105. https://doi.org/10.1016/J.ENVPOL.2023.121105

214. Singh, Simranjeet, Amith G. Anil, Sutripto Khasnabis, Vijay Kumar, Bidisha Nath, Varun Adiga, TS Sunil Kumar Naik et al. "Sustainable removal of Cr (VI) using graphene oxide-zinc oxide nanohybrid: Adsorption kinetics, isotherms and thermodynamics." *Environmental Research* 203 (2022): 111891. https://doi.org/10.1016/j.envres.2021.111891

215. Sinha, R., Kumar, R., Abhishek, K., Shang, J., Bhattacharya, S., Sengupta, S., ... & Sharma, P. (2022). Single-step synthesis of activated magnetic biochar derived from rice husk for hexavalent chromium adsorption: equilibrium mechanism, kinetics, and thermodynamics analysis. *Groundwater for Sustainable Development*, *18*, 100796. https://doi.org/10.1016/j.gsd.2022.100796

216. Sipponen, M. H., Lange, H., Crestini, C., Henn, A., & Österberg, M. (2019). Lignin for nano-and microscaled carrier systems: Applications, trends, and challenges. *ChemSusChem*, *12*(10), 2039. doi: 10.1002/cssc.201900480

217. Sobhanardakani, S., Tayebi, L., & Hosseini, S. V. (2018). Health risk assessment of arsenic and heavy metals (Cd, Cu, Co, Pb, and Sn) through consumption of caviar of Acipenser persicus from Southern Caspian Sea. *Environmental Science and Pollution Research*, *25*(3), 2664-2671. https://doi.org/10.1007/s11356-017-0705-8

218. Sohni, S., Hassan, T., Khan, S. B., Akhtar, K., Bakhsh, E. M., Hashim, R., ... & Khan, S. A. (2023). Lignin nanoparticles-reduced graphene oxide based hydrogel: A novel strategy for environmental applications. *International journal of biological macromolecules*, *225*, 1426-1436.

219. Soliman, N. K., & Moustafa, A. F. (2020). Industrial solid waste for heavy metals adsorption features and challenges; a review. *Journal of Materials Research and Technology*, *9*(5), 10235-10253. https://doi.org/10.1016/j.jmrt.2020.07.045

220. Song, Y. H., Chakraborty, G., Mahata, M. K., & De, R. (2024). Functionalized nanomaterials: health and safety. In *Functionalized Nanomaterials for Cancer Research* (pp. 561-577). Academic Press.

221. Tabassum, R. A., Shahid, M., Dumat, C., Niazi, N. K., Khalid, S., Shah, N. S., ... & Khalid, S. (2019). Health risk assessment of drinking arsenic-containing groundwater in Hasilpur, Pakistan: effect of sampling area, depth, and source. *Environmental Science and Pollution Research*, *26*(20), 20018-20029. https://doi.org/10.1007/s11356-018-1276-z

222. Tahoon, M. A., Siddeeg, S. M., Salem Alsaiari, N., Mnif, W., & Ben Rebah, F. (2020). Effective heavy metals removal from water using nanomaterials: A review. *Processes*, *8*(6), 645. **https://doi.org/10.3390/pr8060645**

223. Tan, K. L., & Hameed, B. H. (2017). Insight into the adsorption kinetics models for the removal of contaminants from aqueous solutions. *Journal of the Taiwan Institute of Chemical Engineers*, *74*, 25-48. https://doi.org/10.1016/j.jtice.2017.01.024

224. Thakur, A., Kumar, A., & Singh, A. (2024). Adsorptive removal of heavy metals, dyes, and pharmaceuticals: Carbon-based nanomaterials in focus. *Carbon, 217,* 118621.

225. Theivasanthi, T., Christma, F. A., Toyin, A. J., Gopinath, S. C., & Ravichandran, R. (2018). Synthesis and characterization of cotton fiber-based nanocellulose. *International journal of biological macromolecules*, *109,* 832-836. https://doi.org/10.1016/j.ijbiomac.2017.11.054

226. Thilakarathna, R. C. N., Siow, L. F., Tang, T. K., & Lee, Y. Y. (2023). A review on application of ultrasound and ultrasound assisted technology for seed oil extraction. *Journal of food science and technology, 60*(4), 1222-1236.

227. Tian, D., Hu, J., Bao, J., Chandra, R. P., Saddler, J. N., & Lu, C. (2017). Lignin valorization: Lignin nanoparticles as high-value bio-additive for multifunctional nanocomposites. *Biotechnology for biofuels*, *10*(1), 1-11. https://doi.org/10.1186/s13068-017-0876-z

228. Tian, G., Zhong, X., Wu, X., & Wang, Z. (2021). Self-Assembly Preparation of Nano-Lignin/Cationic Polyacrylamide Complexes. Polymers, 13(11), 1726.

229. Tran, H. N., You, S. J., Hosseini-Bandegharaei, A., & Chao, H. P. (2017). Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: a critical review. *Water research*, *120,* 88-116. https://doi.org/10.1016/j.watres.2017.04.014

230. Tripathy, S., Sahu, S., Patel, R. K., Panda, R. B., & Kar, P. K. (2021). Efficient removal of Cr (VI) by polyaniline-modified biochar from date (Phoenix dactylifera) seed. *Groundwater for Sustainable Development, 15,* 100653.

231. Van, H. T., Nguyen, L. H., Mac, D. H., Vu, T. T., Ha, L. T., & Nguyen, X. C. (2019). Removal of Cr (vi) from aqueous solution using magnetic modified biochar derived from raw corncob. *New Journal of Chemistry, 43*(47), 18663-18672.

232. Vickram, A. S., Kumar, G., Dey, N., Karunakaran, R., Anbarasu, K., Patel, A. K., ... & Ponnusamy, V. K. (2023). Valorization of nano-based lignocellulosic

derivatives to procure commercially significant value-added products for biomedical applications. *Environmental research*, *216*, 114400.

233. Vijayaram, S., Razafindralambo, H., Sun, Y. Z., Vasantharaj, S., Ghafarifarsani, H., Hoseinifar, S. H., & Raeeszadeh, M. (2023). Applications of Green Synthesized Metal Nanoparticles—A Review. *Biological Trace Element Research*, 1-27. https://doi.org/10.1007/s12011-023-03645-9

234. Wang, B., Lan, J., Bo, C., Gong, B., & Ou, J. (2023). Adsorption of heavy metal onto biomass-derived activated carbon. *RSC advances*, *13*(7), 4275-4302.

235. Wang, B., Sun, D., Wang, H. M., Yuan, T. Q., & Sun, R. C. (2018). Green and facile preparation of regular lignin nanoparticles with high yield and their natural broad-spectrum sunscreens. *ACS sustainable chemistry & engineering*, *7*(2), 2658-2666. https://doi.org/10.1021/acssuschemeng.8b05735

236. Wang, S., & Ali, N. (2023). Spherical lignin nanostructures synthesis, functionalization, and removal of cationic dyes. *Journal of Water Process Engineering*, *54*, 103924. https://doi.org/10.1016/j.jwpe.2023.103924

237. Wang, X., Li, X., Peng, L., Han, S., Hao, C., Jiang, C., ... & Fan, X. (2021). Effective removal of heavy metals from water using porous lignin-based adsorbents. *Chemosphere*, *279*, 130504.

238. Watkins, D., Nuruddin, M., Hosur, M., Tcherbi-Narteh, A., & Jeelani, S. (2015). Extraction and characterization of lignin from different biomass resources. *Journal of Materials Research and Technology*, *4*(1), 26-32.

239. Wijaya, C. J., Ismadji, S., & Gunawan, S. (2021). A Review of Lignocellulosic-Derived Nanoparticles for Drug Delivery Applications: Lignin Nanoparticles, Xylan Nanoparticles, and Cellulose Nanocrystals. *Molecules*, *26*(3), 676. **https://doi.org/10.3390/molecules26030676**

240. Worku, L. A., Bachheti, R. K., Tadesse, M. G., Bachheti, A., Ali, D., Kumar, G., ... & Almarzoug, M. H. (2023). Synthesis of lignin nanoparticles from Oxytenanthera abyssinica by nanoprecipitation method followed by ultrasonication for the nanocomposite application. Journal of King Saud University-Science, 35(7), 102793.

241. Wu, C., McClements, D. J., He, M., Zheng, L., Tian, T., Teng, F., & Li, Y. (2021). Preparation and characterization of okara nanocellulose fabricated using sonication or high-pressure homogenization treatments. *Carbohydrate Polymers*, *255*, 117364. https://doi.org/10.1016/j.carbpol.2020.117364

242. Wu, Z., Zhang, H., Ali, E., Shahab, A., Huang, H., Ullah, H., & Zeng, H. (2023). Synthesis of novel magnetic activated carbon for effective Cr (VI) removal via synergistic adsorption and chemical reduction. *Environmental Technology & Innovation*, *30*, 103092.

243. Xiao, D., Ding, W., Zhang, J., Ge, Y., Wu, Z., & Li, Z. (2019). Fabrication of a versatile lignin-based nano-trap for heavy metal ion capture and bacterial inhibition. *Chemical Engineering Journal*, *358*, 310-320. https://doi.org/10.1016/j.cej.2018.10.037

244. Yadav, A., Raghav, S., Srivastava, A., Jangid, N. K., & Srivastava, M. (2024). Comparative Study of Nickel-Iron Composite with Fe3O4 Nanoparticles for the Adsorption of Chromium from Aqueous Medium. *Water, Air, & Soil Pollution*, *235*(4), 1-22.

245. Yang, W., Rallini, M., Natali, M., Kenny, J., Ma, P., Dong, W., ... & Puglia, D. (2019). Preparation and properties of adhesives based on phenolic resin containing lignin micro and nanoparticles: A comparative study. Materials & Design, 161, 55-63.

246. Ye, J., Wang, Y., Xu, Q., Wu, H., Tong, J., & Shi, J. (2021). Removal of hexavalent chromium from wastewater by Cu/Fe bimetallic nanoparticles. *Scientific Reports*, *11*(1), 10848.https://doi.org/10.1038/s41598-021-90414-0

247. Yin, H., Liu, L., Wang, X., Wang, T., Zhou, Y., Liu, B., ... & Lü, X. (2018). A novel flocculant prepared by lignin nanoparticles-gelatin complex from switchgrass for the capture of Staphylococcus aureus and Escherichia coli. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *545*, 51-59. https://doi.org/10.1016/j.colsurfa.2018.02.033

248. Ying, S., Guan, Z., Ofoegbu, P. C., Clubb, P., Rico, C., He, F., & Hong, J. (2022). Green synthesis of nanoparticles: Current developments and limitations. *Environmental Technology & Innovation*, *26*, 102336. https://doi.org/10.1016/j.eti.2022.102336

249. Yoganand, K. S., & Umapathy, M. J. (2017). Green methodology for the recovery of Cr (VI) from tannery effluent using newly synthesized quaternary ammonium salt. *Arabian Journal of Chemistry*, *10*, S1227-S1234. https://doi.org/10.1016/j.arabjc.2013.02.022

250. Younesi-Kordkheili, H., & Pizzi, A. (2023). Improving the properties of phenol-lignin-glyoxal as a wood adhesive by lignin nanoparticles. *European Journal of Wood and Wood Products*, *81*(2), 507-512. https://doi.org/10.1007/s00107-022-01904-5

251. Zhang, Z., Terrasson, V., & Guénin, E. (2021). Lignin nanoparticles and their nanocomposites. *Nanomaterials*, *11*(5), 1336. **https://doi.org/10.3390/nano11051336**

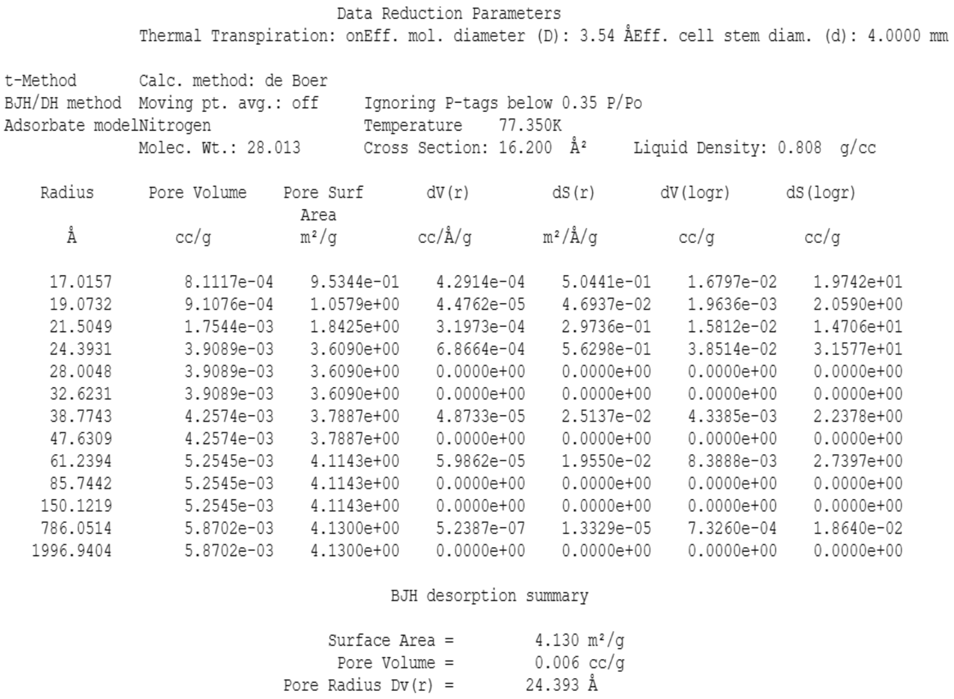
252. Zhao, M., Wang, X., Wang, S., & Gao, M. (2024). Cr-containing wastewater treatment based on Cr self-catalysis: a critical review. *Frontiers of Environmental Science & Engineering*, *18*(1), 1.

253. Zou, T., Sipponen, M. H., Henn, A., & Österberg, M. (2021). Solvent-Resistant Lignin-Epoxy Hybrid Nanoparticles for Covalent Surface Modification and High-Strength Particulate Adhesives. *ACS nano*, *15*(3), 4811-4823. https://doi.org/10.1021/acsnano.0c09500

254. Zuo, C., Xu, Y., Hui, X. Y., Xu, L. H., Wen, J. L., & Yuan, T. Q. (2024). Cascade fractionation of bamboo shoot shells into high-yield xylose, easily digestible cellulose and high-quality lignin nanoparticles by tailored catalytic hydrothermal–hydrated alkaline deep eutectic solvents pretreatment. *Chemical Engineering Journal*, 149622.

APPENDIX A

BET Analysis



```
                                     Data Reduction Parameters
               Thermal Transpiration: onEff. mol. diameter (D): 3.54 ÅEff. cell stem diam. (d): 4.0000 mm

t-Method       Calc. method: de Boer
BJH/DH method  Moving pt. avg.: off     Ignoring P-tags below 0.35 P/Po
Adsorbate modelNitrogen                 Temperature    77.350K
               Molec. Wt.: 28.013       Cross Section: 16.200  Å²     Liquid Density: 0.808  g/cc

    Radius      Pore Volume    Pore Surf       dV(r)         dS(r)       dV(logr)      dS(logr)
                                 Area
       Å           cc/g          m²/g         cc/Å/g        m²/Å/g         cc/g          cc/g

     17.0157        8.1117e-04    9.5344e-01    4.2914e-04    5.0441e-01    1.6797e-02    1.9742e+01
     19.0732        9.1076e-04    1.0579e+00    4.4762e-05    4.6937e-02    1.9636e-03    2.0590e+00
     21.5049        1.7544e-03    1.8425e+00    3.1973e-04    2.9736e-01    1.5812e-02    1.4706e+01
     24.3931        3.9089e-03    3.6090e+00    6.8664e-04    5.6298e-01    3.8514e-02    3.1577e+01
     28.0048        3.9089e-03    3.6090e+00    0.0000e+00    0.0000e+00    0.0000e+00    0.0000e+00
     32.6231        3.9089e-03    3.6090e+00    0.0000e+00    0.0000e+00    0.0000e+00    0.0000e+00
     38.7743        4.2574e-03    3.7887e+00    4.8733e-05    2.5137e-02    4.3385e-03    2.2378e+00
     47.6309        4.2574e-03    3.7887e+00    0.0000e+00    0.0000e+00    0.0000e+00    0.0000e+00
     61.2394        5.2545e-03    4.1143e+00    5.9862e-05    1.9550e-02    8.3888e-03    2.7397e+00
     85.7442        5.2545e-03    4.1143e+00    0.0000e+00    0.0000e+00    0.0000e+00    0.0000e+00
    150.1219        5.2545e-03    4.1143e+00    0.0000e+00    0.0000e+00    0.0000e+00    0.0000e+00
    786.0514        5.8702e-03    4.1300e+00    5.2387e-07    1.3329e-05    7.3260e-04    1.8640e-02
   1996.9404        5.8702e-03    4.1300e+00    0.0000e+00    0.0000e+00    0.0000e+00    0.0000e+00

                                           BJH desorption summary

                                    Surface Area =         4.130 m²/g
                                     Pore Volume =         0.006 cc/g
                               Pore Radius Dv(r) =        24.393 Å
```

APPENDIX B

LIST OF PUBLICATIONS

i. Kumar, A., & Kumar, V. (2023). Coconut coir derived nanolignin for the removal of chromium (VI) from aqueous solution: Adsorption Characteristic and Mechanism. *Chemistry Africa*, *7*(2), 953-968.https://doi.org/10.1007/s42250-023-00818-w [SJR: 0.353, Q:3, IF: 2.6, Publisher : Springer Nature]

ii. Kumar, A., & Kumar, V. (2022). A comprehensive review on application of lignocellulose derived nanomaterial in heavy metals removal from wastewater. *Chemistry Africa*, *6*(1), 39-78. https://doi.org/10.1007/s42250-022-00367-8. [SJR: 0.353, Q:3, IF: 2.6, Publisher : Springer Nature]

iii. Kumar, A., & Kumar, V. (2023). A schematic representation of removal of heavy metal from synthetic water by nanoparticles derived from lignocellulosic biomass. Registration Number: L-123887/2023, Copyrights, Govt. of India

LIST OF CONFERENCES

1. Oral paper presentation on “Removal Of The Hexavalent Form Of Chromium From Aqueous Solution By Nanolignin Derived From Coconut Coir” in the International Conference on Sustainable Experimentation and Modeling in Civil Engineering (SEMCE-2023) held on August 10-11, 2023, organized by the School of Civil Engineering, Lovely Professional University, Punjab in association with the Department of Civil Engineering, Dr B R Ambedkar National Institute of Technology, Jalandhar.
2. Oral Presentation on the topic entitled Green Lignocellulose Derived Nano-materials for Wastewater Treatment and Remediation: A Review in the International Conference on Bioengineering and Biosciences (ICBB-2022) held on 18-19 November 2022 organized by the Department of Biotechnology, School of Bio-engineering and Biosciences in association with the Society of Bioinformatics for Experimenting Scientists (Bioclues) organized at Lovely Professional University, Punjab.

LIST OF WORKSHOPS

1. Participated in one week short term course on ‘’Water quality monitoring and treatment’’ organized by department of chemical engineering, Dr B R Ambedkar National Institute of Technology , Jalandhar from April 27-1 May, 2023.

Chemistry Africa
https://doi.org/10.1007/s42250-023-00818-w

ORIGINAL ARTICLE

Coconut Coir Derived Nanolignin for the Removal of Chromium (VI) from Aqueous Solution: Adsorption Characteristic and Mechanism

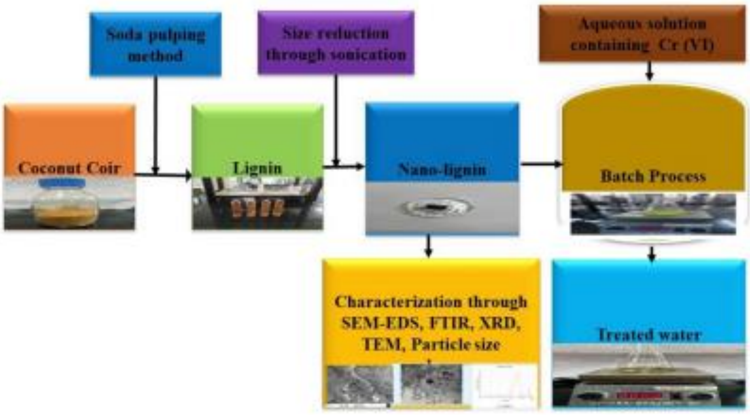
Ajay Kumar[1] · Vineet Kumar[1]

Received: 27 July 2023 / Accepted: 23 October 2023

Abstract

Heavy metals such as chromium-loaded wastewater from anthropogenic activities greatly concern the environment and human health. Industries in electroplating, dyes, pigments, and tanning extensively use chromium and its compounds. Several conventional techniques such as membrane separation, coagulation, precipitation, and flocculation are intensively investigated to remove chromium from wastewater. The removal of chromium using the adsorption technique by green nanomaterial is one of the promising techniques. Lignin has been extracted from coconut coir by the soda pulping method and nanolignin was obtained through the ultrasonication method. The obtained nanolignin from coconut coir was characterized by particle size analyzer, Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDS), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET). The chromium's maximum removal efficiency was 92.8% at acidic pH of 2, nanoadsorbent dosage (0.03 g), and contact time (80 min) as investigated in the batch study. The kinetic study of Cr (VI) was well represented by pseudo-second order and isotherm data were best fitted with the Langmuir model. Thus, nanolignin can be used as an adsorbent for the removal of Cr (VI) from wastewater.

Graphical Abstract



Keywords Nanolignin · Chromium (VI) · Adsorption · Coconut coir · Kinetics

---

Extended author information available on the last page of the article

Chemistry Africa
https://doi.org/10.1007/s42250-022-00367-8

ORIGINAL ARTICLE

A Comprehensive Review on Application of Lignocellulose Derived Nanomaterial in Heavy Metals Removal from Wastewater

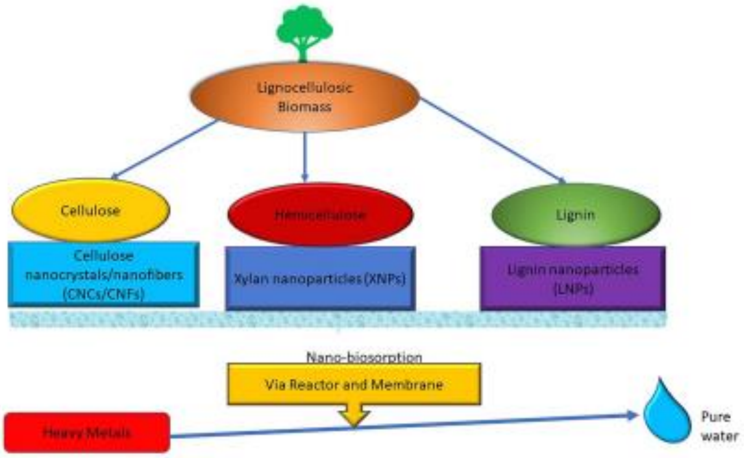
Ajay Kumar[1] · **Vineet Kumar**[1]

Received: 13 January 2022 / Accepted: 18 April 2022

Abstract

In the present scenario, heavy metals in wastewater are among the most severe environmental problems. Wastewater treatments remain a critical issue to date despite advancements in technologies. Global transition for greener and sustainable materials focused on lignocellulosic derived nanomaterials for wastewater treatment and investigated as one of the suitable solutions in industrial scale for environmental remediation. This review provides detailed information about the production of lignocellulosic-based nanomaterial, their adsorption kinetics, applications of reactors, and membranes methods for large-scale remediation of heavy metals from wastewater. The nanosized lignin and cellulose show superior adsorption behavior for the adsorption of heavy metals. Nanocellulose based membranes and filters have been developed to decrease the concentration of heavy metals from wastewater. Several reactors such as batch, continuous, fixed bed, and fluidized bed have been studied to remove heavy metals based on the adsorption phenomenon. The different thermodynamic and kinetic models of lignocellulose-based nanomaterials in context with heavy metal removal have been summarized. The future perspective and challenges linked to lignocellulosic-based nanomaterials and their viability and commercialization have been highlighted in the present review.

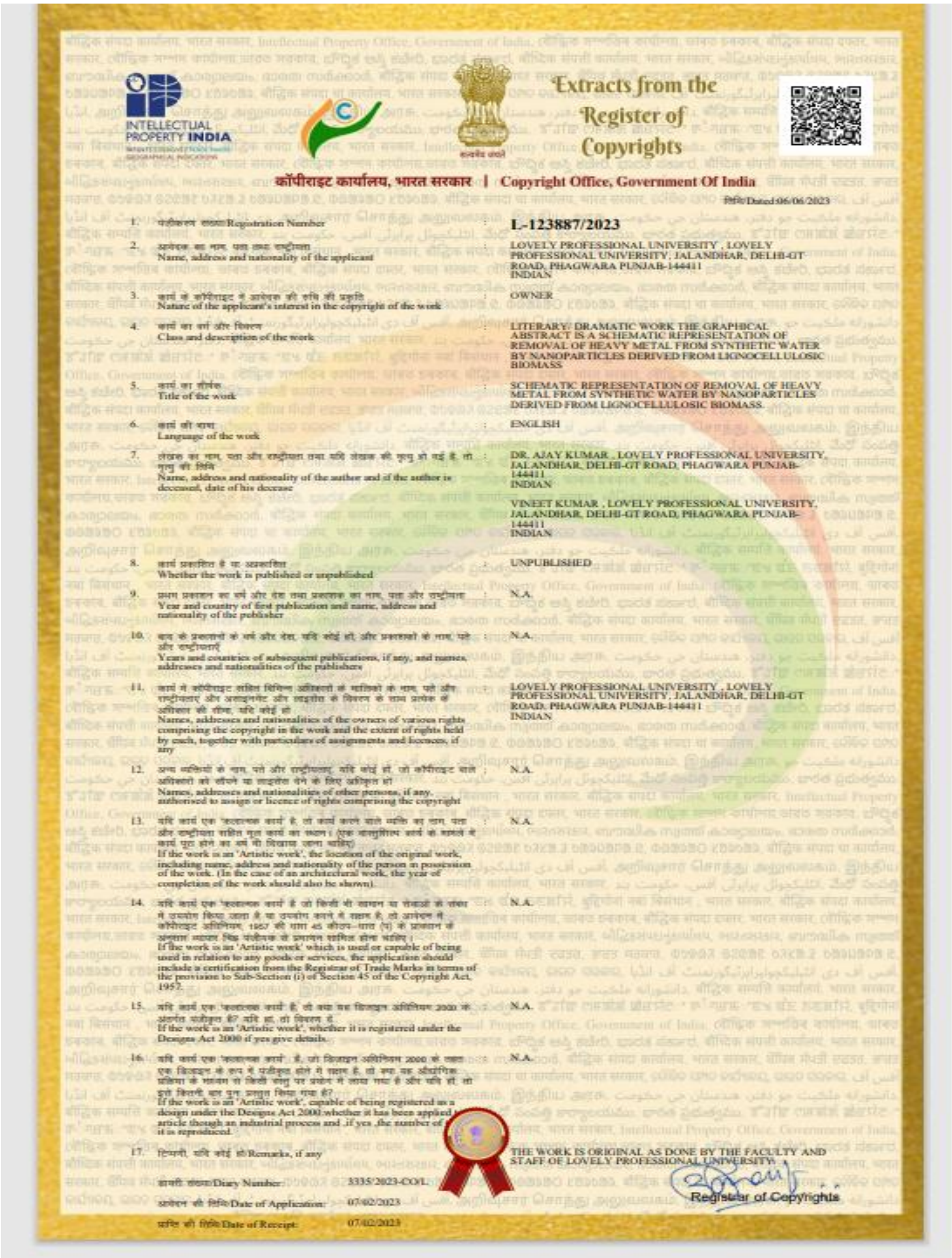
Graphical Abstract



Keywords Lignocellulosic biomass · Nanomaterial · Reactor · Membrane · Adsorption · Models

---

Extended author information available on the last page of the article



INTELLECTUAL PROPERTY INDIA

Extracts from the Register of Copyrights

कॉपीराइट कार्यालय, भारत सरकार | Copyright Office, Government Of India

तिथि/Dated 06/06/2023

1.	पंजीकरण संख्या/Registration Number	L-123887/2023
2.	आवेदक का नाम, पता तथा राष्ट्रीयता Name, address and nationality of the applicant	LOVELY PROFESSIONAL UNIVERSITY , LOVELY PROFESSIONAL UNIVERSITY, JALANDHAR, DELHI-GT ROAD, PHAGWARA PUNJAB-144411 INDIAN
3.	कार्य में कॉपीराइट में आवेदक की रुचि की प्रकृति Nature of the applicant's interest in the copyright of the work	OWNER
4.	कार्य का वर्ग और विवरण Class and description of the work	LITERARY/ DRAMATIC WORK THE GRAPHICAL ABSTRACT IS A SCHEMATIC REPRESENTATION OF REMOVAL OF HEAVY METAL FROM SYNTHETIC WATER BY NANOPARTICLES DERIVED FROM LIGNOCELLULOSIC BIOMASS
5.	कार्य का शीर्षक Title of the work	SCHEMATIC REPRESENTATION OF REMOVAL OF HEAVY METAL FROM SYNTHETIC WATER BY NANOPARTICLES DERIVED FROM LIGNOCELLULOSIC BIOMASS.
6.	कार्य की भाषा Language of the work	ENGLISH
7.	लेखक का नाम, पता और राष्ट्रीयता तथा यदि लेखक की मृत्यु हो गई है, तो मृत्यु की तिथि Name, address and nationality of the author and if the author is deceased, date of his decease	DR. AJAY KUMAR , LOVELY PROFESSIONAL UNIVERSITY, JALANDHAR, DELHI-GT ROAD, PHAGWARA PUNJAB-144411 INDIAN VINEET KUMAR , LOVELY PROFESSIONAL UNIVERSITY, JALANDHAR, DELHI-GT ROAD, PHAGWARA PUNJAB-144411 INDIAN
8.	कार्य प्रकाशित है या अप्रकाशित Whether the work is published or unpublished	UNPUBLISHED
9.	प्रथम प्रकाशन का वर्ष और देश तथा प्रकाशक का नाम, पता और राष्ट्रीयता Year and country of first publication and name, address and nationality of the publisher	N.A.
10.	Years and countries of subsequent publications, if any, and names, addresses and nationalities of the publishers	N.A.
11.	Names, addresses and nationalities of the owners of various rights comprising the copyright in the work and the extent of rights held by each, together with particulars of assignments and licences, if any	LOVELY PROFESSIONAL UNIVERSITY , LOVELY PROFESSIONAL UNIVERSITY, JALANDHAR, DELHI-GT ROAD, PHAGWARA PUNJAB-144411 INDIAN
12.	Names, addresses and nationalities of other persons, if any, authorised to assign or licence of rights comprising the copyright	N.A.
13.	If the work is an 'Artistic work', the location of the original work, including name, address and nationality of the person in possession of the work. (In the case of an architectural work, the year of completion of the work should also be shown).	N.A.
14.	If the work is an 'Artistic work' which is used or capable of being used in relation to any goods or services, the application should include a certification from the Registrar of Trade Marks in terms of the provision to Sub-Section (i) of Section 45 of the Copyright Act, 1957.	N.A.
15.	If the work is an 'Artistic work', whether it is registered under the Designs Act 2000 if yes give details.	N.A.
16.	If the work is an 'Artistic work', capable of being registered as a design under the Designs Act 2000 whether it has been applied to article though an industrial process and ,if yes ,the number of times it is reproduced.	N.A.
17.	टिप्पणी, यदि कोई हो/Remarks, if any	THE WORK IS ORIGINAL AS DONE BY THE FACULTY AND STAFF OF LOVELY PROFESSIONAL UNIVERSITY.

डायरी संख्या/Diary Number: 3335/2023-CO/L

आवेदन की तिथि/Date of Application: 07/02/2023

प्राप्ति की तिथि/Date of Receipt: 07/02/2023

Registrar of Copyrights

Certificate No. 287490

SEMCE
International Conference on Sustainable Experimentation
and Modelling in Civil Engineering

LOVELY
PROFESSIONAL
UNIVERSITY
Transforming Education Transforming India

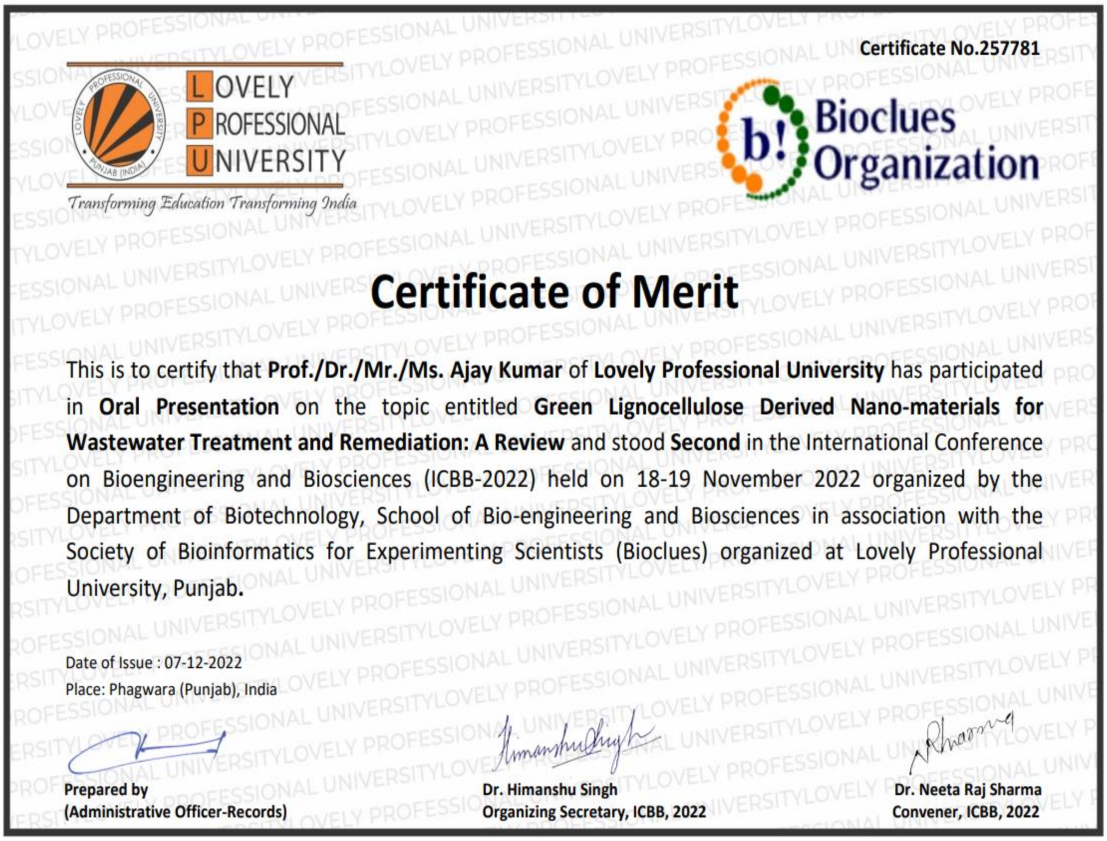
Certificate of Paper Presentation

This is to certify that **Dr./Mr./Ms. Ajay Kumar** of **Lovely Professional University, Phagwara** has presented a paper entitled **"Removal Of The Hexavalent Form Of Chromium From Aqueous Solution By Nanolignin Derived From Coconut Coir"** in the International Conference on **Sustainable Experimentation and Modeling in Civil Engineering (SEMCE-2023) held on August 10-11, 2023,** organized by the School of Civil Engineering, Lovely Professional University, Punjab in association with the Department of Civil Engineering, Dr B R Ambedkar National Institute of Technology, Jalandhar.

Date of Issue : 29-08-2023
Place : Phagwara (Punjab), India

Karan Singh

Prepared by **(Administrative Officer-Records)**	**Program chair** **(SEMCE-2023)**	**General Chair** **(SEMCE-2023)**	**Organizing Secretary** **(SEMCE-2023)**



Certificate No.257781

LOVELY
PROFESSIONAL
UNIVERSITY
Transforming Education Transforming India

Bioclues
Organization

Certificate of Merit

This is to certify that **Prof./Dr./Mr./Ms. Ajay Kumar** of **Lovely Professional University** has participated in **Oral Presentation** on the topic entitled **Green Lignocellulose Derived Nano-materials for Wastewater Treatment and Remediation: A Review** and stood **Second** in the International Conference on Bioengineering and Biosciences (ICBB-2022) held on 18-19 November 2022 organized by the Department of Biotechnology, School of Bio-engineering and Biosciences in association with the Society of Bioinformatics for Experimenting Scientists (Bioclues) organized at Lovely Professional University, Punjab.

Date of Issue : 07-12-2022
Place: Phagwara (Punjab), India

Prepared by
(Administrative Officer-Records)

Dr. Himanshu Singh
Organizing Secretary, ICBB, 2022

Dr. Neeta Raj Sharma
Convener, ICBB, 2022

Certificate No.: NITJ/CH/WQMT/2023211107

डा बी आर अम्बेडकर राष्ट्रीय प्रौद्योगिकी संस्थान, जालंधर

Dr B R Ambedkar National Institute of Technology,
Jalandhar-144027, Punjab (India)

Self-Sponsored Online Short-Term Course on
"Water Quality Monitoring & Treatment"
(April 27- May 1, 2023)

Certificate

This is to certify that Prof./ Dr./ Mr./ Ms./ Er. ____**AJAY KUMAR**____ from **Lovely Professional University, Punjab** has participated in the one week self-sponsored online short-term course on **"Water Quality Monitoring & Treatment"**, organized by Department of Chemical Engineering, Dr B R Ambedkar National Institute of Technology, Jalandhar from April 27 - May 1, 2023.

N. Divya
Dr Neetu Divya
Coordintor

Dr Deepak Sahu
Coordintor

Dr Anjireddy Bhavanam
Coordintor

List of Other Publications During Ph.D work

1. Sharma, R., Jasrotia, K., Singh, N., Ghosh, P., Srivastava, S., Sharma, N. R., ... & **Kumar, A**. **(2020).** A comprehensive review on hydrothermal carbonization of biomass and its applications. *Chemistry Africa*, *3*, 1-19. [SJR: 0.353, Q:3, IF: 2.6, Publisher : Springer Nature]
2. Kour, D., Kaur, T., Devi, R., Yadav, A., Singh, M., Joshi, D., ... **Kumar, A**. & Saxena, A. K. **(2021).** Beneficial microbiomes for bioremediation of diverse contaminated environments for environmental sustainability: present status and future challenges. *Environmental Science and Pollution Research*, *28*, 24917-24939. [SJR: 0.944, Q:1, IF: 5.8, Publisher : Springer Nature]
3. Sharma, M., Singh, J., Baskar, C., & **Kumar, A**. **(2019).** A comprehensive review of renewable energy production from biomass-derived bio-oil. *BioTechnologia. Journal of Biotechnology Computational Biology and Bionanotechnology*, *100*(2). [SJR:0.188, Q4, Publisher : Polish Academy of Sciences, Poland]
4. **Kumar, A. (2021).** Current and future perspective of microalgae for simultaneous wastewater treatment and feedstock for biofuels production. *Chemistry Africa*, *4*, 249-275. [SJR: 0.353, Q:3, IF: 2.6, Publisher : Springer Nature]
5. Barman, P., Kadam, R., & **Kumar, A. (2023).** Lignin-based adsorbent for effective removal of toxic heavy metals from wastewater. *Emergent Materials*, 1-21. [SJR: 0.593, Q:2, IF: 3.8, Publisher : Springer Nature]

6. Singh, S., Naik, T. S. S. K., Shehata, N., Aguilar-Marcelino, L., Dhokne, K., Lonare, S., ... **Kumar, A** & Dehghani, M. H. **(2022).** Novel insights into graphene oxide-based adsorbents for remediation of hazardous pollutants from aqueous solutions: A comprehensive review. *Journal of Molecular Liquids*, 120821. [SJR: 0.914, Q:1, IF: 6.0, Publisher :Elsevier]

7. Sahay, P., Mohite, D., Arya, S., Dalmia, K., Khan, Z., & **Kumar, A. (2023).** Removal of the emergent pollutants (hormones and antibiotics) from wastewater using different kinds of biosorbent—a review. *Emergent Materials*, *6*(2), 373-404. [SJR: 0.593, Q:2, IF: 3.8, Publisher : Springer Nature]

8. Bhatia, A., Koul, P., Dhadwal, A., Kaur, K., & **Kumar, A. (2021).** Current and Future Prospective of Lignin Derived Materials for the Removal of Toxic Dyes from Wastewater. *Analytical Chemistry Letters*, *11*(5), 635-660. [Scopus index, Publisher: Taylor & Francis]
9. **Kumar, A.,** Singh, J., & Baskar, C. **(2020).** Bioenergy: Fungal lipase-mediated biodiesel process technology. In *New and Future Developments in Microbial Biotechnology and Bioengineering* (pp. 137-157). Elsevier. [Book chapter]
10. **Kumar, A.,** & Singh, J. **(2020).** Global scenario and future prospects of the potential microbiomes for sustainable agriculture. In *New and Future Developments in Microbial Biotechnology and Bioengineering* (pp. 311-330). Elsevier. [Book chapter]
11. **Kumar, A.,** Singh, J., & Baskar, C. **(2018).** Microbial Fuel Cell: Green Bioenergy Process Technology. In *Microbial Cell Factories* (pp. 109-123). CRC Press. [Book Chapter]
12. Sharma, M., Singh, J., Baskar, C., & **Kumar, A. (2018).** A comprehensive review on biochar formation and its utilization for wastewater treatment. Pollut. Res, 37, S1-S18. [SJR:0.159, Publisher : EM International]
13. **Kumar, A.,** Kumar, V., & Singh, J. **(2019)**. Role of fungi in the removal of heavy metals and dyes from wastewater by biosorption processes. *Recent Advancement in White Biotechnology Through Fungi: Volume 3: Perspective for Sustainable Environments*, 397-418. https://doi.org/10.1007/978-3-030-25506-0_16 [Book chapter, Publisher : Springer Nature]
14. **Kumar, A.,** & Singh, J. **(2020).** Biofilms forming microbes: diversity and potential application in plant–microbe interaction and plant growth. *Plant microbiomes for sustainable agriculture*, 173-197. [Book chapter, Publisher : Springer Nature]
15. **Kumar, A**., Deb, R., & Singh, J. **(2018).** Bioethanol production from renewable biomass by yeast. *Fungi and their Role in Sustainable Development: Current Perspectives*, 427-448. [Book chapter, Publisher: Springer Nature]
16. **Kumar, A.,** Singh, J., & Baskar, C. **(2020).** Lactic acid production and its application in pharmaceuticals. *Bioactive Natural products in Drug Discovery*, 467-484. [Book chapter, Publisher: Springer Nature]