



Faculty of Resource Science and Technology

***Melia azedarach* Activated Carbon for Heavy Metals Removal: Isotherm,
Kinetic and Response Surface Methodology Study**

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Melia azedarach Activated Carbon for Heavy Metals Removal: Isotherm,
Kinetic and Response Surface Methodology Study

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ABSTRACT

Excessive heavy metals discharge into the environment has become a great concern worldwide and needs an effective long-term solution. *Melia azedarach* tree is a member of the *Meliaceae* family and is used as a source of hard wood; however, the leaves and twigs are burnt due to lack of industrial applications. In this study, biomass from *Melia azedarach* leaves and twigs was used to prepare activated carbons via molten salt synthesis with ZnCl_2 as activator, for the removal of Cu(II) , Pb(II) and Ni(II) ions from aqueous medium. Both activated carbons were characterised, evaluated for batch adsorption and fitness with the kinetic and isotherm models. The central composite design (CCD) was applied to optimise the removal of Cu(II) , Pb(II) and Ni(II) by relating the mutual interactions of the factors including adsorbent dosage, initial metal concentration and contact time. The surface area of activated carbon from *Melia azedarach* leaves ($121.592 \text{ m}^2\text{g}^{-1}$) and twig ($91.423 \text{ m}^2\text{g}^{-1}$) was substantially larger than the feedstock leaves ($1.02 \text{ m}^2\text{g}^{-1}$) and twigs ($0.485 \text{ m}^2\text{g}^{-1}$). The batch adsorption from both activated carbons for Pb(II) and Ni(II) removal followed the Freundlich isotherm, while Cu(II) adsorption followed the Temkin isotherm. Applying central composite design in response surface methodology, the optimised removal efficiency for Cu(II) , Pb(II) , and Ni(II) using *Melia azedarach* leaves activated carbon as adsorbent was determined to be 98.63%, 99.52% and 88.18% respectively while optimised adsorption capacity was found to be 192.12 mgg^{-1} , 170.94 mgg^{-1} , 160.77 mgg^{-1} . On the other hand, the optimised removal efficiency for Cu(II) , Pb(II) , and Ni(II) using *Melia azedarach* twigs activated carbon as adsorbent was found to be 99.66%, 95.05% and 97.53% respectively while optimised adsorption capacity was determined to be 172.32 mgg^{-1} , 254.59 mgg^{-1} , 232.16 mgg^{-1} , optimised through central composite design in response surface methodology. The activated carbon derived from *Melia azedarach* biomass has demonstrated the capacity

to be a value-added product as an adsorbent capable of adsorbing heavy metals from aqueous medium.

Keywords: Agricultural and horticultural wastes, biomass utilisation, green adsorbents, response surface methodology, water pollution

Melia azedarach Karbon Teraktif untuk Penyingkiran Logam Berat: Kajian Metodologi Permukaan Isoterma, Kinetik dan Gerak Balas

ABSTRAK

Pelepasan logam berat yang semakin meningkat ke alam sekitar telah menjadi kebimbangan besar yang memerlukan penyelesaian yang boleh dipercayai dan jangka panjang. Berikutan sintesis garam lebur dengan ZnCl_2 sebagai pengaktif, biojisim daripada daun dan ranting Melia azedarach digunakan untuk menyediakan karbon teraktif untuk penyingkiran ion Cu(II) , Pb(II) , dan Ni(II) daripada medium akuas. Kedua-dua karbon teraktif telah dicirikan, dinilai untuk penjerapan kelompok, dan kesesuaian dengan model kinetik dan isoterma. Reka bentuk komposit pusat (CCD) digunakan untuk mengoptimumkan penjerapan kelompok dengan mengaitkan interaksi bersama faktor termasuk dos penjerap, kepekatan logam awal dan masa sentuhan. Luas permukaan karbon teraktif daun Melia azedarach ($121.592 \text{ m}^2\text{g}^{-1}$) dan ranting ($91.423 \text{ m}^2\text{g}^{-1}$) jauh lebih besar daripada daun ($1.02 \text{ m}^2\text{g}^{-1}$) dan bahan suapan ranting ($0.485 \text{ m}^2\text{g}^{-1}$). Penjerapan kelompok oleh kedua-dua karbon teraktif untuk penyingkiran Pb(II) dan Ni(II) mengikuti isoterma Freundlich, tetapi penjerapan Cu(II) mengikuti isoterma Temkin. Pada pembolehubah proses yang dioptimumkan, penyingkiran optimum Cu(II) 99.50%, Pb(II) ialah 100%, dan Ni(II) ialah 89.17% oleh karbon teraktif daun Melia azedarach. Manakala kapasiti penjerapan optimumnya didapati ialah 189.44 mgg^{-1} untuk Cu(II) , 171.83 mgg^{-1} untuk Pb(II) dan 158.56 mgg^{-1} untuk Ni(II) . Dengan karbon teraktif ranting Melia azedarach, penyingkiran optimum ialah 99.50% Cu(II) , 100% Pb(II) , dan 89.17% Ni(II) . Manakala kapasiti penjerapan optimum ranting Melia azedarach didapati 189.44 mgg^{-1} untuk Cu(II) , 171.83 mgg^{-1} untuk Pb(II) dan 158.56 mgg^{-1} untuk Ni(II) . Kajian ini penting kerana karbon teraktif yang diperolehi daripada biojisim Melia azedarach telah menunjukkan kapasiti untuk menjadi

produk nilai tambah sebagai penjerap yang mampu menyerap logam berat daripada medium akueus.

*. **Kata kunci:** Sisa pertanian, penggunaan biojisim, penjerap hijau, metodologi permukaan tindak balas, pencemaran air*

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LIST OF ABBREVIATIONS

AC	Activated carbon
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CCD	Central composite design
CGS	Centre for Graduate Studies
CHNS	Carbon, Hydrogen, Nitrogen, Sulphur
DOE	Design of Experiment
EDX	Energy Dispersive X-Ray
EPA	Environmental Protection Agency
FAAS	Flame atomic absorption spectrometer
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared
LAC	Leaves Activated Carbon
HM	Heavy Metal
IUPAC	International Union of Pure and Applied Chemistry
MSS	Molten Salt Synthesis
RLP	Raw leaves powder
RMSE	Root Mean square error
RTP	Raw twigs powder
TAC	Twig Activated Carbon
UNIMAS	Universiti Malaysia Sarawak
2FI	Two Factor interaction

CHAPTER 1

INTRODUCTION

1.1 Study Background

Heavy metals contamination of the surface and groundwater has rapidly become an environmentally growing worldwide issue and threatening to human health (Razak et al., 2020). Sources of heavy metals contamination in the environment include industries like metallurgies, ceramics (Ngaini et al., 2021), paints, adhesives (Ghasemi et al., 2020), electroplating, mining, battery manufacturing (Wang & Wang, 2018), printing, fuels (Venkateswarlu et al., 2019), petroleum refineries, computer and television screens, roof and stained glass windows production (Kaya et al., 2020) and pesticides (Ullah et al., 2020). In addition to these, coal combustion and household wastes (Sen et al., 2018), typically contain significant amounts of metals with the potential to be poisonous, demanding extensive waste treatment (Adenuga et al., 2019).

Heavy metals like copper, lead and nickel, can accumulate in living tissues through the food chain, which eventually: causing damage to biosphere (Razak et al., 2020). In humans, heavy metal poisoning can cause high blood pressure, nausea, vomiting, disorientation, liver failure, brain haemorrhage, heart and renal disorders (Amin et al., 2019). According to the United States Environmental Protection Agency (US-EPA), the maximum contamination level in drinking water for Pb(II) is 0.05 mgL^{-1} (Aboli et al., 2020) and 0.25 mgL^{-1} for Cu(II) (Razak et al., 2020). While, based on World Health Organisation (WHO) guidelines, the limit for Ni(II) is 0.02 mgL^{-1} (Guo et al., 2020). In tandem to US-EPA guidelines, the permissible limits for Pb(II), Cu(II) and Ni(II) in wastewater are 0.01 mgL^{-1} ,

2.5 mgL⁻¹ and 2 mgL⁻¹ respectively (Biswas et al., 2019). In order to preserve a healthy ecosystem, it is necessary to treat the heavy metal contaminated wastewater, before being released into water bodies (Taşar & Özer, 2020).

Several techniques have been employed for the removal of heavy metals from wastewater from either via physical (i.e. evaporation-condensation, reverse osmosis, membrane filtration) or chemical methods (i.e. ion exchange, chemical precipitation, solvent extraction) (Ibrahim et al., 2020). These traditional methods, nevertheless, have significant drawbacks (Herrera-Barros et al., 2020) such as solvent extraction restrictions, higher preparation costs, several phases involved and poor quality discharge (Adenuga et al., 2019; Crini & Lichtfzouse, 2019). The coagulation and flocculation methods have several drawbacks, including insufficient heavy metal removal, high chemical use and increased sludge generation (Jin et al., 2020; Surendran & Baral., 2018).

Chemical methods which involve chemical precipitation is a slow process involving different chemicals in large quantities; and huge amounts of sludge that needs further treatment (Sen et al., 2018; Zamora-ledezma et al., 2021). While, ion-exchange process involves high capital involvement and high operation cost, suitable for low concentrations only, highly sensitive to effluents pH and requires physiochemical pre-treatment to avoid damage to beads of organic matters (Adenuga et al., 2019; Siong et al., 2021). Meanwhile, the physical approaches, which involve a process based on membrane-based technologies, has several limitations such as high energy requirements, higher operation and maintenance costs, and limited flowrates (Siong et al., 2021; Wang et al., 2018). Electrochemical technologies involves huge capital investments, high operation costs due to electricity

supply; and ineffective at lower metal ion concentrations (Chen et al., 2020; Zamora-ledezma et al., 2021).

Adsorption is one of the versatile and efficient approaches often employed for the treatment of heavy metal-contaminated wastewater due to its operational simplicity, sludge-free operation and adsorbent reusability in long-term applications (Cao et al., 2019). Commercial activated carbon has been utilised for decades due to its qualities including high surface area, adsorption capacity, ion selectivity, thermal stability, resistance to transportation losses, ease of activation and regeneration (Ghasemi et al., 2020). However, its high cost is the principal obstacle to the industrial application for wastewater treatment (Ansari et al., 2018). Therefore, it is worthwhile to conduct extensive research on the preparation of low-cost adsorbents with specific properties and their utilisation for the removal of various pollutants in aqueous media (Georgieva et al., 2020). Agricultural and horticulture waste materials render prospective adsorbents for heavy metals removal from wastewater and an economical alternate to comparatively expensive activated carbon with comparable qualities by utilising widely available free resources (Hashem et al., 2020). Adsorbents made from agricultural and horticulture wastes have been demonstrated to be fairly effective in extracting heavy metals from wastewater even at very low concentrations (Surendran & Baral, 2018).

1.2 *Melia azedarach*

Melia azedarach tree is found all over the world including Asia, Europe, north and south America however it is native to India, Pakistan, Australia and south east Asia (Majid et al., 2021). A few previous studies have utilised various parts of *Melia azedarach* biomass

with limited physio-chemical modification techniques to produce adsorbent and application for the removal of different heavy metals from aqueous medium.

An adsorbent prepared by grinding and washing the *Melia azedarach* leaves and bark removed 90% of As(III) and As(V) (Sarwar et al., 2015). *Melia azedarach* leaves treated with dilute NaOH and HCl, adsorbed 98.25% and 97.4% of Pb(II) and 97.4% and 98% of Fe(II) ions respectively (Khokhar et al., 2015). *Melia azedarach* powdered wood pyrolyzed at 400 °C treated with Fe(NO₃)₃ removed 99.8% Cr(VI) (Zhang et al., 2018). The optimum adsorption of BR 46 and Cu(II) ions by powdered *Melia azedarach* deadwood was found to be 92.07% and 92.72% respectively (Davoudi et al., 2018). *Melia azedarach* seed shells were pulverised, treated with HCl and carbonised at 550 °C to remove 66% of Cd(II) and 62% of Pb(II) (Ullah et al., 2020). Powdered *Melia azedarach* branches treated with conc. H₂SO₄ exhibited an adsorption capacity of 4.32 mgg⁻¹ for Cr₂O₄⁻² ions removal from aqueous medium (Nosheen et al., 2021).

The *Melia azedarach* seed shells activated carbon has capability to remove 66% and 62%, Cd(II) and Pb(II) respectively (Ullah et al., 2020). Because the *Melia azedarach* plant is abundantly grown for lignocellulosic hard wood for use in furnishings and other construction-related products (Shah et al., 2020), its biomass such as leaves and twigs, is burnt since it has no industrial application (Khokhar et al., 2015).

1.3 Problem Statement

Adsorption has been recognised as one of the most widely used and efficient technologies for heavy metals removal from wastewater due to its operational simplicity, minimal sludge generation and adsorbent reusability in ongoing applications. Commercial

activated carbon has been utilised as an adsorbent for decades due to its remarkable properties; nonetheless, the high cost is the primary barrier to industrial application for wastewater treatment. Consequently, substantial research on the preparation of low-cost activated carbons with specified characteristics for application as adsorbents for the removal of diverse contaminants in aqueous environments is worthwhile. Utilising the locally abundant horticulture waste, such as *Melia azedarach*, appears to be a potential alternative to derive an economical and efficient activated carbon that can be used as an adsorbent for the removal of heavy metals from aqueous medium. A number of previous studies have reported application of *Melia azedarach* biomass as an adsorbent without considerable physiochemical modification, resulting in a low adsorption capacity for heavy metals.

The preparation of activated carbons from *Melia azedarach* leaves and twigs as well as its application as an adsorbent for aqueous media contaminants such as heavy metals, has yet to be explored. Thus, the fundamental purpose of this work is to prepare activated carbons utilising *Melia azedarach* leaves and twigs, as well as to explore the applicability for removal of Copper Cu(II), Lead Pb(II) and Nickle Ni(II) ions from aqueous medium. The optimisation of process variables including adsorbent dosage, initial metal concentration and contact time is also required.

A green cost-effective process, molten salt synthesis (MSS) offers the benefit of completing both the carbonisation and activation processes in a single step, reducing process complexity and time requirements (Pang et al., 2021). With a low melting point of 290 °C, zinc chloride (ZnCl₂) is one of the salts commonly used to produce high yields of porous carbonaceous materials with a high specific surface area from a range of biomass sources (Youssef et al., 2020). This approach for carbonising biomass to generate diverse

microstructures is currently gaining a lot of attention in the sectors of energy, environment and resource sustainability (Yang et al., 2020). However, this process has seldom been used to produce activated carbon from biomass (Shang et al., 2015). In this work, activated carbon was produced from *Melia azedarach* leaves and twigs adopting MSS with ZnCl_2 as activator at 500 °C.

Numerous studies have shown that the capacity of the biosorbents to remove heavy metal ions improved when pH rose from 1 to 5, peaking at pH 5.0 (Balasubramanian et al., 2020; Huang et al., 2020; Ilangovan et al., 2017; Razak et al., 2020; Sajjadi et al., 2019). Due to the high concentration of H^+ ions in low pH solutions, protons and metal ions may compete for adsorption sites, limiting the heavy metal ions adsorption on the adsorbent (Rahim et al., 2019). Additionally, when the active sites are protonated, the surface becomes positively charged and subsequent metal ion adsorption in solution on the surface is less likely to happen due to charge repulsions (Ilangovan et al., 2017). At higher pH (>6), due to the possibility of heavy metal ions precipitating as hydroxides, higher pH values (>6) make it impossible to determine an accurate adsorption capacity (Kongsune et al., 2021). Based on the reported findings, in the present study of heavy metals adsorption by LAC and TAC, pH was fixed near pH 5 for kinetic study, fitness with isotherm models as well as for the process optimisation study.

The initial concentration of the adsorbate plays a key role in the adsorption process because it provides the necessary mass transfer driving force between the solution and the adsorbent (Aboli et al., 2020). However, because the adsorbent's surface only has a finite number of active sites where adsorbate ions can attach, it is thought that the likelihood of ions interacting with this small binding zone decreases with increasing concentration. As a

result, higher adsorption efficiency can be attained despite the fact that poor adsorption capacity values at lower initial concentrations are an expected outcome. An increase in initial concentration results in an increase in the adsorption capacity at equilibrium, being a critical driving factor for the mass transfer between the aqueous solution and the solid phase to overcome the resistance (Kaya et al., 2020). In accordance with the literature review, the effectiveness of LAC and TAC as adsorbents at both low and high metal concentration levels was tested using a variety of initial metal concentrations for kinetic study, fitness with isotherm models as well as for the process optimisation study.

To estimate how well an adsorbent can perform for a particular concentration of an adsorbate, the effect of adsorbent dosage must be evaluated in an adsorption process (Aboli et al., 2020). An adsorbent's surface area, size and shape of the pores, and availability of unoccupied active sites on the surface all affect how quickly heavy metal ions migrate from the solution to the adsorbent's surface (Ghasemi et al., 2020). The adsorption percentage depends on the amount of heavy metal ions being transported from the bulk liquid phase to the available adsorption site which decreases gradually thus adsorption percentage increases with time until saturation (Ouyang et al., 2019). Adsorption capacity may decrease occasionally when adsorbent dosage rises, but it may also increase adsorption in other situations (Kaya et al., 2020). Based on the wider surface area and other characterisation data, both LAC and TAC were employed for heavy metal ions removal at lower range of adsorbent dosage for kinetic study, fitness with isotherm models as well as for the process optimisation study.

Another crucial aspect of understanding adsorption is the contact time between the adsorbent and the solution containing the adsorbate at which the process achieves

equilibrium (Anitha et al., 2020). Conclusively, the adsorbent dosage, initial metal concentration and contact time were selected among the independent variables, adsorption capacity and removal efficiency (% Removal) were studied as depended variables in heavy metal ions adsorption on LAC and TAC. On the other hand, pH, temperature and rotation speed were kept constant as per literature review discussed earlier.

1.4 Objectives

The objectives of this study were:

- i. To prepare activated carbon through molten salt synthesis method using *Melia azedarach* leaves and twigs biomass as precursor and characterise the resulting activated carbon using physiochemical methods.
- ii. To study the prepared activated carbon's ability to adsorb Cu(II), Pb(II) and Ni(II) ions from aqueous medium as well as to study the adsorption process using different kinetic models and isotherm models.
- iii. To optimise the different variables involved in the adsorption process of Cu(II), Pb(II) and Ni(II) ions on *Melia azedarach* activated carbon using the Central Composite Design in Response Surface Methodology.

1.5 Chapter Summary

The scope of this study includes the following:

1. The production of activated carbon from *Melia azedarach* leaves and twigs via MSS approach and characterisation of the resulting activated carbon.

2. Application of *Melia azedarach* leaves activated carbon (LAC) and *Melia azedarach* twigs activated carbon (TAC) as adsorbent in laboratory-scale batch adsorption study to evaluate the removal efficiency and adsorption capacity for Cu(II), Pb(II), and Ni(II) ions from aqueous medium.
3. Optimisation of Cu(II), Pb(II) and Ni(II) adsorption by LAC and TAC via response surface methodology (RSM). Three process variables including adsorbent dosage, initial metal concentration and contact time were evaluated as independent variables while adsorption capacity and removal efficiency were studied as dependent variables. Other process variables including temperature, solution pH and agitation speed were kept constant throughout the optimisation study.
4. The novelty within the scope of this study is the preparation and characterisation of activated carbon using *Melia azedarach* leaves and twigs biomass, application as adsorbent for heavy metals removal from aqueous medium and evaluation of the adsorption process with reference to four kinetic models and four isotherm models.
5. A distinctive component of this work is the optimisation of the heavy metals' adsorption process with three independent variables and two dependent variables since adsorption capacity and removal efficiency (% Removal) have seldom been optimised jointly. In the majority of research, one dependent variable is evaluated in the optimisation of the adsorption process.

1.6 Chapter Summary

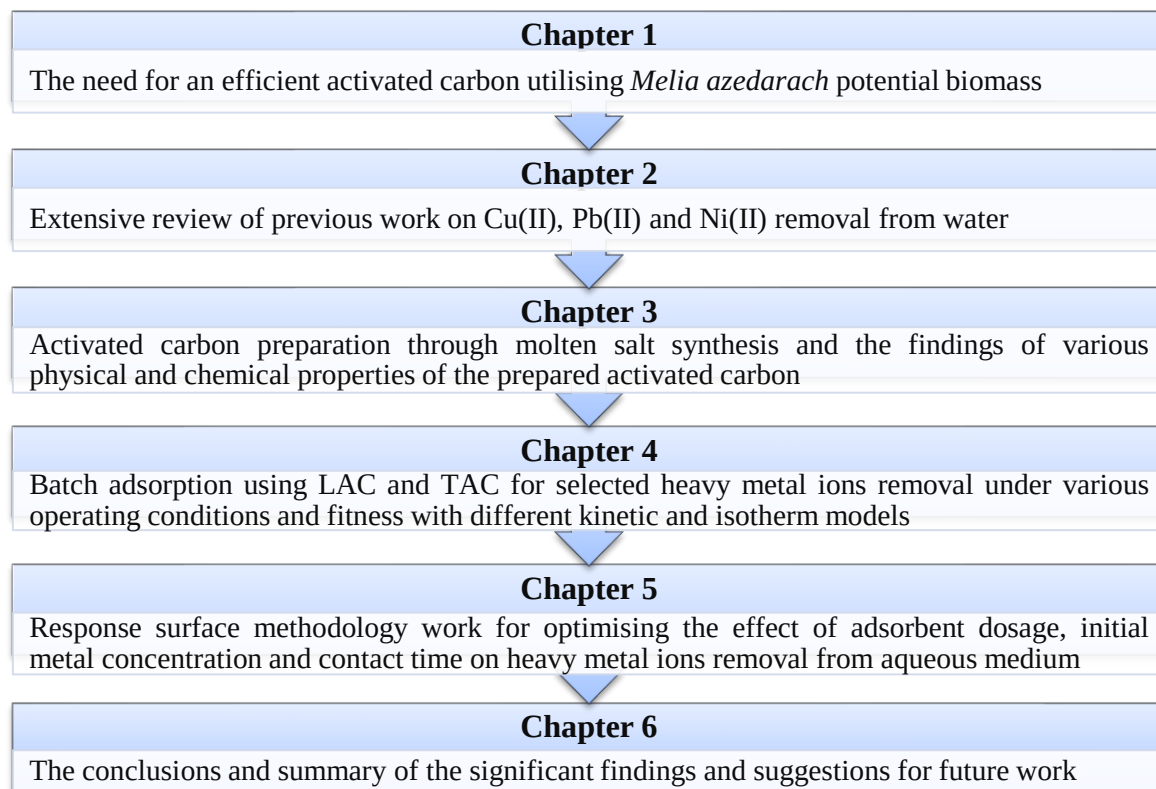


Figure 1.1: Chapter wise thesis organisation

CHAPTER 2

LITERATURE REVIEW

2.1 *Melia azedarach* Biomass

Urban forest provides many benefits to both human and natural systems including temperature and microclimatic modification, pollution mitigation, noise reduction, biodiversity and habitat enhancement, and recreational opportunities (Lan et al., 2022). Grass and leaves collected from public parks, private gardens and roadside greenery, as well as small branches and herbaceous green material are defined as green waste (Langsdorf et al., 2021). Leaf waste accounts for ~46% of the total dry weight of green waste in the United States of America (Lan et al., 2022). The massive amount of waste leaves dropped and accumulated by plants each year has an environmental impact since these leaves serve as an ideal substrate for rodent and insect growth and reproduction as well as a reason of sewage drain blocking in autumn (Abdel-Aziz et al., 2021). Incineration is not recommended because of dioxin and CO₂ emission, which increase the phenomenon of global warming (Abdel-Aziz et al., 2021). The effective of the green wastes will aid in the reduction of environmental pollution and forest fire incidents, which would otherwise endanger life (Isaac & George, 2022). Hence, among other reasons, incorporating fallen leaves into a productive industry is advantageous (Abdel-Aziz et al., 2021).

Melia azedarach belongs to *Meliaceae* family of flowering plants, which includes mostly trees and shrubs in the Sapindales order (Deb et al., 2018). There a several common names such as Bakain, Drek, Chinaberry, Persian lilac and many more (Sharma et al., 2013). *Melia azedarach* trees can grow up to 12 meter in length, with a solid trunk and spreading

branches (Hussein & Al-Marzoqi, 2020). It is a deciduous tree native to Southeast Asia (Deb et al., 2018) and is often found in India, China, Australia, Pakistan, and Iran (Davodi et al., 2019b). As a true urban survival, it grows well in a broad range of conditions, including alkaline soil, where other trees might struggle (Gilman et al., 2018). It has been successfully imported and naturalised globally as an ornamental plant due to its exceptional tolerance to harsh conditions and strong capacity to compete for nutritional resources, as well as its quick growth and plentiful seed production (M'rabet et al., 2017).

Melia azedarach leaves are dark green in colour, bipinnately and odd-pinnately compound, oval in shape, deciduous in persistence, with a blade length of 1-2 feet and leaflet length of 1-2.5 inches (Gilman et al., 2018). *Melia azedarach* leaf has a number of chemical constituents, including kampherol, quercetin, stigmasterol, β -sitosterol, campesterol, phytol, beta-carotene, tocopherol and squalene, 1-eicosanol, and other (Deb et al., 2018).

Melia Azedarach wood is a lignocellulosic material and mainly consists of hemicelluloses, cellulose, and lignin (Dolatabadi et al., 2018). *Melia azedarach* tree is a valuable source for paper pulp, logistics packing-case, furniture production (Zhang et al., 2018). It has been suggested that it can be helpful in remediation of tannery effluent-polluted ecosystems (Davodi et al., 2019b). Every year, a massive amount of *Melia azedarach* wastes such as wood, sawdust, bark, branches and leaves are produced, which is a potential biomass with environmental consequences (Zhang et al., 2018).

2.2 Heavy Metals Pollutions

Heavy metals pollution has increased significantly due to recent rapid industrial development, in addition to other human inputs (Kumar et al., 2019). It has been reported by

WHO that most heavy metals are teratogenic, mutagenic and carcinogenic as the contents exceed the tolerance standards (Cao et al., 2019). Heavy metals present in high concentrations in all rural, urban, and industrial wastewaters (Takdastan et al., 2019). High quantities of highly toxic heavy metals in the environment is a result of technological innovation, industrialisation, agricultural practices and urbanisation (Adenuga et al., 2019). Millions of tonnes of dangerous heavy metals are dumped into the environment every year through wastewater and the discharge is growing with each passing year (Lin et al., 2020). Due to severe toxicity, extensive sources and non-biodegradability, heavy metal pollution has significant negative environmental consequences (Chen et al., 2020). In other words, by polluting the water sources, heavy metals endanger humans, aquatic life and the environment (Lam et al., 2019).

Toxic heavy metals can enter the body through a variety of routes, including contaminated food, drink, or dust inhalation. The food crops irrigated with wastewater account for over 70% of human heavy metal intake (Aslam et al., 2017). Heavy metals contaminated water and food can cause serious health problems in human, including high blood pressure, nausea, vomiting, hepatic dysfunction, cerebral haemorrhage, heart and kidney damage (Amin et al., 2019), arthritis, hypertension, attention deficit hyperactivity disorder, renal failure, cirrhosis (Cao et al., 2019), skin illnesses, brain damage, liver damage, anaemia, ulcers, hepatitis and cancer (Baby and Hussein, 2020). Due to these reason, several studies reported on the applications, toxicity and ramifications of heavy metals Cu(II), Pb(II) and Ni(II).

2.2.1 Cu(II)

Cu(II) is used in a variety of industrial processes including manufacturing of paints, machinery pulp, construction industries (Qin et al., 2019), electrical appliances, electronics, automotives, batteries, fungicides, algicides, insecticides, fertilisers and pesticides (Cibati et al., 2017). Though Cu(II) is essential for human health in minute levels, excessive ingestion can cause renal damage, miscarriages, nervous system disorders, vomiting, headaches, nausea, respiratory problems, abdominal discomfort (Fotsing et al., 2020), lethargy, DNA damage, gastrointestinal bleeding and hypertension (Mahdi et al., 2018), Wilson's disease, insomnia, osteoporosis and leukaemia, diarrhoea and metabolic disorders in humans (Razak et al., 2020). The permitted limits for Cu(II) in drinking water have been specified in Table 2.1 by International Regulatory Agencies to protect humans from its hazardous effects (US-EPA, 2011; WHO, 2017).

2.2.2 Pb(II)

Pb(II) is used to produce paints, pipes, bullets, alloys, batteries, ceramics, glass (Liu et al., 2019), electroplating, pulp and paper, lead smelting, metal finishing (Sajjadi et al., 2019), as well as in households, electronics, incinerators and fuel (Kaur et al., 2020). Due to its non-biodegradability, Pb(II) can accumulate in the food chain, and constitute a major health risk to humans (Zhu et al., 2018).

Pb(II) can enter the human organic system by gastrointestinal absorption or inhalation (Babu et al., 2018). Excessive Pb(II) intake can damage the nervous and reproductive systems as well as cause cancer, kidney failure, lung disorders, hypertension, anaemia, mental development, liver, kidney, nervous system malfunction, red blood cell

damage (Du et al., 2020), encephalopathy, hepatitis, nephritic syndrome (Liu et al., 2019), allergy, mental retardation and brain damage (Maity & Ray, 2018). Pb(II) poisoning can cause arthralgia, digestive issues, headaches, intracranial pressure, renal illness and nervous system dysfunction in children (Sajjadi et al., 2019). Table 2.1 shows the permitted limits for heavy metals in drinking water, set by international regulatory bodies to protect humans from their hazardous effects (US-EPA, 2011; WHO, 2017).

2.2.3 Ni(II)

Ni(II) is a transition metal that is resistant to water, air and alkali corrosion (Anitha et al., 2020) and is used in non-ferrous metal processing industries (An et al., 2019), including stainless steel manufacturing, coins, metallic alloys, super alloys, nonferrous metals, batteries, electroplating, forging, mineral processing, paints and steam-electric power plants (Anitha et al., 2020). Skin allergies, lung fibrosis, cancer (Mahdi et al., 2018), liver, renal, neurological, genetic and reproductive problems in humans, can be caused by Ni(II) contamination (Anitha et al., 2020). Table 2.1 shows the maximum allowable Ni(II) content in drinking water as specified by (WHO, 2017).

Table 2.1: Permissible limits of heavy metals in drinking water

Contaminant	US-EPA Maximum contaminants level (mgL⁻¹)	WHO Provisional guidelines (mgL⁻¹)
Cu(II)	1.3	2
Pb(II)	0.015	0.01
Ni(II)	-	0.07

2.3 Heavy Metals Removal Techniques

Several studies reported on the removal of heavy metal from wastewater using a range of physical and chemical methods (Sajjadi et al., 2019). The following are the pros and cons of the most often applied techniques for heavy metal removal from aqueous medium:

Coagulation and flocculation are two of the most basic and cost-effective water and wastewater treatment methods which are related to each other (Kumar et al., 2021). Coagulation is an extra ordinarily stable process of destabilising suspended particles in water while flocculation is the process of forming larger flocs from destabilised particles (Zinicovscaia & Cepoi, 2016). Chemical coagulants such as alum, ferric chloride, and ferrous sulphate are commonly employed as coagulants in metal separation from aquatic environments to induce the formation of suspended particles (Kumar et al., 2021). Flocculation is the process of combining suspended particles in the form of large clumps or agglomerates utilising polymer-based flocculants (Zinicovscaia & Cepoi, 2016). Production of sludge, transfer of toxic compounds into solid phase (Gupta et al., 2020)

Membrane filtration techniques offer a number of advantages, including low energy needs, high separation efficiency, simple equipment requirements, and straightforward heavy metals separation (Naghdali et al., 2019). Reverse osmosis, ultrafiltration, hyperfiltration, and electrodialysis are examples of filtration systems (Kumar et al., 2021). A membrane is a selective layer that makes contact between two homogenous phases and has a porous or non-porous structure to remove varied size contaminants (Azimi et al., 2017). High operating cost, relatively high membrane material cost, vulnerability of membrane system to scaling, microorganisms, compaction and the productivity loss over time (Kumar

et al., 2021). Overall, this membrane procedure a costly treatment option that demands a high level specialised skill to operate (Naghdali et al., 2019).

Chemical precipitation is a simple, easily automated treatment process for the removal of heavy metals higher concentrations from wastewaters (Azimi et al., 2017). Hydroxide precipitation and sulphide precipitation are two types of precipitation and the applied chemicals react with metal ions in wastewater to produce insoluble precipitates that are separated by sedimentation or filtering (Zinicovscaia & Cepoi, 2016). Negative aspects of chemical precipitation include the discharge of toxic fumes and the formation of colloidal precipitates, which cause problems for separation through filtration or settling processes (Zhao et al., 2016).

The ion exchange process is a chemical method for removing dissolved ions such as heavy metals from contaminated water in which the dissolved ions exchange with ions in a reversible ion-exchange material while the material's structure remains unchanged during the ion exchange process (Kumar et al., 2021). Synthetic ion exchange resins come in a variety of strengths, including strong anionic exchangers and weak cationic exchangers (Azimi et al., 2017). In addition to synthetic resins, natural silicate minerals and natural zeolites are widely used commercially due to their low cost and excellent capability to remove metal ions under varied conditions (Zhao et al., 2016). Some of the key benefits of using an ion-exchange technique to remove heavy metals from wastewater are Higher selectivity, potential metal recovery and reduced sludge (Azimi et al., 2017). The downsides of the ion-exchange process include a high initial capital need owing to synthetic resin, maintenance expenses, the continual need for resins regeneration, higher operation costs, and leftover sludge management (Zhao et al., 2016).

Given the limitations of the aforementioned techniques, it is critical to find safe, low-cost, and practicable alternatives for heavy metals removal from the environment (Adenuga et al., 2019).

2.4 Adsorption

Adsorption has become a popular and profitable alternative to conventional wastewater treatment techniques due to its economic feasibility, high efficiency (Zaidi et al., 2018), adaptability, design versatility, low power use, no harmful by-products (Bonilla-Petriciolet et al., 2017). Adsorbate is a material that is adsorbed on the surface of another substance, whereas adsorbent is the substance on whose surface the adsorption occurs (Patel, 2019). However, adsorbent type, fluid characteristics, target pollutants, operating conditions, process composition, rejuvenation and solid waste disposal, have an impact towards economic and technological viability of adsorption process (Carolin et al., 2017). Adsorption has been reported as an efficient technique for heavy metals removal from aqueous medium (Amin et al., 2019).

2.4.1 Classification of Adsorption Process

The comparison of two main types of adsorption processes i.e. physisorption (physical adsorption) and chemisorption (chemical adsorption) (Bonilla-Petriciolet et al., 2017) has been summarised in Table 2.2.

Table 2.2: Comparison of physisorption and chemisorption processes (Králík, 2014)

Property	Physical adsorption	Chemisorption
Binding forces	Van der Waals	Covalent and ionic bonds
Adsorption heat	10-40 KJ mol ⁻¹	Between 20 and 400 KJ mol ⁻¹

Table 2.2 continued

Chemical transformation	No chemical change involves	New compounds are formed on the surface of the adsorbent
Multilayer's structure	Adsorbate deposits in multilayers on the surface of adsorbent	No
Reversibility	Adsorbate can be recovered through desorption	Desorption involves severe chemical treatment
Energy required for activation	Very low	Excessive
Adsorbate–adsorbent Interaction specificity	Very low	High
Impact of temperature	Unfavorable	Positive impact

Chemical adsorption is distinguished by chemical interactions between the adsorbate and the adsorbent, which result in the formation of covalent or ionic bonds (Burakov et al., 2018). While, physical adsorption is characterised by non-specific increase in adsorbate concentration at the contact (i.e., not depending on the nature of the material) van der Waal forces (Burakov et al., 2018). Physical adsorption is a reversible phenomenon while chemical adsorption is an irreversible phenomenon (Bonilla-Petriciolet et al., 2017). Comparative demonstration of physisorption and chemisorption on the surface of an adsorbent has been presented in Figure 2.1.

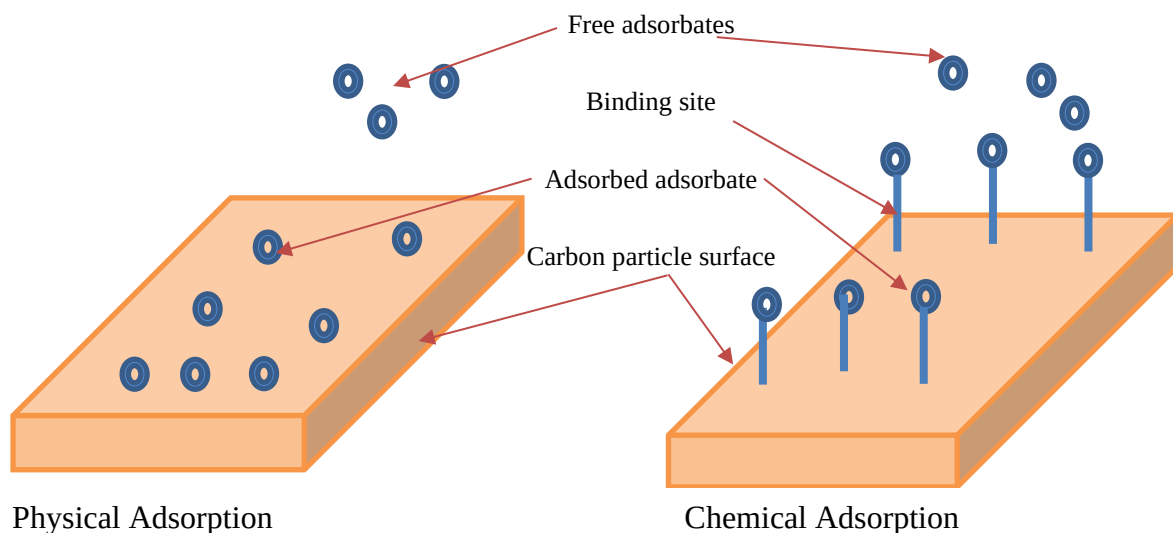


Figure 2.1: Comparison of a) physisorption, b) chemisorption (Nandiyanto et al., 2020)

2.4.2 Adsorption Mechanism

The nature of adsorption process is governed by the nature of the adsorbate as well as the adsorbent's properties (Saleem et al., 2019). Previous studies have shown that activated carbon as an adsorbent exhibits both physisorption and chemisorption simultaneously in heavy metals adsorption (Wang et al., 2020). In addition to precipitation, the mechanisms involved in heavy metals adsorption by activated carbon include complexation and ion exchange (Gao et al., 2019). Ion exchange occurs when adsorbate ions exchange with ions and ligands from the adsorbent, while minerals and functional groups on the adsorbent engage in precipitation and complexation (Wang et al., 2020). Complexation is the coordination of adsorbate with functional groups on the adsorbent through hydrogen bonding or donation of lone pair electron (Zhao et al., 2020). The functional groups in activated carbon that include oxygen (carboxyl, phenolic, and lactonic) create negative charges on the surface, allowing them to form complexes with heavy metals (Gao et al., 2019). In addition to functional groups, different mineral groups play major roles in heavy

metals adsorption via surface complexation, electrostatic interaction and precipitation processes (Bandara et al., 2020). Mineral ions K(I), Na(II), Mg(II), Ca(II), Fe(III), Al(III) on the adsorbent surface exchange with heavy metal ions while complexation occurs with the amino group (Pineda et al., 2020). Figure 2.2 summarises different mechanism involved in the adsorption of heavy metals with activated carbon.

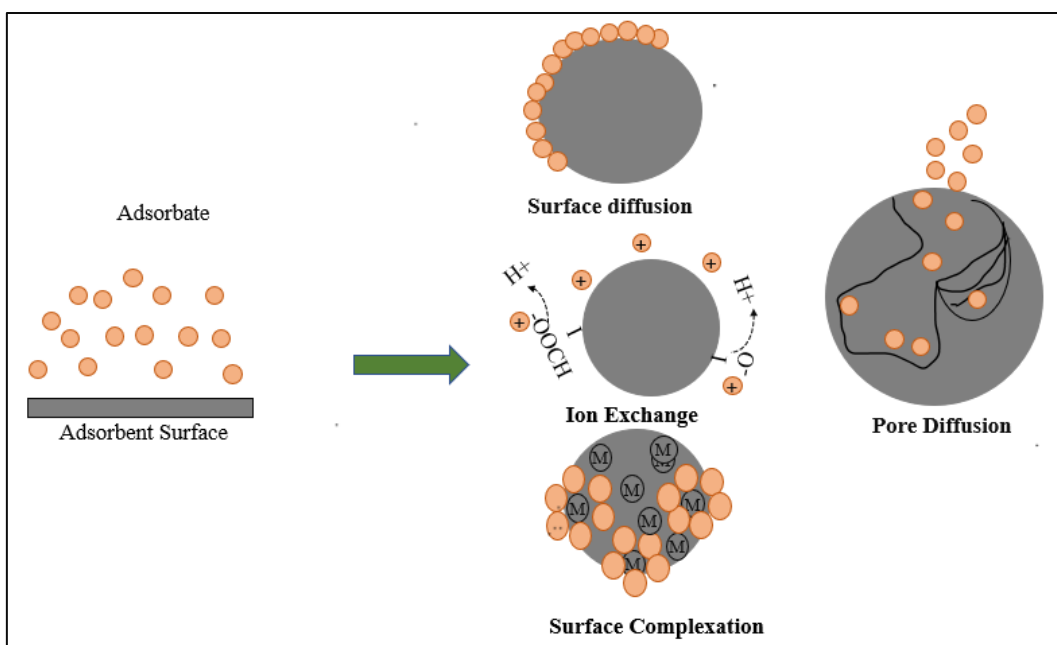
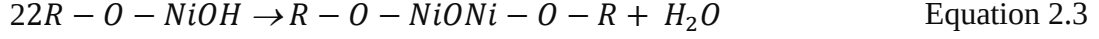
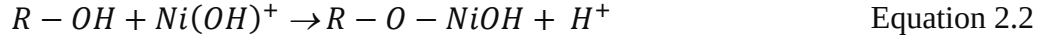


Figure 2.2: Visual illustration of different adsorption mechanisms

In adsorption process, co-precipitation between OH⁻ and metal ions occurs as expressed in equation 2.1 (Al-Onazi et al., 2021). Ion-exchange occurs between the hydrogen of the hydroxyl group and Ni(OH)⁺ group as shown in equation 2.2 (Balasubramanian et al., 2020). While the complexation reaction was represented by equation 2.3 and 2.4 (An et al., 2019). It was concluded that Ni(II) settled in the form of nickel hydroxide and complexed nickel oxide on the adsorbent surface (Guo et al., 2020).



2.5 Adsorption Kinetics

Kinetic studies of the adsorption process are carried out through by examining the rate-limiting step and data from experiments that evolved over time and fitting these findings to different kinetic models such as Pseudo-First-Order (PFO), Pseudo-Second-Order (PSO) (Ngaini et al., 2021), Elovich model (Ahmad et al., 2018), intraparticle diffusion of Weber and Morris (ID-WM) (Shafiq et al., 2021).

2.5.1 Pseudo-First-Order (PFO) Equation

The Pseudo-first order rate equation was proposed for the first time by Lagergren in 1898 (Kaur et al., 2020) and its nonlinear rate equation can be expressed as equation 2.5 (Qu et al., 2020; Tran et al., 2017) while linear forms can be expressed as equation 2.6 (Tran et al., 2017) and equation 2.7 (Tsamo et al., 2018; Ngaini et al., 2021).

$$q_t = q_e(1 - e^{-k_1 t}) \quad \text{Equation 2.5}$$

$$\log(q_e - q_t) = -\frac{k_1}{2.303} t + \log(q_e) \quad \text{Equation 2.6}$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{Equation 2.7}$$

While both q_e and q_t refer to the amount of heavy metal that is adsorbed in every unit mass of adsorbent at equilibrium and time t (min), K_1 ($L \min^{-1}$) refers to the Pseudo-First-Order rate constant obtained from the slop of liner plot of $\ln(q_e - q_t)$ versus t (Ngaini et al., 2021).

In majority of the adsorption studies, Pseudo-First-Order equation is only valid for the first 20-30 min of contact time; but not over the whole adsorbate range (Ho & McKay, 1998). Different studies followed different expression of pseudo first order rate equation, as equation 2.5 (Ahmad et al., 2018; Qu et al., 2020), equation 2.6 (Venkateswarlu et al., 2019; Shafiq et al., 2021), equation 2.7 (Yin et al., 2019; Gao et al., 2020; Kongsune et al., 2021). Table 2.3 contains several studies with adsorption process flowing Pseudo-First-Order kinetics.

2.5.2 Pseudo-Second-Order (PSO) Equation

The second-order rate equation was first introduced by Blanchard R. J. in 1984, however, Ho Y. S. published the nonlinear form the PSO equation for solid-liquid adsorption systems in 1995, as mentioned in equation 2.8 (Tran et al., 2017), while four linear forms have been reported as equation 2.9 (Tsamo et al., 2018; Ngaini et al., 2021) and equation 2.10-2.12 (Tran et al., 2017), as reported in the literature.

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad \text{Equation 2.8}$$

Equation 2.9 gives, Type 1 linear expression of PSO with a plot of t/q_t against t :

$$\frac{t}{q_t} = \left(\frac{1}{q_e} \right) t + \frac{1}{k_2 q_e^2} \quad \text{Equation 2.9}$$

Equation 2.10 gives, Type 2 linear expression of PSO with a plot of $1/q_t$ against $1/t$:

$$\frac{1}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) \frac{1}{t} + \frac{1}{q_e} \quad \text{Equation 2.10}$$

Equation 2.11, Type 3 linear expression with a plot of q_t against q_t/t :

$$q_t = \left(\frac{1}{k_2 q_e} \right) \frac{q_t}{t} + q_e \quad \text{Equation 2.11}$$

Equation 2.12, Type 4 linear expression with a plot of q_t/t against q_t :

$$\frac{q_t}{t} = -(k_2 q_e) q_t + k_2 q_e^2 \quad \text{Equation 2.12}$$

Initial rate h ($\text{mgg}^{-1} \text{min}$) is determined by using equation 2.13 which is derived from Type 1 linear expression of PSO with t approaching to zero (Jin et al., 2020).

$$h = k_2 q_e^2 \quad \text{Equation 2.13}$$

Where q_e and q_t denotes the amount of heavy metal adsorbed in every unit mass of adsorbent at equilibrium and time t (min), k_2 ($\text{gmg}^{-1} \text{min}^{-1}$) refers to the pseudo second order rate constant obtained from the slop of liner plot of t/q_t versus t (Ngaini et al., 2021). The affinity between the adsorbent and the adsorbate can speed up the adsorbate's initial adsorption (Tran et al., 2017). Different studies followed different expression of pseudo order rate equation (Equation 2.4) (Ahmad et al., 2018; Qu et al., 2020), Equation 2.5 (Gao et al., 2020; Shafiq et al., 2021; Wang, 2020), Equation 2.6 (Kongsune et al., 2021). Table 2.3 contains several studies with adsorption process flowing Pseudo-Second-Order kinetics.

2.5.3 Elovich Equation

The Elovich model explains the chemisorption-controlled heterogeneous diffusion process (Jin et al., 2020). This model kinetic was first proposed by Roginsky-Zeldovich in

1934. non-linear expression is in equation 2.14 while simplified linear expression is in and equation 2.15 (Omid et al., 2020) :

$$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t) \quad \text{Equation 2.14}$$

$$q_t = \frac{1}{\beta} \ln(t) + \frac{1}{\beta} \ln(\alpha\beta) \quad \text{Equation 2.15}$$

Where q_t is the amount of metal ions adsorbed after time t in min and q_e is the amount adsorbed when the process reaches equilibrium, α is the initial adsorption rate (mg/(g min)) and β is a constants for desorption constant (gmg⁻¹) (Gao et al., 2020) and a linear plot of q_t versus $\ln t$ gives slope of $(1/\beta)$ and an intercept of $(1/\beta).\ln(\alpha\beta)$ (Tran et al., 2017). Several studies reported to follow the linear expression of Elovich rate equation, as of equation 2.11 (Gao et al., 2020; Babu et al., 2018; Saraeian et al., 2018). Table 2.3 contains several studies with adsorption process flowing Elovich Model kinetics.

2.5.4 Intra-Particle Diffusion and Film Diffusion

The intra-particle diffusion model can help with identification of adsorption mechanisms and prediction of the rate-controlling step (Taşar & Özer, 2020). The intra-particle diffusion model, as developed by Weber and Morris model, is used to adsorption processes in which adsorbate diffuses toward adsorbent, as shown in equation 2.16 (Khan et al., 2020).

$$q_t = K_{dif} t^{0.5} + C \quad \text{Equation 2.16}$$

Where K_{dif} (mgg⁻¹ min^{1/2}) is intra-particle diffusion rate constant and C (mgg⁻¹) is a constant related to boundary layer thickness (Kaya et al., 2020). K_{dif} and C values are derived

from slope and intercept by plotting q_t against $t^{0.5}$, the boundary layer effect increases with the increase in value of C and vice versa (Khan et al., 2020), while value of C near to zero implies that intraparticle diffusion can be the rate-limiting step (Abdallah et al., 2019)

The liquid film diffusion model is used to explore whether the boundary influences the adsorption process (Kongsune et al., 2021), and its mathematical expression is as shown in equation 2.17 (Alguacil et al., 2018).

$$\ln (1 - F) = -K_{fd} t \quad \text{Equation 2.17}$$

Where K_{fd} is the film diffusion rate constant, $F = q_t/q_e$ is the accomplishment of equilibrium in fractional form (Alguacil et al., 2018; Kongsune et al., 2021). Film diffusion and intraparticle diffusion are both physical processes with slow kinetics and are significant in adsorption kinetics (Shi et al., 2019). Film diffusion can be at the first stage, followed by intraparticle diffusion as the second stage (Abdallah et al., 2019). Table 2.3 contains several studies with adsorption process flowing Diffusion Model kinetics.

Table 2.3: Kinetic model fitness for heavy metals adsorption by various biomass-based adsorbents with chemical/thermal treatment

Adsorbent Source	Modification	Metal ions	Adsorption Capacity (mgg ⁻¹)	Kinetic reaction	Reference
Bagasse	Treated with urea, dimethyl formamide and phosphoric acid	Pb(II)	161.6	PSO	(Huang et al., 2020)
		Cu(II)	41.30	PFO	
Spent mushroom compost	Carbonised at 500 °C for 3 h in limited O ₂ flow	Pb(II)	62.4	I-D	(Abdallah et al., 2019)
Rice Husk	Cellulosic grafting with hydroxy ethyl methacrylate monomer, acrylic acid and potassium persulphate	Ni(II)	85.32	PSO	(Kumar et al., 2019)
		Pb(II)	118.06	PSO	
		Cu(II)	84.82	PSO	
<i>Artocarpus odoratissimus</i> leaves	Treated with NaOH and EDTA	Pb(II)	154.8	PSO	(Zaidi et al., 2018)
Grape pomace	Enzyme treated, pyrolyzed at 700 °C	Pb(II)	134	PSO	(Jin et al., 2020)
Walnut shell	Treated with H ₂ SO ₄ and NaOH, CS ₂ , MgSO ₄	Pb(II)	12.75	PSO	(Lu & Guo, 2019)

Table 2.3 continued

Sago bark	Microwave pyrolyzed at 400 °C, for 15 min, treated with 20% NaOH for 2 h, dried, then 5 M HCl for 2 h, washed and dried	Cu(II)	0.35	PSO	(Wahi et al., 2022)
		Ni(II)	-	PSO	
		Pb(II)	-	PSO	
Cauliflower leaves	Pyrolyzed at 600 °C for 2 h	Pb(II)	177.82	PSO	(Ahmad et al., 2018)
		Cu(II)	53.96	Elovich	
Banana Peel	Pyrolyzed at 600 °C for 2 h	Pb(II)	247.1	PSO	
		Cu(II)	75.99	Elovich	

Note: PFO = Pseudo First Order; PSO = Pseudo Second Order; I-D = Intraparticle diffusion

2.6 Adsorption Isotherms

Adsorption isotherms' structure provides a qualitative analysis of the sorption process and the extent to which the adsorbate covers the surface of the adsorbent, which assists in determining the process feasibility for a certain application as well as adequate adsorbent selection and determination of adsorbent dosage needed for the adsorption process (Kongsune et al., 2021). The adsorption data is assessed using four frequently used isotherm models to determine the nature of the adsorption equilibrium (Ghosh et al., 2020).

Depending on the number of variables, a broad set of adsorption isotherm models can be categorised based on number of parameters (Tran et al., 2017). Henry isotherm is the type of isotherms involving one parameter only (Wang & Guo, 2020). The examples of isotherms involving two parameters include Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm (Zaidi et al., 2018). While Sips, Redlich-Peterson, Khan, and Toth isotherms are the examples of three parameters isotherms (Hashem et al., 2020). Koble-Corrigan, Weber-van Vliet, Fritz-Schlunder and Baudu isotherms are the examples of isotherms involving more than three-parameters (Tran et al., 2017). Some of these isotherm models are being described in detail below, along with pertinent equations.

2.6.1 Langmuir Isotherm

The theoretical Langmuir equation was initially applied to the adsorption of gases on a solid surface, by Langmuir in 1918 (Ahmad et al., 2018). Langmuir isotherm is based on the assumptions: i) on the adsorbent's surface, there are a certain number of accessible sites with the same energy level; ii) the adsorption process is of reversible nature (Hasana et al., 2020); iii) once the adsorbate has covered all of the sites on the adsorbent surface, no further

adsorption can occur (Biswas et al., 2019); iv) there is no adsorbate-adsorbate interaction in an adsorption process (Tran et al., 2017). Equation 2.18 is the non-linear expression of Langmuir model, while equations 2.19-2.22 are different linear expressions of Langmuir isotherm (Zaheer et al., 2019).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{Equation 2.18}$$

Type 1 linear expression of Langmuir Model (Hanes-Woolf linearisation)

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \text{Equation 2.19}$$

Type 2 linear expression of Langmuir Model (Lineweaver-Burk linearisation)

$$\frac{1}{q_e} = \left(\frac{1}{q_m K_L} \right) \frac{1}{C_e} + \frac{1}{q_m} \quad \text{Equation 2.20}$$

Type 3 linear expression of Langmuir Model (Eadie-Hoffsee linearisation)

$$q_e = \left(\frac{-1}{K_L} \right) \frac{q_e}{C_e} + q_m \quad \text{Equation 2.21}$$

Type 4 linear expression of Langmuir Model (Scatchard linearisation)

$$\frac{q_e}{C_e} = -K_L q_e + q_e K_L \quad \text{Equation 2.22}$$

Where q_m (mgg^{-1}) denotes adsorbent's maximum monolayer adsorption capacity, q_e (mgg^{-1}) denotes adsorption capacity at equilibrium, C_e (mgL^{-1}) denotes the quantity of adsorbate in the solution at equilibrium, K_L (Lmg^{-1}) represents the Langmuir constant which is related to adsorbate-adsorbent affinity and can be correlated with the adsorbent's suitable area and porosity, implying that adsorbents with larger surface area and pore volume have a higher adsorption capacity (Ayawei et al., 2017). The plots for different linearised forms of

Langmuir isotherm model are as C_e/q_e against C_e for equation 2.19, $1/q_e$ against $1/C_e$ for equation 2.20, q_e versus q_e/C_e against C_e for equation 2.21 and q_e/C_e versus q_e for equation 2.22 (Zaheer et al., 2019). Magnitude of q_m and K_L are obtained from slope and intercept of straight lines respectively (Lodhi et al., 2019). The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the separation factor R_L which can be expressed in equation 2.23 (Ayawei et al., 2017).

$$R_L = \frac{1}{1+k_L C_e} \quad \text{Equation 2.23}$$

The value of R_L demonstrates the isotherm type, ($0 < R_L < 1$) indicates as favourable, ($R_L > 1$) implies to unfavourable, ($R_L = 0$) implies to irreversible and ($R_L = 1$) entails to linear isotherm (Jin et al., 2020).

Different studies followed different expression of Langmuir model isotherm (equation 2.18 (Pineda et al., 2020; Yin et al., 2019), equation 2.19 (Omid et al., 2020; Venkateswarlu et al., 2019), equation 2.20 (Liu et al., 2019; Shafiq et al., 2021), equation 2.21 and equation 2.22 (Tran et al., 2016). Recent studies which have reported the adsorption of Cu(II), Pb(II) and Ni(II) by activated adsorbents, fitting with Langmuir model have been referred in Table 2.4.

2.6.2 Freundlich Isotherm

The Freundlich isotherm was initially depicted by Freundlich H. M. in 1906 which is dependent on a heterogeneous surface with a non-uniform distribution of adsorption heat through a multilayer adsorption process (Zaheer et al., 2019). Equation 2.24 and equation 2.25 express the non-linear and linear forms of Freundlich isotherm model respectively (Tsamo et al., 2018):

$$q_e = K_F C_e^{\frac{1}{n}} \quad \text{Equation 2.24}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{Equation 2.25}$$

Where C_e (mgL^{-1}) denotes total amount of adsorbate in solution at equilibrium, q_e (mgg^{-1}) denotes the adsorbate concentration adsorbed at equilibrium, K_F ($\text{mgg}^{-1} \cdot (\text{Lmg}^{-1})$). $1/n$ is named as Freundlich constant, $1/n$ is called Freundlich intensity parameter, The parameters of the Freundlich equation can be obtained from the K_F is equal to the value of intercept and n is equal to slope of the straight line of the plot $\log q_e$ versus $\log C_e$ (Zaheer et al., 2019). The slope and intercept plot of $\log q_e$ against $\log C_e$ provides the value of heterogeneity factor $1/n$ and K_F , the value of $1/n$ indicates the favourability of the adsorption process, if $n = 1$, adsorption is linear; $n < 1$, it is chemical and $n > 1$, adsorption is physical favorable process (Zaheer et al., 2019).

Different studies followed different expression of Freundlich model isotherm, as equation 2.24 (Mahdi et al., 2019; Qu et al., 2021) while equation 2.25 (Lodhi et al., 2019; Saraeian et al., 2018). Several studies have been reported in which adsorption data fits the Freundlich Model isotherm, as mentioned in Table 2.4. Some studies have reported that the experimental data appear to fit with both the Langmuir and Freundlich isotherms, suggesting that in given circumstances, sorption occurred through adsorption as well as absorption (Ilangoan et al., 2017).

2.6.3 Temkin Isotherm:

In 1940, Temkin and Pyzhev presented this adsorption isotherm model which is based on the assumption that interactions between the adsorbate and the adsorbent produce

heat during adsorption (Kongsune et al., 2021). It's Refer to a term that is widely used to characterise heterogeneous surfaces having non-uniform binding energy distributions (Saraeian et al., 2018). This isotherm relates to chemical adsorption on solid adsorbents and adsorbates in aqueous medium (Kongsune et al., 2021). The nonlinear and linear forms of Temkin model are in equation 2.26 and equation 2.27 respectively (Zaheer et al., 2019).

$$q_e = \left(\frac{RT}{b_T} \right) \ln(A_T \cdot C_e) \quad \text{Equation 2.26}$$

$$q_e = \left(\frac{RT}{b_T} \right) \ln A_T + \left(\frac{RT}{b_T} \right) \ln C_e \quad \text{Equation 2.27}$$

Where q_e (mgg^{-1}) denotes the adsorbate's quantity adsorbed at equilibrium, R is universal gas constant ($\text{JK}^{-1}\text{mol}^{-1}$) and T is the absolute temperature in Kelvin (Sen et al., 2018). Where A_T and b_T are named as Temkin parameters and calculated as slope and intercepts of the plots of q_e versus $\ln C_e$ respectively. As per Temkin isotherm if value of $b_T < 20 \text{ J mol}^{-1}$, it means that the physisorption is dominating the chemisorption (Zaheer et al., 2019). Several studies have been published in which adsorption data matches the Temkin Model isotherm, with a few instances included in Table 2.4.

2.6.4 Redlich-Peterson Isotherm

Redlich and Peterson devised three parameters empirical isotherm which incorporates features of both Langmuir and Freundlich equations (Ahmad et al., 2018). This model can be applied to illustrate adsorption equilibrium across a broad range of adsorbate concentrations in both homogeneous and heterogeneous systems (Tsamo et al., 2018). The nonlinear and linear form of this model are expressed in equation 2.28 and equation 2.29 (Ayawei et al., 2017).

$$q_e = \frac{A C_e}{1 + B C_e^\beta} \quad \text{Equation 2.28}$$

$$\ln \left(\frac{C_e}{q_e} \right) = \beta \ln C_e - \ln A \quad \text{Equation 2.29}$$

Redlich-Peterson constants, β and A can be determined from a $\ln(C_e/q_e)$ versus $\ln C_e$ plot, as slope and intercept respectively (Ayawei et al., 2017). When the exponent β is close to zero, the sorption process fits better with the Freundlich model, implying monolayer adsorption and when β is close to 1.0, the data fits better with the Langmuir isotherm model (Ahmad et al., 2018). Examples of adsorption process fitting with Redlich-Peterson model have been referred in Table 2.4.

Table 2.4: Isotherm models fitness of heavy metals adsorption by different biomass-based adsorbents with chemical/thermal treatment

Adsorbent Source	Modification	Metal ions	Adsorption Capacity (mgg ⁻¹)	Isotherm	Reference
Bagasse	Treated with urea, dimethyl formamide and phosphoric acid	Pb(II)	161.6	Langmuir	(Huang et al., 2020)
		Cu(II)	41.30	Langmuir	
Spent mushroom compost	Carbonised at 500 °C for 3 h in limited O ₂ flow	Pb(II)	62.4	Langmuir	(Abdallah et al., 2019)
Mangosteen shell	Treated with conc. H ₂ SO ₄ at 150 °C for 24 h, washed with NaHCO ₃ sol.	Ni(II)	57.14	Langmuir	(Anitha et al., 2020)
Rice Husk	Cellulosic grafting with hydroxy ethyl methacrylate monomer, acrylic acid and potassium persulphate	Ni(II)	85.32	Langmuir	(Kumar et al., 2019)
		Pb(II)	118.06	Langmuir	
		Cu(II)	84.82	Temkin	
Sago bark	Microwave pyrolyzed at 400 °C, for 15 min.	Cu(II)	7.09	D-R	(Wahi et al., 2022)
		Ni(II)	-	Freundlich	

Table 2.4 continued

<i>Artocarpus odoratissimus</i> leaves	Treated with NaOH and EDTA	Pb(II)	154.8	R-P	(Zaidi et al., 2018)
Sago bark	Microwave pyrolyzed at 400 °C, for 15 min, treated with 20% NaOH for 2 h, dried, then 5 M HCl for 2 h, washed and dried	Cu(II)	0.35	Temkin	(Wahi et al., 2022)
		Ni(II)	-	Freundlich	
		Pb(II)	-	Freundlich	
Cauliflower leaves	Pyrolyzed at 600 °C for 2 h	Pb(II)	177.82	R-P	(Ahmad et al., 2018)
		Cu(II)	53.96	R-P	
Banana Peel	Pyrolyzed at 600 °C for 2 h	Pb(II)	247.1	R-P	
		Cu(II)	75.99	R-P	
Grape pomace	Enzyme treated, pyrolyzed at 700 °C	Pb(II)	134	Temkin	(Jin et al., 2020)
Walnut shell	Treated with H ₂ SO ₄ and NaOH, CS ₂ , MgSO ₄	Pb(II)	12.75	Temkin	(Lu & Guo, 2019)

Note: D-R = Dubinin-Radushkevich; R-P = Redlich-Peterson

2.6.5 Error Functional Analysis for Linear Models

The error functions are frequently used to compare the results of non-linear and linear models in adsorption investigations (Shah et al., 2020) and determination coefficient R^2 is one of the most commonly used to determine the error functions (Zheng et al., 2019). The determination of R^2 , equation 2.30 (Zheng et al., 2019).

$$R^2 = \frac{\sum_{i=1}^p q_{e \text{ isotherm}} - q_{e \text{ exp}}}{\sum_{i=1}^p [(q_{e \text{ isotherm}} - q_{e \text{ exp}})^2 + (q_{e \text{ isotherm}} - q_{e \text{ exp}})^2]} \quad \text{Equation 2.30}$$

Where $q_{e \text{ exp}}$ is the adsorption capacity (mgg^{-1}) derived from the experimental data and $q_{e \text{ isotherm}}$ is the adsorption capacity (mgg^{-1}) derived from the theoretical model's calculations, p is the number of parameters in the specified model and n represents the number of experimental data (Zheng et al., 2019).

2.7 Factor Affecting Adsorption of Heavy Metals:

Adsorption capacity is significantly influenced by adsorbent dosage, adsorbate initial concentration, solution pH, temperature and contact time, all of which need to be evaluated during the adsorption process (Chen et al., 2020).

2.7.1 Sorbent Dosage

Adsorbent dosage is critical in the adsorption process because it can be used to evaluate the adsorbent's ability to remove a certain concentration of an adsorbate (metal ions) (Biswas et al., 2019). To determine the optimal amount of adsorbent for maximal adsorption efficiency, a series of experiments are carried out while maintaining other process variables constant, such as pH, initial ion concentration and contact duration, constant (Al-Onazi et al., 2021). Table 2.5 lists a number of recent studies that utilised modified adsorbents derived

from various agricultural and horticulture wastes to adsorb Cu(II), Pb(II) and Ni(II) at adsorbent dosages ranging from 0.1 gL⁻¹ to 10 gL⁻¹. This suggests that the adsorbent dosage in this range has mostly been studied for heavy metals adsorption using modified adsorbent derived from agricultural and horticulture wastes.

With the increase in adsorbent dosage in an adsorption process, the adsorption capacity boosts to a certain level till achieving the highest adsorption capacity and then drops with further increase in adsorbent dosage (Biswas et al., 2019; Qin et al., 2019). At constant metal ion concentrations, increasing adsorbent dosage may cause adsorbent aggregation, reducing effective surface area and confining active sites, resulting in a decreased adsorption capacity to extract metal ions from aqueous medium (Aboli et al., 2020; Qin et al., 2019). It can be due to the reason that with an increase in adsorbent dosage, solid to liquid ratio increases, occasionally obstructing the active sites and resulting in reduced adsorption capacity (Biswas et al., 2019). In some situations, increasing the adsorbent dosage allows the metal ions access to a more porous surface and a greater number of appropriate active sites, allowing them to readily diffuse and adsorb in the adsorbent structure, resulting in increased adsorption efficiency (Choudhary et al., 2020).

Table 2.5: Effect of Adsorbent dosage on Adsorption Efficiency using modified adsorbents

Adsorbent Source	Modification	Metal	Dosage (gL ⁻¹)	pH	Temp (°C)	Contact time (min)	Initial Conc. (ppm)	Removal %	Adsorption Capacity (mgg ⁻¹)	Reference
<i>Punica Granatum</i> rind	Treated: with FeCl ₃ , and CH ₃ COONa, Temp: 70 °C, Time : 2 h	Pb(II)	0.1	5	28	120	20	96.68	46.18	(Venkateswarlu et al., 2019)
Peanut shell	Stage 1: Pyrolysis Temp: 500 °C, Time: 2 h, Stage 2: Treated with KMnO ₄ , and KOH Temp: 300 °C, Time: 1 h	Ni(II)	0.1	6	25	60	20	90	87.15	(An et al., 2019)

Table 2.5 continued

Ginkgo shells	Stage 1: Pyrolysis Temp: 300 °C, Stage 2: Treated with H ₂ SO ₄ , KMnO ₄ , H ₂ O ₂ Temp: 20 °C, 35 °C, 98 °C	Cu(II)	0.5	7	25	100	25	83.6	41.6	(Qin et al., 2019)
<i>Opuntia ficusindica</i> Cladodes	Stage 1: Pyrolysis Temp: 400 °C Time: 1 h, Stage 2: Treated with NaOH, Temp: 500 °C Time: 1 h	Cu(II)	0.6	6	30	2880	10	91	49.36	(Choudhary et al., 2020)
		Ni(II)	0.6	6	30	2880	10	89	44.35	
<i>Citrus limetta</i>	Pyrolysis Temp: 700 °C, Time: 3 h	Ni(II)	1	6	25	60	5	97.54	58.139	(Aboli et al., 2020)
		Pb(II)	1	6	25	60	5	99.53	69.82	

Table 2.5 continued

Coffee grounds	Treated: with HCl Temp: at boiling Time: 2 h	Pb(II)	1.5	6	30	75	100		61.6	(Babu et al., 2018)
Date palm	Pyrolysis Temp: 800 °C	Cu(II) Pb(II)	1.8 1.8	5.5 4.5		180 60	100 100	75 99	41 98.9	(Amin et al., 2019)
Cocoa cortex	Stage 1: Treated: with NaOH Temp: 70 °C Time: 2 h Stage 2: Treated: with Sodium alginate and CaCl ₂	Cu(II)	2	4.17	25	220	100	95.32		(Fotsing et al., 2020)
<i>Artocarpus odoratissimus</i> leaves	Treated: with EDTA Temp: room temp Time: 2 h	Pb(II)	2	5	25	60	100	80	53.26	(Zaidi et al., 2018)

Table 2.5 continued

<i>Artocarpus odoratissimus</i> leaves	Treated: with NaOH Temp: room temp Time: 2 h	Pb(II)	2	5	25	60	100	85	109.7	(Zaidi et al., 2018)
Oil Palm residue	Stage 1: Treated with dimethyl sulfoxide Time: 24 h at 120 rpm Stage 2: Treated with tetra ethyl silicate and alumina nano particles Time: 12 h at 120 rpm	Ni(II)	5	6	28	120	100	81	-	(Herrera-Barros et al., 2020)
Date seed	Stage 1: Carbonisation Temp: 550 °C Time: 3 h Stage 2: Treated with NaOH Time: 2 h	Ni(II)	10	6	23	60	58.7	94	19.54	(Mahdi et al., 2018)
		Cu(II)	10	6	23	60	63.55	94	26.75	

2.7.2 Effect of Initial Metal Concentration

Higher initial metal ion concentration enhances adsorption capacity by increasing the concentration gradient and decreasing mass transfer resistance (Biswas et al., 2019). However, due to the presence of surplus ions in the system, greater initial concentration increases the competition to adhere to an adsorbent surface, reducing total removal efficiency for the metal ions (Amin et al., 2019). As the forces driving the adsorption process develop in proportion to the increase in adsorbate concentration, adsorption capacity rises linearly as the initial adsorbate concentration rises (Taşar & Özer, 2020). Table 2.6 summarises the studies with a wide range of initial concentration of adsorbates Cu(II), Pb(II) and Ni(II) and their removal from aqueous medium utilising modified adsorbents prepared from diverse agricultural and horticulture wastes.

Several studies reported that maximum removal occurred for a certain level of initial concentration and then removal efficiency decreased with the increase in initial concentration (Biswas et al., 2019; Rodriguez et al., 2018; Qin et al., 2019). Contrarily, adsorption capacity found to be increasing with increasing initial concentration keeping other factor like adsorbent dose, solution pH and temperature, constant (Kongsune et al., 2021).

Table 2.6: Effect of initial metal concentration sorption by modified adsorbents

Adsorbent Source	Modification	Metal	Dosage (gL ⁻¹)	pH	Temp (°C)	Contact time (min)	Initial Conc. (ppm)	Removal %	Adsorption Capacity (mgg ⁻¹)	Reference
Rice husk ash	Treated: with Mg(NO ₃) ₂ , and Fe(NO ₃) ₃ Temp: room temp Time: 20 min agitation, left for 24 h	Pb(II)	0.5	5	25	480	10	99.09	100.58	(Yu et al., 2018)
Mangosteen shell	Treated: with conc. H ₂ SO ₄ , Temp: 150 °C, Time for 24 h	Ni(II)	0.6	6.29	25	30	10	99	57.14	(Anitha et al., 2020)
Coffee husk	Stage 1: Pyrolysis Temp: 500 °C, Time: 1 h Stage 2: Carbonised Temp: 800 °C Time: 30 min	Ni(II)	1	6	55	1440	45	90.8	57.14	(Rodriguez et al., 2018)

Table 2.6 continued

Spent Coffee	Stage 1: Pyrolysis	Ni(II)	0.8	6	55	1440	45	65.2	51.91	(Rodriguez et al., 2018)
	Temp: 500 °C									
	Time: 1 h									
	Stage 2: Carbonised									
	Temp: 800 °C									
Pinecones	Time: 30 min									(Biswas et al., 2019)
	Stage 1: Pyrolysis	Ni(II)	1	5.5	40	180	50	84	156	
	Temp: 500 °C									
	Time: 1 h									
	Stage 2: Treating with sodium alginate									
	Time: 6 h with magnetic stirring	Cu(II)	1	5.5	40	180	50	84	112	
	Stage 3: Treated with CaCl ₂									

Table 2.6 continued

Peanut shell	Stage 1: Treated with ZnCl ₂ , Temp: 80 °C Time: 2 h Stage 2: Pyrolysis Temp: 500 °C Time: 1 h	Pb(II)	0.5	5	1	60	50	70	135	(Liu et al., 2018)
Long-root <i>Eichhornia</i> <i>crassipes</i>	Stage 1: Treated with KOH, Time: 12 h Stage 2: Carbonisation Temp: 600 °C, Time: 1 h Stage 3: Pyrolysis, Temp: 800 °C, Time: 2 h	Ni(II)	1	6	30	150	58.69	80	56.93	(Cao et al., 2019)
		Cu(II)	1	6	30	150	63.5	80	137.13	

Table 2.6 continued

Softwood pine	Stage 1: Pyrolysis	Ni(II)	10	5.5	22	720	100	73.5	90.9	(Sajjadi et al., 2019)
	Temp: 600 °C									
	Stage 2: Treated with CO ₂									
	Time: 30 mint									
	Stage 3: 20 kHz ultrasonic treatment in CO ₂ environment									
	Time: 60 Sec									
	Stage 4: Treated with H ₃ PO ₄									
	Temp: 50 °C, Time: 3hr									
	Stage 5: Treated with urea									
	Temp: room temp									
	Time: 8 h									

Table 2.6 continued

Date palm	Pyrolysis at 800 °C	Cu(II)	1.8	4.5	30	60	100	99	41	(Amin et al., 2019)
		Pb(II)	1.8	4.5	30	60	100	99	98.9	
Banan Peel	Pyrolysis at 600 °C	Cu(II)	2.5	6	22	1440	200	-	75.99	(Ahmad et al., 2018)
	Time: 2 h									
Cauliflower leaves	Pyrolysis at 600 °C	Cu(II)	2.5	6	22	1440	200	-	53.66	
	Time: 2 h									
Neem leaves	Treated with polyethylene glycol, acrylamide, and 2-hydroxy ethyl methacrylate	Pb(II)	0.25	6	30	80	400	57	575	(Maity & Ray, 2018)
	Temp: 30 °C, Time: 40 min									
<i>Caragana korshinskii</i>	Pyrolysis	Pb(II)	3	6	25	180	600	90	220.94	(Wang, 2020)
	Temp: 650 °C									
	Time: 3 h									

2.8 Effect of pH

In the adsorption of heavy metals from aqueous solution, pH is one of the significant parameters (Jain et al., 2020). Table 2.7 summarises different adsorption studies which have reported broad pH range of 2-9 for Pb(II) adsorption, 2-7 for Cu(II) adsorption 5-6 for Ni(II) adsorption using different adsorbents based on agricultural and horticulture wastes.

At lower pH, hydrogen ions compete for accessible adsorption sites on the adsorbent due to the increasing concentration of hydrogen ions in the aqueous medium (Qin et al., 2019), as well as with the adsorbate ions (Lin et al., 2019). This competition results in decreased metal adsorption (Ilangoan et al., 2017) and with rise in the pH, the negative charge on the adsorbent surface increases which facilitates metal adsorption (Qin et al., 2019). However different studies have reported that maximum adsorption of Pb(II) was found at pH 6 because at a pH higher than 6, the metal ions precipitates forming metal hydroxide consequently decreasing adsorption (Baby & Hussein, 2020; Taşar & Özer, 2020). Similar behaviour has been reported in Cu(II) and Ni(II) adsorption too and maximum adsorption was found to be at pH 5, therefore, solution pH should be adjusted to a value of 5-6 to avoid the influence of precipitation on the adsorption process (Abdallah et al., 2019; Fotsing et al., 2020).

Table 2.7: Effect of solution pH on Adsorption of Cu(II), Pb(II) and Ni(II) by modified adsorbents

Adsorbent Source	Modification	Metal	Dosage (g ^L ⁻¹)	pH	Temp (°C)	Contact time (min)	Initial. Conc. (ppm)	Removal %	Adsorption Capacity (mgg ⁻¹)	Reference
Sago hampas; Rice husk	Stage 1: Pyrolysis Temp: 700 °C Time: 6 h, Stage 2: Treated with ethanol, 3-triethoxysilyl propyl amine, Time: 1 h,	Cu(II)	1	2	25	30	5	9	0.4248	(Ngaini et al., 2021)
Cocoa cortex	Stage 1: Treated: with NaOH, Temp: 70 °C, Time: 2 h, Stage 2: Treated: with Sodium alginate and CaCl ₂	Cu(II)	2	4.17	25	220	100	95.32	19.54	(Fotsing et al., 2020)

Table 2.7 continued

Bagasse	Stage 1: Treated with N, N-Dimethyl formamide Temp: 130 °C Time: 1 h Stage 2: Treated with phosphoric acid Temp: 130 °C, Time: 4 h	Cu(II)	0.75	5	25	180	6.35	92.74	40.32	(Huang et al., 2020)
Date seed	Stage 1: Treated with HCl, Temp: 90 °C, Time: 2 min Stage 2: Pyrolysis Temp: 550 °C, Time: 3 h Stage 3: Treated with HCl, Time: 2 h	Cu(II)	10	6	23	60	63.55	94	44.80	(Mahdi et al., 2019)

Table 2.7 continued

Pistachio shells	Stage 1: Pyrolysis Temp: 550 °C, Time: 1 h Stage 2: Steam activation Temp: 900 °C, Time: 10 h. Stage 3: Treated with dil. HCl, Time: 48 h Stage 4: Treated with HNO ₃ , Temp: 60 °C, Time: 12 h	Cu(II)	0.6	6.5	55	180	60	95.29	277.7	(Nejadshafiee & Islami, 2020)
<i>Azadirachta indica</i>	Treated with H ₃ PO ₄ Temp: 260 °C, Time: 20 min	Cu(II)	1	7	25	60	110	59	-	(Al Moharbi et al., 2020)
Peanut hulls	Treated with FeCl ₃ , FeSO ₄ , NH ₄ OH, Temp: 80 °C, Time: 30 min	Ni(II)	4	6	25	30	10	82.8	3.29	(Kucukcongar et al., 2020)

Table 2.7 continued

Date seed	Stage 1: Treated with HCl Temp: 90 °C, Time: 2 min Stage 2: Pyrolysis Temp: 550 °C Time: 3 h Stage 3: Treated with HCl Time: 2 h	Ni(II)	10	6	23	60	63.55	94	40.62	(Mahdi et al., 2019)
Sago hampas; Rice husk	Stage 1: Pyrolysis Temp: 700 °C, Time: 6 h, Stage 2: Treated with ethanol, 3-triethoxysilyl propyl amine , Time: 1 h,	Pb(II)	1	2	25	30	5	9	0.9699	(Ngaini et al., 2021)

Table 2.7 continued

Hazelnut shell	Pyrolysis Temp: 700 °C, Time: 60 min	Pb(II)	3	4	45	90	15	80	11.2	(Kaya et al., 2020)
<i>Eucalyptus</i> leaf	Stage 1: Treated with KOH, Temp: 200 °C, Time: 24 h, Stage 2: Treated with HCl, waste-iron, ZnCl ₂ .	Pb(II)	2	5	25	360	50	-	97.3	(Du et al., 2020)
<i>Arachis</i> <i>Hypogaea</i> Shell	Pyrolysis Temp: 550 °C, Time: 30 min	Pb(II)	2	5.5	20	180	100	89	56.5	(Taşar & Özer, 2020)
Grape pomace	Stage 1: Pyrolysis Temp: 500 °C, Time: 2 h	Pb(II)	1	6.5	25	1440	300	71.7	107	(Jin et al., 2020)

Table 2.7 continued

Jackfruit Peel	Stage 1: Treated with H ₃ PO ₄ Stage 2: Carbonisation Temp: 500 °C, Time: 2 h	Pb(II)	2.5	7	45	180	100	70	10.1	(Ibrahim et al., 2020)
<i>Calophyllum inophyllum</i> spent seedcake	Stage 1: Carbonisation Temp: 500 °C, Time: 45 min, Stage 2: Treated with H ₂ SO ₄ , Time: 48 h, Stage 3: Treated with 400 W microwave, 4 min	Pb(II)	10	9	30	120	25	99.06	52.63	(Adenuga et al., 2019)

2.9 Effect of Contact Time

The impact of contact time is related to availability of active sites on the adsorbent surface as well as the difference of adsorbate concentration between the bulk solution and the adsorbent surface (Abdel-Aziz et al., 2021). Initially, the sorption process is found to be rapid because of enhanced accessibility of active binding sites on the adsorbent surface which is governed by diffusion process from the bulk to the surface, whereas in the final stages, sorption is likely to be attachment controlled process due to a decrease in the available active sites (Adeoye et al., 2020).

Heavy metals sorption often occurs in two stages: an initial quick phase lasting a few minutes, followed by a slower phase that lasts until equilibrium is reached (Dalali & Haggghi, 2016). Increasing the contact time enhances removal efficiency until equilibrium is reached (Sajjadi et al., 2019). This phenomenon can be interpreted as the transfer of metal ions to the unoccupied active sites and diffusion into the adsorbent pores continuing until the saturation of all active sites (Choudhary et al., 2020).

Table 2.8 summarises several different studies which utilised agricultural and horticulture wastes based modified adsorbents for the adsorption of Cu(II), Pb(II) and Ni(II) from aqueous solution and these studies have reported with contact time within a range of 5 min to 48 h.

Table 2.8: Effect of contact time on Adsorption of Cu(II), Pb(II) and Ni(II) by modified adsorbents

Adsorbent Source	Modification	Adsorbate	Dosage (g L ⁻¹)	pH	Temp (°C)	Contact time (min)	Initial Conc. (ppm)	Removal %	Adsorption Capacity (mg g ⁻¹)	Reference
<i>Axonopus compressus</i>	Treated with H ₂ SO ₄ Temp: 180 °C Time: 30 min	Pb(II)	2	4.5	25	5	200	98	191.07	(Yu et al., 2021)
Spent Mushroom Compost	Pyrolysis Temp: 500 °C Time: 3 h	Pb(II)	10	6	20	15	771	99.99	103.5	(Abdallah et al., 2019)
<i>Annona reticulata</i> seeds	Treated with H ₂ SO ₄ Time: 24 h	Cu(II)	0.4	6	30	30	100	99.712	-	(Harsha Vardhan et al., 2020)
<i>Cinnamomum camphora</i>	Stage 1: Treated with NaOH, Time: 4 h, Stage 2: Treated with (CH ₂ CO) ₂ O, Time: 24 h,	Ni(II)	12	5.5	30	30	50	99.05	-	(Wang & Wang, 2018)

Table 2.8 continued

Jujube pit	Pyrolysis	Pb(II)	0.4	6	25	30	150	80	137.1	(Gao et al., 2020)
	Temp: 800 °C									
	Time: 2 h									
Peanut shell	Stage 1: Pyrolysis	Ni(II)	0.1	6	25	60	20	90	87.15	(An et al., 2019)
	Temp: 500 °C									
	Time: 2 h,									
	Stage 2: Treated with KMnO ₄									
	Temp: 60 °C									
	Time: 4 h,									
	Stage 3: Treated with KOH									
	Temp: 300 °C									
	Time: 1 h									

Table 2.8 continued

Banana peel	Stage 1: Carbonisation Temp: 500 °C Time: 2 h, Stage 2: Treated with FeSO ₄ and FeCl ₃ Temp: 50 °C Time: 30 min Stage 3: Treated with NaOH Time: 60 min	Cu(II)	1	6	25	120	200	91		(Oladipo et al., 2019)
Rice Straw	Stage 1: Carbonisation Temp: 420 °C, Time: 4 h Stage 2: Treated with KMnO ₄ Temp: 80 °C, Time: 24 h.	Pb(II)	1	5	20	480	207	99.14	63.25	(Tan et al., 2018)

Table 2.8 continued

Kenaf fibre	Stage 1: Treated with dimethyl formamide, Temp: room temp Time: 24 h Stage 2: Treated with urea and phosphoric acid, Temp: 150 °C, Time 2 hr	Cu(II)	3.33	5	25	1080	200	88.2	176.4	(Razak et al., 2020)
Coffee husk	Stage 1: Pyrolysis Temp: 500 °C, Time: 1 h, Stage 2: Carbonised Temp: 800 °C, Time: 30 min	Ni(II)	0.8	6	55	1440	45	90.8	57.14	(Rodriguez et al., 2018)

Table 2.8 continued

Rice Straw	Pyrolysis	Pb(II)	1.25	5	25	2880	200	97	0.85	(Zhao et al., 2020)
	Temp: 550 °C, Time: 2 h									
<i>Opuntia ficusindica</i> Cladodes	Stage 1: Pyrolysis	Cu(II)	0.6	6	30	2880	10	91	49.36	(Choudhary et al., 2020)
	Temp: 400 °C, Time: 1 h,									
	Stage 2: Treated with NaOH									
	Stage 3: Carbonisation									
	Temp: 500 °C, Time: 1 h									
<i>Opuntia ficusindica</i> Cladodes	Stage 1: Pyrolysis	Ni(II)	0.6	6	30	2880	10	89	44.35	(Choudhary et al., 2020)
	Temp: 400 °C, Time: 1 h,									
	Stage 2: Treated with NaOH									
	Stage 3: Carbonisation									
	Temp: 500 °C, Time: 1 h									

2.10 Effect of Temperature

Temperature is a critical factor that must be analyzed to identify its impact on the adsorption capacity and efficiency of the adsorbent (Abdallah et al., 2019). In order to anticipate the thermodynamic nature of the sorption process, the effect of temperature on the sorbent's sorption capacity is examined (Lodhi et al., 2019). Increasing the temperature reduces the viscosity of the bulk solution and consequently increases the speed of ion/molecule diffusion along with the sorbent's outer layer, resulting in improved sorption performance (Ghasemi et al., 2020).

The increase in metal ions removal percentage with temperature can be attributed to a higher affinity of active positions for metal ions or an increase in binding positions on the adsorbent outer layer (Ghasemi et al., 2020). This can result in a chemisorption type of interaction mechanism (Mustapha et al., 2019) and an endothermic adsorption process (Gao et al., 2020). However, once the temperature is raised above a particular point, the removal percentage of metal ions declines gradually (Tang et al., 2020). The weakening of adsorptive interactions between the metal ions and the adsorption sites of the adsorbent could be the cause (Tang et al., 2020). This refers to the physisorption mechanism, which is involved in the sorption process (Kebede et al., 2018). When the metal ion removal percentage reduces with the increase in temperature, this indicates that temperature is not a contributing factor in the adsorption process; rather the process is exothermic and spontaneous (Lu & Guo, 2019). Table 2.9 highlights a number of studies that have documented the impact of temperature on the adsorption of Cu(II), Pb(II) and Ni(II) from aqueous medium utilising modified adsorbent prepared from agricultural and horticulture wastes throughout a wide range of temperature (15-65 °C).

Table 2.9: Effect of Temperature on Adsorption of Cu(II), Pb(II) and Ni(II) by modified adsorbents

Adsorbent Source	Modification	Adsorbate	Dosage (gL ⁻¹)	pH	Temp (°C)	Contact time (min)	Initial Conc. (ppm)	% Removal	Adsorption Capacity (mgg ⁻¹)	Reference
Spent Mushroom Compost	Carbonisation Temp: 500 °C, Time: 3 h	Pb(II)	10	6	20	15	771	99.99	103.5	(Abdallah et al., 2019)
Pomegranate Peel	Stage 1: Treated with H ₃ PO ₄ and ZnCl ₂ Time: 24 h, Stage 2: Pyrolysis Temp: 500 °C Time: 60 min	Pb(II)	0.5	6.5	23	90	100	93.1	68.6	(Al-Onazi et al., 2021)
<i>Axonopus compressus</i>	Treated: with H ₂ SO ₄ Temp: 180 °C, Time: 30 min	Pb(II)	2	4.5	25	5	200	98	191.07	(Yu et al., 2021)

Table 2.9 continued

Mangosteen shell	Stage 1: Treated with conc. H ₂ SO ₄ Temp: 150 °C, Time: 24 h, Stage 2: Treated with NaHCO ₃ , Time: 24 h	Ni(II)	0.6	6.29	25	30	10	99	57.14	(Anitha et al., 2020)
Peanut shell	Stage 1: Pyrolysis Temp: 500 °C, Time: 2 h Stage 2: Treated with KMnO ₄ and KOH	Ni(II)	0.1	6	25	60	20	90	87.15	(An et al., 2019)
Pomelo Peel	Stage 1: Treated with FeCl ₃ , Na ₂ CO ₃ , PEG, and C ₂ H ₆ O ₂ , Time: 10 h Stage 2: Carbonisation Temp: 550 °C, Time: 4 h	Pb(II)	1	5	25	360	500	99.8	205.391	(Chen et al., 2020)

Table 2.9 continued

Pomelo Peel	Stage 1: Treated with FeCl ₃ , Na ₂ CO ₃ , PEG, and C ₂ H ₆ O ₂ , Time: 10 h Stage 2: Carbonisation Temp: 550 °C, Time: 4 h	Cu(II)	1	6	25	360	500	51.60	81.909	(Chen et al., 2020)
<i>Annona reticulata</i> seeds	Treated with H ₂ SO ₄	Cu(II)	0.4	6	30	30	100	99.712	-	(Harsha Vardhan et al., 2020)
<i>Tectona grandis</i> leaves	Pyrolysis Temp: 650 °C Time: 60 min	Ni(II)	3	6	30	120	25	92.46	32.89	(Vilvanathan et al., 2018)

Table 2.9 continued

Mangosteen peel	Stage 1: Carbonisation Temp: 700 °C, Time: 70 min Stage 2: Treated with ZnCl ₂ , Stage 3: Carbonisation Temp: 600 °C, Time: 2 h.	Pb(II)	0.67	5	30	180	50	-	130	(Kongsune et al., 2021)
Stem internodes of sugarcane tops	Step 1: Carbonisation Temp: 350 °C, Time: 3 h, Stage 2: Treated with limewater, Time: 2 h, Stage 3: Treated with (NH ₄) ₂ HPO ₄ , Time : 2 h, five times	Pb(II)	1	5	45	1440	328.6	98.18	325.85	(Zhu et al., 2018)

Table 2.9 continued

Pistachio shells	Stage 1: Pyrolysis Temp: 550 °C, Time: 1 h Stage 2: Steam activation, Temp: 900 °C, Time: 10 h Stage 3: Treated with dil. HCl, Time: 48 h Stage 4: Treated with HNO ₃ , Temp: 60 °C, Time: 12 h	Cu(II)	0.6	6.5	55	180	60	95.29	277.7	(Nejadshafiee & Islami, 2020)
Rice husk	Stage 1: Cellulose extraction with NaOH Stage 2: Treated with humic acid	Ni(II)	10	6	60	1440	100	95	12.41	(Basu et al., 2019)

2.11 Desorption and Regeneration

For a successful economic adsorption operation, the adsorbent must have a higher regenerative capability (Omidi et al., 2020). The regenerative studies with reference to different adsorbents including activated carbons, biochars and modified adsorbents have been reported in some recent studies (Babu et al., 2018). The manganese dioxide-loaded biochar used to remove Cd(II) and Pb(II) from aqueous medium was regenerated with 0.1M HNO₃ and rinsed with 120 mL of distilled water at 298 K and the concentration of Pb(II) and Cd(II) in effluent was <0.001 mgL⁻¹ after regeneration (Zhang et al., 2020). Biosorbent made from Punica granatum rind extract and treated with Ferric chloride, sodium acetate and dimercaptosuccinic acid, after absorbing Pb(II) from aqueous solution was regenerated using 0.01M HCl, with a maximum desorption percentage of 91% at 1.5 pH (Venkateswarlu et al., 2019). Under the same adsorption circumstances, the regenerated adsorbents exhibited 75.1% Pb(II) removal, implying that the adsorbent is reusable (Venkateswarlu et al., 2019). Desorption of Cd(II) ions from biochar derived from cinnamon and cannabis using 0.1M NaOH was 95.5% and 93%, respectively, whereas using 0.1M HCl, the desorption values were 99% and 99.5%, respectively (Omidi et al., 2020). Milkweed carbon was desorbed by treating with 0.1M HCl and rate of desorption was almost linear with time, reaching maximum 59% Pb(II) desorption in 60 min; however, desorption can be increased further by lowering pH and rising temperature, but higher desorption percentage at lower pH can come at the cost of adsorbent matrix degradation (Ilangovan et al., 2017).

2.12 Adsorbents

In the last decade, there has been a significant increase in the number of studies on the use of adsorption methods and a variety of adsorbents have been evaluated and reported

(Zaidi et al., 2018). In addition to capacity, the selection criteria for an adsorbent includes its abundance, low cost and environmental friendliness (Zaidi et al., 2018). Solid materials of mineral, organic, or biological origin, with diverse chemical forms and geometrical surface structures, have been used as adsorbents (Crini et al., 2019). Activated carbons, zeolites, clays, nano-magnetic particles, are some of the commercially successful adsorbents (Kebede et al., 2018).

An adsorbent should have the following characteristics to be commercially successful including large surface area with sufficient partition into micropores and mesopores (Ghasemi et al., 2020), pertinent surface chemistry i.e., availability of functional groups capable of binding the adsorbate by forming surface complexes (Abdallah et al., 2019). To be economically viable, an adsorbent should have high selectivity for acute separation, be capable of high adsorption with low dosage, (Aboli et al., 2019), and have convenient kinetics such as sorption rate and rapid transportation characteristics (Zaidi et al., 2018). Successful adsorbent features include heat and chemicals resistance (Li et al., 2020), being sparingly soluble in the surrounding medium to reduce loss and retain efficiency (Singh, et al., 2017) and being sufficiently hard and mechanically robust to survive in application (Marsh & Francisco, 2013).

2.12.1 Adsorbents Classification

For selecting an efficient adsorbent, high surface areas, large pore volumes, porosity with varying extents of micropores, mesopores and macropores are among the significant characteristics considered (Ghasemi et al., 2020). A plot of relative pressure verses volume adsorbed obtained by measuring the amount of N₂ gas adsorbed onto the adsorbent surface and the subsequent amount desorbed at constant temperature, is named as N₂ adsorption-

desorption isotherm (Wang et al., 2020) which has been reported as the best model for the determination of adsorbent surface area, pore size distribution and total pore volume (Aboli et al., 2020). A large specific surface area increases the number of small pores (Luo et al., 2019) which is another significant feature that improves the adsorbent's capacity to adsorb by increasing the opportunities for adsorbent molecules to get onto surface (Choi, 2019). Micropores is classified with a diameter less than 2 nm, mesopores and macropores between the range of 2 nm and 50 nm and more than 50 nm, respectively (Lu et al., 2020). With sub division of micropores, ultra-micropores have a diameter of less than 0.7 nm, medium-sized micropores have a diameter of greater than 0.7 nm but less than 0.9 nm and super-micropores have a diameter of less than 0.9 nm (Bardestani et al., 2019).

In liquid phase applications, carbon-based adsorbents typically have a larger number of mesopores or a transient range of pores, allowing aqueous solution to flow freely through macropores and mesopores into the internal microporous region, resulting in faster kinetics of adsorbate-adsorbent interactions (Chowdhury, 2013). Macroporous or mesoporous carbons are applied to remove large molecules, while microporous carbons are better for removing smaller molecules from aqueous medium (Gisi et al., 2016). Macroporous carbons has bulk density $> 1.0 \text{ cm}^3\text{g}^{-1}$, mesoporous carbon has bulk density between $0.85 \text{ cm}^3\text{g}^{-1}$ and $1.0 \text{ cm}^3\text{g}^{-1}$ and microporous carbon has bulk density $< 0.85 \text{ cm}^3\text{g}^{-1}$ (De et al., 2016). According to American Water Work Association, the bulk density of activated carbon should not be less than $0.25 \text{ cm}^3\text{g}^{-1}$ for practical application (Adane et al., 2020).

Figure 2.3 illustrates the classification of cost-effective adsorbent precursors for liquid phase applications.

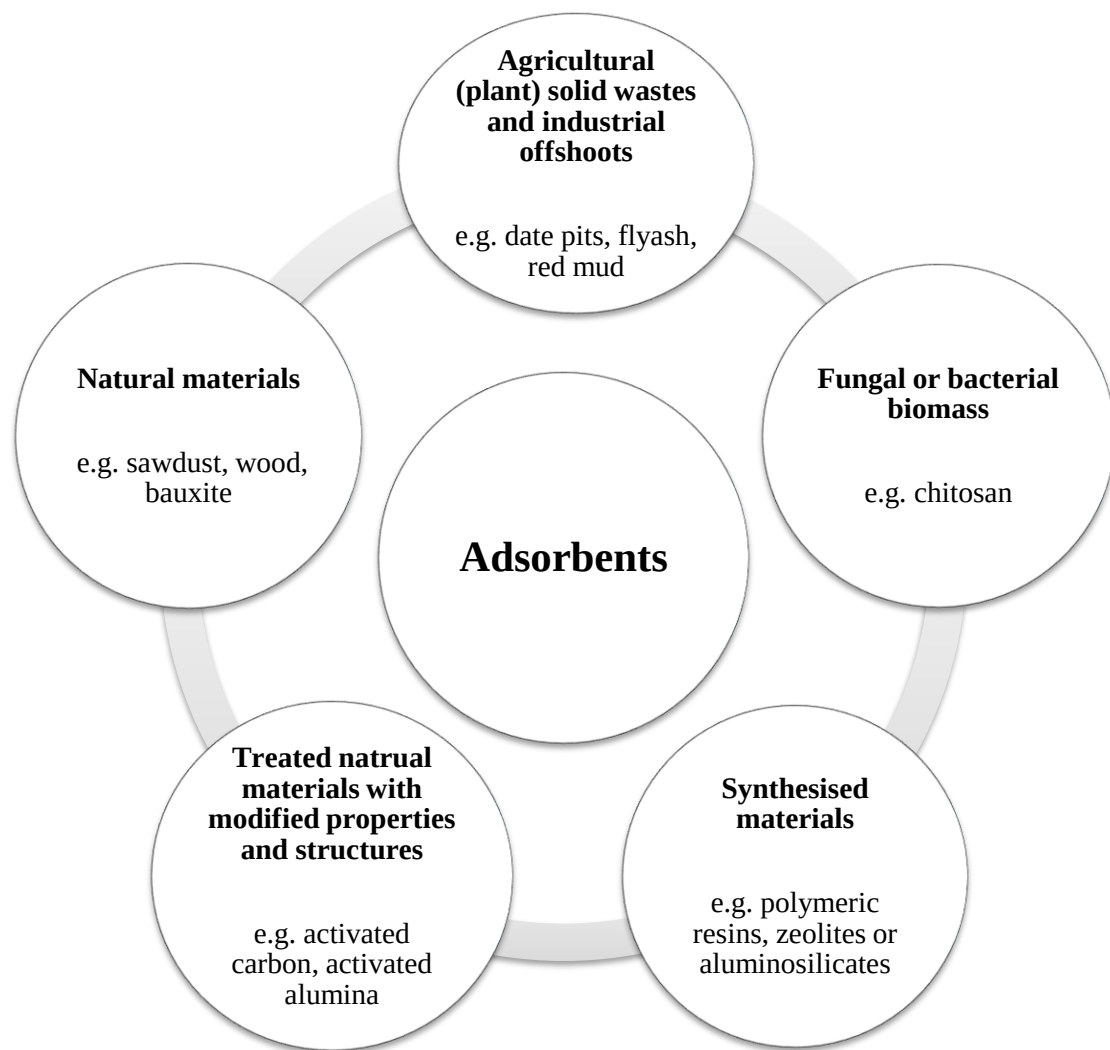


Figure 2.3: Classification of Adsorbents (Crini et al., 2019)

Coal is the basic source material utilised in the industrial production of activated carbon, which is expensive and finds limited application nowadays (Burakov et al., 2018). Many natural and synthetic materials have been identified as adsorbent feedstocks (Lin et al., 2020) and several attempts have recently been undertaken to utilise non-conventional materials to generate cheaper and more effective adsorbents (Kongsune et al., 2021). Generally, activated carbon derived from agricultural and horticulture wastes biomass has been reported as effective and trustworthy adsorbent due to its large surface area, micro-

porous structure, uniform distribution of pore sizes, exorbitant porosity, high surface reactivity, excellent mechanical stability and superior adsorption capacity (Dai et al., 2018).

2.12.2 Natural Adsorbents and Precursors

Many researchers have studied various adsorbents for the removal of heavy metals from wastewater utilising a variety of feedstocks, including natural and synthetic materials (Kongsune et al., 2021). Carbon-rich materials has become the main focus because these adsorbents have proven to be efficient at removal of contaminants from wastewater (Lin et al., 2020). Agricultural and horticulture wastes have grabbed the researchers' interest because of their natural abundance, low cost and little processing requirements, making these adsorbents a viable alternative to commercial activated carbon (Liu et al., 2019; Hashem et al., 2020).

Recent decades have witnessed an increase in the development of adsorbents derived from plant-based sources (Morin-Crini et al., 2020). *Artocarpus odoratissimus* leaves (Zaidi et al., 2018), *Adenanthera pavonina* seeds (Sen et al., 2018), oil palm frond (Shilawati et al., 2018), leaves of jackfruit, mango, rubber (Nag et al., 2019), globe artichoke (Fernández-López et al., 2019), *Albizia lebbbeck* pods (Mustapha et al., 2019), corncob (Cerrahoğlu & Bingöl, 2019), milled olive stone (Amar et al., 2020), *Citrus limetta* leaves (Aboli et al., 2020), ground olive stone (Amar et al., 2020), rice husk (Wang et al., 2020), *Citrus limetta* leaves (Aboli et al., 2020), pomelo peel (Yaoning et al., 2020), pomegranate peel, date pit (Al-Onazi et al., 2021), palm kernel shells (Baby et al., 2021), have been studied as adsorbents for the removal of heavy metals from waste water.

The efficiency of an adsorbent is influenced by its physical structure, pore size and availability of different functional groups integrated during the activation process (Fahmi et al., 2019). Agricultural and horticulture wastes biomass comprises of various organic compounds such as lignin, cellulose and hemicelluloses (Adeoye et al., 2020), as well as a variety of functional groups such as carboxyl, carbonyl, phenol, quinone, lactone groups and others on its graphite layers, providing a diverse range of adsorption target (Alguacil et al., 2018). Acidic, alkaline and neutral activating agents are most prevalent and capable to impart different functional groups to the adsorbents' surface (Baby et al., 2021). The relative surface functional groups of the adsorbent material are examined using FTIR, in wavenumber range of 400–4000 cm^{-1} (Ibrahim et al., 2020).

High surface areas and large pore volumes are critical features of adsorbents in order to attain a high adsorption capacity (Ghasemi et al., 2020). The identification of materials with significant affinity for the required sorbate, broad surface area, chemical stability and facile regeneration is driving biosorbent synthesis research (Herrera-Barros et al., 2020). The most reliable methods for determining the specific surface area and pore size distribution of porous material are based on gas physisorption equilibrium isotherms for nitrogen, argon, or carbon dioxide adsorbates (Bardestani et al., 2019). Brunauer-Emmett-Teller theory (BET) is a popular method for calculating specific surface area that extends the Langmuir monolayer adsorption model to multilayer layers (Kaya et al., 2020). Pore volume is also determined using BET theory (Ansari et al., 2018). The Barrett-Joyner-Halenda method is implemented to calculate the pore size (Cai et al., 2021).

2.12.3 Activated Natural Adsorbents

Agricultural and horticulture wastes is a valuable source of carbonaceous matter with a porous structure (Baby & Hussein, 2020) however, the properties of untreated adsorbents are still insufficient for effective adsorbate removal and to be a substitute for commercial grade activated carbon (Ibrahim et al., 2019). Activation through different physical and chemical modifications, rather than depending just on basic drying and grinding, might potentially increase the use of agricultural waste biomass (Kongsune et al., 2021). Successful activation increases the surface area of a carbonaceous agricultural waste material by forming new pores or enlarging existing pores, which improves the adsorption capacity of the adsorbent (Negara et al., 2020).

Mechanical activation through ball mill, physical activation by means of steam treatment, gas purgation, natural minerals impregnation, magnetic modification (Ahmad et al., 2018). Chemical modification of adsorbents, such as treatment with different acids and/or bases, different coatings, treatment with organic solvents and treatment with surfactants, have all received a lot of attention due to their incredible effectiveness at activating adsorbents (Marsh & Francisco, 2013). Chemical activation has been used to increase porosity, generate mesopores & micropores and construct hierarchical pore structures (Ilangovan et al., 2017). The chemical interaction between the chemical component of biomass's precursor and activation agents would provide enough heat to compensate for the temperature required for precursor activation, decreasing the activation temperature in the chemical activation approach (Lei et al., 2020). Dehydrating agents including H_2SO_4 (Nosheen et al., 2021), NaOH (Khokhar et al., 2015), KOH (Ghasemi et

al., 2020), H_3PO_4 (Ibrahim et al., 2019), and ZnCl_2 (Al-Onazi et al., 2021; Hong et al., 2019) are often used in chemical activation.

Many studies reported physical modifications such as Carbonisation and pyrolysis of the agricultural and agro-industrial wastes, for example, pyrolysis of rice straw 350 °C and 550 °C for 2 h (Zhao et al., 2020), pyrolysis of *Eucalyptus camdulenis* at 600 °C for 6 h (Shafiq et al., 2021), pyrolysis of *Caragana korshinskii* at 650 °C for 3 h (Wang, 2020), pyrolysis of grape pomace waste at 500 °C and 700 °C (Jin et al., 2020), Carbonisation of pumpkin fruit hulls at 450 °C for 5 h (Ghasemi et al., 2020). Several kinds of different chemical modification have also been reported as exhausted coffee grounds were treated with HCl at boiling for 2 h (Babu et al., 2018), *Axonopus compressus* biomass was mixed evenly with conc. H_2SO_4 , heated at 180 °C for 30 min, the resulting black matter was washed with deionised water repeatedly until neutral pH, dried (Yu et al., 2021), oil palm residue was treated with dimethyl sulfoxide, tetra ethyl-o-silicate (Herrera-Barros et al., 2020), hay straw (Lin et al., 2019). Combination of chemical and physical modification treatments, for example, palm kernel shell was treated with H_3PO_4 for 2 h and then carbonised at 500 °C for 2 h (Baby & Hussein, 2020), *Calophyllum inophyllum* spent seedcake was carbonised at 500 °C for 45 min before being treated with dil. H_2SO_4 for 48 h before being microwaved in an oven at 400W for 4 min (Adenuga et al., 2019).

2.13 Activated Carbon

The Environmental Protection Agency (EPA) has recognised activated carbons as well-known that adsorbent material as one of the most efficient techniques used for heavy metal removal because of large specific surface areas, well-developed internal porous structures and multiple surface functional groups (Cao et al., 2019). The term "Activated

Carbon" refers to a family of non-crystalline porous carbonaceous materials with a large internal surface area that are extensively used as adsorbents in wastewater and emissions treatment (Saleem et al., 2019). Activated carbon cannot be characterised by a structural formula (Abdulrazak et al., 2017). However, the structure consists of microcrystalline graphite, amorphous carbon and single-plane reticular carbon, with microcrystalline graphite accounting for the major part of it but differing from graphite and cannot be converted to graphite even when heated above 2000 °C; hence named as non-graphite microcrystal (Baby et al., 2021). The activated carbon's porous structure is enhanced by the microcrystalline structure (Lei et al., 2020). The most common activators are acidic, alkaline and neutral types, which impart unique functional groups onto the surface of the activated carbon and consequently increase the adsorption efficiency (Baby et al., 2021). The distinctive characteristics of activated carbon as an adsorbent include a well-developed surface area ranging from 500 to 2000 m²g⁻¹ (Fahmi et al., 2019), an appropriate distribution of pore sizes and the presence of active sites, particularly oxygen functional groups which enhances surface reactivity (Abdallah et al., 2019).

Due to the activated carbon's exorbitant cost on the market, new adsorbents with comparable performance and lower prices are needed (Mustapha et al., 2019). Different carbon-containing materials such as agricultural wastes, newspapers trash and various parts of the plants, can be utilised to synthesise activated carbons (Baby et al., 2021). Early research on the practicality of using naturally available biomass resources as adsorbents or precursors for the production of activated adsorbents and while a few of these are currently employed in commercial scale activated carbon production, more resources are required to fulfil the demand (Saleem et al., 2019).

2.14 Molten Salt Synthesis

Substantial research has been carried out in recent years on innovative ways for the preparation of porous carbon materials and molten salt synthesis is regarded as an emerging and promising technique with tremendous potential in producing customised production of porous carbon (Pang et al., 2021). Molten salt synthesis (MSS) differs from conventional methods used for activated carbon preparation as in this technique both carbonisation and activation can be performed in a single step by application of a salt/multi-salt with a low melting point as the molten medium, consequently decreasing process complexity and reaction time (Gupta & Mao, 2021). The most widely employed activators in conventional carbonaceous material activation are acids, alkalis and potassium hydroxide, and these activation reagents are hazardous in nature, and the severely corroding/oxidising action during carbonisation results in a poor yield of carbon product (Bassey et al., 2021). Contrarily, environmental friendliness, low cost, ease of operation, and scalability are among the advantageous features of MSS (Gupta & Mao, 2021).

The molten salt synthesis (MSS) approach employs one or more than one low melting point salts as the molten medium for the desired synthesis (Bassey et al., 2021). The molten salt offers a suitable flux environment (from 100 °C to over 1000 °C) with the solubility and diffusivity necessary for solid-phase reactions, allowing the synthesis temperature to be significantly reduced (Dai et al., 2019). Molten salts can increase carbon product output by emitting less carbon than a typical high temperature carbonisation process (Tian et al., 2021). Molten salts initiate the reactions at significant rates without the need of expensive and specialised catalysts (Dai et al., 2019). Molten salts are a good thermo-chemical medium with excellent heat storage/transfer capabilities and can serve as in-built template and pore-

forming agent for making porous structure (Tian et al., 2021). The electrochemical redox reactions of the electrode materials and/or electrolyte are primarily responsible for the molten salt electrosynthesis of carbon compounds in principle (Pang et al., 2021).

MSS also expresses excellent ability to react with the impurities in biomass precursor and result in carbon with high-purity (Tian et al., 2021). The carbonaceous precursor tends to generate richer pore texture and/or specific morphology during the carbonisation process with the assistance of molten salt (Pang et al., 2021). For application in energy storage N, S-codoped hierarchically porous carbon nanosheets were prepared through molten salt synthesis using ginkgo biloba leaf as a precursor, KCl template, and K_2CO_3 activation step (Tian et al., 2021). Corn cob based activated carbon was prepared through MSS with zinc chloride as activator and applied as adsorbent for the removal of mercury (Duan et al., 2019). Three different types of biomass including corn straw, bamboo powder and sawdust were subjected to zinc chloride activator in MSS to obtain microporous activated carbon and applied for the removal of elemental mercury (Hong et al., 2019). Mangosteen peel biomass was subjected to zinc chloride activator in MSS and the resulting activated carbon was applied for removal of lead metal ions from the aqueous medium (Kongsune et al., 2021).

2.15 *Melia azedarach* Tree and Botanical Background

Melia azedarach is a *Meliaceae* family member that is also known as chinaberry tree or Persian lilac (Amiri et al., 2020). The mature tree has a rounded crown with a capacity to grow 7–12 meters height (Davodi et al., 2019). It is endemic to Asia's Himalaya region and can be found in India, China, Australia, Pakistan and Iran and is well suited to warm weathers, poor soils and seasonal droughts (Van & Matsumura, 2018). It is largely utilised for providing hard lignocellulosic wood principally used for making furniture, construction

industry-related goods (Shah et al., 2020) due to its comparatively fine grains, quite durable, resistant to termites and insects and easy to work qualities (Van & Matsumura, 2018).

2.15.1 *Melia azedarach* Leaves

Melia azedarach is also used for medical purposes in several countries, although poisoning has been reported in humans and domestic animals after eating leaves or fallen fruits, even grasshoppers do not consume the leaves due to their pesticide characteristics (Majid et al., 2021). The leaves can grow to be up 50 cm long (Sarwar et al., 2015) and are a waste product with no industrial use (Khokhar et al., 2015). According to preliminary phytochemical investigation, *Melia azedarach* leaves contain alkaloids, carbohydrates, lipids, protein and amino acids, saponins, sterols, triterpenoids, esters, thiols, cyanogenic glycosides, tannins, flavonoids, and phenolic compounds (Deb et al., 2018).

Leaves and bark of the *Melia azedarach* tree were subjected to drying and grinding in combined form to applied to remove arsenic from aqueous medium (Sarwar et al., 2015). Deadwood of *Melia azedarach* tree was ground and soaked in 10% HCl sol for specified duration, rinsed, dried, ground, sieved and applied as an adsorbent for Cu(II) removal from aqueous solution (Dolatabadi et al., 2018).

2.16 Response Surface Methodology

Earlier sections summarised the impact of various factors on heavy metal adsorption using various adsorbents. However, the majority of the published research concentrated on establishing the ideal parameters associated with the highest adsorption capacity, which was usually done by altering one element while leaving the others constant. Such experimental designs may be time-consuming, as well as require a large number of samples at a higher

cost (Praveena et al., 2019). Multivariate experimental designs are gaining popularity in the realm of scientific research due to diverse advantages over traditional approaches, such as simultaneous exploration of several control factors, swift implementation, cost-effectiveness (Jain et al., 2020).

Response Surface Methodology (RSM), since its inception by Box and Wilson in 1951, has been referred to as a reliable Design of Experiments (DOE) tool for different applied sciences (Taheri, 2022). In traditional heavy metals adsorption studies, the influence of different variables is evaluated by varying one variable at a time while keeping the rest of the parameters constant (Adane et al., 2020). The primary disadvantage of such approach is that it does not include the interaction impact of all the variables under evaluation, also excessive experiments are required to be carried out (Biswas et al., 2019). Due to these limitations of the traditional approach, the application of RSM for process optimisation has gained attention among researchers in recent decades (Jain, et al., 2020).

A few recently reported optimisation studies using RSM include Cu(II) and Ni(II) adsorption by sodium alginate treated pinecones biochar (Biswas et al., 2019), Pb(II) adsorption by neem leaves based bio-composite (Maity & Ray, 2018), Cu(II) adsorption by activated carbon based on pistachio shells (Nejadshafiee & Islami, 2020), Pb(II) adsorption by pyrolyzed activated sludge (Makshut et al., 2020), Cu(II) adsorption by acid-base treated coconut shell biochar (Hasana et al., 2020), Pb(II) adsorption by activated carbon based on de-oiled soya (Sujatha & Sivarethinamohan, 2021).

The principal RSM techniques utilised to design the experiments are central composite design, Box–Behnken design and Doehlert design (Jain et al., 2020). Second-

order (quadratic) polynomial model, Central Composite Design (CCD), is the most acceptable experimental technique (Adane et al., 2020). It is a preferable option to complete factorial, three-level design since it involves fewer experiments while delivering comparable findings (Sabah et al., 2020). Equation 2.31 can be used to get the total number of experiments (N) (Jain et al., 2020).

$$N = 2^k + 2k + C_0 \quad \text{Equation 2.31}$$

Where “N” is the number of experiments, “C₀” represents the number of center points and “k” is the number of variables (Rasoulzadeh et al., 2020). Only a few studies have been conducted utilising RSM for the removal of heavy metals from wastewater in the literature and the researchers must manually tune each and every parameter (pH, contact time, adsorbent dosage, initial concentration, temperature) (Jain et al., 2020). For the modelling and optimisation experiment, utilisation of different types of software including Design expert (Adane et al., 2020), R-software have been reported (Rasoulzadeh et al., 2020).

2.17 Conclusion

Adsorbents derived from renewable, abundant and low-cost raw materials, particularly agricultural and horticulture wastes biomass, have recently attracted a lot of interest. Based on the literature review, the characteristics of an adsorbent are dependent on the type of feedstock used and the activation procedure utilised. Owing to the abundance of *Melia azedarach* trees grown for wood, management of biomass including leaves and twigs, has becomes an issue due to lack of commercial application. *Melia azedarach* biomass has been reported to be utilised in biosorbents preparation in several studies (Khokhar et al., 2015; Nosheen et al., 2021; Sarwar et al., 2015); however, no study has reported significant

physio-chemical activation on *Melia azedarach* leaves and twigs biomass. Several publications have investigated the influence of different variables on the adsorption process, however applying response surface methods to optimise these effects is still infrequent. Using low-cost agricultural and horticulture wastes to prepare activated carbon, characterising their surface morphological features and conducting subsequent metal ions adsorption in batch adsorption systems could be advantageous in managing the *Melia azedarach* waste biomass.

CHAPTER 3

SYNTHESIS AND PHYSIOCHEMICAL CHARACTERISATION OF ACTIVATED CARBON FROM *Melia azedarach* LEAVES AND TWIGS

3.1 Overview

Studies have shown that activated carbon (AC) is an excellent adsorbent materials for pollutant removals from wastewater (Baby et al., 2021). There are hundreds of commercial activated carbons on the market, each with its unique set of characteristics and specific applications (Marsh & Francisco, 2013). For instance, AC is commercially available for removal of heavy metals (Al-Onazi et al., 2021; Anitha et al., 2020; Nejadshafiee & Islami, 2020), dyes (Ebadollahzadeh & Zabihi, 2020; Han et al., 2020; Jawad & Abdulhameed, 2020), and pesticides (Derylo-Marczewska et al., 2019; Mohammad et al., 2020; Nejadshafiee & Islami, 2020a).

The effectiveness of applying AC as an adsorbent materials is mainly due to its following characteristics: large surface area with micropores and mesopores (Rodriguez et al., 2018), the availability of functional groups, selectivity of feedstock (Zaidi et al., 2018), rapid sorption (Cao et al., 2019), resistance to heat and chemical effects, sufficiently hard, resistance to crushing and corrosion (Liu et al., 2019), regeneratable and relatively lower production cost compared to other types of adsorbents (Qu et al., 2020). Most commercial activated carbon is made of synthetic materials, often manufactured using non-renewable resources as feedstock (Choudhary et al., 2020). Qualities including wide surface area, adsorption capacity, ion selectivity, thermal stability, resistance to transportation losses, and ease of activation and regeneration make them effective adsorbents for pollutant removal

(Ghasemi et al., 2020). However, the greatest barrier to its industrial implementation for wastewater treatment is its high production cost (Ansari et al., 2018).

Agricultural wastes have gained researchers' interest for the few recent decades due to their natural abundance, low cost and biocompatibility (Liu et al., 2019). Agricultural wastes offer unique surface characteristics and have been utilised to produce hybrid metal oxide catalysts, bio-energy sources and adsorbents for different pollutants (Qin et al., 2019). By employing readily available free resources, agricultural waste-based adsorbents provide a low-cost alternative to the more expensive synthetic activated carbon (Hashem et al., 2020). Adsorbents derived from plant-based agricultural waste involves inexpensive feedstock with lower production costs yet comparative adsorption capacity (Ghasemi et al., 2020). However, the complexity of bio-resource structure make it challenging to transform bio-resource into commercially successful products (Luo et al., 2019).

The release of dissolved organics from waste biomass may result in secondary contamination (Qin et al., 2019). Thus, physical and chemical treatments have been used to improve the properties of adsorbents derived from agricultural waste, apart from traditional method via drying (Liu et al., 2018). Successful activation expands the surface area of the carbonaceous agricultural waste materials by forming new pores or widening existing pores, increasing the adsorbent's capacity (Negara et al., 2020). The availability of active functional groups present on the surface of AC such as hydroxyl, carbonyl and carboxyl have considerably improved the adsorption effectiveness (Nejadshafiee et al., 2020).

The AC's porous structure and characteristics are highly influenced by the activation technique and raw material qualities (Lin et al., 2021). Carbonisation aids the elimination of

moisture, volatile compounds and other aromatics (Piriya et al., 2021). Chemical activation is widely employed in the preparation of AC due to its short processing time with low heating requirement (Gupta & Mao, 2021b), high carbon output (Youssef et al., 2020), adequate pore structure (Lin et al., 2021) and high specific surface area (Duan et al., 2019). The chemical interaction between the chemical composition of biomass's precursor and activation agents would provide enough heat to compensate for the temperature required for precursor activation, which subsequently decreases the temperature during chemical activation (Lei et al., 2020). Dehydrating agents including H_2SO_4 , H_3PO_4 , NaOH , KOH and ZnCl_2 are often used in the chemical activation (Ibrahim et al., 2019). Aside from strong acid/alkali, ZnCl_2 is the most widely utilised activation agent in AC production (Lin et al., 2021).

Molten salt synthesis (MSS) is a green cost-effective process for the synthesis of porous carbon (Shang et al., 2015). The MSS method has the advantage of completing both the carbonisation and activation processes in a single step, reducing the complexity of the process and the time required (Tian et al., 2021). Currently, this process has gained a lot of attention in the fields of energy, environment and resource sustainability for carbonising/pyrolyzing biomass to produce various microstructures (Yang et al., 2020).

The MSS approach uses molten salt to create a sufficient flux environment (from 100 °C to over 1000 °C) with the solubility and diffusivity required for solid-phase reactions, lowering the synthesis temperature significantly (Gupta & Mao, 2021a). Chlorides, sulphates, carbonates and hydroxides are common salts used in MSS because of their low costs and widespread availability (Shang et al., 2015). Zinc chloride (ZnCl_2) having a low melting point of 290 °C, is one of the salts that are widely employed to produce high yields of porous carbonaceous materials with a high specific surface area from a variety of biomass

sources (Youssef et al., 2020). Additionally, various nano powders have also been made using this process, including ferrites, titanates, niobates, mullite, aluminium borate and wollastonite (Gupta & Mao, 2021a). However, for manufacturing activated carbon from biomass, this method has been rarely utilised (Shang et al., 2015).

Melia azedarach tree, a member of *Meliaceae* family, normally grows to 7–12 meters height (Davodi et al., 2019). It is indigenous to Asia's Himalaya region and can be found in India, China, Australia, Pakistan and Iran (Van & Matsumura, 2018). It is mostly utilised for providing hard lignocellulosic wood which is primarily used in furniture, and construction-related goods (Shah et al., 2020). *Melia azedarach* leaves and twigs are burned because of not finding any industrial application (Khokhar et al., 2015).

In this work, described are the physiochemical characteristics of the AC produced via molten salt synthesis, employing *Melia azedarach* leaves and twigs as carbon precursors and ZnCl_2 as the pore generator. The potential of the prepared AC as adsorbent was evaluated based on the physicochemical characteristics.

3.2 Materials and Methods

3.2.1 Materials

Melia azedarach leaves and twigs were collected from the suburbs of Faisalabad city in Punjab, Pakistan. Leaves samples were washed with distilled water to remove contaminants and sun-dried for 4-5 days depending on weather conditions prior to oven drying (90 °C, 3 h) as shown in Figure 3.1 (a) and (b). The sample was then ground using food grinder (Panasonic, MX-7995) and sieved to the particle size of <125 µm. Twigs samples were washed, sun-dried, cut into 2-3 cm pieces and crushed with mortar and pestle

prior to grinding and sieving to the particle size of $<125\ \mu\text{m}$. Ground and sieved forms of leaves and twigs are shown in Figure 3.1 (c) and (d). Chemical reagents employed in this study are as follows: zinc chloride, ZnCl_2 (98% purity, R&M Chemicals, Malaysia) was used for activated carbon preparation; sodium hydroxide, NaOH (99%, Merck, Germany) and hydrochloric acid, HCl (33-38% purity, Fisher Chemical, Malaysia) were used for pH adjustment. Vanadium pentoxide (Fisher Chemical, Malaysia) was used as catalyst in elemental analysis. Potassium bromide (99%, Merck, Germany) was used for pellet formation in FTIR analysis.



Figure 3.1: *Melia azedarach* (a) leaves, (b) twigs, (c) leaves powder and (d) twigs powder

3.2.2 Molten Salt Synthesis

Activated carbon from *Melia azedarach* leaves and twigs was prepared through molten salt synthesis following Liu et al (2018), by changing pyrolysis with Carbonisation. Raw *Melia azedarach* leaves powder (RLP) and twigs powder (RTP) were impregnated with ZnCl_2 (10%, 100 mL) in separate experiments. The mixture was stirred continuously at 85 °C for 2 h, cooled to room temperature. The settled down matter was shifted to the crucibles and was oven-dried at 105 °C for 24 h. The solid was carbonised in a muffle furnace (Protherm ECO 110/15, Turkey) at 500 °C for 2 h. After Carbonisation, the black solid was cooled to room temperature, crushed, thoroughly washed with distilled water and oven-dried (105 °C, 12 h), ground and sieved to obtain activated carbon 0.5 mm particle size and labelled as LAC and TAC for *Melia azedarach* leaves activated carbon and *Melia azedarach* twigs activated carbon, respectively.

3.2.3 Physiochemical Characterisation

Several characterisation analyses were conducted on RLP, RTP, LAC and TAC samples. The purpose of the analyses was to determine the physicochemical properties change of *Melia azedarach* leaves and twigs after conversion to activated carbon and to evaluate its potential use as heavy metal adsorbent.

3.2.3.1 Proximate Analyses

The proximate analyses of samples were carried out using standard methods for the determination of moisture content, ash content and volatile content. In addition, proximate determination of fixed carbon content and bulk density of the samples were conducted based

on methods described in previous studies (Adane et al., 2020). Each analysis was carried out in triplicates and the mean results were reported with standard deviation.

Moisture content analysis was carried out following ASTM D3173 (2013). A porcelain crucible with a lid was heated, cooled to room temperature and placed in a desiccator (30 min) before being weighed. Sample (1 g) was placed in the crucible, covered with lid and dried in a preheated oven (105 °C, 3 h). The dried sample was cooled to room temperature and weighed. The drying, cooling and weighing processes were repeated until a consistent sample weight was obtained. The moisture percentage of each sample was calculated following equation 3.1.

$$\text{Moisture content, wt\%} = \frac{(W_i - W_o) - (W_f - W_o)}{(W_i - W_o)} \times 100 \quad \text{Equation 3.1}$$

Where W_o = weight of empty crucible, W_i = weight of crucible with sample before heating and W_f = weight of crucible with sample after heating.

Ash content analysis was carried out following ASTM D3174 (2018). Sample (1 g) was placed in a pre-weighed porcelain crucible and placed in a cold furnace, where it was progressively heated to 500 °C. Heating was continued for 1.5 h, cooled to room temperature, placed in a desiccator and weighed. Equation 3.2 was used to calculate the ash content of each sample.

$$\text{Ash content, wt\%} = \frac{(W_f - W_o)}{(W_i - W_o)} \times 100 \quad \text{Equation 3.2}$$

Volatile matter content determination was conducted based on ASTM D 3175 (2020). Sample (1 g) was heated in an oven (500 °C, 10 min). Calculation of weight loss

percentage and volatile content percentage was carried out using equation 3.3 and equation 3.4 respectively.

$$\text{Weight loss, wt\%} = \frac{(W_i - W_o) - (W_f - W_o)}{(W_i - W_o)} \times 100 \quad \text{Equation 3.3}$$

$$\text{Volatile matter content, wt\%} = \text{Weight loss \%} - \text{Moisture \%} \quad \text{Equation 3.4}$$

Fixed carbon is the residue remaining after the sample particle heated to the extent at a specified temperature and the volatile stuff had been removed ASTM D3172 (2013). In this study, fixed carbon content (wt%) was calculated based on the difference in total percentage of moisture, ash and volatile matter contents from the total percentage of the sample, as per equation 3.5.

$$\text{Fixed carbon, wt\%} = 100 - [\text{moisture} + \text{ash} + \text{volatile}] \% \quad \text{Equation 3.5}$$

Bulk density determination was conducted by filling the sample into a 25 cm³ glass cylinders to a specified volume (Ekpete et al., 2017). To compact the material to a consistent volume, each cylinder was patted for at least 1–2 min (Abdulrazak et al., 2017). After overnight drying at 105 °C in an oven (Ekpete et al., 2017), the sample mass were transferred out of the cylinder, weighed and equation 3.6 was implemented to calculate the bulk density (Abdulrazak et al., 2017).

$$\text{Bulk density} = \frac{\text{Dry mass of the adsorbent (g)}}{\text{Sample volume (cm}^3\text{)}} \quad \text{Equation 3.6}$$

3.2.3.2 Elemental Analyses

The carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content of samples were determined using CHN Elemental Analyzer (Thermo Fisher Scientific, Flash EA1112,

USA). Samples were oven-dried at 105 °C overnight and kept in sealed glass voiles, mixed with vanadium pentoxide (combustion accelerator) before analysis (Singh et al., 2017). The proportion of oxygen was calculated using the difference method as per equation 3.7 (Tatjana, et al., 2018).

$$\% \text{ Oxygen} = 100 - (\text{carbon} + \text{hydrogen} + \text{nitrogen} + \text{sulpher})\% \quad \text{Equation 3.7}$$

The O/C, H/C, and N/C ratios were computed using elements molar concentrations and each ratio was derived by dividing the element's total weight by its molecular weight (Zhao et al., 2019).

3.2.3.3 Surface Morphology Analysis

The surface morphological aspects of the samples were studied using field emission scanning electron microscopy (FESEM) equipped with energy dispersive X-ray (EDX), (JEOL JSM-IT500HR, Japan). Dried samples were adhered to a specimen stub with carbon-based adhesive tape and were coated with gold (5 nm) under vacuum (1 min) before analysis.

3.2.3.4 Surface Area and Pore Analyses

The specific surface area, pore volume and pore radius of the raw and activated carbon samples were determined with Brunauer-Emmett-Teller (BET) method by using Quantachrome ASiQWin automated gas sorption analyzer (Autosorb iQ, USA). All raw and activated carbon samples were degassed prior to analysis at 105 °C for 8 h.

3.2.3.5 Functional Groups Analysis

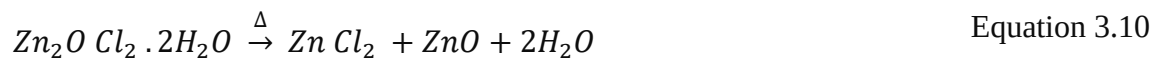
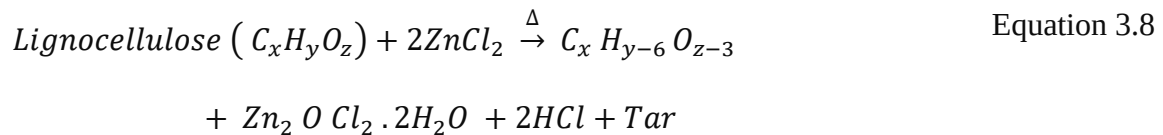
The functional groups present in the raw and AC samples were investigated using Fourier Transform Infrared (FTIR) spectroscopy (Thermo Scientific/Nicolet iS10, USA).

Samples were homogenously mixed with dried KBr in a 1:10 ratio to form pellets for analysis. The pellets were inserted in the sample holder inside the analysis chamber for analysis. The spectra were measured from 400 to 4000 cm⁻¹ wavelength.

3.3 Results and Discussion

3.3.1 Mechanism of pore activation via ZnCl₂

In this study, RLP and RTP were impregnated with ZnCl₂ which is a strong dehydrating agent with a low melting point (283–293 °C), followed by drying and Carbonisation. The combination of organic and inorganic phases progressively became homogenous during Carbonisation as the temperature increased and the salt liquefied (Yang et al., 2020). At elevated temperature, the molten ZnCl₂ accelerated the bond breakage and consequently removal of hydroxyl and carbonyl groups present in RLP and RTP (Luo et al., 2019). The process resulted in the generation of micropores on the surface of the afforded activated carbon, as expressed in Eq. 3.8 (Li et al., 2020).



Due to the slippage of a significant number of weaker biopolymer chains, the molten ZnCl₂ could be uniformly mixed with the thermoplastic phase of the biopolymer (Ma, 2017). At the same time, zinc oxide chloride hydrate (Zn₂OCl₂ · 2 H₂O) was formed utilising the water generated in bond breaking (Equation 3.9) (Li et al., 2020) which was further

decomposed to ZnCl_2 gas due to increased temperature (Equation 3.10) (Ma, 2017). Subsequently, the gas diffusion made pathways through the thermoplastic phase, creating the pore structure of the final product (Li et al., 2020).

3.3.2 Proximate Analyses

The proximate analysis results of raw *Melia azedarach* leaves and twigs (RLP and RTP, respectively) and their activated carbon samples (LAC and TAC) are depicted in Table 3.1. Results showed that the moisture content of the RLP and RTP were 6.12% and 6.28% respectively and that both were lower than 10%, making them potential feedstock for activated carbon (Kaya et al., 2020). On the other hand, LAC and TAC were found to have moisture contents of 1.14% and 4.75% respectively, which were much lower than those of the precursors. The moisture content reduction in the activated carbons was due to water removal during the carbonisation process as well as prolonged heating during the drying of the activated carbon (Choudhary et al., 2020). Reduction in moisture content of LAC and TAC is also due to the modification of RLP and RTP with a strong dehydrating agent ZnCl_2 (Ghasemi et al., 2020), the mechanism of dehydration due to ZnCl_2 has been explained in equation 3.8 -3.10 (Li, et al., 2020; Ma, 2017).

The volatile matter concentration of various biomass precursors has been previously reported to range from 48% to 87% (Kaya et al., 2020). The volatile components of RLP and RTP were found to be 63.96% and 71.87%, respectively. It was clear from comparing these raw materials' moisture contents to the literature that both had potential to serve as suitable precursors for activated carbon. After modification, the volatile contents of activated carbons (LAC and TAC) were lower than respective precursor (RLP and RTP). During high-temperature carbonisation, the decomposition of lignin, cellulose and hemicellulose

components of the biomass occurred (Choudhary et al., 2020). Hemicellulose decomposes at 250 °C to 320 °C, cellulose decomposes at 320 °C to 380 °C while lignin decompose gradually up to 900 °C (Qiao et al., 2019). Being volatile components, hemicellulose and cellulose are mainly responsible for the mesopores and macropores of produced activated carbon, in contrast to lignin which has a high thermal stability and a relatively low reactivity that enable it to withstand the corrosive reactions occurring during the modification process (Hong et al., 2019). During modification, the fibrous structures of the biomass precursor were destroyed during modification (Ngaini et al., 2021) and organic extracts of low molecular mass were eliminated as volatile matter and assisted in the formation of pore structures on the surface of activated carbon (Hong et al., 2019).

Table 3.1: Physicochemical properties of feedstock and activated carbon

Material	Proximate Analysis				Bulk Density (cm ³ g ⁻¹)
	Moisture	Ash Matter	Volatile	Fixed	
	Content (%)	(%)	Matter (%)	Carbon (%)	
RLP	6.12 ± 0.40	7.99 ± 2.88	63.96 ± 3.03	21.93 ± 5.85	0.543 ± 0.022
RTP	6.28 ± 0.69	3.95 ± 2.23	71.87 ± 1.08	12.02 ± 5.11	0.474 ± 0.008
LAC	1.14 ± 1.45	71.01 ± 6.43	15.66 ± 2.18	17.91 ± 2.13	0.365 ± 0.003
TAC	4.75 ± 0.88	44.59 ± 5.20	17.38 ± 1.66	33.07 ± 3.26	0.368 ± 0.004

Ash content is a combination of incombustible minerals including calcium, magnesium, iron, sodium, and potassium found in the biomass (Hasana et al., 2021). The ash content in the AC was higher (LAC 71.01%; TAC 44.59%) compared to the raw samples (RLP 7.99%, RTP 3.95%). Ash content increased after modification, indicating that ZnCl₂ treatment enhanced the inorganic solid fractions (Makshut et al., 2020). LAC was found to

have a higher ash content than TAC, indicating that LAC contained relatively more minerals than TAC (Abdallah et al., 2019).

Fixed carbon is fundamentally a combination of carbon along with small quantities of oxygen, hydrogen, nitrogen, and sulphur (Hasana et al., 2021). The primary source of fixed carbon in the biomass precursor is lignin, whereas hemicellulose and cellulose combine to make up the volatile components (Hong et al., 2019). The fixed carbon content of LAC (17.91%) was found to be somewhat lower than RLP (21.93%). However, the fixed carbon content in TAC increased to 33.07% from 12.02% in RTP. The difference in lignin concentration between TAC and LAC can be the reason for TAC's higher fixed carbon content (Hong et al., 2019). The fact that the fixed carbon in activated carbon can develop the structure of carbons into pores is another sign of a potential improvement of the adsorption sites (Hasana et al., 2021).

To be practically fit for use, the bulk density of an activated carbon should be higher than $0.25 \text{ cm}^3\text{g}^{-1}$ according to American Water Work Association's specifications (Adane et al., 2020), along with better filterability as an adsorbent (Bayuo et al., 2020). The bulk density of LAC was determined to be $0.365 \text{ cm}^3\text{g}^{-1}$ while TAC was found to have bulk density of $0.368 \text{ cm}^3\text{g}^{-1}$. The findings showed that both LAC and TAC had acceptable bulk densities that met the intended criterion and had good filterability. Different classes of activated carbon can also be distinguished based on the bulk density: macroporous carbon has a bulk density greater than $1 \text{ cm}^3\text{g}^{-1}$ (pore space volume per gramme of carbon), mesoporous carbon has a bulk density between $0.85 \text{ cm}^3\text{g}^{-1}$ and $1.0 \text{ cm}^3\text{g}^{-1}$, and microporous carbon has a bulk density less than $0.85 \text{ cm}^3\text{g}^{-1}$ (Gisi et al., 2016). Bulk density of both LAC

and TAC indicated that both the activated carbons were of microporous in nature with bulk density less than $0.85 \text{ cm}^3\text{g}^{-1}$.

3.3.3 Elemental analysis

The CHNS analysis results are illustrated in Figure 3.2. The C contents in LAC increased to 56.80% from 51.61% while TAC's carbon content increased to 65.42% from 39.89% in raw biomass. Volatile compounds in the biomass were degraded during Carbonisation at 500°C in the presence of ZnCl_2 , resulting in higher graphitisation and consequently increased carbon content in the resultant activated carbon (Kongsune et al., 2021).

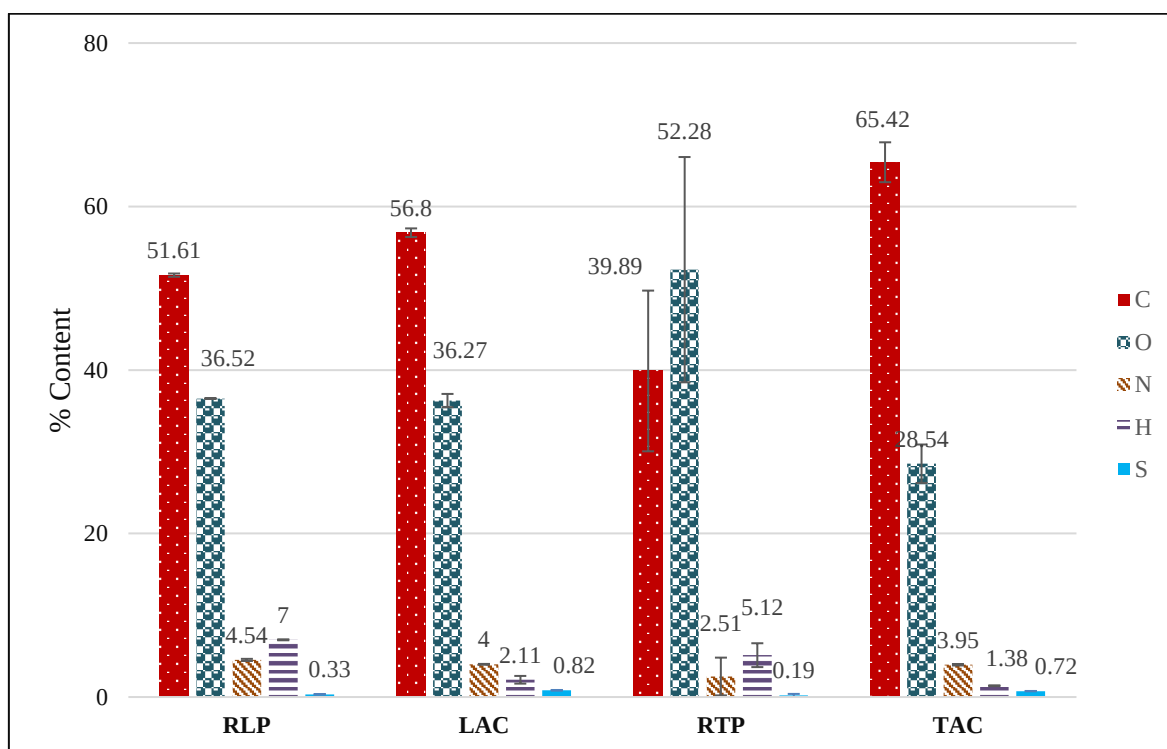


Figure 3.2: Elemental analysis of the raw samples (RLP and RTP) and activated carbon (LAC and TAC)

H/C content of both LAC and TAC are lower than the respective feedstock which indicates that the activation with ZnCl_2 and Carbonisation has increased the aromaticity of both the activated carbons (Gao et al., 2019). As H/C molar ratio ≤ 0.3 , shows a high degree of aromatic structures whereas $\text{H/C} \geq 0.7$ indicates non-aromatic structures (Bandara et al., 2020) therefore H/C ratio of 0.04 and 0.02 of LAC and TAC respectively express the formation of aromatic and aliphatic structures while 0.64 and 0.44 O/C ratio of LAC and TAC indicates the stability of both the activated carbons (Wang, 2020). The ratio of O/C to H/C is directly related to aromatics, biodegradability and polarity; thus, this ratio affects the removal of organic and inorganic contaminants (Choi, 2019). A high carbon percentage in activated carbon demonstrates its suitability as a porous adsorbent, whereas a high amount of hydrogen, nitrogen and sulphur provides the benefit of maintaining the functional groups that are necessary for the adsorbent's adsorption capacity (Rahim et al., 2019).

3.3.4 Surface Morphology Analysis

The surface morphological features of feedstocks RLP, RTP, as well as activated carbons LAC and TAC samples were studied before and after adsorption using FESEM as shown in Figure 3.3 and 3.4.

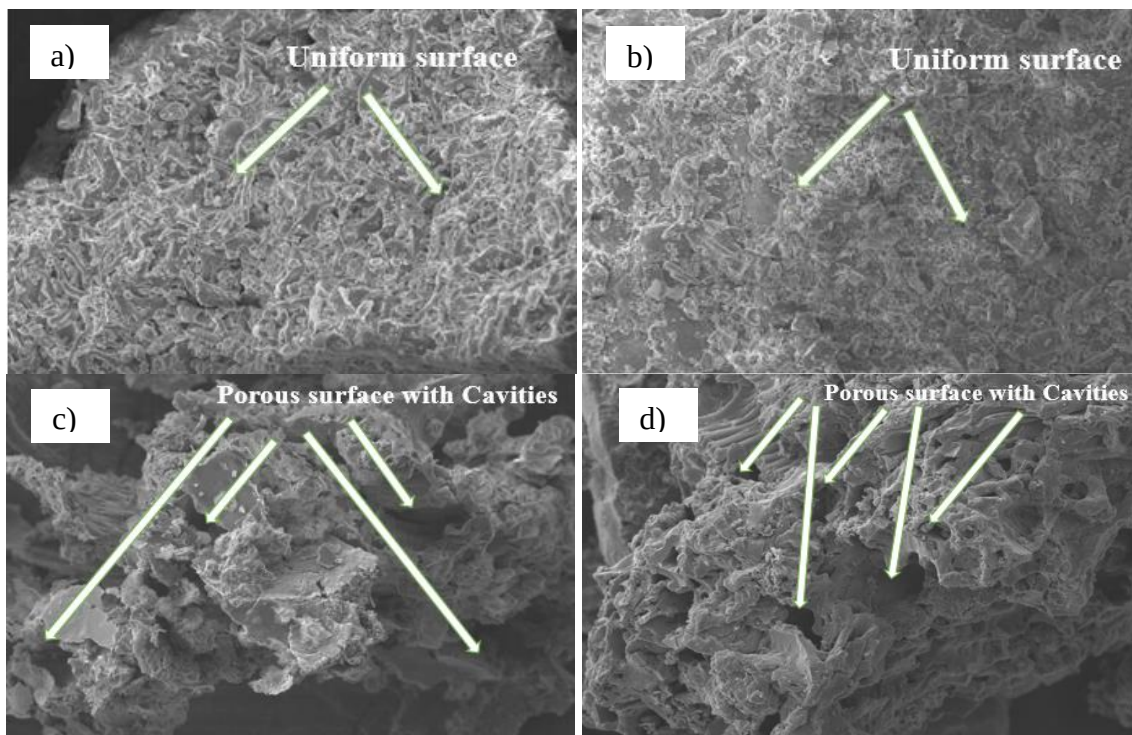


Figure 3.3: FESEM images of *Melia azedarach* (a) leaves powder (RLP); (b) twigs powder (RTP); (c) leaves activated carbon (LAC); and (d) twigs activated carbon (TAC) , at 1000X magnification and 10 μm spatial resolution

Figures 3.3 (c) and (d) show FESEM micrographs of LAC and TAC, respectively. It can be seen that both AC contain pores on the surface, whereas Figures 3.3 (a) and (b) depict that RLP and RTP have uniform surfaces without pore (Ghasemi et al., 2020). The irregular cavities with a wide range of sizes on the surface of both LAC and TAC show that these cavities were generated in *Melia azedarach* leaves and twigs during molten salt synthesis (Luo et al., 2019). The proximate analysis revealed that RLP and RTP include a considerable quantity of volatile compounds that disperse during activation and zinc chloride was adsorbed there (Piriya et al., 2021) Porosity increased when the temperature went over 300 $^{\circ}\text{C}$ due to the swelling effect of ZnCl_2 , pore channel structures emerged and numerous microparticles were generated (Li et al., 2020). With the temperature increases above 450 $^{\circ}\text{C}$, these

microparticles collapsed or fractured, leading to an increase in surface area due to the formation of a massive number of mesopores and macropores (Lin et al., 2021).

Based on FESEM images of LAC and TAC in Figure 3.3 (c) and (d), the surface of both the AC was porous with a significant number of irregular pores, making LAC and TAC suitable for the adsorption of contaminants from an aqueous medium (Aboli et al., 2020). The N₂ adsorption-desorption isotherm findings further show that the activated carbon LAC and TAC contain a large number of mesopores. It is also evident that the BET surface area increased from 1.020 m²g⁻¹ to 121.592 m²g⁻¹ in LAC and from .485 m²g⁻¹ to 91.423 m²g⁻¹ in TAC from the relevant feedstock. Heavy metal adsorption takes place primarily in mesopores, which offer routes for heavy metal ions to reach active adsorption sites and enhance rapid adsorption (Mahdi et al., 2018).

FESEM micrographs in Figure 3.4(a-f) show that the surface pores on both the LAC and TAC were approximately covered with the deposition of Pb (II), Cu (II) and Ni (II) ions during adsorption. As pores were filled with some irregular, crystalline structures which supported the adsorption of metal ions from an aqueous medium.

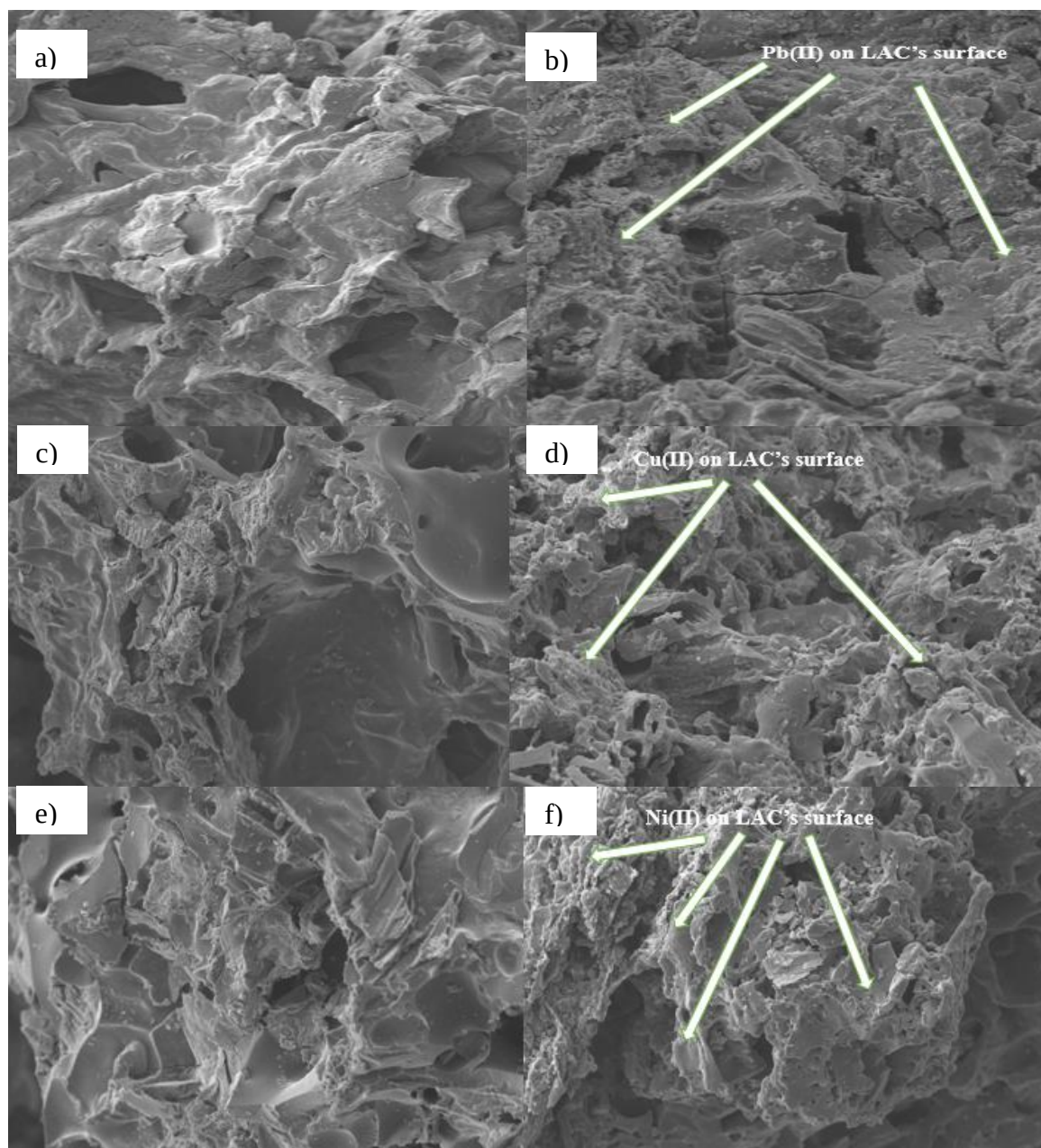


Figure 3.4: FESEM images of activated carbon(a) LAC A/Pb(II) adsorption; (b) TAC A/Pb(II); (c) LAC A/Cu(II) adsorption; (d) TAC A/Cu(II) adsorption; (e) LAC A/Ni(II) adsorption and (f) TAC A/Ni(II) adsorption at 1000X magnification and 10 μm spatial resolution

3.3.5 EDX Analysis

The surface elements of the feedstock and the activated carbon samples were identified using EDX analysis. As demonstrated in Table 3.2, RLP contains carbon, oxygen,

sulfur, calcium, Magnesium, silicon and potassium, whereas LAC contains zinc and chlorine following activation. Some compounds found in RTP were identical to those found in RLP while sodium and aluminium were also discovered. Sulphur, calcium, silicon, sodium and potassium were removed from TAC during activation process. Carbon has been one of the most main constituent of the analyzed samples of LAC and TAC and the proportion of carbon found in EDX analysis was almost similar to elemental analysis (Aboli et al., 2020).

Table 3.2: EDX analysis of elements % mass of RLP, RTP, LAC and TAC

Content Element	%Mass			
	RLP	LAC	RTP	TAC
Carbon	57.44 $\pm$ 0.04	63.52 $\pm$ 23.12	60.92 $\pm$ 0.07	70.55 $\pm$ 0.06
Oxygen	36.80 $\pm$ 0.08	12.51 $\pm$ 1.77	33.64 $\pm$ 0.13	10.45 $\pm$ 0.04
Sulphur	0.39 $\pm$ 0.01	0.11 $\pm$ 0.33	0.47 $\pm$ 0.02	n.d.
Calcium	2.69 $\pm$ 0.04	1.42 $\pm$ 0.02	1.28 $\pm$ 0.05	n.d.
Magnesium	0.59 $\pm$ 0.01	0.48 $\pm$ 0.01	0.72 $\pm$ 0.33	0.37 $\pm$ 0.01
Silicon	0.52 $\pm$ 0.01	0.24 $\pm$ 0.02	0.24 $\pm$ 0.02	n.d.
Sodium	n.d.	n.d.	0.74 $\pm$ 0.01	0.58 $\pm$ 0.01
Aluminium	n.d.	n.d.	0.27 $\pm$ 0.02	n.d.
Potassium	1.57 $\pm$ 0.03	n.d.	2.49 $\pm$ 0.06	n.d.
Chlorine	n.d.	3.75 $\pm$ 8.92	n.d.	0.54 $\pm$ 0.02
Zinc	n.d.	19.36 $\pm$ 12.04	n.d.	18.05 $\pm$ 0.04
Total	100	100	100	100

n. d. : not detected

The results of the EDX analysis (Table 3.2) of both activated carbon LAC and TAC confirmed the presence of zinc and Cl (Duan et al., 2019). Results indicate that these studies ions have been attached to active functional groups of the feedstock during activation (Maity & Ray, 2018). The presence of Zinc in LAC and TAC can also take part in the adsorption of heavy metals through a chelation mechanism due to identical energy levels (Du et al., 2020).

3.3.6 Pore Structure Analyses

Surface area, pore volume and pore structure were determined using Quantachrome ASiQWin automated gas sorption analyzer supplied by Quantachrome and calculations were carried out using Brunauer-Emmett-Teller (BET) method. As pre-treatment for analysis, samples were degassed under vacuum at 105 °C for 8 h before analysis at 77K to eliminate any moisture content from the solid surface. To evaluate the impact of activation on the surface area and pore structure, the N₂ adsorption/desorption isotherms were obtained, as shown in Figure 3.5.

The IUPAC recommendations were used to examine the N₂ adsorption-desorption isotherms of activated carbon, LAC and TAC , which comprise six separate isotherms and six related hysteresis loops (Thommes et al., 2015). In Figure 3.5, both adsorption isotherms are of Type IV, indicating that they are mesoporous (Choudhary et al., 2020). In the adsorption-desorption isotherm, LAC exhibited a broad hysteresis at a relative pressure (P/P_0) of 0.2–0.8 region while TAC exhibited a sharper hysteresis in the range of 0.24-0.9 relative pressure. Hysteresis in the LAC isotherm was found to be H4 type while in TAC, both H3 and H4 imply the presence of aggregate assemblages creating slit-like pores of varied sizes (Oladipo et al., 2019). Collectively based on isotherms and hysteresis, both LAC and TAC are found to be mesoporous (Venkateswarlu et al., 2019) which are

characteristically demonstrated by commercial adsorbents, numerous oxide gels and mesoporous molecular sieves (Thommes et al., 2015). Previous research has shown that utilising ZnCl_2 as an activator can produce mesoporous activated carbon (Hong et al., 2019) and the findings in this work confirmed the same capability of ZnCl_2 activation on *Melia azedarach* leaves and twigs biomass.

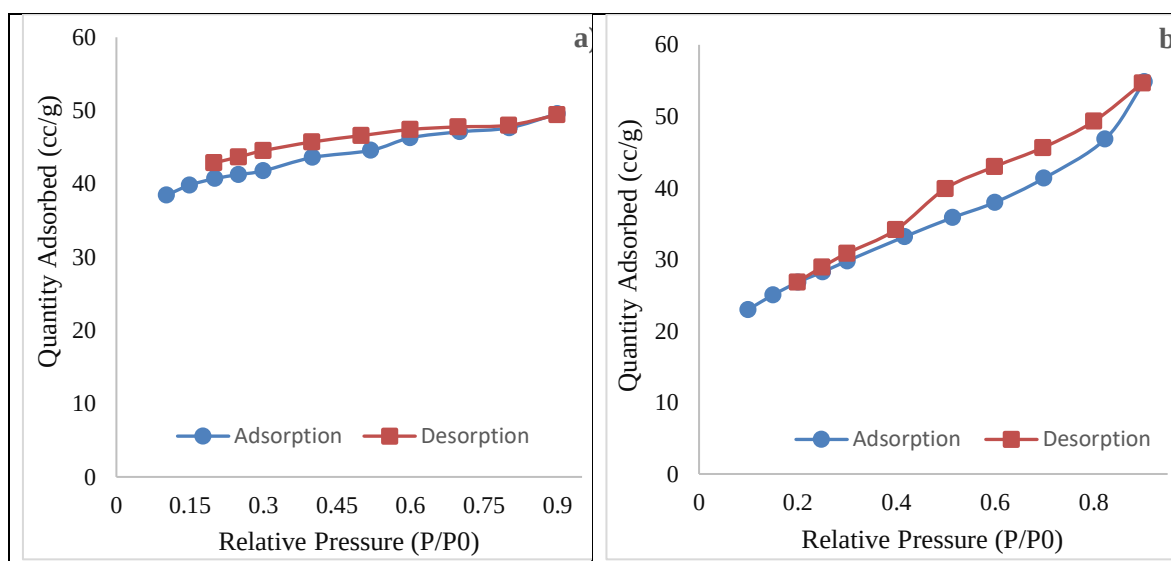


Figure 3.5: N_2 Adsorption-desorption isotherm curves for a) LAC ; b) TAC

Table 3.3 shows that LAC has a surface area of $121.592 \text{ m}^2\text{g}^{-1}$, compared to $1.020 \text{ m}^2\text{g}^{-1}$ of RLP. The surface area of TAC was found to be $91.223 \text{ m}^2\text{g}^{-1}$, compared to $0.485 \text{ m}^2\text{g}^{-1}$ of RTP. The surface area of the activated carbon influences physical adsorption as a larger surface area facilitates metal ions uptake while chlorine present on the surface of activated carbon due to ZnCl_2 activation participates in oxidising metal ions in the aqueous solution resulting in chemical adsorption (Duan et al., 2019).

Table 3.3: Surface area, pore volume and diameter of feedstock and activated carbon

Material		BET Surface area (m²g⁻¹)	Pore Volume (m³g⁻¹)	Pore size (°A)	Reference
Peanut shells	activated with ZnCl ₂ , pyrolysis at 500 °C	1807	0.725	-	(Liu et al., 2018)
Carbonised the mangosteen peels	at 700 °C	45.31	0.02	-	(Kongsune et al., 2021)
Groundnut shell, rice husk and soya bean shell Composite	was pyrolyzed at 400 °C for 30 min, impregnated with KCl sol. overnight	849.63	0.4967	-	(Obayomi et al., 2019)
Carbonised the mangosteen peels	at 700 °C, impregnated with ZnCl ₂ , then 600 °C carbonised	423.99	0.22	-	(Kongsune et al., 2021)
Pyrolyzed Barley straw	at 500 °C	1.43	0.0094	-	(Jazini et al., 2018)
Pyrolyzed <i>Melia azedarach</i> wood	at 400 °C, treated with Ferric nitrate	5.219	0.017	-	(Zhang et al., 2018)

Table 3.3 continued

Pyrolyzed Shell at 550 °C	Peanut	1.78	0.00047	-	(Taşar & Özer, 2020)
RLP		1.020	0.00361	9.1591	This study
RTP		0.485	0.00467	14.8854	This study
LAC		121.592	0.08485	1.26087	This study
TAC		91.423	0.07666	1.86025	This study

Previously, it has been reported that the adsorption capacity increases proportionately with the surface area, regardless of the types of adsorbent (Razak et al., 2020). The surface area and pore volume achieved in this study are lower than those obtained in previous research with different types of biomass using ZnCl_2 activation in conjunction with pyrolysis. However, as compared to pyrolysis and other chemical activations, the surface area and pore volume obtained in this study are significantly higher.

3.3.7 Functional groups Analyses

Figure 3.6 shows the FTIR Spectra of RLP and LAC. In RLP, there are peaks on 2915, 2849 cm^{-1} symmetric -C-H stretching band, 1621 for -COOH group (Jin et al., 2020), 1396 cm^{-1} mention the existence of the -C-H bending group (Singh et al., 2017). Peaks at 2885 cm^{-1} reflect the presence of CH stretch of methyne groups, 2163 cm^{-1} , 1987 cm^{-1} , 1555 cm^{-1} , 1026 cm^{-1} represents symmetric -C-O stretching band of -OCH₃ group, while peaks at 873 cm^{-1} and 689 cm^{-1} represents the aromatic -C-H band (Jin et al., 2020). In RLP, a strong intense peak at 1625 cm^{-1} , corresponded to aromatic groups, while a weak peak at 1750 cm^{-1} attributed to carbonyl compounds. In LAC, carbonyl group was disappeared and a modest peak close to 1600 cm^{-1} indicating the removal of volatile compounds and breakage of double

bons during activation (Nandiyanto et al., 2019). In RLP, peaks at 1558 cm^{-1} , 1539 cm^{-1} attributed to C=C of aromatic ring (Fotsing et al., 2020) and 1211 cm^{-1} corresponded to -CO stretching vibration were disappeared after activation (Anitha et al., 2020). In RLP, a strong peak at 1030 cm^{-1} indicated the presence of C-O of ethers, cellulose alcohols which was transformed to a weaker peak in LAC (Fotsing et al., 2020). After the activation process, a few new peaks appeared in LAC, including at 3554 cm^{-1} which corresponded -OH dimeric stretching and a strong peak at 790 cm^{-1} corresponded the -C-Cl stretch of aliphatic chloro compounds (Nandiyanto et al., 2019).

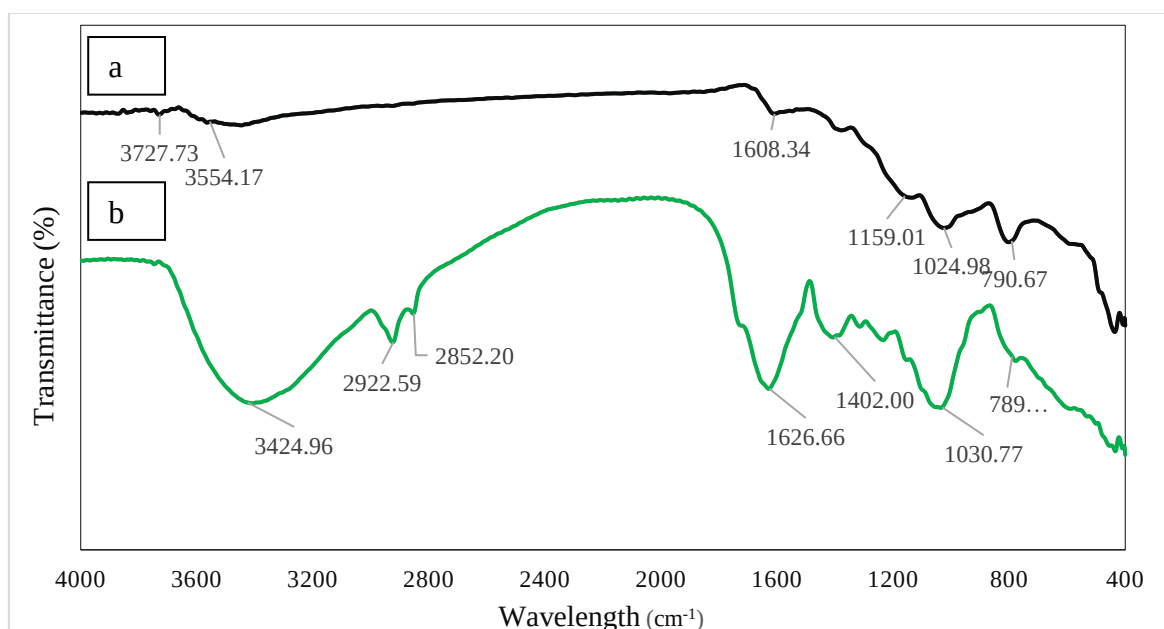


Figure 3.6: FTIR Spectra: a) *Melia azedarach* leaves raw powder (RLP) and b) activated carbon (LAC)

Figure 3.7 contains FTIR spectra of RTP and TAC. In RTP, strong peaks on $3000\text{--}3600\text{ cm}^{-1}$ corresponded OH group of alcohols, aromatic compounds, which reduced in TAC after activation process (Nandiyanto et al., 2019). A peak at 2918 cm^{-1} corresponded C-H asymmetric/symmetric stretching of aliphatic acids/polysaccharides which disappears in

TAC (Fotsing et al., 2020). In RTP, there is a peak at 1627 cm^{-1} , indicates alkyl stretch or aromatic compounds, in TAC, there is peak shift to 1610 cm^{-1} indicating changes happened during activation (Al-Onazi et al., 2021). A peak at 1747 cm^{-1} indicates carbonyl compounds in RTP while in TAC, this peak is absent indicating the removal of volatile compounds during activation (Nandiyanto et al., 2019). In RTP, there are several small peaks in between $1000\text{--}1500\text{ cm}^{-1}$ indicating C-O, C-O-C, C-O antisymmetric stretching of ether, alcohol, polysaccharides and all these are not visible in TAC, another set of functional groups involved in activation (Fotsing et al., 2020), In RTP. there is strong peak at 1014 cm^{-1} indicate presence of C–O of ethers, cellulose alcohols which persisted in TAC with a shift to 1026 cm^{-1} as a weak smaller peak (Fotsing et al., 2020). After activation, in TAC, new peak appeared at 790 cm^{-1} indicating C-Cl stretch of aliphatic chloro compounds which was not visible in RTP (Nandiyanto et al., 2019).

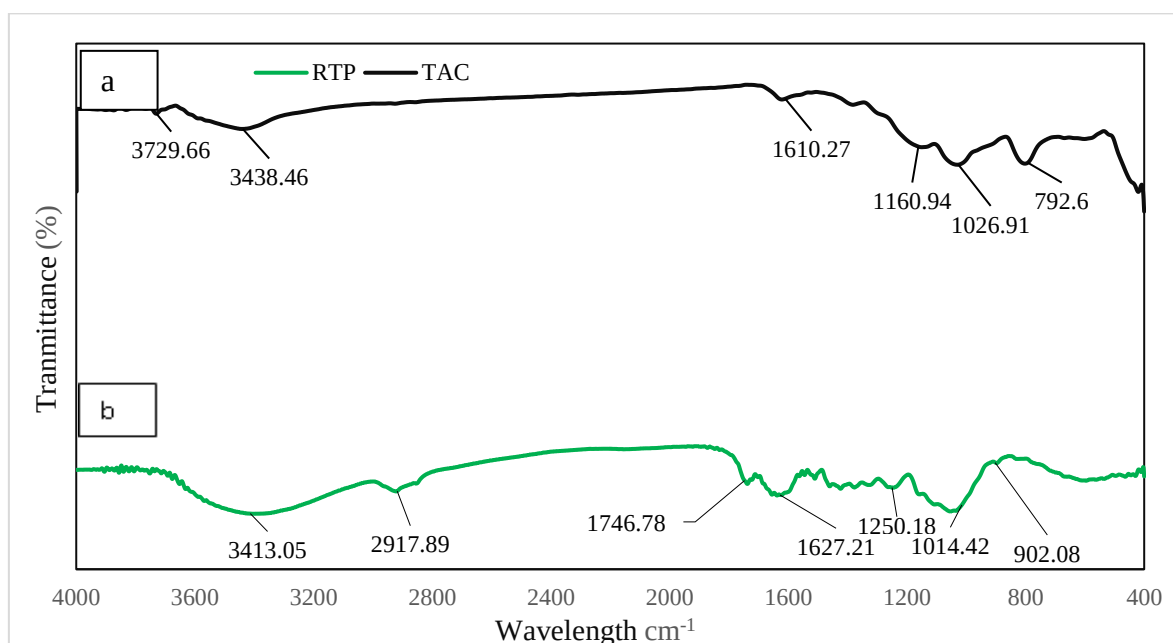


Figure 3.7: FTIR Spectra: a) *Melia azedarach* leaves raw powder (RTP) and b) activated carbon (TAC)

3.4 Conclusion

Melia azedarach leaves and twigs were effectively transformed into mesoporous activated carbon with enhanced surface area and functional groups availability, through Molten Salt Synthesis. Proximate analysis revealed that the addition of inorganic components in the form of ZnCl_2 reduced the moisture and volatile content of LAC and TAC while increasing the ash content. Carbon content increased during Molten Salt Synthesis, as measured by CHNS elemental analysis and EDX analysis, and LAC and TAC both were found to be carbon-rich. Bulk density of LAC and TAC were found to be $0.365 \text{ cm}^3\text{g}^{-1}$ and $0.368 \text{ cm}^3\text{g}^{-1}$ which complies the American water Work Association's minimum bulk density requirement for commercial activated carbon. The BET surface area of LAC and TAC were found to be $121.592 \text{ m}^2\text{g}^{-1}$ and $91.423 \text{ m}^2\text{g}^{-1}$, respectively. LAC and TAC were determined to be mesoporous activated carbon based on N_2 adsorption-desorption isotherm and supported by FESEM analysis. Both LAC and TAC contain several functional groups such as carboxyl, hydroxyl and other oxygen containing groups, as per FTIR analysis. Based on these findings, LAC and TAC demonstrate the ability to function as excellent adsorbents for heavy metals removal from aqueous medium.

CHAPTER 4

HEAVY METALS REMOVAL BY ACTIVATED CARBON BASED ON *Melia azedarach* LEAVES AND TWIGS: ADSORPTION ISOTHERM AND KINETICS STUDY

4.1 Introduction

Heavy metal contamination in aquatic ecosystems has increased at an alarming rate in recent decades as a result of a variety of human activities, including mining, industrial, household, and municipal waste disposal, agriculture, and wastewater discharge (Bandara et al., 2020). Heavy metal contamination has serious environmental repercussions due to its high toxicity, widespread distribution, and non-biodegradability (Anitha et al., 2020). Heavy metals damage humans, aquatic life, and the environment by poisoning water supplies (Balasubramanian et al., 2020).

Cu(II) finds application in a wide range of industrial operations, including the production of paints, machinery pulp, construction industries (Qin et al., 2019), as well as electrical appliances, electronics, automotives, batteries, pesticides and fertilisers (Cibati et al., 2017). Industries in which Pb(II) is used include paints, pipes, bullets, alloys, batteries, ceramics, glass, electroplating, pulp and paper, (Ibrahim et al., 2020), lead smelting, metal finishing, as well as in households, electronics, incinerators and in fuel (Wang, 2020). Ni(II) is being used in different industries including stainless steel and other metallic alloys, batteries, electroplating, mineral processing, paints and steam-electric power plants (Anitha et al., 2020).

Cu(II) is required to the human body in small amounts, but high levels can cause kidney damage, miscarriages, nervous system abnormalities, following vomiting, headache,

nausea, respiratory difficulties, stomach discomfort, liver and gastrointestinal haemorrhage, and brain damage (Fotsing et al., 2020). Excessive Pb(II) intake can be linked to cancer, damage the nervous and reproductive systems as well as cause cancer, kidney failure, (Kongsune et al., 2021), lung disorders, hypertension, anaemia, mental development, liver, kidney, nervous system malfunction, red blood cell damage (Alguacil et al., 2018). Ni(II) is harmful to humans, causing skin allergies, lung fibrosis, cancer liver, renal, neurological, genetic and reproductive problems (Mahdi et al., 2018). The maximum allowable content of Cu(II), Pb(II) and Ni(II) in drinking water have been specified by international regulatory authorities like US-EPA and WHO.

Several studies have reported on the preparation of activated carbon from various agricultural and horticultural wastes and its application for heavy metals removal from aqueous medium. Activated carbon was prepared by treating powdered peanut shell with ZnCl_2 followed by pyrolysis at 500 °C and oxidised by treating with HNO_3 , H_3PO_4 , and KOH respectively and its adsorption capacity was determined to be 135 mgg^{-1} when applied as adsorbent to remove Pb(II) ions from aqueous medium (Liu et al., 2018). Water suspension of pulverised winemaking waste cluster stalks was prepared by combing with water at high temperature and pressure for 3 h, with high speed constant stirring, filtered, and the resultant product was dried and activated with KOH at 800 °C for 2 h under a N_2 atmosphere, and the resultant activated carbon had an adsorption capacity of 58 mgg^{-1} for Pb(II) removal (Alguacil et al., 2018). Coffee husk and spent coffee were pyrolyzed separately at 500 °C for 1 hr, followed by activation at 800 °C for 30 mint and the resulting activated carbon was applied as an adsorbent for Ni(II) removal with adsorption capacities of 57.14 mgg^{-1} and 51.91 mgg^{-1} respectively (Hernández et al., 2018).

In other studies of activated carbon preparation from agricultural wastes, *Opuntia ficusindica* Cladodes were pyrolyzed at 400 °C for 1 h and activated with NaOH and carbonised at 500 °C for 1 hr and the Cu(II) and Ni(II) adsorption capacity of the resultant activated carbon was 49.36 mgg⁻¹ and 44.35 mgg⁻¹ respectively (Choudhary et al., 2020). The dried *Citrus limetta* leaves were pyrolyzed at 700 °C for 3 h and the obtained activated carbon had an adsorption capacity of 69.82 mgg⁻¹ for removing Pb(II) ions from water (Aboli et al., 2020). Jujube sawdust was mixed with H₃PO₄, then pyrolyzed at 450 °C for 1 hr, and the resultant un-oxidised activated carbon was found to have 29.98 mgg⁻¹ adsorption capacity for Pb(II) removal (Khan et al., 2020). Mangosteen peels were carbonised at 700 °C, mixed in ZnCl₂ sol. then activated at 600 °C for 2 hr, yielding activated carbon with a Pb(II) adsorption capacity of 130 mgg⁻¹ (Kongsune et al., 2021).

A few studies have been published on the utilisation of *Melia azedarach* biomass feedstock as an adsorbent for heavy metals from aqueous medium. Removal of As(III) and As(V) by dried and ground *Melia azedarach* leaves and bark was reported by (Sarwar et al., 2015). Lead and iron adsorption efficiency of *Melia azedarach* leaves treated with diluted HCl and NaOH was studied by (Khokhar et al., 2015). Powdered *Melia azedarach* wood was pyrolyzed at 400 °C followed by Fe(NO₃)₃ impregnation was evaluated for Cr(VI) removal by (Zhang et al., 2018). Powdered *Melia azedarach* branches were modified with conc. H₂SO₄ for 24 h and applied as adsorbent for the removal of Cr₂O₄⁻² from aqueous medium (Nosheen et al., 2021). Activated carbon was prepared with *Melia azedarach* seed shells by treating with HCl, carbonising at 550 °C for 4 h which removed 66% for Cd(II) and 62% for Pb(II) with 2 gL⁻¹ dosage, 40 mgL⁻¹ initial conc., pH 5 and 120 min contact time (Ullah et al., 2020). Most of these studies have described the use of *Melia azedarach* biomass as an

adsorbent without significant physiochemical modification, leading in a low adsorption capacity or removal efficiency for heavy metals.

Based on previous studies, *Melia azedarach* biomass appeared to be a potential alternative for producing an economical and efficient activated carbon that can be used as an adsorbent for the removal of heavy metals from aqueous medium. The application of activated carbon derived from *Melia azedarach* leaves and twigs, as an adsorbent to remove heavy metals from aqueous medium, has yet to be documented. A thorough understanding of the adsorption mechanism is also required.

The aim of the present work is to study the adsorption of divalent metal ions Cu(II), Pb(II) and Ni(II) by using activated carbons derived from *Melia azedarach* leaves and twigs. Adsorption isotherm models and kinetic study was used to evaluate the adsorption behaviour in different parameters.

4.2 Materials and Methods

4.2.1 Adsorbent

In the present study, activated carbon prepared from *Melia azedarach* leaves (LAC) and *Melia azedarach* twigs (TAC) were applied as adsorbent for the adsorption of Cu(II), Pb(II) and Ni(II) heavy metal ions. The activated carbons LAC and TAC were both prepared through molten salt synthesis (MSS) method. The preparation method and physiochemical characteristics of LAC and TAC were discussed in Chapter 3.

4.2.2 Preparation of Stock Solution for Adsorption Study

Chemical reagents used as adsorbate in this study including lead Nitrate; $\text{Pb}(\text{NO}_3)_2$ (99% purity, R&M Chemicals, Malaysia), copper sulphate; $\text{Cu}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ (99% purity,

Johchem Scientific, Malaysia), Ni(II) standard solution (1000 mgL⁻¹ solution, Merk, Germany). For pH adjustment, sodium hydroxide, NaOH (99%, Merck, Germany) and hydrochloric acid, HCl (33-38% purity, Fisher Chemical, Malaysia) were used. Pb(II) and Cu(II) Stock solutions were prepared by dissolving 1.6 g of lead nitrate and 3.93 g of copper sulphate individually in a 1 L volumetric flask to obtain 1000 mgL⁻¹ of each single solute, then diluting with de-ionised water to achieve the desired concentration. For Ni(II), 1000 ppm standard solution (Merck) was used. Stock solution was freshly diluted to the concentrations of 5 mgL⁻¹, 10 mgL⁻¹, 15 mgL⁻¹, 20 mgL⁻¹, 25 mgL⁻¹, 30 mgL⁻¹, 35 mgL⁻¹, 40 mgL⁻¹, 45 mgL⁻¹ and 50 mgL⁻¹.

4.2.3 Adsorption Study

i) Effect of Contact Time

In this study, contact time effect on the batch adsorption process was investigated using 50 ml of the adsorbate solutions containing 50 ppm initial concentrations of Cu(II), Pb(II) and Ni(II) with 1 gL⁻¹ dosage of prepared adsorbent (LAC and TAC) at 25 ± 2 °C in individual studies with rotation at 150 rpm in an orbital shaker. Adsorption capacity and heavy metal removal efficiency of the adsorbent was calculated using equation 4.1 and equation 4.2 respectively.

$$q_e = \frac{C_o - C_e}{W} \times V \quad \text{Equation 4.1}$$

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \times 100 \quad \text{Equation 4.2}$$

ii) Effect of Initial Concentration

In this study, effect of initial metal concentration on the batch adsorption process was investigated using 50 ml of the adsorbate solutions containing 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 ppm initial concentrations of each Cu(II), Pb(II) and Ni(II) independently with 1 gL⁻¹ dosage of prepared adsorbent (LAC and TAC) at 25 ± 2 °C in individual studies with rotation at 150 rpm in an orbital shaker for a contact time of 120 min.

iii) Adsorption isotherm Study

The adsorption isotherm depicts the amount of adsorbate on the adsorbent as a function of concentration at constant temperature, and specified contact time and adsorbent dosage (Taşar and Özer, 2020). The adsorption isotherm data at equilibrium must be calculated while designing an adsorption system (Shafiq et al., 2021). The adsorption capacity, isotherm intensity, and the mechanism of adsorption should be determined for adsorption isotherm (Razak et al., 2020). Thus, the experimental results were evaluated by applying the Langmuir, Freundlich, Temkin, and Dubinin- Radushkevich (D-R) isotherm models, which have been used extensively to describe the adsorption process. The theories and equations related to the above adsorption isotherms were described in Chapter 2.

iv) Kinetic Study

For the application of an adsorbent for removal of adsorbate from aqueous medium, adsorption rate and its dynamic behaviour are essential elements which are necessary to be explored. The structure and features of activated carbon vary with the feedstocks used as well as modifications carried out. Activated carbon characteristics including aromaticity, porosity, surface area, polarity, affect the adsorption rate and capacity (Abdallah et al., 2019). For an adsorbent's performance evaluation, kinetic parameters can be used to identify

the rate-limiting step and the requisite contact time for the adsorption process (Kaya et al., 2020). For adsorption rate limiting step evaluation, four most often employed models: Pseudo- First-Order (PFO), Pseudo-Second-Order (PSO), Elovich model and Weber-Morris model (WM) were applied and best fitting kinetic model was selected with the highest correlation coefficient (R^2) between experimental and theoretical data (Abdallah et al., 2019). In this study, linearised forms of the PFO, PSO, Elovich Model and WM as described in equation 2.7, equation 2.9, equation 2.16 and equation 2.17 respectively (Chapter 2) were followed to evaluate the adsorption kinetics of Pb(II), Cu(II) and Ni(II) by LAC and TAC.

v) Functional Groups Analysis

The functional groups present on the surface of both activated carbons, before and after heavy metal Cu(II), Pb(II) and Ni(II) ions adsorption were investigated using Fourier Transform Infrared (FTIR) spectroscopy (Thermo Scientific/Nicolet iS10, USA).

4.3 Results and Discussion

4.3.1 Effect of Contact Time

Figure 4.1 shows the adsorption of Cu(II), Pb(II) and Ni(II) ions onto LAC as a function of contact time. All three metals Cu(II), Pb(II) and Ni(II) ions showed rapid uptake by LAC in the first 40 min then the process slowed down and at 120 min, the equilibrium was established. At equilibrium the % removal by LAC as well as metal ions adsorption capacity was found in the sequence of Pb(II) > Cu(II) > Ni(II).

In adsorption by LAC, after 10 min contact time, the percentage removal was determined as 46.45% for Pb(II), 22.53% for Cu(II) and 19.52% for Ni(II), while adsorption capacity was found to be 23.23 mgg⁻¹ for Pb(II), 11.27 mgg⁻¹ for Cu(II) and 9.76 mgg⁻¹ for

Ni(II). This is aligned with the fact that metals with higher electronegativity are more attracted to hydrous substances and exhibit increased % removal from aqueous medium (Choudhary et al., 2020). The electronegativity of Pb(II), is 2.33 which is higher than 1.91 and 1.90 of Cu(II) and Ni(II) respectively (Lou et al., 2017), % removal and adsorption capacity of Pb(II) is also higher than Cu(II) and Ni(II). The metal ions with larger ionic radius are preferentially adsorbed compared to the metal ions with smaller ionic radius (Oladipo et al., 2019). Pb(II), has ionic radius of 1.32 Å, which is greater than 0.72 Å of Cu(II) and 0.70 Å of Ni(II) which supports the results that Pb(II) adsorption by LAC was more than Cu(II) and Ni(II) (Lou et al., 2017). The metal ions with smaller ionic radii and higher electronegativity exhibit better binding affinity to the surface functional groups such as -OH and -COOH, available on the activated carbon as per FTIR analysis (Bandara et al., 2020). Therefore, ion exchange and surface complexation are likely major mechanisms of heavy metal sorption by LAC (Bandara et al., 2020). Charge to radius ratio (Z/r) of 1.51, 2.78 and 2.86 respectively and lower Z/r expresses the higher binding capability of metal ions to the solid surface (Lou et al., 2017). The adsorption capacity sequence of Pb(II) > Cu(II) > Ni(II) is supported by the fact that at similar ionic radius of Cu(II) and Ni(II), Z/r ratio affect the adsorption capacity inversely (Lou et al., 2017).

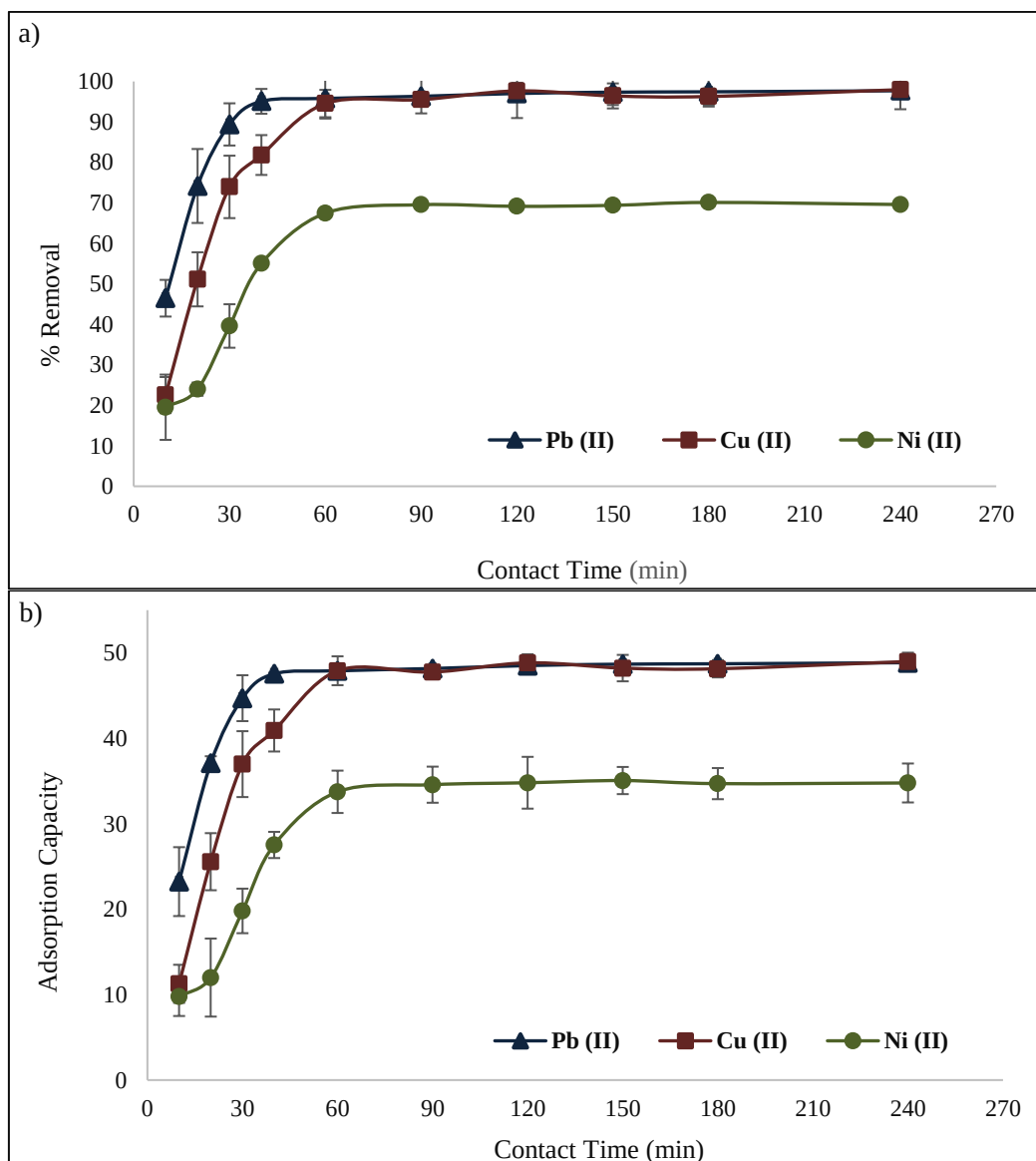


Figure 4.1: Effect of contact time on Pb(II), Cu(II) and Ni(II) ions adsorption by LAC from aqueous solutions; in terms of a) % removal and b) adsorption capacity at 1 gL^{-1} adsorbent dosage, pH 5, 26°C temperature, 50 mgL^{-1} initial concentration and 150 rpm stirring rate

Figure 4.2 shows the adsorption of Pb(II), Cu(II) and Ni(II) ions onto TAC as a function of contact time. All three metals Pb(II), Cu(II) and Ni(II) ions showed rapid uptake by TAC in the first 40 min then the process slowed down and at 120 min, the equilibrium

was established. At equilibrium the % removal by TAC as well as metal ions adsorption capacity was found in the sequence of Cu(II)> Ni(II)> Pb(II) which is different from LAC.

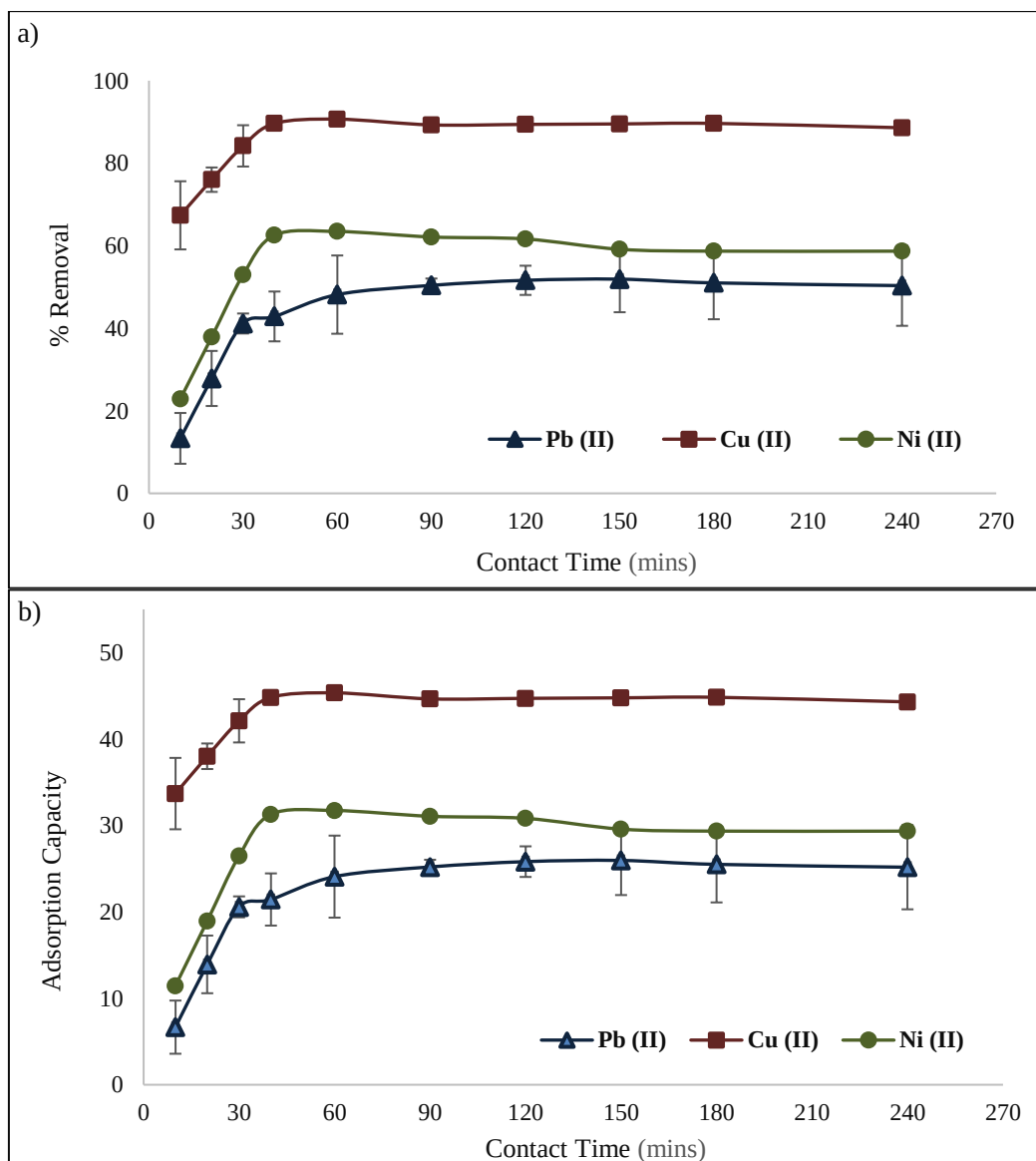


Figure 4.2: Effect of contact time on Pb(II), Cu(II) and Ni(II) ions adsorption by TAC from aqueous solutions; in terms of a) % removal and b) adsorption capacity at 1 gL⁻¹ adsorbent dosage, pH 5, 26 °C temperature, 50 mgL⁻¹ initial concentration and 150 rpm stirring rate

LAC expressed the adsorption capacity and removal percentage in the sequence Pb(II) > Cu(II) > Ni(II) while TAC expressed the removal efficiency in the order Cu(II) >

Ni(II) > Pb(II). Heavy Metals removal by biosorbents consists of three subsequent steps: mass transfer, intraparticle diffusion and metal uptake on sorption sites (Wang et al., 2018). The higher adsorption rate at the process start is due to more readily available adsorption sites, which slows down with the time due to fewer available adsorption sites, followed by a plateau indicating the inception of equilibrium (Abdallah et al., 2019). The amount of solute dispersion within equilibrium contact time is a significant factor in batch sorption since it affects the entire mass transfer process (Kucukcongar et al., 2020). Therefore, the contact time was adjusted to 120 min in the following experiments to assure adsorption equilibrium.

Adsorbents prepared from biomass precursors through different physiochemical modifications were compared with LAC and TAC for the removal of Pb(II), Cu(II) and Ni(II) ions and results were compiled in Table 4.1. In the present work, *Melia azedarach* leaves activated carbon resulted in 96% removal efficiency and 47.9 mgg⁻¹ adsorption capacity for Pb(II) removal at 1 gL⁻¹ adsorbent dose and 50 ppm initial concentration. In the present work, *Melia azedarach* twigs activated carbon resulted in 48% removal efficiency and 24 mgg⁻¹ adsorption capacity for Pb(II) removal at 1 gL⁻¹ adsorbent dose and 50 ppm initial concentration. Baby et al., (2021) reported that palm kernel shell-based adsorbent prepared via three step modification resulted in 90% removal efficiency and 38 mgg⁻¹ adsorption capacity for Pb(II) removal at 2 gL⁻¹ adsorbent dose and 40 ppm initial concentration. Kaya et al., (2020) reported that hazelnut shell-based adsorbent prepared by pyrolysis resulted in 71% removal efficiency and 8.8 mgg⁻¹ adsorption capacity for Pb(II) removal at 3 gL⁻¹ adsorbent dose and 45 ppm initial concentration. Srisuwan et al., (2018) reported that sunflower seed husk-based adsorbent prepared through chemical treatment

followed by carbonisation, resulted in 96.98% removal efficiency and 9.7 mgg^{-1} adsorption capacity for Pb(II) removal at 5 gL^{-1} adsorbent dose and 100 ppm initial concentration.

In adsorption of Cu(II) by *Melia azedarach* leaves activated carbon resulted in 96% removal efficiency and 47.9 mgg^{-1} adsorption capacity at 1 gL^{-1} adsorbent dose and 50 ppm initial concentration. *Melia azedarach* twigs activated carbon resulted in 90.7% removal efficiency and 45.34 mgg^{-1} adsorption capacity for Cu(II) removal at 1 gL^{-1} adsorbent dose and 50 ppm initial concentration. Cibati et al., (2017) reported that *Miscanthus x giganteus*-based adsorbent prepared through pyrolysis followed by chemical modification, resulted in 57.15% removal efficiency and 15.70 mgg^{-1} adsorption capacity for Cu(II) removal at 20 gL^{-1} adsorbent dose and 250 ppm initial concentration. Amin et al., (2019) reported that date palm-based adsorbent prepared through high temperature pyrolysis, resulted in 75% removal efficiency and 41.0 mgg^{-1} adsorption capacity for Cu(II) removal at 1.8 gL^{-1} adsorbent dose and 1270.8 ppm initial concentration.

In adsorption of Ni(II) by *Melia azedarach* leaves activated carbon resulted in 70% removal efficiency and 33.74 mgg^{-1} adsorption capacity at 1 gL^{-1} adsorbent dose and 50 ppm initial concentration. *Melia azedarach* twigs activated carbon as Cu(II) adsorbent resulted in 60% removal efficiency and 31.7 mgg^{-1} adsorption capacity at 1 gL^{-1} adsorbent dose and 50 ppm initial concentration. Basu et al., (2019) reported that rice husk-based adsorbent prepared via chemical modification, resulted in 95% removal efficiency and 12.41 mgg^{-1} adsorption capacity for Ni(II) removal at 10 gL^{-1} adsorbent dose and 10 ppm initial concentration (Rodriguez et al., 2018) reported that coffee husk-based adsorbent prepared through chemical modification, resulted in 65% removal efficiency and 52 mgg^{-1} adsorption capacity for Ni(II) removal at 0.8 gL^{-1} adsorbent dose and 120 ppm initial concentration.

Based on the comparison in Table 4.1, it can be concluded that both the removal efficiencies and adsorption capacities of activated carbons LAC and TAC were comparable to those of adsorbents prepared from different biomass using different physiochemical modifications. LAC and TAC demonstrated comparably better results at minimal adsorbent dosage of 1 gL⁻¹. Both LAC and TAC are effective adsorbents for the removal of heavy metals from aqueous medium, reflecting the feasibility of the resource recycling path to prepare high performance activated carbons using *M. azedarach* leaves and twigs. The surface area of LAC was found to be 121.592 m²g⁻¹ in contrast to 91.423 m²g⁻¹ of TAC, as described in Table 3.3 in Chapter 3. As mentioned in Table 4.1, LAC performed comparatively better than TAC in terms of removal efficiency and adsorption capacity. . As an adsorbent, an activated carbon's adsorption capacity and removal efficiency are function of properties including aromaticity, porosity, surface area, polarity, and so on (Abdallah et al., 2019). Therefore, higher surface area can be the reason behind the better adsorption results of LAC than TAC.

Table 4.1: Comparative effectiveness of LAC and TAC adsorbents

Feedstock	Modification	Metal ion	Adsorbent Dosage (g L ⁻¹)	Removal Efficiency (%)	Adsorption Capacity (mg g ⁻¹)	Reference
<i>Melia azedarach</i> leaves	Molten salt synthesis with ZnCl ₂ at 500 °C.	Pb(II)	1	96	47.9	This work
		Cu(II)	1	96	47.9	
		Ni(II)	1	70	33.74	
<i>Melia azedarach</i> twigs	Molten salt synthesis with ZnCl ₂ at 500 °C.	Cu(II)	1	90.7	45.34	This work
		Ni(II)	1	60	31.7	
		Pb(II)	1	48	24.0	
Palm kernel shells	Treated with H ₃ PO ₄ , carbonised at 500 °C, then treated with HNO ₃	Pb(II)	2	90	38	(Baby et al., 2021)
Hazelnut shell	Pyrolysis at 500 °C for 60 min	Pb(II)	3	71	8.8	(Kaya et al., 2020)
Sunflower seed husks	Treated with K ₂ CO ₃ sol. for 24 h, washed and carbonised at 400 °C	Pb(II)	5	96.98	9.7	(Srisuwan et al., 2018)

Table 4.1 continued

<i>Miscanthus x giganteus</i>	Pyrolysis at 600 °C for 10 mins and activation with H ₂ O ₂	Cu(II)	20	57.15	14.28	(Cibati et al., 2017)
Date palm	Pyrolyzed at 800 °C	Cu(II)	1.8	75	41	(Amin et al., 2019)
Rice Husk	Treated with NaOH and with humic acid	Ni(II)	10	95	12.41	(Basu et al., 2019)
Coffee Husk	Pyrolysis at 500 °C for 1 h in N ₂ flow, then activation at 800 °C for 30 min	Ni(II)	0.8	65	52	(Rodiguez et al., 2018)

4.3.2 Effect of Initial Concentration

As the initial metal concentration of an aqueous solution provides propellant to resist mass transfer between water and the solid material, this parameter has a substantial influence on the adsorption process (Kucukcongar et al., 2020). The influence of initial concentration of Cu(II), Pb(II) and Ni(II) ions on removal efficiency and adsorption capacity of LAC is shown in Figure 4.3. The removal efficiency of LAC for Cu(II), Pb(II) and Ni(II) ions was higher at lower initial concentration, as shown in Figure 4.3 (a). At lower concentrations, the number of metal ions available in the solution is lesser than the number of readily accessible active sites on the adsorbent surface, hence rate of adsorption is higher but the amount adsorbed per unit mass of adsorbent is lesser (Khan et al., 2020). The removal efficiency of LAC for Cu(II), Pb(II) and Ni(II) ions decreased with an increase in initial concentration. As the metal ions bind with the adsorbent surface, the number of accessible and active sites reduces, slowing the rate of adsorption and consequently heavy metals ions removal efficiency from the aqueous medium (Kaur et al., 2020).

The adsorption ability of LAC to adsorb Cu(II), Pb(II) and Ni(II) ions increased with increasing initial concentration from 5 mgL⁻¹ to 50 mgL⁻¹, as illustrated in Figure 4.3 (b), and was determined to be greatest at maximum initial concentration. The enhanced adsorption capacity of the adsorbent from aqueous medium with increasing initial metal ion concentration is attributed to coverage of all the active sites of the adsorbent surface by an increased number of metal ions in the solution (Khan et al., 2020).

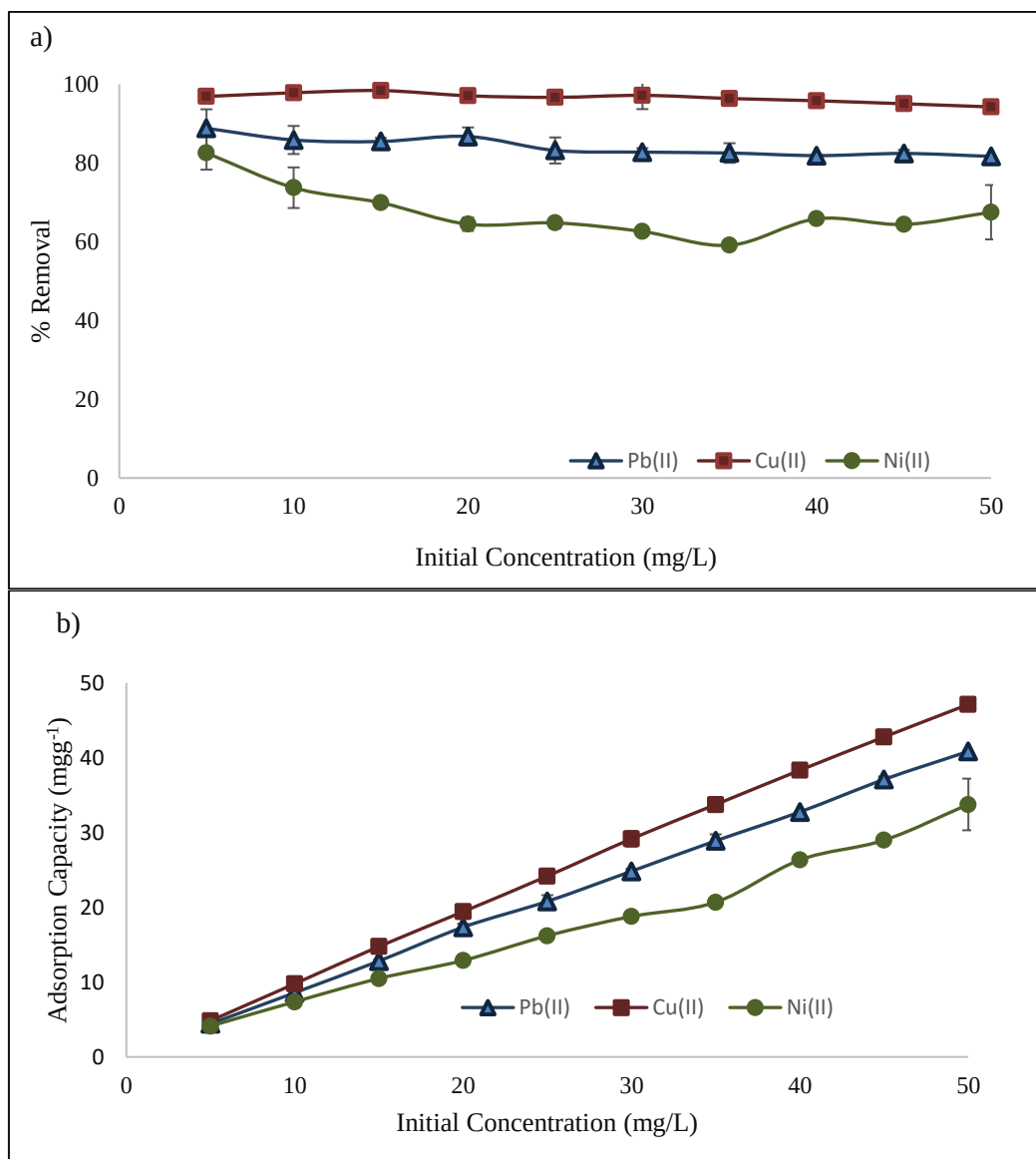


Figure 4.3: Effect of initial concentration on Pb(II), Cu(II) and Ni(II) ions adsorption by LAC from aqueous solutions; in terms of a) % removal and b) adsorption capacity at 1 gL⁻¹ adsorbent dosage, pH 5, 26 °C temperature, 120 contact time and 150 rpm stirring rate

The influence of initial concentration of Cu(II), Pb(II) and Ni(II) ions on removal efficiency and adsorption capacity of TAC is shown in Figure 4.4. The removal efficiency of TAC for Cu(II), Pb(II) and Ni(II) ions was higher at lower initial concentration, and the removal efficiency of LAC for Cu(II), Pb(II) and Ni(II) ions decreased with an increase in

initial concentration, as shown in Figure 4.4 (a). As the metal ions bind with the adsorbent surface, the number of accessible and active sites reduces, slowing the rate of adsorption and consequently heavy metals ions removal efficiency from the aqueous medium (Ngaini et al., 2021)

The adsorption ability of TAC to adsorb Cu(II), Pb(II) and Ni(II) ions increased with increasing initial concentration from 5 mgL⁻¹ to 50 mgL⁻¹, as illustrated in Figure 4.4 (b) and was determined to be greatest at maximum initial concentration. The increased adsorption capacity of the adsorbent from aqueous medium with increasing initial concentration is attributed to an increased number of metal ions in the solution covering all active sites on the adsorbent surface (Razak et al., 2020).

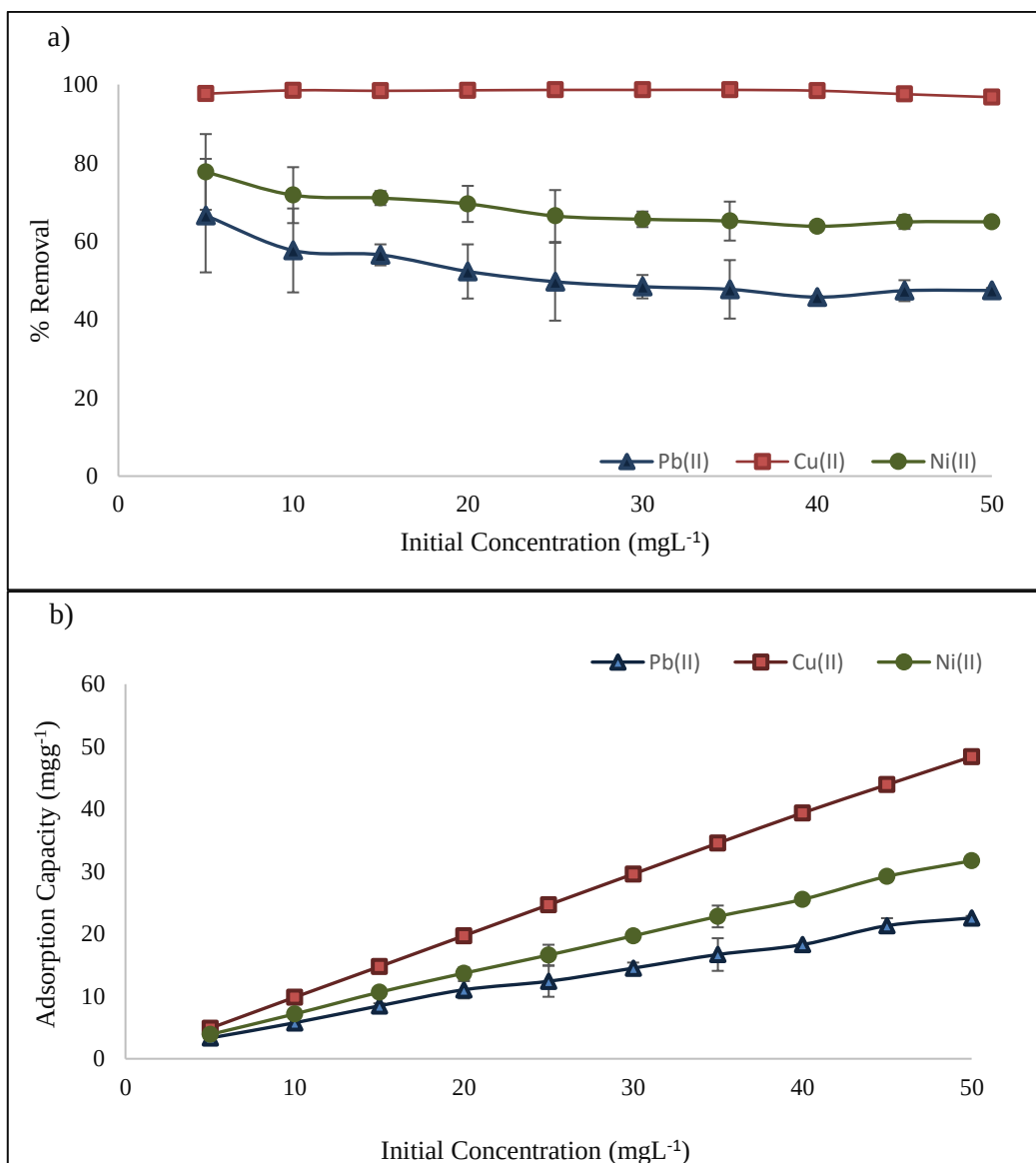


Figure 4.4: Effect of initial concentration on Pb(II), Cu(II) and Ni(II) ions adsorption by TAC from aqueous solutions; in terms of a) % removal and b) adsorption capacity at 1 gL⁻¹ adsorbent dosage, pH 5, 26 °C temperature, 120 min contact time and 150 rpm stirring rate

The mechanism of metal ion interaction with activated carbon at varied concentration was depicted in Figure 4.5. Rapid adsorption rate was observed at preliminary stage with low initial metal concentration, can be ascribed to the greater number of accessible active sites in terms of functional groups as well as pores on the surface of AC (Choudhary et al.,

2020). A steadier increase in adsorption rate continued with the concentration kept increasing, indicating strong interactions between metal ions and the AC's surface (Fotsing et al., 2020). The adsorption capacity as well as removal efficiency increased with increasing initial metal concentration, most likely due to accelerated diffusion of metal ions from the solution to the surface of the AC (Fotsing et al., 2020). Near the equilibrium, metal ions build-up on AC's surface hinders the diffusion of molecules into the pores, leading to a slower adsorption rate (Balasubramanian et al., 2020). This phenomenon can be elucidated that the mass transfer of metal ions to the unoccupied active sites and the diffusion into the pores of AC continued till the saturation of all active sites (Kongsune et al., 2021).

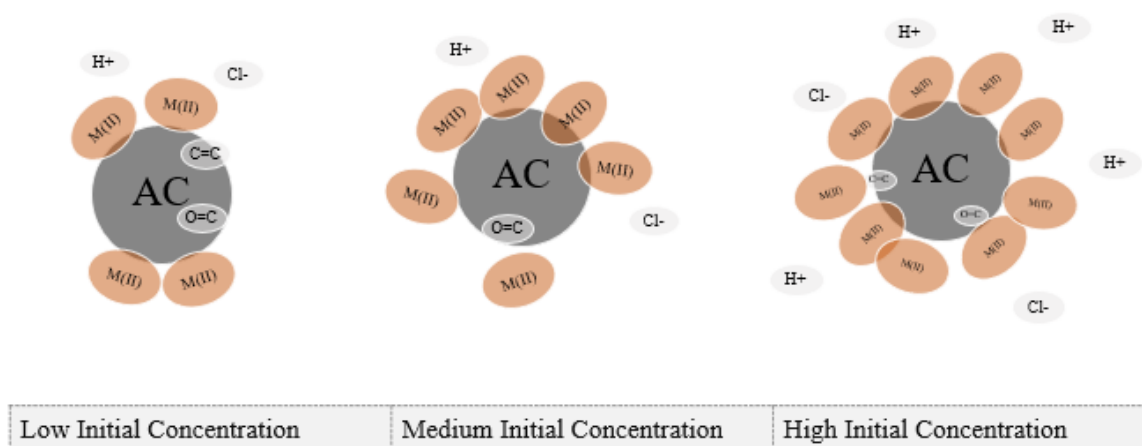


Figure 4.5: Mechanism of M(II) ions interaction with activated carbon at lower to higher initial concentration. M(II) represents Pb(II), Cu(II) and Ni(II)

4.3.3 Adsorption Isotherms

To evaluate the adsorptive behaviour of LAC and TAC in the removal of Cu(II), Pb(II) and Ni(II) metal ions from aqueous medium, adsorption process was analyzed with

reference to fitness with four most frequently applied two factors isotherm models including Langmuir, Freundlich, Temkin and Redlich isotherm models.

The type-1 linearised form of Langmuir model, mentioned as equation 2.19 in Chapter 2, was applied. For the calculation of separation factor (R_L), a dimensionless parameter of the Langmuir adsorption isotherm, equation 2.23 in Chapter 2 was used. Alignment of experimental data of Pb(II), Cu(II) and Ni(II) adsorption by LAC and TAC, with Langmuir model in Figure 4.6, The calculated parameters based on the slopes and intercepts of the above-mentioned expressions, have been summarised in Table 4.2.

With LAC as adsorbent, R_L was found to be 0.0034, 0.0081 and 0.061 for the adsorption of Ni(II), Pb(II) and Cu(II) respectively. With TAC as adsorbent, R_L was found to be 0.003, 0.005 and 0.129 for the adsorption of Ni(II), Pb(II) and Cu(II) respectively. For adsorption of all the three metals by both the adsorbents, R_L was greater than zero and less than 1 which indicates that the adsorption of Cu(II), Pb(II) and Ni(II) by LAC and TAC was a favourable process with irreversible nature (Jin et al., 2020).

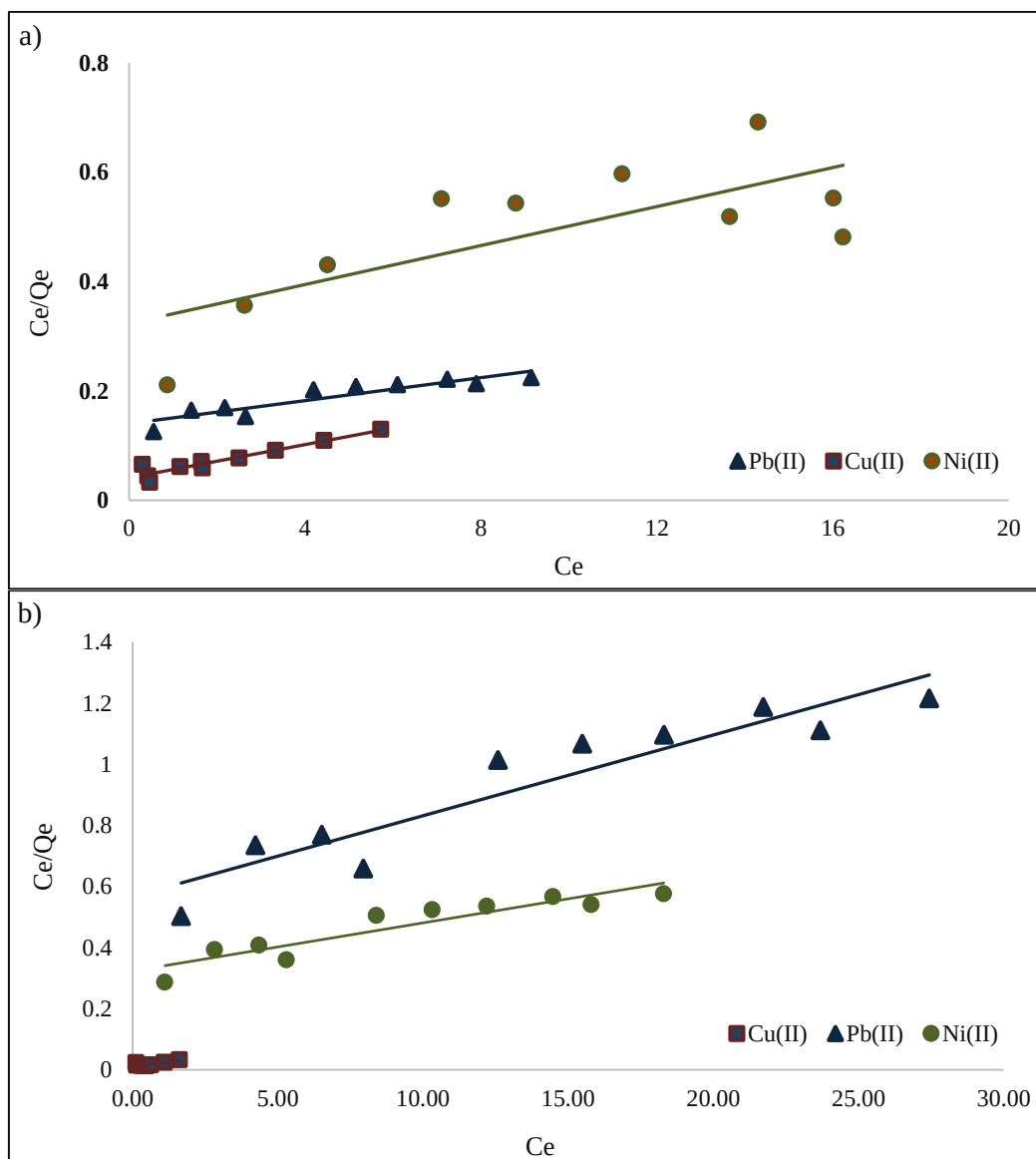


Figure 4.6: Langmuir isotherm plot for metal ions adsorption by a) LAC and b) TAC: at 5-50 ppm initial concentration, 25 °C temperature, 120 min time and 1 gL⁻¹ adsorbent dosage

The Linear expressions of Freundlich isotherm described as equation 2.25 in Chapter 2, was followed to evaluate the fitness of adsorption process as shown in Figure 4.7. The calculated parameters based on the slopes and intercepts of the above-mentioned expressions, have been summarised in Table 4.2. In adsorption by LAC, Freundlich heterogeneity factor n for Pb(II), Cu(II) and Ni(II) was found to be 0.79, 0.68 and 0.68. In

adsorption by TAC, Freundlich heterogeneity factor $1/n$ for Pb(II), Cu(II) and Ni(II) was found to be 0.68, 0.83 and 0.75. The value of n is related with the adsorption process favourability, $n=0$ indicates linear adsorption, $n < 1$ indicates chemical adsorption while $n > 1$ indicates favourability of physical adsorption process (Zaheer et al., 2019). As for the adsorption of Pb(II), Cu(II) and Ni(II) by both LAC and TAC, n is greater than zero and less than 1 which indicates predominant chemical adsorption.

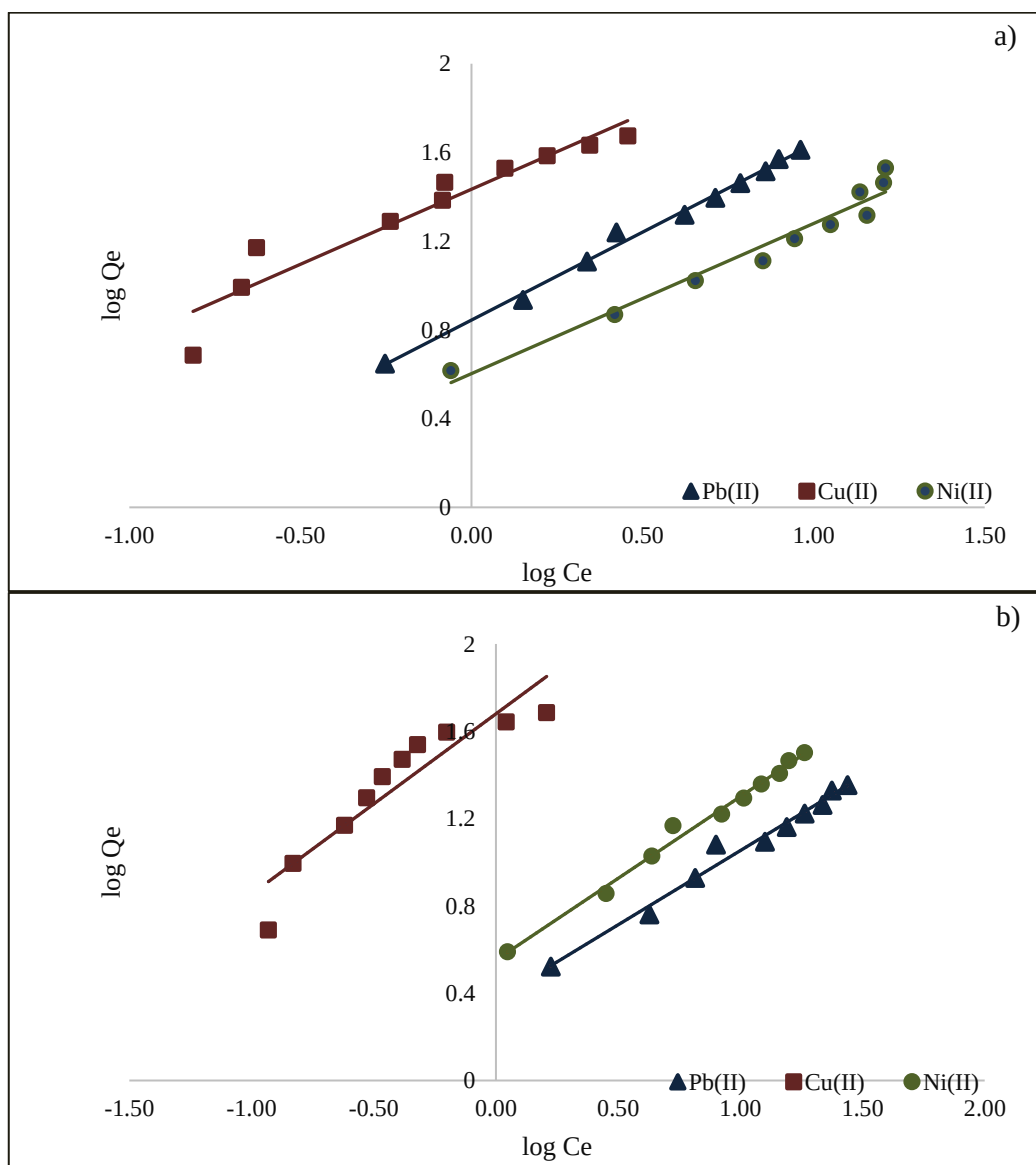


Figure 4.7: Freundlich isotherm plot for metal ions adsorption by a) LAC and b) TAC: at 5-50 ppm initial concentration, 25 °C temperature, 120 min time and 1 gL⁻¹ adsorbent dosage

Linear expression of Temkin isotherm described as equation 2.27 in Chapter 2, was followed to evaluate the fitness of adsorption process which can be seen in Figure 4.8. The calculated parameters based on the slopes and intercepts of the above-mentioned expressions, have been summarised in Table 4.2.

For the adsorption by LAC, B_t for Pb(II), Cu(II) and Ni(II) removal, 6.296, 30.833, 0.3784 while for the adsorption by TAC, B_t for Pb(II), Cu(II) and Ni(II) removal, 2.77, 43.29, 1.37. As per Temkin isotherm, the value of $b_T < 20 \text{ Jmol}^{-1}$ means that the physisorption is dominating the chemisorption (Zaheer et al., 2019). Therefore, in the adsorption of Pb(II) and Ni(II) by both LAC and TAC is predominantly physisorption while adsorption of Cu(II) by both LAC and TAC was predominantly chemisorption.

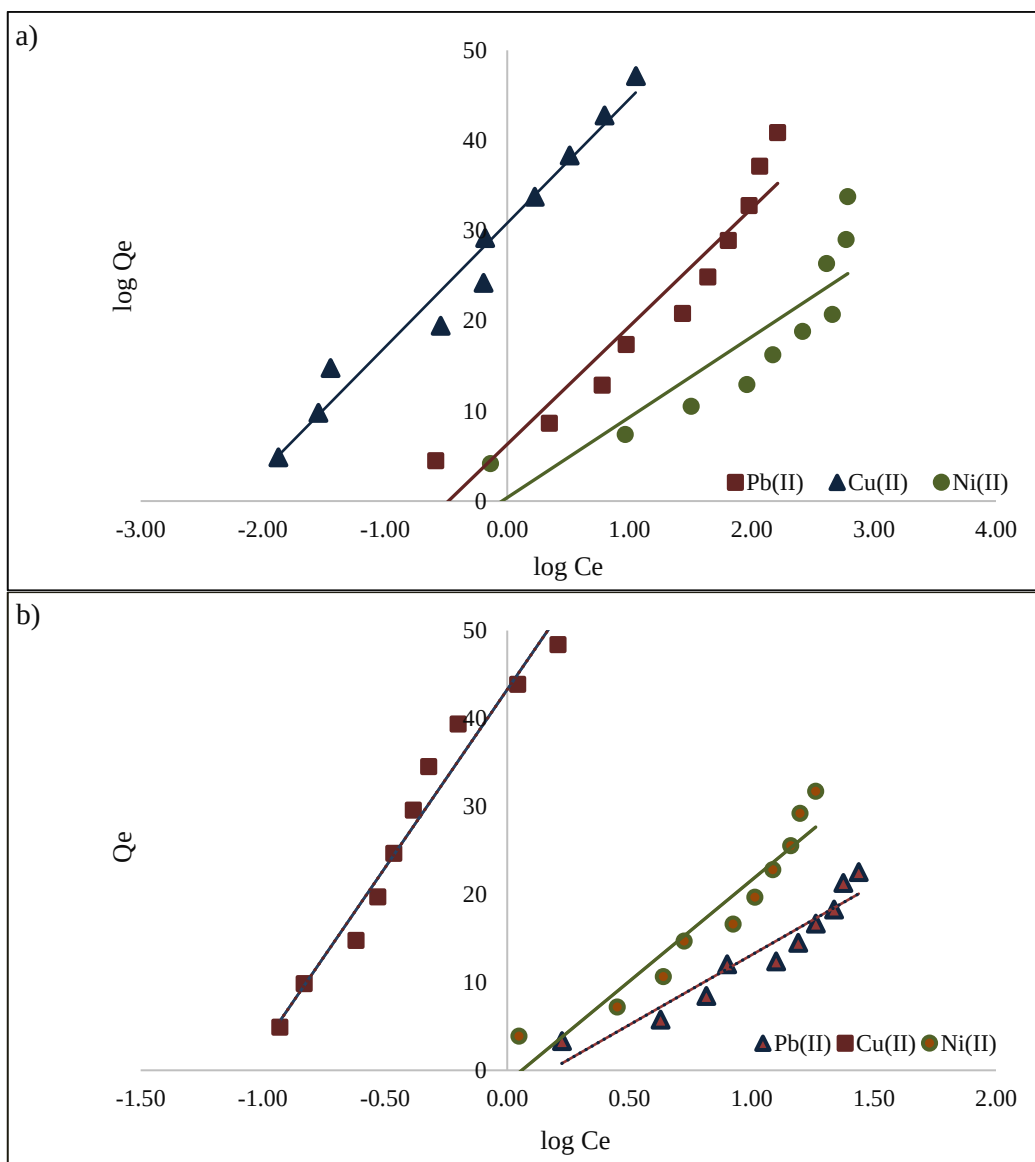


Figure 4.8: Temkin isotherm plot for metal ions adsorption by a) LAC and b) TAC: at 5-50 ppm initial concentration, 25 °C temperature, 120 min time and 1 gL⁻¹ adsorbent dosage

Linear expression of Redlich-Peterson isotherm expressed as equation 2.31 in Chapter 2 was followed to evaluate the fitness of adsorption process with for LAC and TAC as shown in Figure 4.9. The calculated parameters based on the slopes and intercepts of the above-mentioned expressions, have been summarised in Table 4.2.

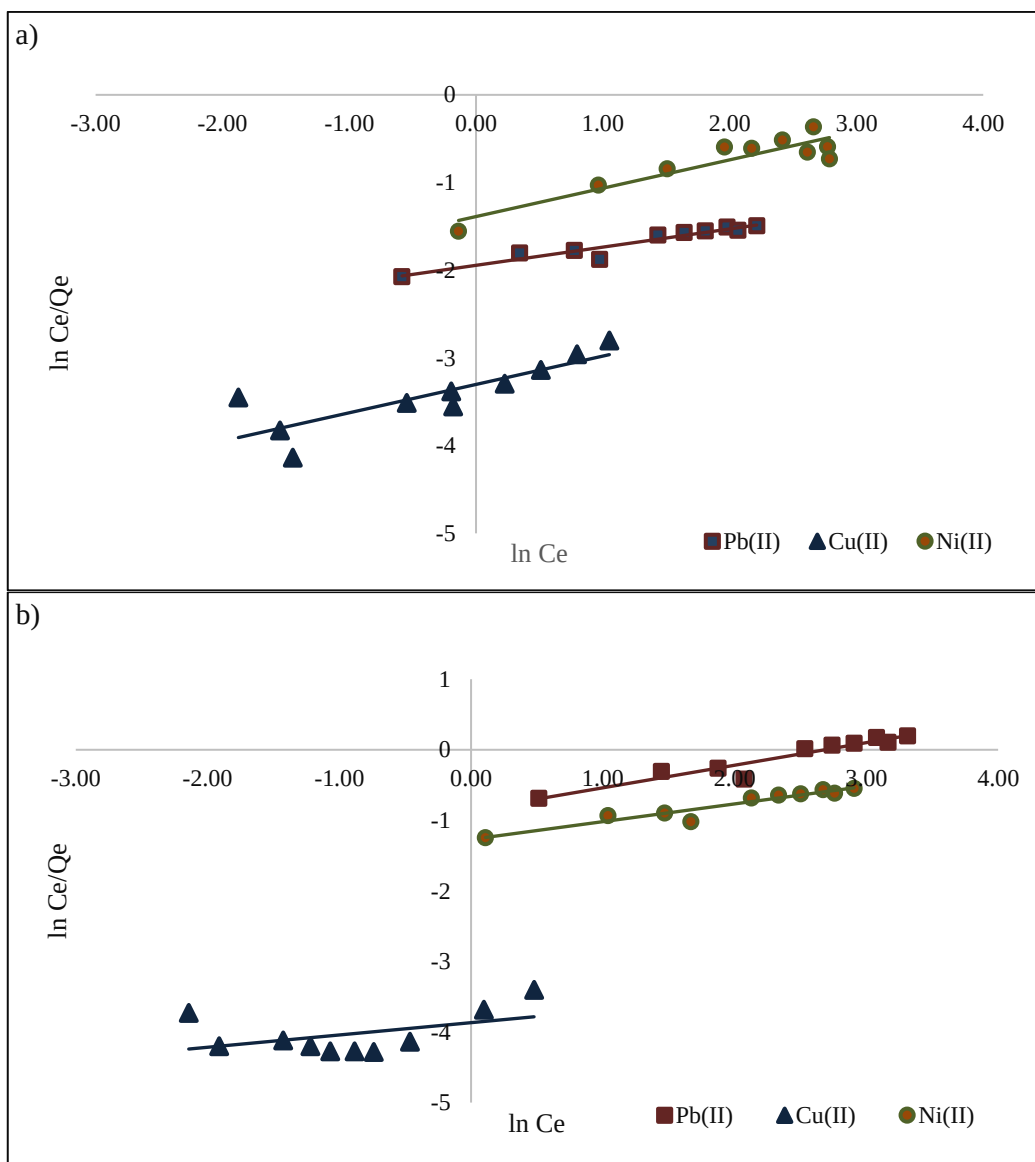


Figure 4.9: Redlich-Peterson isotherm plot for metal ions adsorption by a) LAC, b) TAC: at 5-50 ppm initial concentration, 25 °C temperature, 120 min time and 1 gL⁻¹ adsorbent dosage

In adsorption by LAC, β value for Pb(II), Cu(II) and Ni(II) were found to be 0.32, 0.21 and 0.32 while in adsorption by TAC, was 0.17, 0.32 and 0.25. When the exponent β is close to zero, the sorption process fits better with the Freundlich model, implying monolayer adsorption, and when β is close to 1.0, the data fits better with the Langmuir isotherm model (Ahmad et al., 2018). As all the β values are near to zero and away from 1,

therefore, heavy metals adsorption by LAC and TAC were better fit Freundlich model instead of Langmuir Model.

According to the results summarised in Table 4.2, the values of correlation coefficients (R^2) indicate that though all the models adequately explained the adsorption process, however the Freundlich model better explained the mechanism for the adsorption of Pb(II) and Ni(II) ions by both LAC and TAC, as shown in Figure 4.7, indicating a heterogeneous adsorptive process (Shi et al., 2019). Cu(II) adsorption by both LAC ($R^2 = 0.9722$) and TAC ($R^2 = 0.9649$) fitted with Temkin model as per results are shown in Figure 4.8 and the relevant parameters given in Table 4.2.

The Temkin isotherm suggests that the heat of adsorption of all molecules in layer reduces linearly with adsorbent surface coverage due to adsorbate-adsorbent interactions, also the adsorption energy is not uniform (Jin et al., 2020). This meant that Ni(II) adsorption by LAC and TAC was a multilayer on an uneven surface with a higher equilibrium binding energy “ a_T ”, indicating that multilayer adsorption with chemical binding played a major role in the process, which was consistent with the adsorption kinetic studies (Lu & Guo, 2019).

Table 4.2: Isotherm models parameters for heavy metals adsorption by LAC and TAC

Model	Adsorbent	Parameters	Pb(II)	Cu(II)	Ni(II)
Langmuir	LAC	Q_m	95.238	65.7895	56.179
		K	13.352	2.7039	18.164
		R_L	0.0081	0.061	0.0034
		R^2	0.8421	0.9049	0.5544

Table 4.2 continued

Freundlich	TAC	Q_m	37.879	92.593	63.694
		K	21.485	1.185	20.605
		R_L	0.005	0.129	0.003
		R^2	0.8777	0.5961	0.8571
	LAC	N	0.7926	0.6768	0.6769
		K	2.3264	4.1959	1.0284
		R^2	0.9936	0.911	0.9568
	TAC	N	0.6800	0.8256	0.7487
		K	1.4524	5.3639	1.7362
		R^2	0.9797	0.8593	0.9896
Temkin	LAC	A_t	30.111	31.711	20.533
		B_t	6.2961	30.833	0.3784
		R^2	0.9046	0.9722	0.7706
	TAC	A_t	15.88	40.516	22.996
		B_t	2.7658	43.291	1.3689
		R^2	0.9157	0.9649	0.9100
	LAC	A	3.3021	1.944	1.3879
		β	0.3232	0.2074	0.3231
		R^2	0.7001	0.8348	0.9142
Redlich-Peterson	TAC	A	3.8676	0.8593	1.2703
		β	0.1744	0.32	0.2513
		R^2	0.2142	0.9146	0.9146

4.3.4 Adsorption Kinetics

Figures 4.7 and 4.8 illustrate the quantities of Cu(II), Pb(II) and Ni(II) adsorbed by LAC and TAC as a functions of the contact time (0–240 min). The adsorption capacities of both the adsorbents increased with time and eventually stabilised when equilibrium was attained. Cu(II), Pb(II) and Ni(II) adsorption by both the LAC and TAC were faster in the initial phases, likely because adsorption largely happened on the outer surfaces of these activated carbons. Metal ions gradually penetrate into the pores of activated carbon with increasing time, further interacting with internal active sites, where the adsorption process is relatively slow (Zhang et al., 2018). The rate controlling steps of the adsorption process can be effectively investigated by different kinetic models. In this study, linearised forms of the Pseudo First Order described as equation 2.2 in Chapter 2, was followed to evaluate the adsorption kinetics of Pb(II), Cu(II) and Ni(II) by LAC and TAC.

Figure 4.10 (a) and (b) depict the linear plot of $\log(q_e - q_t)$ vs t with reference to PFO for the adsorption of Cu(II), Pb(II) and Ni(II) by LAC and TAC respectively. Table 4.3 provides the rate constants, correlation coefficients and theoretical adsorption capacities obtained from the linear plot of the model. Theoretical q_e derived from PFO is very low compared to actual adsorption capacity as well as R^2 is in between 0.678 to 0.816 for LAC and 0.053 to 0.523 for TAC.

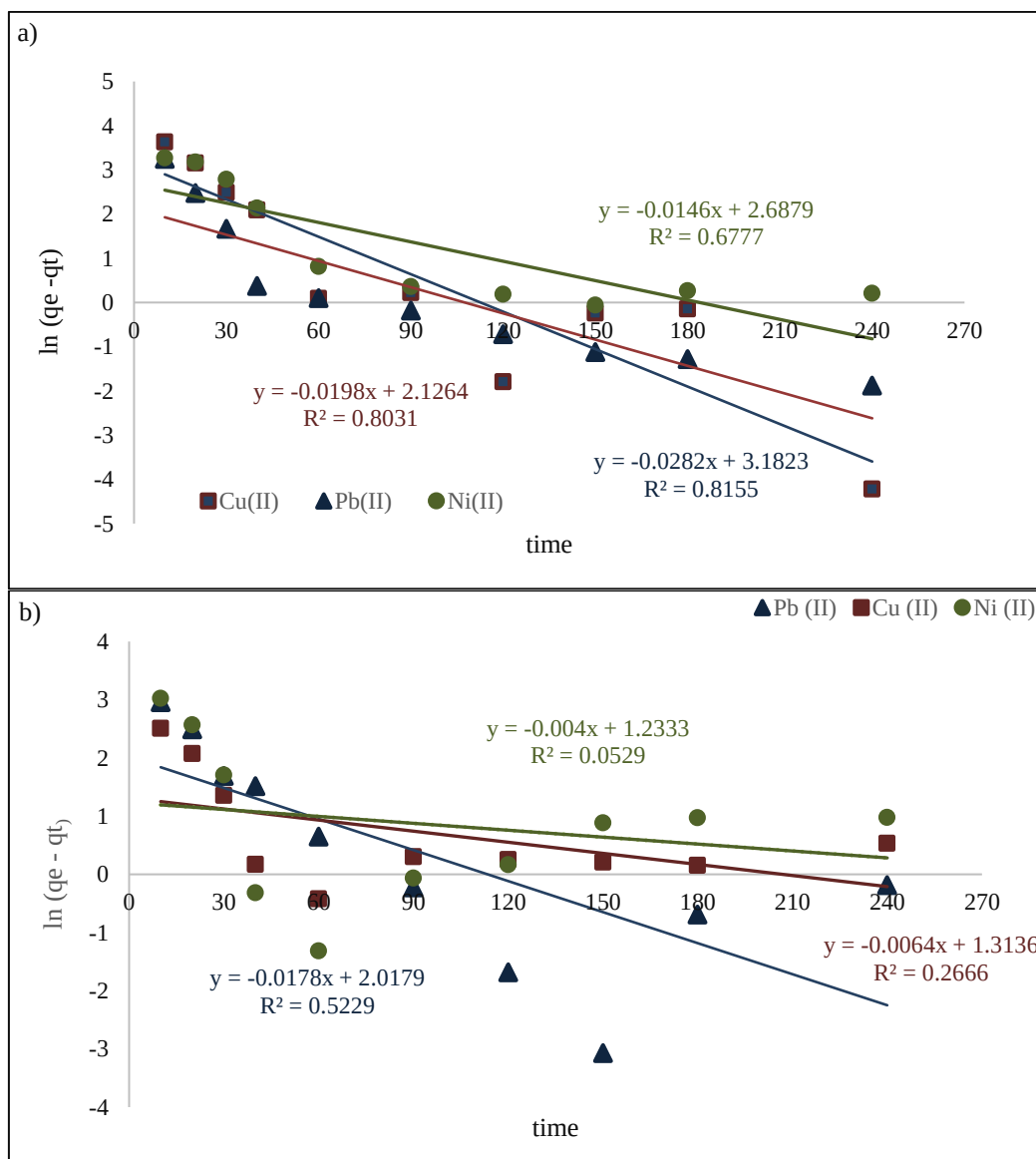


Figure 4.10: Pseudo-first-order plot for adsorption of Pb(II), Cu(II) and Ni(II) by a) LAC b) TAC

Figure 4.11 (a) and (b) depict the linear plot of t vs t/q_t with reference to PSO for the adsorption of Cu(II), Pb(II) and Ni(II) by LAC and TAC respectively. Table 4.3 provides the rate constants, correlation coefficients and theoretical adsorption capacities obtained from the linear plot of the PSO model. Theoretical q_e derived from PSO is comparable with

the actual adsorption capacity as well as R^2 is in between 0.9799 to 0.9988 for LAC and 0.9898 to 0.9996 for TAC and overall close to 1.

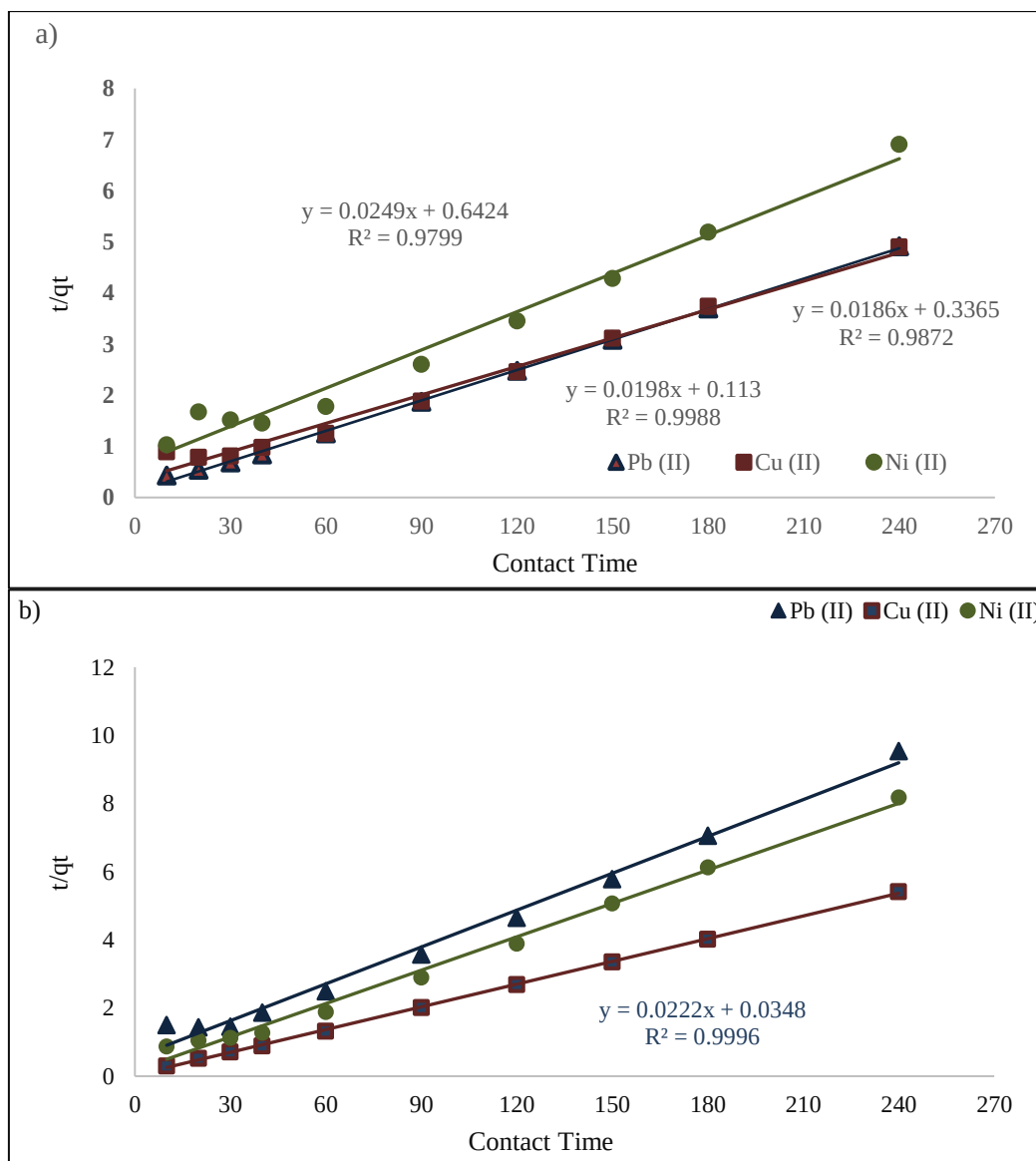


Figure 4.11: PSO plot for adsorption of Pb(II), Cu(II), and Ni(II) by a) LAC and b) TAC

Figure 4.12 (a) and (b) depict the linear plot of $\ln t$ vs q_t with reference to Elovich Model for the adsorption of Cu(II), Pb(II) and Ni(II) by LAC and TAC respectively. Table 4.3 provides the model constants and correlation coefficients obtained from the linear plot

of the model. For Elovich Model, the R^2 is in between 0.7648 to 0.8720 for LAC and 0.6711 to 0.8708 for TAC.

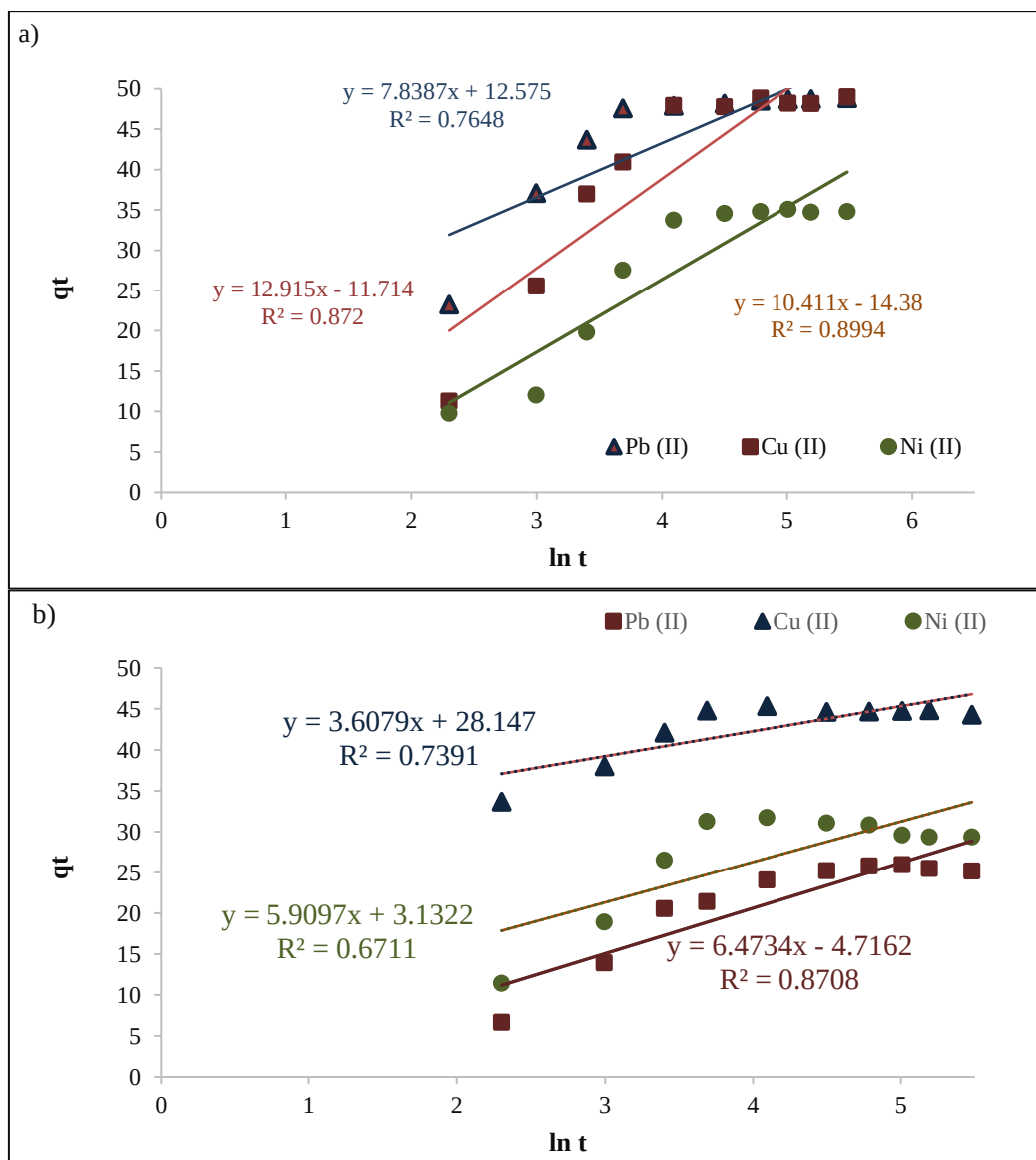


Figure 4.12: Elovich Model plot for heavy metals adsorption by a) LAC and b) TAC

The WM model was studied to assess if intraparticle diffusion is the rate limiting step during the overall adsorption process by LAC and TAC adsorbents. Figure 4.13 shows the linear plot of Q_t vs $t^{0.5}$ for adsorption of Cu(II), Pb(II) and Ni(II) by LAC adsorbent while

the linear plot of Q_t vs $t^{0.5}$ for adsorption of Cu(II), Pb(II) and Ni(II) by TAC adsorbent has been shown in Figure 4.14. The parameters of the WM models are shown in Table 4.2. The intercept of plot “C” represents for the thickness of the boundary layer, smaller the value of “C”, lower the boundary effect during the adsorption process and a “C” value of zero suggests that intraparticle diffusion could be the rate-limiting (Khan et al., 2020). Figures 4.13 and Figure 4.14 show the WM kinetic model plot for Pb(II), Cu(II) and Ni(II) adsorption by LAC and TAC respectively. Two separate parts were obtained from this plot before the and after equilibrium, first stage in the dotted line represents film diffusion while second stage in solid line represents intraparticle diffusion step (Abdallah et al., 2019). The straight lines for Pb(II), Cu(II) and Ni(II) did not pass through the origin in either case, but they were close to it because the intercept "C" values range from 1.97 to 3.33 for LAC and 0.89 to 1.67 for TAC, though in TAC case it is closer to zero than LAC but still not zero, indicating that the boundary effect is not significant.

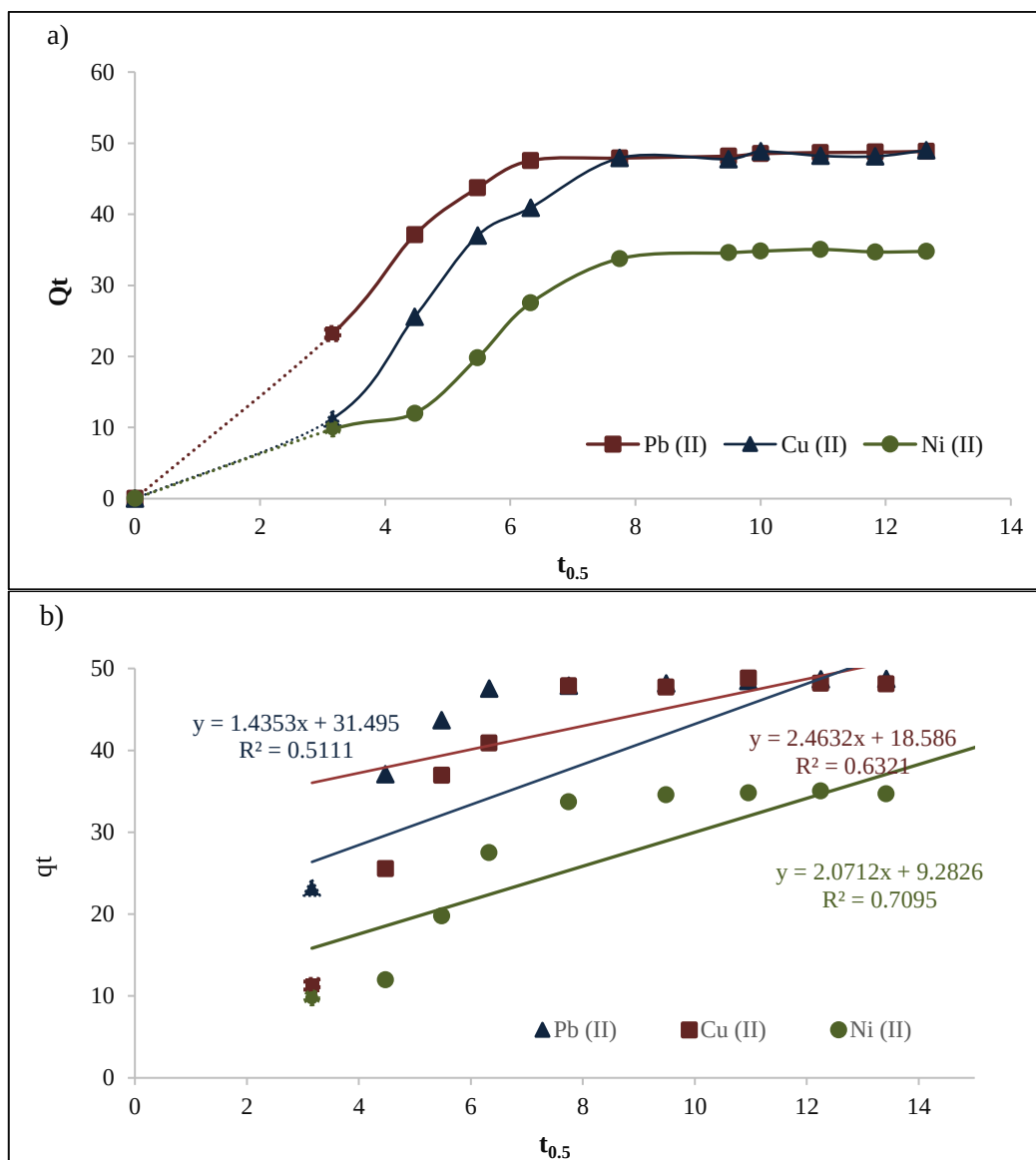


Figure 4.13: Weber-Morris Model plot for heavy metals adsorption by LAC
a) before equilibrium b) after equilibrium

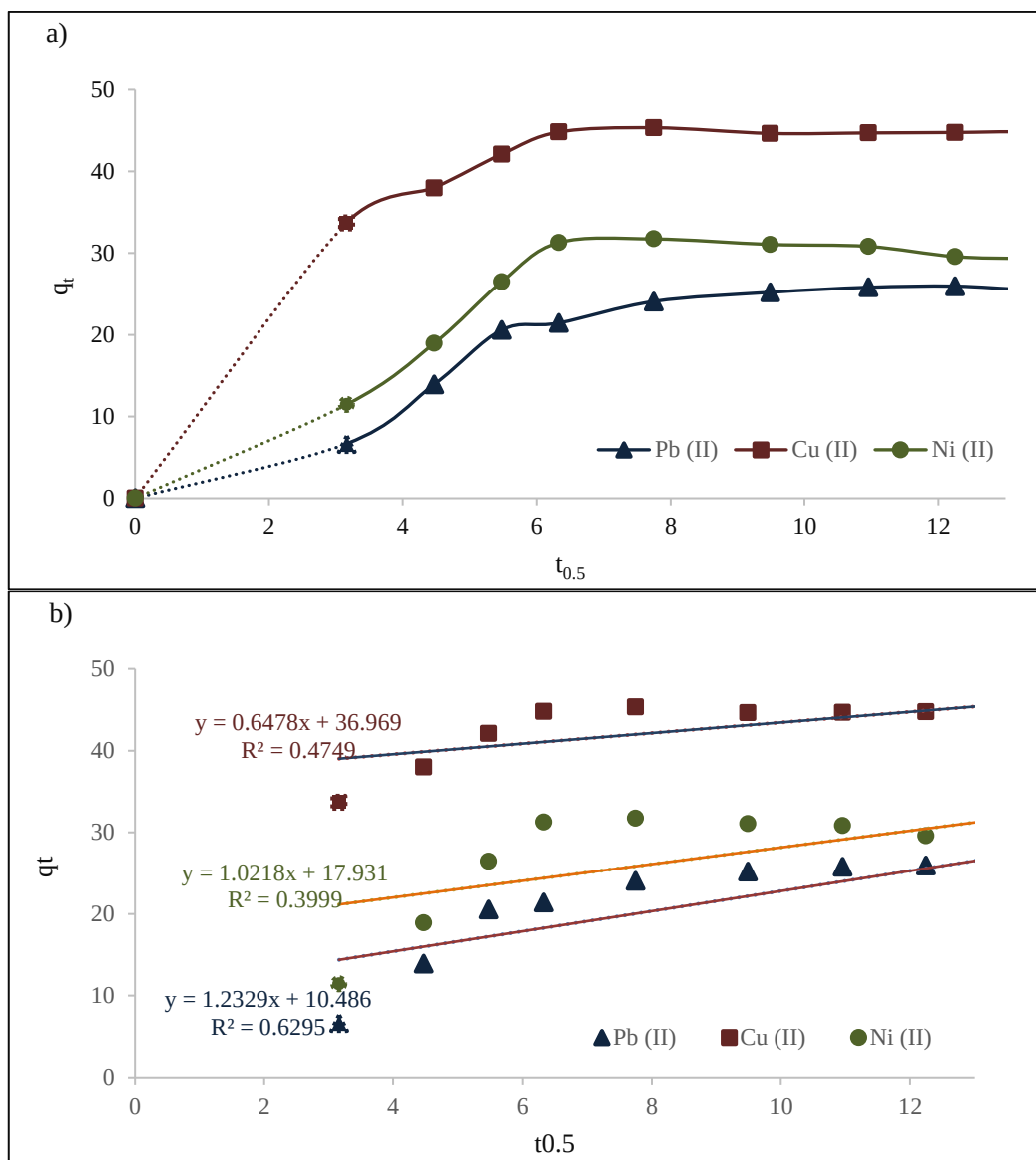


Figure 4.14: Weber-Morris model plot for heavy metals adsorption by TAC
a) before equilibrium b) after equilibrium

In order to correctly establish the kinetic model of the system, all of the data from the PFO, PSO, Elovich model and Weber Morris model were evaluated. The kinetic model with the average correlation coefficients closest to 1 is the most appropriate for the system and the $Q_{e \text{ exp}}$ (mgg^{-1}) values obtained experimentally are closer to the $Q_{e \text{ cal}}$ (mgg^{-1}) values derived from the model equations. When the findings in Table 4.2 are evaluated in this context, it is established that adsorption of Cu(II), Pb(II) and Ni(II) ions by both LAC and

TAC is more suited with the pseudo second order kinetic model because the correlation coefficients R^2 are higher when compared to the other kinetic models studied. Several previous studies on heavy metals removal by adsorbents such as activated carbon and modified biochar based on agricultural and horticultural wastes biomass have reported a Pseudo second order kinetic model (Jin et al., 2020; Lu & Guo, 2019; Mahdi et al., 2019; Wahi et al., 2022).

Table 4.3: Kinetic models parameters for heavy metals adsorption by LAC and TAC

Model		Adsorbent	Parameters	Pb(II)	Cu(II)	Ni(II)
Pseudo Order	First	LAC	Q_e (mgg ⁻¹)	0.8204	0.9722	0.9855
			K_1 (Lmin ⁻¹)	4.6845	7.0106	5.9214
			R^2	0.8031	0.8155	0.6777
		TAC	Q_e (mgg ⁻¹)	0.9936	0.9824	0.9960
			K_1 (Lmin ⁻¹)	2.8939	4.4454	2.7162
			R^2	0.2666	0.5229	0.0529
Pseudo Second Order		LAC	Q_e (mgg ⁻¹)	50.5051	53.7634	40.1606
			K_2 (Lmin ⁻¹)	0.0035	0.0010	0.0010
			R^2	0.9988	0.9872	0.9799
		TAC	Q_e (mgg ⁻¹)	27.778	45.4555	30.675
			K_2 (Lmin ⁻¹)	0.0024	0.0139	0.0062
			R^2	0.9898	0.9996	0.9928
Elovich Model		LAC	α	5.214	38.989	2.616
			β	0.077	0.128	0.096
			R^2	0.8720	0.7648	0.8994

Table 4.3 continued

Weber-Morris Model	TAC	α	8818.60	3.124	0.871
		β	0.277	0.155	0.169
		R^2	0.7391	0.8708	0.6711
	LAC	C	1.969	3.332	2.783
		K_1	28.148	13.094	4.852
		R^2	0.602	0.731	0.809
	TAC	C	0.897	1.669	1.437
		K_1	35.356	7.7226	15.025
		R^2	0.5748	0.7291	0.4995

Evaluation on findings in Table 4.3 established that adsorption of Pb(II), Cd(II) and Ni(II) ions by both LAC and TAC is more suited with the Pseudo Second Order kinetic model because the correlation coefficients R^2 are higher when compared to the other kinetic models studied. Pseudo second order kinetic model was reported in majority of the previous investigations including Mahdi et al., (2019), Jin et al., (2020), Lu & Guo (2019), Wahi et al., (2022), employing activated carbon and modified biochar based on agricultural biomass feedstock, as adsorbent for heavy metals removal.

Correlation coefficient R^2 values for Pb(II), Cu(II) and Ni(II) by LAC were in 0.76-0.89 range and by TAC were in 0.67-0.87 range indicating that all three metal ions were absorbed by chemisorption without desorption (Shafiq et al., 2021). The interactions between the metal ions and the functional groups available on the surface of the adsorbent were equally important in adsorption motivation in Pb(II), Cu(II) and Ni(II) ions adsorption by LAC and TAC and a charge transfer complex pattern on the adsorbent surface may have

controlled the adsorption processes, but external mass transport intraparticle diffusion was also involved in the adsorption process (Cao et al., 2019).

The theoretical adsorption capacity Q_e calculated by PSO is closer to Q_e experimental than the value calculated by PFO as shown in Table 4.3 indicate that chemisorption was more involved than physisorption (Kumar et al., 2019). In the Elovich model, adsorption constant ' α ' for all metal ions adsorption by LAC and TAC, are good however higher values for Cu(II) in LAC and of Pb(II) in TAC further suggest the stronger adsorption capacity of LAC and TAC to adsorb metal ions while minimum desorption constant ' β ' demonstrated stronger interactions of metal ions on the adsorption sites of the LAC and TAC (Kumar et al., 2019).

4.3.5 FTIR Analysis after Heavy Metals Adsorption

Figure 4.15 and 4.16 contain the FTIR spectra of LAC and TAC with a comparison of before adsorption and after adsorption.

In LAC, 3443 cm^{-1} before adsorption shifted to 3456 cm^{-1} in the form a bigger peak in LAC after Pb(II) adsorption, shifted to 3430 cm^{-1} after Cu(II) adsorption, a small peak at 3420 cm^{-1} in LAC after Ni(II) adsorption. In LAC, peak at 1618 cm^{-1} shifted to 1630 cm^{-1} after Cu(II) adsorption, 1618 cm^{-1} after Pb(II) adsorption, while several small peaks appeared $1540\text{-}1623\text{ cm}^{-1}$ after Ni(II) adsorption. Peak at 1018 cm^{-1} in LAC, shifted to 1013 cm^{-1} after Pb(II) adsorption, shifted to 1019 after Cu(II) adsorption and shifted to 1023 cm^{-1} after Ni(II) adsorption. Before adsorption peak at 797 cm^{-1} shifted to 795 cm^{-1} after Pb(II) adsorption, 816 cm^{-1} after Cu(II) adsorption, 797 cm^{-1} after Ni(II) adsorption.

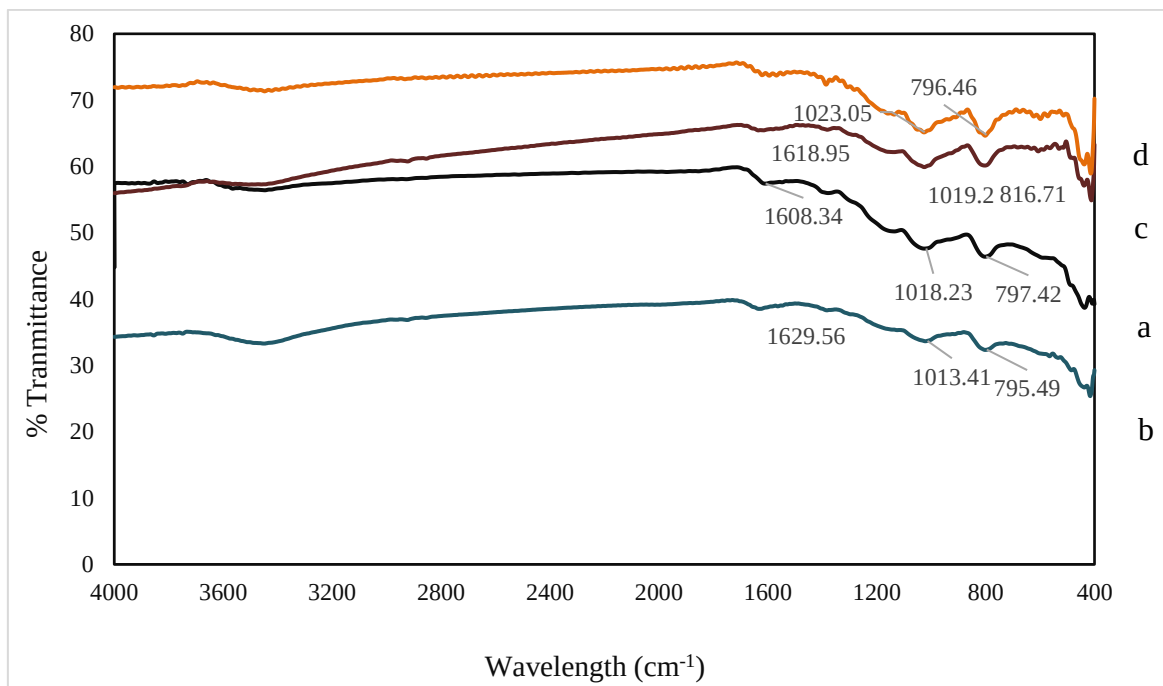


Figure 4.15: FTIR Spectra of LAC, a) before adsorption, b) after Pb(II) adsorption, c) after Cu(II) adsorption and d) after Ni(II) adsorption

FTIR spectrum of LAC before and after adsorption of Cu(II), Pb(II) and Ni (II) shows that most of the peaks shifted predicting that heavy metals are incorporated inside the activated carbon due to the interaction of active functional group after the adsorption process (Anitha et al., 2020; Babu et al., 2018). The change in intensity of peaks after adsorption may be because of the metal ions binding (Anitha et al., 2020).

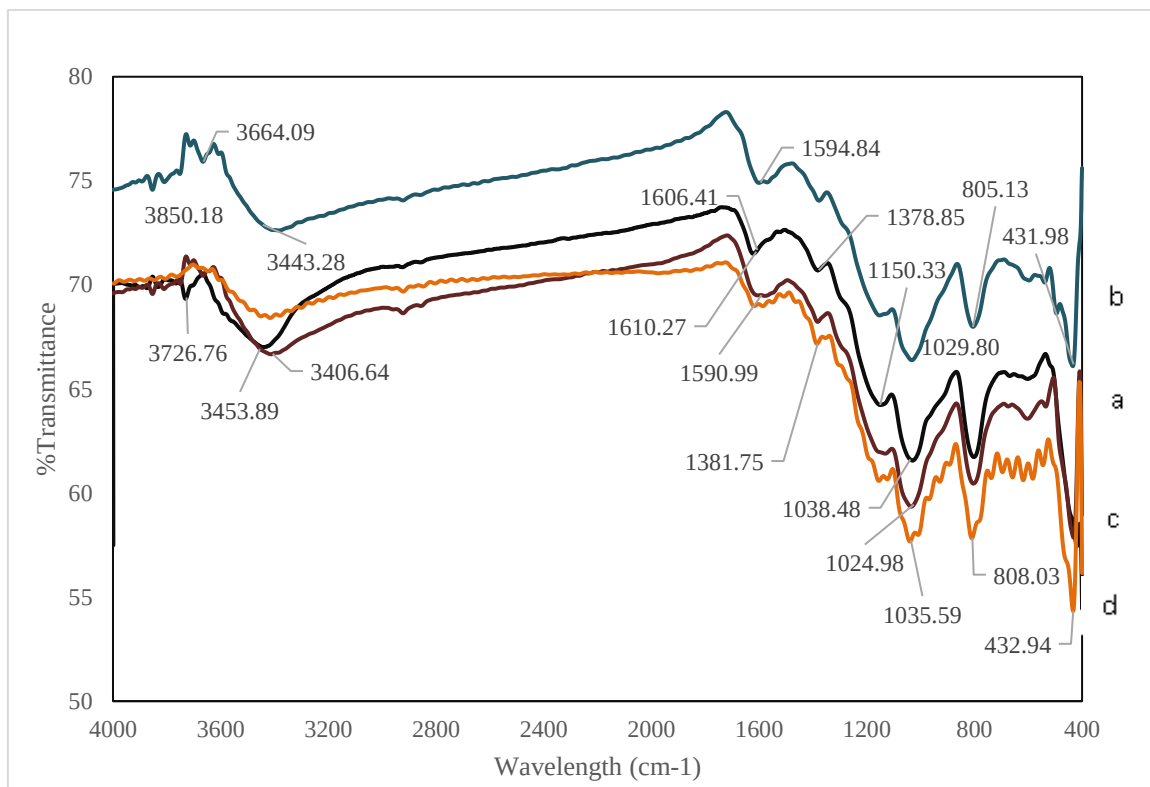


Figure 4.16: FTIR Spectra of TAC, a) before adsorption, b) after Pb(II) adsorption, c) after Cu(II) adsorption and d) after Ni(II) adsorption

Figure 4.16 shows the spectra of TAC, before and after heavy metals adsorption. The behaviour is identical to LAC. There are shifts in peaks indicating the involvement of functional groups in adsorption as explained earlier. Surface functional groups are significant in adsorption capacity because heavy metals adsorption can occur through complexation or ion exchange mechanisms in which different metal ion interact with –COOH, –C–O and –OH groups, to form complexes, which can result in extraction of heavy metal from aqueous medium (Liu et al., 2018).

4.3.6 Adsorption Mechanism

The adsorption mechanisms of AC were explored according to the results of SEM, EDX, BET, FTIR, kinetic and isotherm models fitness for the adsorption experiments (Lu

& Guo, 2019). As larger surface area facilitates the uptake metal ions, the surface area of LAC ($121.592 \text{ m}^2\text{g}^{-1}$) and TAC ($91.223 \text{ m}^2\text{g}^{-1}$) influenced physical adsorption (Duan et al., 2019). Based on the analysis presented in Figure 4.11 and Table 4.3, the pseudo-second-order model was found to be best fit for explaining the behaviour of heavy metal ions adsorption into LAC and TAC, indicating that the process was of chemisorption nature rather than physisorption due to the involvement of functional groups on AC's surface (Sajjadi et al., 2019). FTIR studies of LAC and TAC as pristine and after heavy metals adsorption, as per Figure 4.15 and Figure 4.16, revealed that functional groups -OH -COOH and -C-O groups also played a vital role in adsorption (Bandara et al., 2020), through complexation and ion exchange mechanisms (Liu et al., 2018). Chlorine present on the surface of activated carbon oxidised metal ions which participates on the surface resulting in chemisorption (Duan et al., 2019).

The value of B_t in the Temkin isotherm for Cu(II) adsorption by LAC and TAC was found to be greater than 20 Jmol^{-1} . In the Freundlich isotherm, heterogeneity factor was found to be $0 < n < 1$ for the adsorption of Pb(II), Cu(II) and Ni(II) by both LAC and TAC which indicated predominant chemical adsorption (Zaheer et al., 2019). On the other hand, the value of B_t in the Temkin isotherm for Pb(II) and Ni(II) adsorption by LAC and TAC was found to be less than 20 Jmol^{-1} . These results corroborated the conclusion that chemisorption predominated Cu(II) adsorption while physisorption predominated in Pb(II) and Ni(II) adsorption (Zaheer et al., 2019). Though the interactions between the metal ions and the functional groups available on adsorbent surface were vital in adsorption of Pb(II), Cu(II) and Ni(II) ions into LAC and TAC, however external mass transport intraparticle diffusion was also involved in the adsorption process (Cao et al., 2019).

4.4 Conclusion

Melia azedarach leaves and twigs activated carbons were applied in a laboratory scale batch adsorption process to remove Cu(II), Pb(II) and Ni(II) ions from aqueous medium. Both *Melia azedarach* leaves and twigs activated carbon demonstrated excellent adsorption capacity at low adsorbent dosage, as per comparison of experimental results with the recent studies. LAC expressed maximum removal of Cu(II), Pb(II) and Ni(II) as 97.67%, 97.03% and 69.60% respectively, at 50 ppm initial concentration, 1 gL⁻¹ adsorbent dosage, 5 solution pH, 26 °C temperature and 120 min contact time. For these process conditions, the adsorption capacity of LAC for Cu(II), Pb(II) and Ni(II) removal, was determined to be 48.63 mgg⁻¹, 48.51 mgg⁻¹ and 34.80 mgg⁻¹ respectively. TAC expressed maximum removal of Cu(II), Ni(II) and Pb(II) as 89.41%, 51.63% and 61.64% respectively, at 50 ppm initial concentration, 1 gL⁻¹ adsorbent dosage, 5 solution pH, 26 °C temperature and 120 min contact time. For these process conditions, the adsorption capacity of LAC for Cu(II), Ni(II) and Pb(II) removal, was determined to be 44.71 mgg⁻¹, 30.82 mgg⁻¹ and 25.81 mgg⁻¹ respectively. For Pb(II) and Ni(II) adsorption, the equilibrium data followed a Freundlich isotherm, however for Cu(II) adsorption, the Temkin isotherm model was followed by both LAC and TAC. The Cu(II), Pb(II) and Ni(II) ion adsorption by both LAC and TAC followed pseudo second order model kinetics.

CHAPTER 5

OPTIMISATION OF Cu(II), Pb(II) AND Ni(II) ADSORPTION BY *Melia azedarach* ACTIVATED CARBON: A RESPONSE SURFACE METHODOLOGY APPROACH

5.1 Introduction

It is vital for an adsorbent for a large-scale application to optimise adsorption process parameters in order to make the adsorption system comfortable and cost-effective (Biswas et al., 2019). In heavy metals adsorption, the key process variables include initial concentration of adsorbate, adsorbent dosage, solution pH, contact time, and temperature (Al-Onazi et al., 2021). Traditionally, in adsorption process optimisation, one of these parameter is changed while other remain constant and this approach is known as one-variable-at-a-time (OVAT) optimisation (Hasana et al., 2020). The fundamental disadvantage of this technique is that the cumulative influence of all the factors remains unstudied; also, a large number of trials are required to optimise one parameter at a time (Mohd Zahri et al., 2021).

Response Surface Methodology (RSM) is a combination of mathematical and statistical techniques and has been proven to be beneficial in developing, improving and optimising processes (Cerrahoğlu et al., 2019). RSM optimises the number of experimental runs while reducing operational costs and labour requirements by creating an optimal experimental matrix that accounts for the impact of interacting effects (Praveena et al., 2019). Central Composite Design, Box–Behnken Design and Doehlert Design are the three basic RSM designs used for design of experiment (Jain et al., 2020).

The most commonly used RSM design is Central Composite Design (CCD) which employs a second-order (quadratic) polynomial model (Adane et al., 2020). CCD has the benefit over other designs in that it can optimise multifactor problems with an optimal number of experimental investigations (Kaçakgil & Bingöl, 2019). Following the selection of the design matrix and experiments execution, data processing with a specialised software enables the construction of a model and the generation of surface responses (Anfar et al., 2020).

In traditional heavy metals adsorption studies, the OVAT approach has been used to study parameters such as adsorbent dosage, initial metal concentration, solution pH, temperature and contact time (Jain, et al., 2020). In OVAT approach, effect of different variables is studied by varying one factor at a time keeping the rest of the parameters constant (Adane et al., 2020). The fundamental drawback of such technique is that it does not include the interaction effect of all the parameters studied, also in OVAT, a number of experiments are to be carried out (Biswas et al., 2019).

Due to the limitations of the traditional OVAT approach, the employment of RSM with CCD for optimising adsorption of heavy metals has gained attention among researchers in recent decades (Jain, et al., 2020). A few recently reported optimisation studies using RSM include Pb(II) adsorption by neem leaves based bio-composite (Maity & Ray, 2018), Cu(II) and Ni(II) adsorption by sodium alginate treated pinecones biochar (Biswas et al., 2019), Cu(II) adsorption by activated carbon based on pistachio shells (Nejadshafiee & Islami, 2020), Pb(II) adsorption by pyrolyzed activated sludge (Makshut et al., 2020), Cu(II) adsorption by acid-base treated coconut shell biochar (Hasana et al., 2020), Pb(II) adsorption by activated carbon based on de-oiled soya (Sujatha & Sivarethinamohan, 2021). Typically

in these studies, two types of variables were studied: independent variables (factors) such as adsorbent dose, contact time and temperature, while dependent variables (responses) like removal efficiency (%) and adsorption capacity (mgg^{-1}) (Anfar et al., 2020).

Findings from afore-mentioned studies reveal that, RSM provides optimal parameter conditions for the best response (Mohd Zahri et al., 2021). Using a hybrid adsorbent based on sodium alginate biopolymer and pinecone biochar, the optimum conditions for maximum metal ion adsorption for Cu(II) were found to be 47.05 mgg^{-1} at 84.8 mgL^{-1} initial concentration, 1.40 g adsorbent dosage and 36°C system temperature, while for Ni(II) adsorption, the conditions were 28.06 mgg^{-1} at 84.8 mgL^{-1} initial concentration, 1.48 g adsorbent dose and 40°C system temperature (Biswas et al., 2019). Using sago sludge activated carbon, the optimum Pb(II) removal (99.87%) was found to be at 0.5 g of adsorbent, 5 mgL^{-1} initial concentration and 30 min contact time (Makshut et al., 2020). Using acid-base modified coconut shell biochar as adsorbent, maximum Cu(II) removal efficiency 99.50% was found at pH 7, contact time 60 min and particle size of 0.60 mm (Hasana et al., 2020). Activated carbon prepared from de-oiled soya exhibited optimal adsorption capacity of 26.279 mgg^{-1} for Pb(II) removal at 60 mgL^{-1} initial concentration, 4.03 pH , 0.2 g adsorbent dosage and 80 min contact time (Sujatha & Sivarethinamohan, 2021).

The aim of this work was to optimise the adsorption parameters for Cu(II), Pb(II) and Ni(II) ions adsorption by *Melia azedarach* leaves activated carbons (LAC) and *Melia azedarach* twigs activated carbons (TAC) using RSM with CCD approach. The effect of three factors, including adsorbent dosage, initial metal concentration and contact time, on key responses removal efficiency and adsorption capacity was investigated.

5.2 Materials and Methods

5.2.1 Materials

In the present study, activated carbon prepared from *Melia azedarach* leaves (LAC) and *Melia azedarach* twigs (TAC) were applied as adsorbent for the adsorption of Cu(II), Pb(II) and Ni(II) heavy metal ions. Both LAC and TAC were prepared by Molten Salt Synthesis as explained in section 3.2.3 of Chapter 3.

For pH adjustment, sodium hydroxide, NaOH and hydrochloric acid, HCl were used. Pb(II) and Cu(II) stock solutions were prepared by dissolving 1.6 g of lead nitrate and 3.93 g of copper sulphate individually in a 1 L volumetric flask to obtain 1000 mgL⁻¹ of each single solute, then diluting with de-ionised water to achieve the desired concentration. For Ni(II), 1000 ppm standard solution (Merck) was used. Stock solution was freshly diluted to 5 mgL⁻¹, 10 mgL⁻¹, 15 mgL⁻¹, 20 mgL⁻¹, 25 mgL⁻¹, 30 mgL⁻¹, 35 mgL⁻¹, 40 mgL⁻¹, 45 mgL⁻¹ and 50 mgL⁻¹ concentrations.

5.2.2 RSM Adsorption Experiment

In this study, batch adsorption process was carried out at different parameters including initial concentrations of Cu(II), Pb(II) and Ni(II), adsorbent dosage (LAC and TAC) and contact time. Among the constant parameters were the adsorption temperature 25 ± 2 °C, solution pH 5 and 150 rpm agitation speed in an orbital shaker.

RSM with CCD was employed to measure two responses: adsorbent's efficiency in heavy metal removal and adsorbent's adsorption capacity. For this purpose, Design Expert (DX11) by Stat-Ease, Inc. USA, was used to analyze the experimental results for three factors including "A" adsorbent dose, "B" initial concentration and "C" contact time. The

upper (+1) and lower (−1) levels of these factors are summarised in Table 5.1. The following factors were kept constant throughout all experiments: pH 5, adsorption temperature 25 ± 1 °C and rotation speed 150 rpm. A set of 17 experiments calculated by Design Expert were carried out for each heavy metal ion Cu(II), Pb(II) and Ni(II) by each of the adsorbent LAC and TAC, varying configurations as demonstrated in Table 5.2 were performed to determine both the responses.

In this experiment, two types of responses were studied: the removal efficiency and adsorption capacity. Adsorption capacity and heavy metal removal efficiency of the adsorbent was calculated using equation 4.1 and equation 4.2 respectively, as expressed in Chapter 4.

Table 5.1: Range of factors for heavy metals adsorption via CCD

Factors	Units	-1	0	+1
A: Adsorbent dosage	g L^{-1}	1	2.5	4
B: Initial Concentration	ppm	50	175	300
C: Contact Time	min	60	120	180

Table 5.2: Experimental conditions for heavy metals adsorption via CCD

Experimental Run No.	Standard Run No.	Factor A	Factor B	Factor C
1	8	4	300	180
2	11	2.5	10	120
3	10	4.5	175	120
4	3	1	300	60

Table 5.2 continued

5	13	2.5	175	40
6	12	2.5	340	120
7	17	2.5	175	120
8	5	1	50	180
9	4	4	300	60
10	15	2.5	175	120
11	1	1	50	60
12	2	4	50	60
13	7	1	300	180
14	6	4	50	180
15	9	0.5	175	120
16	14	2.5	175	200
17	16	2.5	175	120

Note: Factor A: Adsorbent dosage; Factor B: Initial metal Conc.; Factor C: Contact Time

5.3 Result and Discussion

5.3.1 Cu(II) ions Adsorption by LAC and TAC

5.3.1.1 Cu(II) ions Adsorption by LAC

Using a central composite design with 17 experimental runs, the relationship between the operational parameters for the removal efficiency and adsorption capacity of LAC in terms of Cu(II) removal efficiency and adsorption capacity from aqueous medium was examined. At the experimental conditions specified in Table 5.2, the Cu(II) removal

efficiency of LAC ranged from 41.11% to 98.63% and the adsorption capacity ranged from 3.95 mgg⁻¹ to 192.12 mgg⁻¹ as expressed in Table 5.3.

The maximum Cu(II) removal by LAC was determined to be 98.63% in run 2 at 2.5 gL⁻¹ adsorbent dosage, 10 ppm initial concentration and 120 min contact time while the minimum Cu(II) removal was 41.11% in run 4 at 1 gL⁻¹ adsorbent dosage, 300 ppm initial concentration and 60 min contact time. It indicated that maximum Cu(II) removal was achieved at medium level adsorbent dose (2.5 gL⁻¹), lowest initial concentration (10 ppm) and medium contact time (120 min), whereas minimum Cu(II) removal was expressed with minimum adsorbent dosage, highest initial concentration and shortest contact time. Aside from run 2, which had the highest removal, nine additional runs, including runs 1, 3, 7,8, 10, 12, 14, 16 and 17 had over 80% removal efficiency.

Table 5.3: Exprimental and predicted results for Cu(II) adsorption by LAC

Run	Std.	Factor	Factor	Factor	Removal Efficiency		Ads. Capacity	
		A	B	C	Actual	Predicted	Actual	Predicted
1	8	4	300	180	88.96	87.58	66.72	65.51
2	11	2.5	10	120	98.63	99.71	3.95	-2.21
3	10	4.5	175	120	94.95	94.32	37.12	45.48
4	3	1	300	60	41.11	41.84	123.33	135.22
5	13	2.5	175	40	70.27	66.46	49.19	37.89
6	12	2.5	340	120	77.81	75.37	105.82	104.92
7	17	2.5	175	120	82.33	85.32	57.63	60.23

Table 5.3 continued

8	5	1	50	180	94.69	92.17	47.34	55.75
9	4	4	300	60	78.24	81.36	51.18	45.85
10	15	2.5	175	120	84.41	85.32	53.18	60.23
11	1	1	50	60	66.36	68.34	33.18	37.46
12	2	4	50	60	91.60	91.15	11.45	17.21
13	7	1	300	180	64.04	65.08	192.12	189.44
14	6	4	50	180	98.09	97.95	9.76	0.9406
15	9	0.5	175	120	64.82	64.12	156.86	141.59
16	14	2.5	175	200	84.02	86.49	58.81	63.20
17	16	2.5	175	120	87.57	85.32	61.30	60.23

Among these tests, runs 8 and 14 shown a high level of removal with 50 ppm initial concentration and 180 min contact time, whereas runs 2,3,7,16,17 showed high removal with 175 ppm initial concentration and 120 min contact time with varied adsorbent dosage. The existence of vacant surface-active sites may have caused this sorption disparity and after 120 min, the surface active sites are saturated with Cu(II) ions, resulting in a fairly steady removal efficiency afterwards (Oladipo et al., 2019). After a certain level of metal concentration, removal efficiency decreases due to the quick filling of binding sites on the adsorbent surface, limiting removal efficiencies (Al Moharbi et al., 2020). This can also be due to the fact that at higher concentrations, more metal ions compete for the same accessible binding site, which has become saturated due to increased ion exchange, resulting in more metal ions remaining unabsorbed and a drop in removal efficiency (Hasana et al., 2020).

According to Table 5.3, the highest adsorption capacity of LAC for Cu(II) ions adsorption, was 192.12 mgg^{-1} by run 13 at 1 gL^{-1} adsorbent dosage, 300 ppm initial concentration and 180 min contact time. In addition, three more runs, 15, 4 and 6 had high adsorption capacities of 156.86, 123.33 and 105.82 mgg^{-1} respectively. However, out of the four runs with adsorption capacities greater than 100 mgg^{-1} , three were with initial concentration 300-340 ppm, besides run 15 which expressed high adsorption capacity at 175 ppm initial concentration, 0.5 gL^{-1} adsorbent dosage and 120 min contact time. The lowest adsorption capacity was 3.95 mgg^{-1} in run 2 at 2.5 adsorbent dosage, 10 ppm initial concentration and 120 min contact time. With 50 ppm initial concentration, two more runs, 12 and 14, demonstrated limited adsorption capacity.

The ability of LAC to adsorb Cu(II) increased with increasing initial concentrations, implying that the driving force at the solid-liquid interface was enhanced, allowing the adsorption capacity to rise until the adsorption sites were saturated (Ouyang et al., 2019). It can be concluded that LAC demonstrated near-maximal adsorption capacity from 175 ppm initial concentration at 0.5 gL^{-1} adsorbent dosage, however findings revealed a reduction in adsorption capacity at the same initial concentration of Cu(II) with increased adsorbent dosage up to 4.5 gL^{-1} . The reason might be that higher adsorbent dosage increases adsorbent aggregation, lowering effective surface area and restricting active sites, reducing the adsorbent's adsorption capacity on fixed initial metal concentration (Qin et al., 2019).

Table 5.4. shows the model fitness summary as calculated by Design Expert software based on the adsorption experiments. Results showed that Cu(II) adsorption by LAC can be expressed by quadratic model ($p \leq 0.05$) and the predicted R-squared values were closer to one with respect to other models (Sujatha & Sivarethinamohan, 2021).

Table 5.4: Model fitness sumamry for both the responses in Cu(II) adsorption by LAC

Response		Model Fitness Summary				
	Source	Sequential p-value	Lack of Fit p- value	Adjusted R²	Predicted R²	Remarks
Removal Efficiency	Linear	< 0.0001	0.1213	0.8011	0.6959	
	2FI	0.0808	0.1657	0.8643	0.6863	
	Quadratic	0.0096	0.4405	0.9586	0.8601	Suggested
	Cubic	0.2965	0.5128	0.9737	0.4651	Aliased
Adsorption Capacity	Linear	< 0.0001	0.0253	0.7917	0.6783	
	2FI	0.0589	0.0373	0.8672	0.7896	
	Quadratic	0.0198	0.0870	0.9498	0.8072	Suggested
	Cubic	0.1464	0.1178	0.9811	-0.2472	Aliased

According to analysis of variance for Cu(II) adsorption by LAC, the F-value of the model was found to be 42.15 as described in Table 5.5, which implied the model was significant with only a 0.01% chance that such large F-value could occur due to noise. Values of “Prob > F” less than 0.0500 indicated that the A, B, C, AB, AC, A², C² were significant model terms while other factors which had Prob > F” values greater than 0.1000 were insignificant while the F-value and “Prob > F” for “lack of fit” were 1.53 and 0.4405 respectively, indicated that lack of fit was not significant and there was 44.05% chance that such large value can occur due to noise (Singh & Bhateria, 2020).

Table 5.5: ANOVA results for Cu(II) removal efficiency by LAC

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3642.44	9	404.72	42.15	< 0.0001	significant
A-Ads. dosage	1482.30	1	1482.30	154.38	< 0.0001	
B-Initial Conc.	975.96	1	975.96	101.64	< 0.0001	
C-Contact Time	652.01	1	652.01	67.90	< 0.0001	
AB	139.62	1	139.62	14.54	0.0066	
AC	144.96	1	144.96	15.10	0.0060	
BC	0.1699	1	0.1699	0.0177	0.8979	
A ²	76.18	1	76.18	7.93	0.0259	
B ²	10.17	1	10.17	1.06	0.3377	
C ²	159.88	1	159.88	16.65	0.0047	
Residual	67.21	7	9.60			
Lack of Fit	53.28	5	10.66	1.53	0.4405	not significant
Pure Error	13.93	2	6.97			
Correlation	3709.65	16				
Total						

As mentioned in Table 5.6, for adsorption capacity of LAC to adsorb Cu(II) from aqueous medium, the F-value of the model was found to be 34.64 as per ANOVA results described in Table 5.6, which implied the model was significant with only a 0.01% chance that such large F-value could occur due to noise. Values of “Prob > F” less than 0.0500 indicated that the A, B, C, AB and A² were significant model terms while other factors which had Prob > F” values greater than 0.1000 were insignificant while the F-value and “Prob >

F” for “lack of fit” were 10.78 and 0.0870 respectively, indicated that lack of fit was not significant and there was 8.70% , though this lack of fit was less than required however such results have been reported earlier too (Ghosh et al., 2020).

Table 5.6: ANOVA results for Cu(II) Adsorption capacity by LAC

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	41168.16	9	4574.24	34.64	< 0.0001	significant
A-Ads. dosage	15012.59	1	15012.59	113.67	< 0.0001	
B-Initial Conc.	18915.10	1	18915.10	143.22	< 0.0001	
C-Contact Time	1040.34	1	1040.34	7.88	0.0263	
AB	2388.33	1	2388.33	18.08	0.0038	
AC	597.04	1	597.04	4.52	0.0711	
BC	645.49	1	645.49	4.89	0.0627	
A ²	2266.09	1	2266.09	17.16	0.0043	
B ²	163.60	1	163.60	1.24	0.3025	
C ²	191.71	1	191.71	1.45	0.2674	
Residual	924.49	7	132.07			
Lack of Fit	891.42	5	178.28	10.78	0.0870	not significant
Pure Error	33.07	2	16.54			
Correlation Total	42092.65	16				

The response levels for varied values of each factor can be predicted using the equation in terms of coded factors (Biswas et al., 2019). The high levels of the factors are coded as +1 and the low levels are coded as -1 in the coded equation by default, which is

useful for comparing the factor coefficients to determine the relative effect of the factors (Sujatha & Sivarethinamohan, 2021). In coded form, the equations of the quadratic model for Cu(II) removal efficiency by LAC, are in equation 5.1 whereas equation 5.2 is for adsorption capacity of LAC to adsorb Cu(II) from aqueous medium.

Removal Efficiency

Equation 5.1

$$\begin{aligned} &= +85.32 + 11.33A - 9.22B + 7.51C + 4.18AB \\ &- 4.26AC - 0.1457BC - 3.43A^2 + 1.27B^2 \\ &- 4.98C^2 \end{aligned}$$

Adsorption Capacity

Equation 5.2

$$\begin{aligned} &= +60.23 - 36.04A + 40.58B + 9.49C \\ &- 17.28AB - 8.64AC + 8.98BC + 18.73A^2 \\ &- 5.10B^2 - 5.45C^2 \end{aligned}$$

In equation 5.1 and 5.2, A, B and C represent adsorbent dosage, initial concentration, and contact time respectively. A single factor coefficient represents the influence of a single component, whereas a two-factor coefficient represents the interaction effect of two components and a squared form coefficient represents the influence of quadratic factors (Singh & Bhateria, 2020). The negative signs indicate the inimical effect while the positive signs display coating effects (Hasana et al., 2020). According to equation 5.1, adsorbent dosage and contact time had a favorable effect on Cu(II) removal efficiency of LAC while initial concentration had an opposite effect. Adsorption capacity increased with increasing contact time and initial concentration, but declined with adsorbent dosage, according to equation 5.2.

Three-dimensional response surfaces plotted in Figure 5.1 depict that optimum conditions of different factors for both Cu(II) removal efficiency and adsorption capacity by LAC. The red area/point on the plots shows the highest removal percentage of Cu(II) ion on certain conditions. Figure 5.1(a) shows the combined effect of adsorbent dosage and initial concentration on Cu(II) removal efficiency at 120 min contact time. Figure 5.1(b) shows the combined effect of adsorbent dosage and contact time on Cu(II) removal efficiency at 175 ppm initial concentration. Figure 5.1(c) shows the combined effect of initial concentration and contact time on Cu(II) removal efficiency at 2.5 gL⁻¹ adsorbent dosage. Figure 5.1(d) shows the combined effect of adsorbent dosage and initial concentration on Cu(II) adsorption capacity of LAC at 120 min contact time. Figure 5.1(e) shows the combined effect of adsorbent dosage and contact time on Cu(II) adsorption capacity of LAC, at 175 ppm initial concentration. Figure 5.1(f) shows the combined effect of initial concentration and contact time on Cu(II) adsorption capacity of LAC at 2.5 gL⁻¹ adsorbent dosage.

According to CCD optimisation analysis, the optimum conditions for Cu(II) adsorption by LAC were 3.17 gL⁻¹ adsorbent dosage, 53.57 ppm initial concentration and 140 min contact time. At these conditions, optimum Cu(II) removal was found to be 98.52 ± 0.09% with adsorption capacity of 16.78 ± 0.02 mgg⁻¹. At optimum adsorbent dosage of 1.0 gL⁻¹, initial concentration of 300 ppm and contact time of 180 min, adsorption capacity was found to be 150.05 ± 0.331 mgg⁻¹ with 50.03 ± 1.10 % removal efficiency.

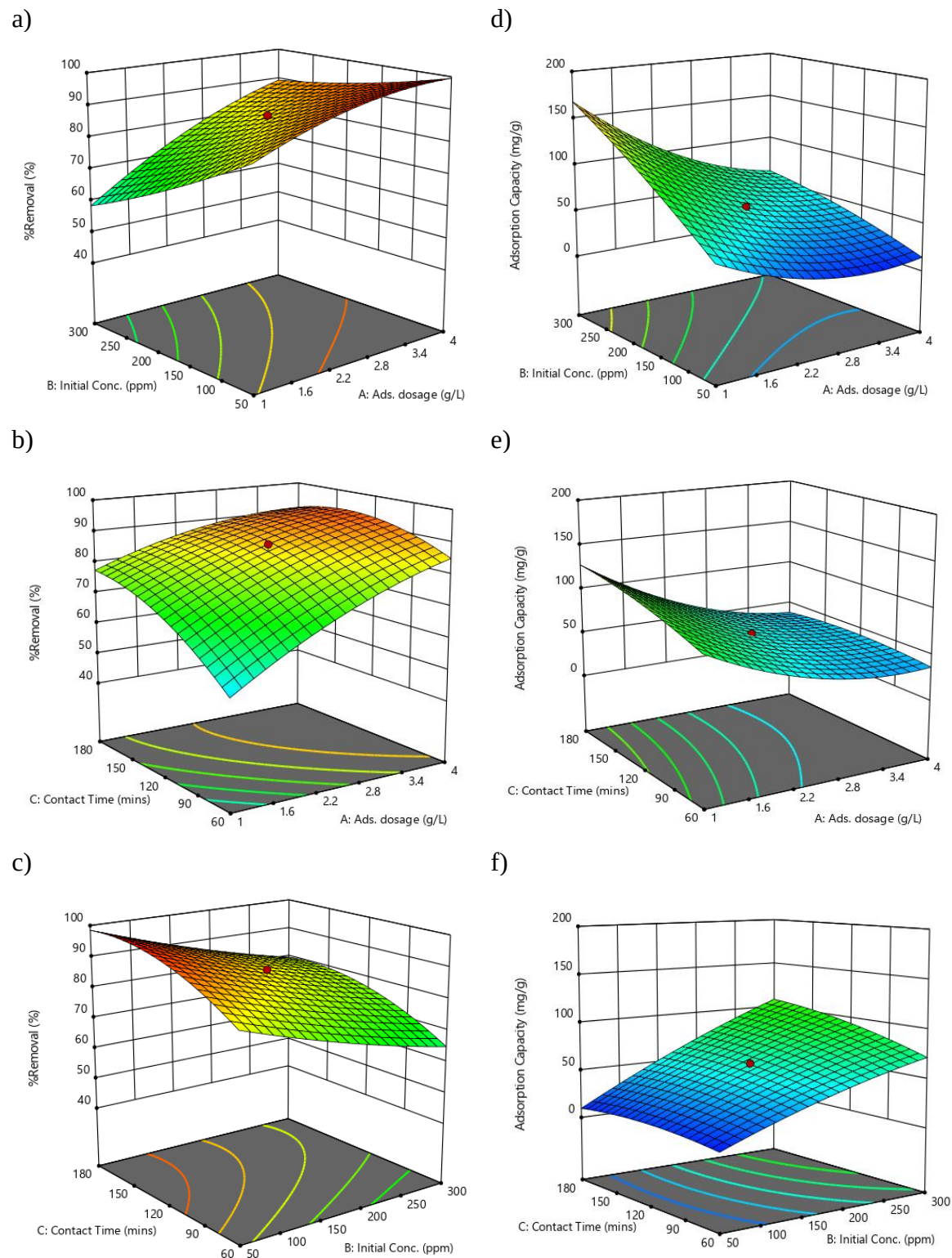


Figure 5.1: 3D response surface graphs illustrating the interlinked effect of adsorbent dosage, initial concentration and contact time on Cu(II) removal efficiency and adsorption capacity of LAC

5.3.1.2 Cu(II) ions Adsorption by TAC

The correlation between the operational factors for the removal efficiency and adsorption capacity of TAC in terms of Cu(II) removal efficiency and adsorption capacity from aqueous medium was explored utilising a central composite design with seventeen experimental runs. Table 5.7 reveals that the Cu(II) removal efficiency by TAC ranged from 45.43% to 99.66% under the given experimental conditions and adsorption capacity ranged from 3.52 mgg⁻¹ to 172.22 mgg⁻¹.

The maximum Cu(II) removal by TAC was 99.66% in run 14 with 4 gL⁻¹ adsorbent dosage, 50 ppm initial concentration and 180 min contact time while minimum Cu(II) removal 45.43% was found in run 4 with 1 gL⁻¹ adsorbent dosage, 300 ppm initial concentration and 60 min contact time. It indicates that maximum Cu(II) removal was expressed with the highest adsorbent dosage (4 gL⁻¹), the longest contact time (180 min) and the lowest initial concentration (50 ppm), whereas the minimum Cu(II) removal was expressed with highest initial concentration, lowest adsorbent dosage and shortest contact time. In addition to run 14, seven other run had above 80% removal efficiency including runs 1, 2, 3, 9, 12, 14 and 17.

Table 5.7: Experimental and predicted Cu(II) adsorption by TAC

Run	Std.	Factor			Removal Efficiency		Ads. Capacity	
		A	B	C	Actual	Predicted	Actual	Predicted
1	8	4	300	180	87.15	86.46	65.36	62.53
2	11	2.5	10	120	88.11	88.18	3.52	-3.60
3	10	4.5	175	120	96.77	98.66	37.76	42.91
4	3	1	300	60	45.43	45.99	136.28	139.47
5	13	2.5	175	40	61.50	61.52	43.05	39.18

Table 5.7 continued

6	12	2.5	340	120	72.31	73.39	98.34	104.07
7	17	2.5	175	120	78.10	79.61	54.67	54.76
8	5	1	50	180	69.12	69.65	34.56	39.86
9	4	4	300	60	80.70	79.67	53.03	48.33
10	15	2.5	175	120	79.60	79.61	50.15	54.76
11	1	1	50	60	56.08	56.27	28.04	31.48
12	2	4	50	60	89.34	89.35	11.17	14.71
13	7	1	300	180	57.44	56.92	172.32	169.38
14	6	4	50	180	99.66	98.60	9.96	7.38
15	9	0.5	175	120	57.67	56.91	131.83	125.32
16	14	2.5	175	200	73.87	74.98	51.71	54.23
17	16	2.5	175	120	82.53	79.61	57.77	54.76

All these run has one similarity of maximum adsorbent dosage different initial concentration and contact time. This underlines the relevance of the increased number of functional groups and active adsorption sites as a result of the increased surface area available with the increased adsorbent dosage (Amin et al., 2019).

According to the results in Table 5.7, the adsorption capacity of TAC for Cu(II) ions was 172.32 mgg⁻¹ by run 13 with 1 gL⁻¹ adsorbent dosage, 300 ppm initial concentration and 180 min contact time. Furthermore, three other runs 4, 15 and 6, had high adsorption capacity 136.28, 131.83 and 98.34 respectively. However, out of four runs with higher adsorption capacity, three had initial concentration 300-340 ppm, with the exception of run 15. Run 2 acquired a minimum adsorption capacity of 3.52 mgg⁻¹ with 2.5 gL⁻¹ adsorbent dosage, 10 ppm initial concentration and 120 min contact time, whereas runs 14 and 12 exhibited lower adsorption capacity with 50 ppm initial concentration. With increasing initial concentrations,

the ability of TAC to adsorb Cu(II) increased, suggesting that the driving force at the solid–liquid interface was increased, allowing the adsorption capacity to rise until the adsorption sites were saturated (Biswas et al., 2019)

Table 5.8 shows the model fitness summary as calculated by the Design Expert software based on the adsorption experiments. Results showed that adsorption of Cu(II) by LAC can be expressed by quadratic model ($p\text{-value} \leq 0.05$), also the values of predicted R-squared were closer to one with respect to other models.

Table 5.8: Model fitness summary for both the responses in Cu(II) adsorption by TAC

Response	Model Fitness Summary					
	Source	Sequential p-value	Lack of Fit p- value	Adjusted R ²	Predicted R ²	Remarks
Removal efficiency	Linear	< 0.0001	0.1690	0.9006	0.8746	
	2FI	0.9382	0.1307	0.8757	0.8090	
	Quadratic	0.0002	0.8098	0.9874	0.9724	Suggested
	Cubic	0.7804	0.5172	0.9814	0.6281	Aliased
Adsorption Capacity	Linear	< 0.0001	0.0299	0.8167	0.7125	
	2FI	0.0270	0.0519	0.9011	0.8609	
	Quadratic	0.0023	0.2188	0.9801	0.9302	Suggested
	Cubic	0.0835	0.6354	0.9950	0.9418	Aliased

According to analysis of variance, the F-value of the model for removal efficiency in Cu(II) adsorption by TAC was 42.15 as shown in Table 5.9 implying that the model was significant with only a 0.01% chance that such large F-value could occur due to noise. Values

of “Prob > F” less than 0.0500 indicated that the A, B, C, C² were significant model terms, whereas other factors with Prob > F” values greater than 0.1000 were insignificant. The F-value and “Prob > F” for “lack of fit” were 0.4245 and 0.8098 respectively, indicating that lack of fit was not significant and there was 80.98% chance that such large value could occur due to noise.

Table 5.9: ANOVA results for Cu(II) removal efficiency by TAC

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	3772.90	9	419.21	140.38	< 0.0001	significant
A-Ads. dosage	2832.60	1	2832.60	948.57	< 0.0001	
B-Initial Conc.	360.62	1	360.62	120.76	< 0.0001	
C-Contact Time	294.16	1	294.16	98.51	< 0.0001	
AB	0.1733	1	0.1733	0.0580	0.8166	
AC	8.57	1	8.57	2.87	0.1341	
BC	3.01	1	3.01	1.01	0.3491	
A ²	6.85	1	6.85	2.29	0.1738	
B ²	2.86	1	2.86	0.9572	0.3605	
C ²	263.71	1	263.71	88.31	< 0.0001	
Residual	20.90	7	2.99			
Lack of Fit	10.76	5	2.15	0.4245	0.8098	not significant
Pure Error	10.14	2	5.07			
Cor Total	3793.80	16				

For adsorption capacity of TAC to adsorb Cu(II) from aqueous medium, the F-value of the model was found to be 88.51 as per ANOVA results described in Table 5.10 which implied the model was significant with only a 0.01% chance that such large F-value could occur due to noise. Values of “Prob > F” less than 0.0500 indicated that the A, B, C, AB, A²

were significant model terms while other factors which had Prob > F” values greater than 0.1000 were insignificant while the F-value and “Prob > F” for “lack of fit” were 3.85 and 0.2188 respectively, indicated that lack of fit was not significant and there was 21.88% chance that a lack of fit value this large could occur due to noise.

Table 5.10: ANOVA results for Cu(II) Adsorption capacity of TAC

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	35535.37	9	3948.37	88.51	< 0.0001	significant
A-Ads. dosage	11037.06	1	11037.06	247.42	< 0.0001	
B-Initial Conc.	19104.76	1	19104.76	428.28	< 0.0001	
C-Contact Time	368.07	1	368.07	8.25	0.0239	
AB	2765.58	1	2765.58	62.00	0.0001	
AC	123.48	1	123.48	2.77	0.1401	
BC	231.76	1	231.76	5.20	0.0567	
A ²	1760.52	1	1760.52	39.47	0.0004	
B ²	42.50	1	42.50	0.9526	0.3616	
C ²	132.73	1	132.73	2.98	0.1282	
Residual	312.26	7	44.61			
Lack of Fit	282.90	5	56.58	3.85	0.2188	not significant
Pure Error	29.36	2	14.68			
Cor Total	35847.63	16				

In coded form, the equations of the quadratic model for removal efficiency of Cu(II) by TAC, are in equation 5.3 whereas equation 5.4 is for adsorption capacity of TAC to adsorb Cu(II) from aqueous medium.

Removal Efficiency

Equation 5.3

$$\begin{aligned} &= +79.61 + 15.66A - 5.60B + 5.05C \\ &+ 0.1472AB - 1.03AC - 0.6131BC - 1.03A^2 \\ &+ 0.6735B^2 - 6.39C^2 \end{aligned}$$

Adsorption Capacity

Equation 5.4

$$\begin{aligned} &= +54.76 - 30.91A + 40.79B + 5.64C \\ &- 18.59AB - 3.93AC + 5.38BC + 16.51A^2 \\ &- 2.60B^2 - 4.53C^2 \end{aligned}$$

In equation 5.3 and 5.4, A, B and C stand for adsorbent dosage, initial concentration, and contact time respectively. The influence of a single component is shown by a single factor coefficient, but the interaction effect of two factors is shown by a two-factor coefficient and the effect of quadratic factors is shown by a squared form coefficient (Singh & Bhateria, 2020). The negative signs indicate the inimical effect and the positive signs display coating effects (Hasana et al., 2020). Adsorbent dosage and contact time had a favorable effect on Cu(II) removal efficiency, as evidenced by the conditions. while initial concentration had an opposite effect. Adsorption capacity increased as the initial concentration increased, also contact time affected positively however adsorption capacity declined with the increase in the adsorbent dosage.

Three-dimensional response surfaces plotted in Figure 5.2 depict the optimum conditions of different factors for both Cu(II) removal efficiency and adsorption capacity by TAC. The red area/point on the plots shows the highest removal of Cu(II) ion on certain conditions. Figure 5.2 (a) shows the combined effect of adsorbent dosage and initial concentration on removal efficiency of Cu(II) at 120 min contact time. Figure 5.2 (b) shows

the combined effect of adsorbent dosage and contact time on removal efficiency of Cu(II) at 175 ppm initial concentration. Figure 5.2 (c) shows the combined effect of initial concentration and contact time on Cu(II) removal efficiency at 2.5 gL⁻¹ adsorbent dosage. Figure 5.2 (d) shows the combined effect of adsorbent dosage and initial concentration on Cu(II) adsorption capacity of TAC at 120 min contact time. Figure 5.2 (e) shows the combined effect of adsorbent dosage and contact time on Cu(II) adsorption capacity of TAC, at 175 ppm initial concentration. Figure 5.2 (f) shows the combined effect of initial concentration and contact time on Cu(II) adsorption capacity of TAC at 2.5 gL⁻¹ adsorbent dosage.

According to CCD optimisation analysis for Cu(II) adsorption by TAC, optimum factors included adsorbent dosage 3.944 gL⁻¹, initial concentration 60 ppm and contact time 153.809 min. For these conditions, maximum Cu(II) removal of 96.28% $\pm$ 0.32 was found along with 14.66 mgg⁻¹ adsorption capacity. While for maximum adsorption capacity was found to be 148.98 mgg⁻¹ $\pm$ 1.55 and 56.93% removal efficiency with found at adsorbent dosage 1.0 gL⁻¹, initial concentration 300 and contact time 180 min as optimum parameters.

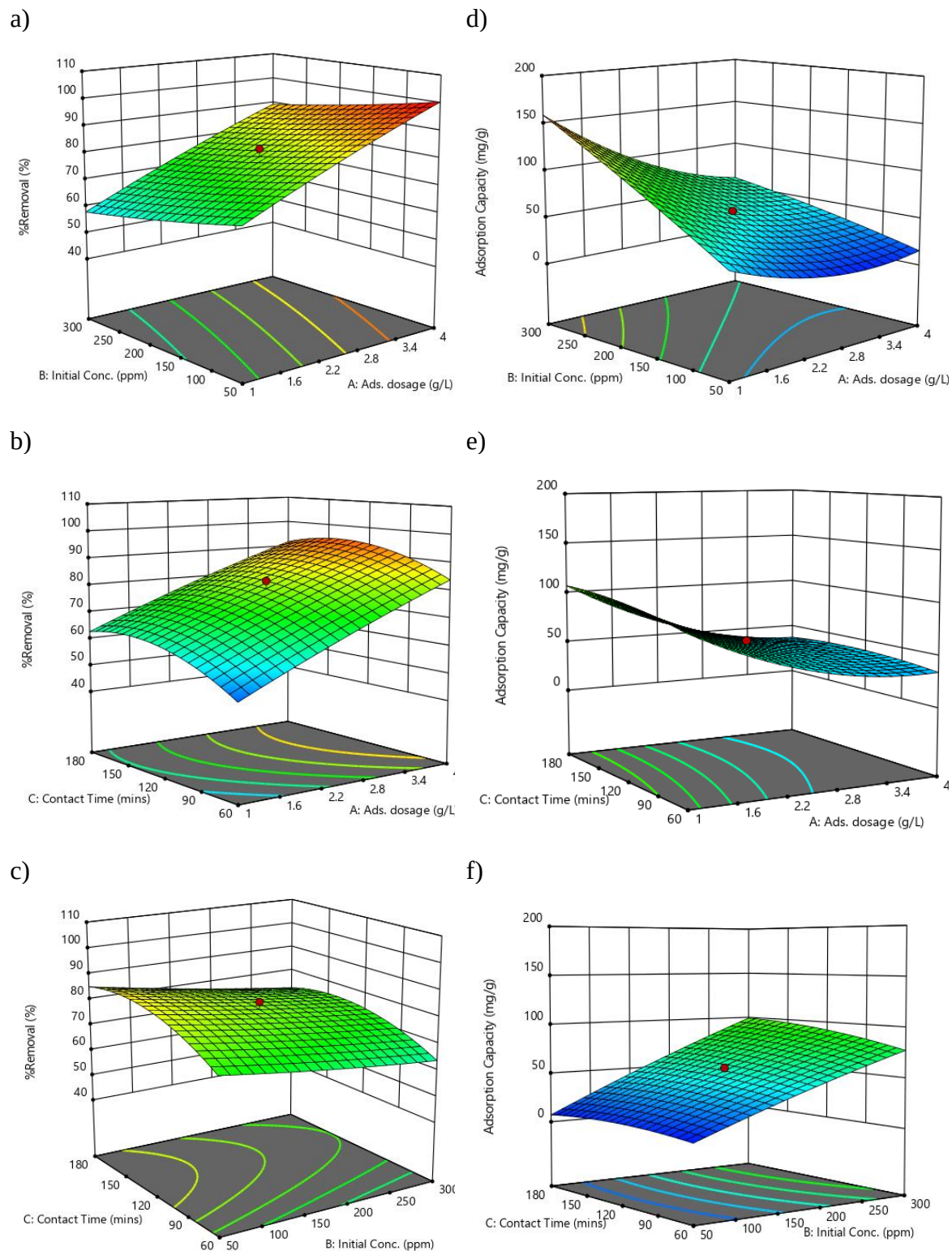


Figure 5.2: 3D response surface graphs illustrating the interlinked effect of adsorbent dosage, initial concentration and contact time on Cu(II) removal efficiency and adsorption capacity of TAC

5.3.2 Pb(II) ions adsorption by LAC and TAC

5.3.2.1 Pb(II) ions adsorption by LAC

The correlation between the operational factors for the adsorption efficiency of LAC in terms of Pb(II) removal efficiency and adsorption capacity from aqueous medium was studied using a central composite design with seventeen experimental runs. For the prescribed experimental conditions, Pb(II) removal by LAC varied from 45.73% to 99.52% and adsorption capacity varied from 3.98 mgg⁻¹ to 170.94 mgg⁻¹ as demonstrated in Table 5.11.

Maximum Pb(II) removal by LAC was found 99.52% in run 2 with 2.5 gL⁻¹ adsorbent dosage, 10 ppm initial concentration and 120 min contact time while minimum Pb(II) removal 45.73% in run 4 was with 1 gL⁻¹ adsorbent dosage, 300 ppm initial concentration and 60 min contact time. It indicates that maximum Pb(II) removal was expressed with medium level adsorbent dose (2.5 gL⁻¹), lowest initial concentration (10 ppm) and medium contact time (120 min), whereas minimum Pb(II) removal was expressed with minimum adsorbent dosage, highest initial concentration and shortest contact time. Aside from run 2, which had the highest removal, eight other runs had removal efficiency of more over 90%, including runs 1, 3, 7, 8, 10, 14, 16 and 17.

Table 5.11: Experimental and predicted results for Pb(II) adsorption by LAC

Run	Std.	Factor			Removal Efficiency		Ads. Capacity	
		A	B	C	Actual	Predicted	Actual	Predicted
1	8	4	300	180	91.26	93.99	68.44	67.22
2	11	2.5	10	120	99.52	101.04	3.98	-1.40
3	10	4.5	175	120	97.28	92.38	37.83	50.40

Table 5.11 continued

4	3	1	300	60	45.73	46.10	128.19	140.59
5	13	2.5	175	40	85.31	83.95	59.71	51.84
6	12	2.5	340	120	78.25	75.40	106.42	103.20
7	17	2.5	175	120	92.05	92.79	64.43	68.06
8	5	1	50	180	94.68	93.13	47.34	58.02
9	4	4	300	60	84.15	86.27	63.11	56.18
10	15	2.5	175	120	91.47	92.79	64.03	68.06
11	1	1	50	60	87.53	85.38	43.77	48.73
12	2	4	50	60	86.02	87.78	10.50	12.43
13	7	1	300	180	56.98	55.79	170.94	172.75
14	6	4	50	180	93.35	93.56	9.25	0.5904
15	9	0.5	175	120	61.70	65.31	165.95	144.96
16	14	2.5	175	200	94.20	94.26	65.94	65.39
17	16	2.5	175	120	93.24	92.79	65.27	68.06

Among these run, 8 and 14 expressed high level of removal efficiency with 50 ppm initial concentration and 180 min contact time while run 2,3,7,16,17 showed high removal efficiency at 175 ppm initial concentration and 120 min contact time with different adsorbent dosage. The existence of vacant surface-active sites may have produced this sorption disparity and after 120 min, the surface active sites are saturated with Pb(II) ions, resulting in a fairly constant removal efficiency afterwards (Kaur et al., 2020). With the increase in metal concentration after a certain level, the removal efficiency decreases due to fast filling of binding sites on the adsorbent surface, limiting removal efficiencies (Amin et al., 2019).

Results in Table 5.11 depict that for Pb(II) ions, maximum adsorption capacity of LAC was 170.94 mgg^{-1} by run 13 with 1 gL^{-1} adsorbent dosage, 300 ppm initial

concentration and 180 min contact time. Furthermore, runs 15, 4 and 6 had high adsorption capacity of 165.95, 128.19 and 106.42 mgg^{-1} respectively. Except for run 15, all four runs with adsorption capacity greater than hundred 100 mgg^{-1} , had an initial concentration of 300-340 ppm. In run 2, the lowest adsorption capacity was 3.98 mgg^{-1} with a 2.5 gL^{-1} adsorbent dosage, 10 ppm initial concentration and 120 min contact time and in addition to it, two other runs, 14 and 12, expressed very low adsorption capacity at an initial concentration of 50 ppm.

The adsorption capacity of LAC increased as the initial concentration of Pb(II) increased due to a rise in the mass transfer driving force and for this reason, the cross over rate of Pb(II) from the bulk solution to the particle surface while removal efficiency decreased due to lack of available sites required (Zhu et al., 2018). It can be affirmed that LAC achieved near-highest adsorption capacity from 175 ppm Pb(II) ions concentration at 0.5 gL^{-1} adsorbent dosage, while at same initial concentration of Pb(II) with increased adsorbent dosage up to 4.5 gL^{-1} , results showed decrease in adsorption capacity.

Table 5.12 shows the model fitness summary as calculated by the Design Expert software based on the adsorption experiments. Results showed that adsorption of Pb(II) by LAC can be expressed by quadratic model ($p\text{-value} \leq 0.05$), also the values of predicted R-squared were closer to one with respect to other models (Ghosh et al., 2020).

Table 5.12: Model fitness summary for both the responses in Pb(II) adsorption by LAC

Response		Model Fitness Summary				
	Source	Sequential p-value	Lack of Fit p- value	Adjusted R ²	Predicted R ²	Remarks
Removal	Linear	0.0024	0.0070	0.5781	0.3425	
Efficiency	2FI	0.0348	0.0116	0.7596	0.3642	
	Quadratic	0.0020	0.0530	0.9537	0.8395	Suggested
	Cubic	0.0496	0.1544	0.9918	0.5040	Aliased
Adsorption	Linear	< 0.0001	0.0008	0.8284	0.7467	
Capacity	2FI	0.2771	0.0009	0.8457	0.7474	
	Quadratic	0.0356	0.0017	0.9305	0.7433	Suggested
	Cubic	0.1309	0.0023	0.9758	-1.0373	Aliased

According to analysis of variance, for Pb(II) removal efficiency by LAC, F-value of the model was found to be 42.15 as described in Table 5.13 expressing that the quadratic model was significant with only a 0.01% chance that such large F-value could occur due to noise. Values of “Prob > F” less than 0.0500 indicated that the A, B, C, AB, A² were significant model terms while other factors which had Prob > F” values greater than 0.1000 were insignificant while the F-value was 18.17 and “Prob > F” for “lack of fit” was 0.053, indicating that lack of fit was insignificant and there was a 5.3% chance that F- value could occur due to noise (Biswas et al., 2019).

Table 5.13: ANOVA results for Pb(II) removal efficiency of LAC

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3647.78	9	405.31	37.59	< 0.0001	significant
A-Ads. dosage	1190.64	1	1190.64	110.41	< 0.0001	
B-Initial Conc.	1083.39	1	1083.39	100.47	< 0.0001	
C-Contact Time	172.81	1	172.81	16.03	0.0052	
AB	713.23	1	713.23	66.14	< 0.0001	
AC	1.96	1	1.96	0.1821	0.6824	
BC	1.88	1	1.88	0.1746	0.6886	
A ²	397.42	1	397.42	36.85	0.0005	
B ²	43.28	1	43.28	4.01	0.0852	
C ²	27.73	1	27.73	2.57	0.1528	
Residual	75.49	7	10.78			
Lack of Fit	73.86	5	14.77	18.17	0.0530	not significant
Pure Error	1.63	2	0.8132			
Cor Total	3723.26	16				

For second response, adsorption capacity of LAC to adsorb Pb(II) from aqueous medium, the F-value of the model was found to be 24.79 as described in Table 5.14 which implied the model was significant with only a 0.02% chance that such large F-value could occur due to noise. Values of “Prob > F” less than 0.0500 indicated that the A, B, AB, A² were significant model terms while other factors which had Prob > F” values greater than 0.1000 were insignificant. For “lack of fit” of the mode, the F-value was 582.67 and “Prob

> F” was 0.0017 respectively, indicated that lack of fit was significant and there were only 0.17% chances that this lack of fit could occur due to noise.

Table 5.14: ANOVA results for Pb(II) adsorption capacity by LAC

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	37019.30	9	4113.26	24.79	0.0002	significant
A-Ads. dosage	14529.44	1	14529.44	87.56	< 0.0001	
B-Initial Conc.	18028.75	1	18028.75	108.64	< 0.0001	
C-Contact Time	298.20	1	298.20	1.80	0.2219	
AB	1157.25	1	1157.25	6.97	0.0334	
AC	223.08	1	223.08	1.34	0.2843	
BC	261.71	1	261.71	1.58	0.2495	
A ²	1792.55	1	1792.55	10.80	0.0134	
B ²	611.14	1	611.14	3.68	0.0965	
C ²	182.28	1	182.28	1.10	0.3294	
Residual	1161.62	7	165.95			
Lack of Fit	1160.82	5	232.16	582.67	0.0017	significant
Pure Error	0.7969	2	0.3984			
Cor Total	38180.92	16				

In analysis of variance for Pb(II) adsorption by LAC, out of the two responses, removal efficiency and adsorption capacity, the quadratic model of the later, was found to be with significant lack of fit and for an effective model, lack of fit should be insignificant (Singh & Bhateria, 2020). However, problem with significance of the “lack of fit” was not

unusual and has been reported by Liu et al., (2022), Ghosh et al., (2020) and Taheri, (2022) to compare the removal of different types of pollutants by different processes. Noise can be a reason for the “lack of fit” but in the present work, it results from high precision of central points, existence of error in other points and negative predicted adsorption capacity (Taheri, 2022).

The equations of the quadratic model for Pb(II) removal efficiency of LAC, in coded form, is in equation 5.5 whereas equation 5.6 is for adsorption capacity of LAC to adsorb Pb(II) from aqueous medium.

Removal Efficiency

Equation 5.5

$$\begin{aligned} &= +92.79 + 10.15A - 9.71B + 3.87C + 9.44AB \\ &- 0.4954AC + 0.4851BC - 7.85A^2 - 2.62B^2 \\ &- 2.07C^2 \end{aligned}$$

Adsorption Capacity

Equation 5.6

$$\begin{aligned} &= +68.06 - 35.46A + 39.62B + 5.08C \\ &- 12.03AB - 5.28AC + 5.72BC + 16.66A^2 \\ &- 9.85B^2 - 5.31C^2 \end{aligned}$$

It is evident from equation 5.5 that in Pb(II) adsorption by LAC, adsorbent dosage and contact time had a favorable effect on removal efficiency, while initial concentration had an opposite effect. Equation 5.6 depicts that the initial concentration and contact time had positive effect on adsorption capacity however it declined with the increase in the adsorbent dosage.

Three-dimensional response surfaces plotted in Figure 5.3 depict that optimum conditions of different factors for both Pb(II) removal efficiency and adsorption capacity by LAC. The red area/point on the plots shows the highest removal of Pb(II) ion on certain conditions. It is shown in Figure 5.3 (a) that the combined effect of adsorbent dosage and initial concentration on Pb(II) removal efficiency at 120 min contact time. Figure 5.3 (b) shows the combined effect of adsorbent dosage and contact time on Pb(II) removal efficiency at 175 ppm initial concentration. Figure 5.3 (c) shows the combined effect of initial concentration and contact time on Pb(II) removal at 2.5 gL^{-1} adsorbent dosage. Figure 5.3 (d) shows the combined effect of adsorbent dosage and initial concentration on Pb(II) adsorption capacity of LAC at 120 min contact time. Figure 5.3 (e) shows the combined effect of adsorbent dosage and initial concentration on Pb(II) adsorption capacity of LAC, at 175 ppm initial concentration. Figure 5.3 (f) shows the combined effect of initial concentration and contact time on Pb(II) adsorption capacity of LAC at 2.5 gL^{-1} adsorbent dosage.

According to CCD optimisation analysis, for LAC in Pb(II) adsorption, the optimum factors were 2.340 gL^{-1} adsorbent dosage, 56.18 ppm initial concentration and 137 min contact time for optimum Pb(II) removal of 98.58% along with 23.67 mgg^{-1} adsorption capacity. For optimum adsorption capacity of 184.93 mgg^{-1} , adsorbent dosage 1.0 gL^{-1} , initial concentration 297 ppm and contact time 178 min were suggested as optimum parameters and removal with these parameters was found to be 62.27%.

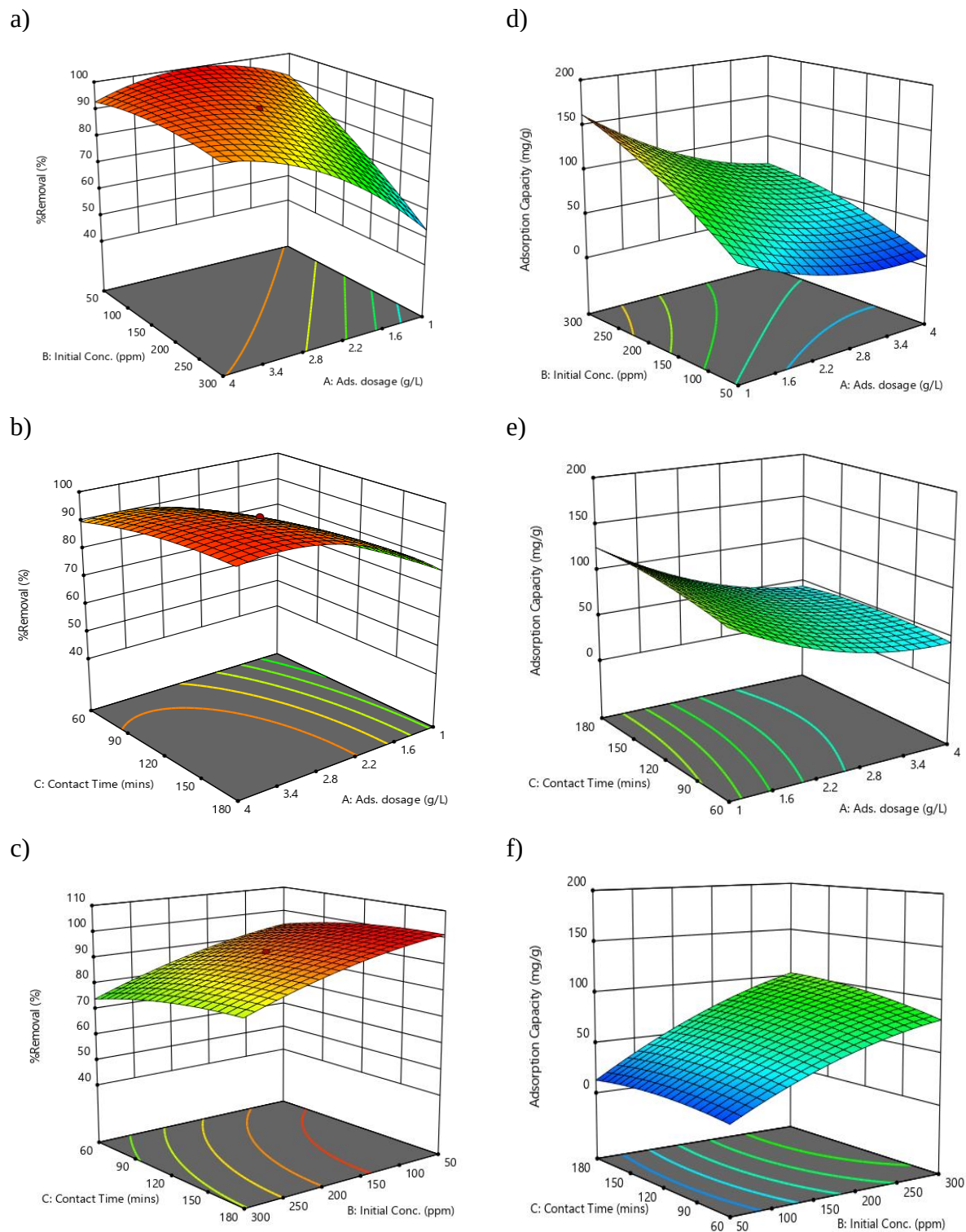


Figure 5.3: Response surface graphs illustrating the interlinked effect of adsorbent dosage, initial concentration and contact time on Pb(II) removal efficiency and adsorption capacity of LAC

5.3.2.2 Pb(II) ions adsorption by TAC

The correlation between the operational factors for the adsorption efficiency of TAC in terms of Pb(II) removal efficiency and adsorption capacity from aqueous medium was studied using a central composite design with seventeen experimental runs. For the prescribed experimental conditions, Pb(II) removal efficiency by TAC varied from 73.09% to 95.05% and adsorption capacity varied from 3.60 mgg⁻¹ to 223.79 mgg⁻¹ as demonstrated in Table 5.15.

Maximum Pb(II) removal efficiency by TAC was found to be 95.05% in run 1 with 4 gL⁻¹ adsorbent dosage, 300 ppm initial concentration and 180 min contact time while minimum Pb(II) removal 73.09% in run 11 was with 1 gL⁻¹ adsorbent dosage, 50 ppm initial concentration and 60 min contact time. It indicates that maximum Pb(II) removal was expressed with maximum level adsorbent dose (4 gL⁻¹), maximum initial concentration (10 ppm) and maximum contact time (180 min), whereas minimum Pb(II) removal was expressed with minimum adsorbent dosage, minimum initial concentration and shortest contact time. Aside from run 1, which had the highest removal efficiency, five other runs had removal efficiency of more than 90%, including runs 2, 3, 9, 14, 16, while seven run including 6, 7, 8, 10, 12, 13, 17 had removal rate of more than 80%.

Table 5.15: Experimental and predicted results for Pb(II) adsorption by TAC

Run	Std.	Factor			Removal Efficiency		Ads. Capacity	
		A	B	C	Actual	Predicted	Actual	Predicted
1	8	4	300	180	95.05	95.31	71.28	64.09
2	11	2.5	10	120	90.11	88.71	3.60	-16.49
3	10	4.5	175	120	94.25	93.80	36.87	44.60

Table 5.15 continued

4	3	1	300	60	74.60	73.79	223.79	224.43
5	13	2.5	175	40	76.34	77.49	53.44	49.42
6	12	2.5	340	120	89.27	89.80	121.41	136.71
7	17	2.5	175	120	85.30	86.62	59.71	60.32
8	5	1	50	180	83.97	84.86	41.98	53.19
9	4	4	300	60	90.05	89.54	60.04	50.92
10	15	2.5	175	120	86.05	86.62	54.21	60.32
11	1	1	50	60	73.09	73.21	36.55	45.82
12	2	4	50	60	88.56	88.41	11.07	16.68
13	7	1	300	180	84.86	85.39	254.59	251.07
14	6	4	50	180	93.05	94.24	9.13	10.58
15	9	0.5	175	120	77.46	77.05	201.10	188.68
16	14	2.5	175	200	91.12	89.11	63.78	63.11
17	16	2.5	175	120	87.45	86.62	61.22	60.32

All of these run had maximum adsorbent dosage at different initial concentration and varied contact time. This means that raising the adsorbent dosage increased the number of functional groups and active adsorption sites accessible due to increased surface area available as the adsorbent dosage increased (Makshut et al., 2020).

According to Table 5.15, the highest adsorption capacity of TAC for Pb(II) ions was 254.59 mgg^{-1} by run 13 with 1 gL^{-1} adsorbent dosage, 300 ppm initial concentration and 180 min contact time. Whereas run 4 and 15 showed adsorption capacities of 223.79 and 201.10 mgg^{-1} respectively. Both run 4 and 13 had adsorption capacity greater than hundred 200 mgg^{-1} with 300 ppm initial concentration , 1 gL^{-1} adsorbent dosage and varied contact time. While run 15, showed 201.10 mgg^{-1} at 0.5 gL^{-1} adsorbent dosage, 175 ppm and 120 min contact time. Run 2, 14 and 12 demonstrated reduced adsorption capacities of 3.98, 9.13 and

11.07 mgg⁻¹ with 10-50 ppm initial concentration s at varied contact time and adsorbent dosage.

The adsorption capacity of TAC increased as the initial concentration of Pb(II) increased due to a rise in the mass transfer driving force and for this reason, the cross over rate of Pb(II) from the bulk solution to the particle surface while removal efficiency decreased due to lack of available sites required (Taşar & Özer, 2020). TAC achieved near-highest adsorption capacity from 175 ppm Pb(II) ions concentration at 0.5 gL⁻¹ adsorbent dosage, however findings revealed a reduction in adsorption capacity at the same initial concentration of Pb(II) with varied adsorbent dosage up to 4.5 gL⁻¹. This might be attributed to saturation at this adsorbent dosage and increasing the adsorbent dosage decreased adsorption capacity due to a higher adsorbent-to-Pb(II) ratio (Biswas et al., 2019).

Table 5.16 shows the model fitness summary as calculated by the Design Expert software based on the adsorption experiments. Results showed that adsorption of Pb(II) by LAC can be expressed by quadratic model (p-value ≤ 0.05), also the values of predicted R-squared were closer to one with respect to other models.

Table 5.16: Model fitness sumamry for both the responses in Pb(II) adsorption by TAC

Response	Model Fitness Summary					Remarks
	Source	Sequential p-value	Lack of Fit p- value	Adjusted R ²	Predicted R ²	
Removal	Linear	< 0.0001	0.1735	0.8845	0.8345	
Efficiency	2FI	0.4026	0.1684	0.8865	0.8235	

Table 5.16 continued

	Quadratic	0.0208	0.3683	0.9565	0.8718	Suggested
	Cubic	0.3258	0.3474	0.9703	-0.0765	Aliased
	Linear	< 0.0001	0.0081	0.7504	0.6115	
Adsorption	2FI	0.0290	0.0139	0.8632	0.7766	
Capacity	Quadratic	0.0041	0.0515	0.9674	0.8893	Suggested
	Cubic	0.0372	0.1856	0.9953	0.7344	Aliased

According to analysis of variance, the F-value of the model for Pb(II) removal efficiency by TAC was 40.07, as described in Table 5.17, indicating that the quadratic model was significant with only a 0.01% probability that such large F-value could occur due to noise. Values of “Prob > F” less than 0.0500 indicated that the A, C, AC, B², C² were significant model terms whereas other factors with Prob > F” values greater than 0.1000 were insignificant while the F-value was 1.98 and “Prob > F” for “lack of fit” was 0.3683, indicating that lack of fit was insignificant and there was a 36.83% chance that F- value could occur due to noise.

Table 5.17: ANOVA results for Pb(II) removal efficiency of TAC

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	733.03	9	81.45	40.07	< 0.0001	significant
A-Ads. Dosage	455.88	1	455.88	224.28	< 0.0001	
B-Initial Conc.	1.98	1	1.98	0.9760	0.3561	
C-Contact Time	219.28	1	219.28	107.88	< 0.0001	

Table 5.17 continued

AB	0.1446	1	0.1446	0.0711	0.7974	
AC	16.97	1	16.97	8.35	0.0233	
BC	0.0013	1	0.0013	0.0006	0.9806	
A ²	2.93	1	2.93	1.44	0.2688	
B ²	14.40	1	14.40	7.08	0.0324	
C ²	22.50	1	22.50	11.07	0.0126	
Residual	14.23	7	2.03			
Lack of Fit	11.84	5	2.37	1.98	0.3683	not significant
Pure Error	2.39	2	1.19			
Cor Total	747.25	16				

The F-value of the model was determined to be 53.80 for the second response, adsorption ability of TAC to adsorb Pb(II) from aqueous medium, as shown in Table 5.18 implying the model was significant with only a 0.01% chance that such a big F-value could arise due to noise. Values of "Prob > F" less than 0.0500 suggested that the A, B, AB and A² were significant model variables, whilst other components with Prob > F" values larger than 0.1000 were inconsequential. The F-value for "lack of fit" of the mode was 18.73 and "Prob > F" was 0.0515, indicating that lack of fit was not significant and that there were only 5.15% odds that this lack of fit might arise due to noise.

Table 5.18: ANOVA results for adsorption capacity of Pb(II) by TAC

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	89910.57	9	9990.06	53.80	< 0.0001	significant
A-Ads. dosage	33733.21	1	33733.21	181.67	< 0.0001	
Table 5.1	38675.44	1	38675.44	208.29	< 0.0001	
C-Contact Time	304.76	1	304.76	1.64	0.2410	
AB	10420.64	1	10420.64	56.12	0.0001	
AC	90.66	1	90.66	0.4882	0.5073	
BC	185.79	1	185.79	1.00	0.3505	
A ²	6479.70	1	6479.70	34.90	0.0006	
B ²	0.0931	1	0.0931	0.0005	0.9828	
C ²	33.66	1	33.66	0.1813	0.6830	
Residual	1299.76	7	185.68			
Lack of Fit	1272.58	5	254.52	18.73	0.0515	not significant
Pure Error	27.18	2	13.59			
Cor Total	91210.33	16				

The quadratic model equation for Pb(II) removal efficiency of TAC are in coded form in equation 5.7 and the adsorption capacity of TAC to adsorb Pb(II) from aqueous medium is in equation 5.8.

Removal Efficiency

Equation 5.7

$$\begin{aligned} &= +86.62 + 6.28A + 0.4156B + 4.36C \\ &+ 0.1344AB - 1.46AC - 0.0127BC - 0.6738A^2 \\ &+ 1.51B^2 - 1.87C^2 \end{aligned}$$

Adsorption Capacity

Equation 5.8

$$\begin{aligned} &= +60.32 - 54.03A + 58.03B + 5.14C \\ &- 36.09AB - 3.37AC + 4.82BC + 31.68A^2 \\ &- 0.1216B^2 - 2.28C^2 \end{aligned}$$

According to equation 5.7 that in Pb(II) adsorption by TAC, adsorbent dosage, initial concentration and contact time had a favorable effect on removal efficiency. According to equation 5.8, the initial concentration and contact time had a beneficial influence on adsorption capacity, but it decreased as the adsorbent dosage increased.

Three-dimensional response surfaces plotted in Figure 5.4 depict the optimum conditions of different factors for both Pb(II) removal efficiency and adsorption capacity by TAC. The red area/point on the plots shows the highest removal efficiency of Pb(II) ion on certain conditions. Figure 5.4 (a) shows the combined effect of adsorbent dosage and initial concentration on Pb(II) removal at 120 min contact time. Figure 5.4 (b) shows the combined effect of adsorbent dosage and contact time on Pb(II) removal at 175 ppm initial concentration. Figure 5.4 (c) shows the combined effect of initial concentration and contact time on Pb(II) removal at 2.5 gL⁻¹ adsorbent dosage. Figure 5.4 (d) shows the combined effect of adsorbent dosage and initial concentration on Pb(II) adsorption capacity of TAC at 120 min contact time. Figure 5.4 (e) shows the combined effect of adsorbent dosage and initial concentration on Pb(II) adsorption capacity of TAC, at 175 ppm initial concentration.

Figure 5.4 (f) shows the combined effect of initial concentration and contact time on Pb(II) adsorption capacity of TAC at 2.5 gL^{-1} adsorbent dosage.

According to CCD optimisation analysis, the optimum conditions for maximum Pb(II) removal of 94.33% along with 12.15 mgg^{-1} adsorption capacity by TAC were 4 gL^{-1} adsorbent dosage, 50 ppm initial concentration and 168 min contact time. For maximum adsorption capacity of 152.29 mgg^{-1} , 1.0 gL^{-1} adsorbent dosage, 300 ppm initial concentration and 180 min contact time were found to be the optimum parameters.

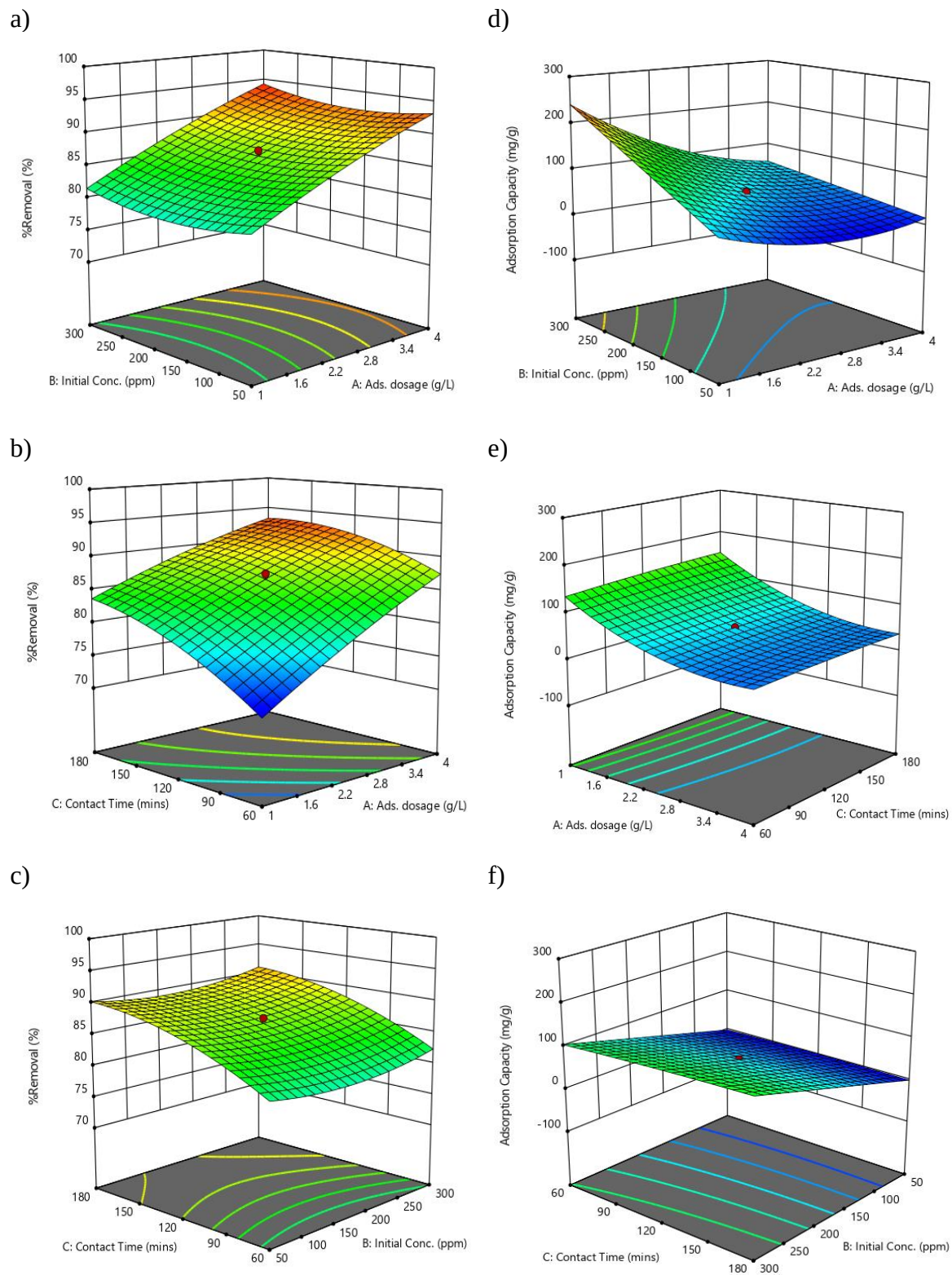


Figure 5.4: 3D response surface graphs illustrating the interlinked effect of adsorbent dosage, initial concentration and contact time on Pb(II) removal efficiency and adsorption capacity of TAC

5.3.3 Ni(II) ions adsorption by LAC and TAC

5.3.3.1 Ni(II) ions adsorption by LAC

The correlation between the operational factors for the adsorption efficiency of LAC in terms of Ni(II) removal efficiency and adsorption capacity from aqueous medium was studied using a central composite design with seventeen experimental runs. For the prescribed experimental conditions as demonstrated in Table 5.1, Ni(II) removal by LAC varied from 30.66% to 88.18% and adsorption capacity varied from 3.53 mgg^{-1} to 160.67 mgg^{-1} .

Maximum Ni(II) removal by LAC was found 88.18% in run 2 with 2.5 gL^{-1} adsorbent dosage, 10 ppm initial concentration and 120 min contact time while minimum Ni(II) removal 30.66% in run 4 was with 1 gL^{-1} adsorbent dosage, 300 ppm initial concentration and 60 min contact time. It indicates that maximum Ni(II) removal was expressed with medium level adsorbent dose (2.5 gL^{-1}), lowest initial concentration (10 ppm), and medium contact time (120 min), whereas minimum Pb(II) removal was expressed with minimum adsorbent dosage, highest initial concentration and shortest contact time. Along with run 2, nine other runs had removal efficiency of more over 70%, including runs 1, 3, 7, 8, 10, 12, 14, 16 and 17. With different adsorbent dosage, run 8, 12 and 14 showed high removal efficiency with initial concentration of 50 ppm and contact time 180 min while as a second category, run 3, 7, 10, 16, 17 showed high removal efficiency at 175 ppm initial concentration and 120 min contact time however run 1 with 300 ppm, 180 min showed above 70% Ni(II) ions removal from aqueous medium.

Table 5.19: Experimental and predicted results for Ni(II) adsorption by LAC

Run	Std.	Factor	Factor	Factor	Removal Efficiency		Ads. Capacity	
		A	B	C	Actual	Predicted	Actual	Predicted
1	8	4	300	180	78.51	77.15	55.88	56.16
2	11	2.5	10	120	88.18	89.34	3.53	0.6852
3	10	4.5	175	120	85.01	84.28	38.06	41.62
4	3	1	300	60	30.66	31.29	99.97	105.99
5	13	2.5	175	40	59.82	56.09	31.88	26.82
6	12	2.5	340	120	67.36	65.00	86.61	86.42
7	17	2.5	175	120	71.88	75.33	50.32	53.62
8	5	1	50	180	84.24	81.62	46.12	50.63
9	4	4	300	60	67.79	70.93	37.85	34.65
10	15	2.5	175	120	75.52	75.33	52.86	53.62
11	1	1	50	60	55.91	57.80	27.96	29.00
12	2	4	50	60	81.15	80.72	9.14	12.68
13	7	1	300	180	53.59	54.54	160.77	158.56
14	6	4	50	180	87.64	87.52	7.95	3.26
15	9	0.5	175	120	54.37	53.92	127.29	120.76
16	14	2.5	175	200	73.57	76.12	53.50	55.58
17	16	2.5	175	120	77.12	75.33	53.98	53.62

Results in Table 5.19 depict that for Ni(II) ions, maximum adsorption capacity of LAC was 160.77 mgg^{-1} by run 13 with 1 gL^{-1} adsorbent dosage, 300 ppm initial concentration and 180 min contact time. Followed by this high adsorption capacity, runs 15, 4 and 6 also exhibited high adsorption capacity of 120.76 mgg^{-1} , 105.99 mgg^{-1} and 86.42 mgg^{-1} respectively. Out of these four with high adsorption capacity, run 13, 4 and 6 had an initial concentration of 300-340 ppm and only run 15 have initial concentration of 175 ppm, 0.5 gL^{-1} adsorbent dosage and 120 min contact time. The lowest adsorption capacity of 3.53

mgg⁻¹ with at 2.5 gL⁻¹ adsorbent dosage, 10 ppm initial concentration and 120 min contact time in run 2 and two other runs, 14 and 12, expressed lower adsorption capacity of 7.95 mgg⁻¹ and 9.14 mgg⁻¹ respectively, at an initial concentration of 50 ppm.

Capacity of LAC increased to adsorb Ni(II) ions as the initial concentration increased, while removal efficiency decreased. This might be because the initial concentration is the driving for the adsorption capacity and as it increases, adsorption capacity increases while removal efficiency decreases owing to the unavailability of unoccupied binding sites (Choudhary et al., 2020). From 175 ppm initial concentration, LAC obtained near-highest adsorption capacity at 0.5 gL⁻¹ adsorbent dosage, while adsorption capacity declined with 4.5 gL⁻¹ adsorbent dosage. This might be because saturation was attained at this adsorbent dosage and increasing the adsorbent dosage reduced adsorption capacity due to a greater adsorbent to available metal ions ratio (Anitha et al., 2020).

Table 5.20 shows the model fitness summary as calculated by the Design Expert software based on the adsorption experiments. Results showed that adsorption of Ni(II) by LAC can be expressed by quadratic model (p-value ≤ 0.05), also the values of predicted R-squared were closer to one with respect to other models.

Table 5.20: Model fitness sumamry for both the responses in Ni(II) adsorption by LAC

Response	Model Fitness Summary					Remarks
	Source	Sequential p-value	Lack of Fit value	Adjusted p- R ²	Predicted R ²	
Removal Efficiency	Linear	< 0.0001	0.1228	0.7981	0.6929	

Table 5.20 continued

	2FI	0.0888	0.1644	0.8593	0.6717	
	Quadratic	0.0081	0.4560	0.9592	0.8623	Suggested
	Cubic	0.2887	0.5660	0.9746	0.5883	Aliased
	Linear	< 0.0001	0.0082	0.7952	0.6829	
Adsorption	2FI	0.0511	0.0126	0.8734	0.8397	
Capacity	Quadratic	0.0006	0.0812	0.9829	0.9270	Suggested
	Cubic	0.1130	0.1330	0.9946	0.6584	Aliased

According to analysis of variance, Ni(II) removal efficiency of LAC, F-value of the model was found to be 42.77 as described in Table 5.21 expressing that the quadratic model was significant with only a 0.01% chance that such large F-value could occur due to noise. Values of “Prob > F” less than 0.0500 indicated that the A, B, C, AB, AC, A², C² were significant model terms while other factors which had Prob > F” values greater than 0.1000 were insignificant while the F-value was 1.45 and “Prob > F” for “lack of fit” was 0.4560, indicating that lack of fit was insignificant with 45.60% chance that F- value could occur due to noise.

Table 5.21: ANOVA results for adsorption capacity of Ni(II) by LAC

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	3672.23	9	408.03	42.77	< 0.0001	significant
A-Ads. Dosage	1497.58	1	1497.58	156.97	< 0.0001	
B-Initial Conc.	975.96	1	975.96	102.30	< 0.0001	

Table 5.21 continued

C-Contact Time	652.01	1	652.01	68.34	< 0.0001	
AB	139.62	1	139.62	14.63	0.0065	
AC	144.96	1	144.96	15.19	0.0059	
BC	0.1699	1	0.1699	0.0178	0.8976	
A ²	79.19	1	79.19	8.30	0.0236	
B ²	7.05	1	7.05	0.7391	0.4184	
C ²	173.60	1	173.60	18.20	0.0037	
Residual	66.78	7	9.54			
Lack of Fit	52.35	5	10.47	1.45	0.4560	not significant
Pure Error	14.44	2	7.22			
Cor Total	3739.01	16				

For adsorption capacity of LAC to adsorb Ni(II) from aqueous medium, the F-value of the model was found to be 103.12 as described in Table 5.22 which implied the model was significant with only a 0.01% chance that such large F-value could occur due to noise. Values of “Prob > F” less than 0.0500 indicated that the A, B, C, AB, AC, BC, A², B², C² were significant model terms. For “lack of fit” of the mode, the F-value was 11.60 and “Prob > F” was 0.0812 respectively, indicated that lack of fit was insignificant with only 8.12% chances that this lack of fit could occur due to noise.

Table 5.22: ANOVA results for adsorption capacity of Ni(II) by LAC

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	28140.34	9	3126.70	103.12	< 0.0001	significant
A-Ads. Dosage	10179.02	1	10179.02	335.71	< 0.0001	
B-Initial Conc.	12111.94	1	12111.94	399.45	< 0.0001	
C-Contact Time	1344.47	1	1344.47	44.34	0.0003	
AB	1513.58	1	1513.58	49.92	0.0002	
AC	482.22	1	482.22	15.90	0.0053	
BC	478.34	1	478.34	15.78	0.0054	
A ²	1553.10	1	1553.10	51.22	0.0002	
B ²	210.32	1	210.32	6.94	0.0337	
C ²	314.91	1	314.91	10.39	0.0146	
Residual	212.25	7	30.32			
Lack of Fit	205.17	5	41.03	11.60	0.0812	not significant
Pure Error	7.07	2	3.54			
Cor Total	28352.59	16				

The equations of the quadratic model for Ni(II) removal efficiency by LAC, in coded form, is in equation 5.9 whereas equation 5.10 is for adsorption capacity of LAC to adsorb Ni(II) from aqueous medium.

Removal Efficiency

Equation 5.9

$$\begin{aligned} &= +75.33 + 11.38A - 9.22B + 7.51C + 4.18AB \\ &- 4.26AC - 0.1457BC - 3.50A^2 + 1.06B^2 \\ &- 5.19C^2 \end{aligned}$$

Adsorption Capacity

Equation 5.10

$$\begin{aligned} &= +53.62 - 29.68A + 32.47B + 10.79C \\ &- 13.75AB - 7.76AC + 7.73BC + 15.51A^2 \\ &- 5.78B^2 - 6.98C^2 \end{aligned}$$

It is evident from equation 5.9 that in Ni(II) adsorption by LAC, adsorbent dosage and contact time had positive impact while initial concentration had negative impact on removal efficiency. According to equation 5.10, both the initial concentration and contact time had positive effect on adsorption capacity while adsorbent dosage had negative impact.

Three-dimensional response surfaces plotted in Figure 5.5 depict the optimum conditions of different factors for both Ni(II) removal efficiency and adsorption capacity by LAC. The red area/point on the plots shows the highest removal of Ni(II) ion on certain conditions. Figure 5.5 (a) shows the combined effect of adsorbent dosage and initial concentration on Ni(II) removal efficiency at 120 min contact time. Figure 5.5 (b) shows the combined effect of adsorbent dosage and contact time on Ni(II) removal efficiency at 175 ppm initial concentration. Figure 5.5 (c) shows the combined effect of initial concentration and contact time on Ni(II) removal efficiency at 2.5 gL⁻¹ adsorbent dosage. Figure 5.5 (d) shows the combined effect of adsorbent dosage and initial concentration on Ni(II) adsorption capacity of LAC at 120 min contact time. Figure 5.5 (e) shows the combined effect of

adsorbent dosage and contact time on Ni(II) adsorption capacity of LAC, at 175 ppm initial concentration Figure 5.5 (f) shows the combined effect of initial concentration and contact time on Ni(II) adsorption capacity of LAC at 2.5 gL⁻¹ adsorbent dosage.

According to CCD optimisation analysis, the optimum conditions for LAC were found to be 3.903 gL⁻¹ adsorbent dosage, 55.984 ppm initial concentration and 157.921 min contact time which gave optimum Ni(II) removal of 89.174% along with 10.303 mgg⁻¹ adsorption capacity. For maximum adsorption capacity of 158.558 mgg⁻¹ along with 54.540% removal efficiency was achieved at 1.0 gL⁻¹ adsorbent dosage, 300 ppm initial concentration and 180 min contact time.

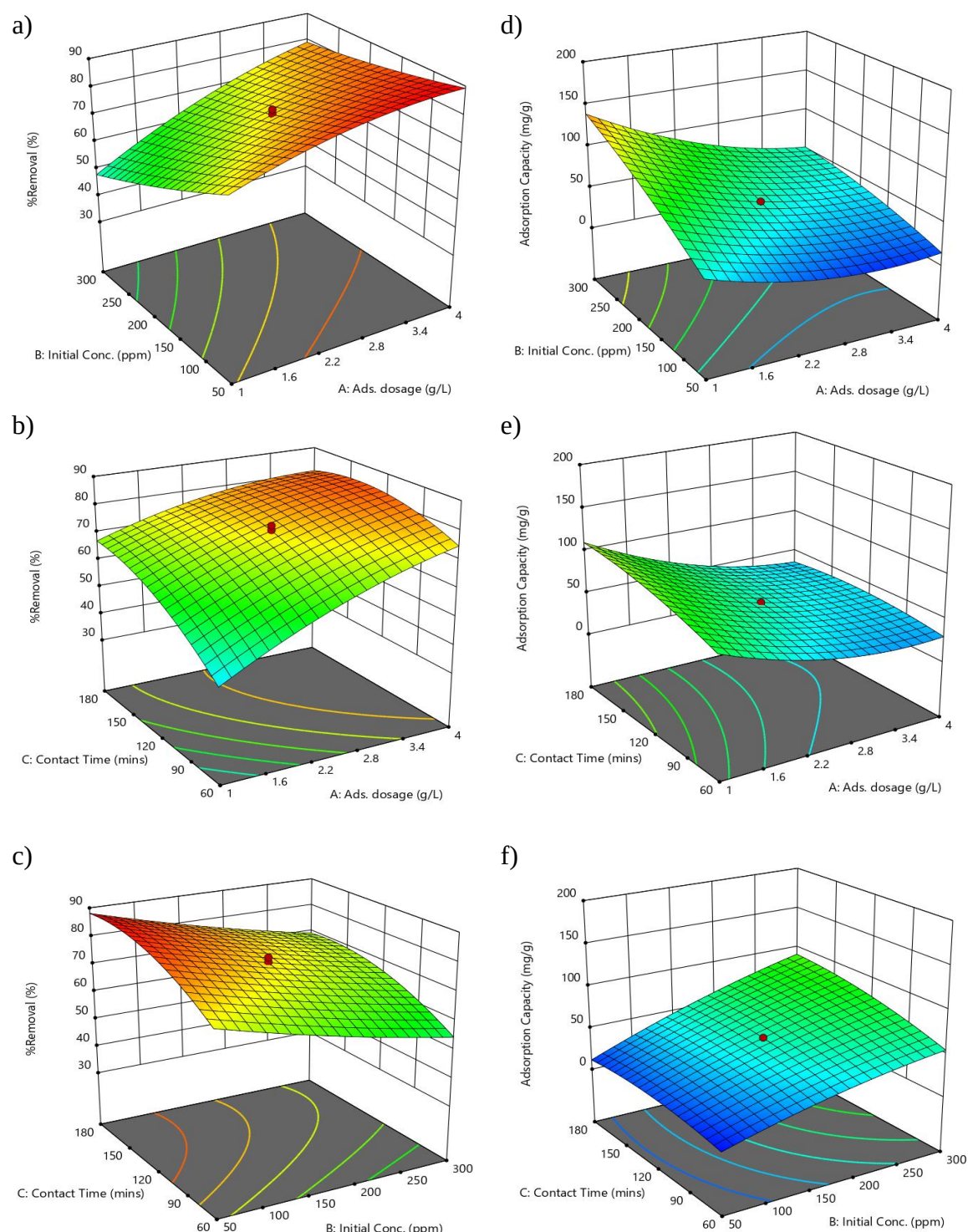


Figure 5.5: 3D response surface graphs illustrating the interlinked effect of adsorbent dosage, initial concentration and contact time on Ni(II) removal efficiency and adsorption capacity of LAC

5.3.3.2 Ni(II) ions adsorption by TAC

The correlation between the operational factors for the adsorption efficiency of TAC in terms of Ni(II) removal efficiency and adsorption capacity from aqueous medium was studied using a central composite design with seventeen experimental runs. For the prescribed experimental conditions, Ni(II) removal efficiency by TAC varied from 39.07% to 97.53% and adsorption capacity varied from 2.45 mgg⁻¹ to 232.16 mgg⁻¹ as demonstrated in Table 5.23.

Maximum Ni(II) removal efficiency by TAC was found 97.53% in run 16 with 2.5 gL⁻¹ adsorbent dosage, 175 ppm initial concentration and 200 min contact time while minimum Ni(II) removal 39.07% in run 12 was with 4 gL⁻¹ adsorbent dosage, 50 ppm initial concentration and 60 min contact time. It indicates that maximum Ni(II) removal was expressed with medium level adsorbent dose (2.5 gL⁻¹), medium level initial concentration (175 ppm) and maximum applicable contact time (200 min), whereas minimum Ni(II) removal was expressed with maximum adsorbent dosage, lower initial concentration and shortest contact time. Along with run 16, five other runs had above 90% removal rate including runs 1, 3, 7, 10 and 17 while four runs 6, 8, 14 and 15 had above 80% removal efficiency. Majority of runs with above 80% removal efficiency, had adsorbent dosage 2.5-4 gL⁻¹, initial concentration 175-300 ppm and contact time 120-180 min. while as a second category, run 8 and 14 showed high removal efficiency at 50 ppm initial concentration, adsorbent dosage 1 gL⁻¹ and 4 gL⁻¹ respectively and for extended contact time of 180 min. Previous research reported that increasing adsorbent dosage and contact time increased Ni(II) removal rate, which could be attributed to available sites (Anitha et al., 2020) and a

rise in removal rate over time suggested that physisorption, in addition to chemisorption, was involved at an earlier stage as a rapid step (Guo et al., 2020).

Table 5.23: Experimental and predicted results for Ni(II) adsorption by TAC

Run	Std.	Factor	Factor	Factor	Removal Efficiency		Ads. Capacity	
		A	B	C	Actual	Predicted	Actual	Predicted
1	8	4	300	180	93.66	95.33	70.24	60.35
2	11	2.5	10	120	61.35	65.10	2.45	-17.20
3	10	4.5	175	120	91.02	89.62	35.75	53.53
4	3	1	300	60	63.51	63.67	190.54	196.63
5	13	2.5	175	40	58.43	59.30	40.90	34.71
6	12	2.5	340	120	81.86	79.62	111.33	119.64
7	17	2.5	175	120	94.20	93.23	65.94	68.06
8	5	1	50	180	85.77	84.04	42.89	57.78
9	4	4	300	60	66.50	67.58	42.38	32.42
10	15	2.5	175	120	95.66	93.23	60.27	68.06
11	1	1	50	60	55.89	53.56	27.94	42.77
12	2	4	50	60	39.07	38.67	4.88	4.64
13	7	1	300	180	77.39	77.13	232.16	237.34
14	6	4	50	180	84.26	83.45	8.03	6.88
15	9	0.5	175	120	84.52	87.40	225.83	196.94
16	14	2.5	175	200	97.53	98.13	68.27	63.34
17	16	2.5	175	120	91.67	93.23	64.17	68.06

Table 5.23 shows that the maximum adsorption capacity of TAC for Ni(II) ions was 232.16 mgg⁻¹ by run 13 with 1 gL⁻¹ adsorbent dosage, 300 ppm initial concentration and 180 min contact time. Following this high adsorption capacity, runs 15, 4 and 6 had high adsorption capacities 225.83 mgg⁻¹, 190.54 mgg⁻¹ and 111.33 mgg⁻¹ respectively. Run 13, 4 and 6 had an initial concentration of 300-340 ppm whereas only run 15 had an initial

concentration of 175 ppm, 0.5 gL⁻¹ adsorbent dosage and 120 min contact time. At the other end, run 2 had the lowest adsorption capacity of 3.53 mgg⁻¹ with 2.5 gL⁻¹ adsorbent dosage, 10 ppm initial concentration and 120 min contact time, whereas runs, 12 and 14 had lower adsorption capacity of 4.88 mgg⁻¹ and 8.03 mgg⁻¹ respectively, with 50 ppm initial concentration.

Capacity of TAC increased to adsorb Ni(II) ions as the initial concentration increased, while removal efficiency decreased. This might be because the initial concentration is the driving for the adsorption capacity and as it increases, adsorption capacity increases while removal efficiency decreases owing to the unavailability of unoccupied binding sites (Kucukcongar et al., 2020). From 175 ppm initial concentration, TAC obtained near-highest adsorption capacity at 0.5 gL⁻¹ adsorbent dosage, while adsorption capacity declined with 4.5 gL⁻¹ adsorbent dosage. This might be because saturation was attained at this adsorbent dosage and increasing the adsorbent dosage reduced adsorption capacity due to a greater adsorbent to available metal ions ratio (Aboli et al., 2020).

Table 5.24 shows the model fitness summary as calculated by the Design Expert software based on the adsorption experiments. Results showed that adsorption of Ni(II) by LAC can be expressed by quadratic model (p-value ≤ 0.05), also the values of predicted R-squared were closer to one with respect to other models.

Table 5.24: Model fitness sumamry for both the responses in Ni(II) adsorption by TAC

Response		Model Fitness Summary				
	Source	Sequential p-value	Lack of Fit p- value	Adjusted R ²	Predicted R ²	Remarks
Removal Efficiency	Linear	0.0070	0.0233	0.5004	0.3300	
	2FI	0.4548	0.0218	0.4941	-0.2119	
	Quadratic	< 0.0001	0.3420	0.9743	0.9233	Suggested
	Cubic	0.2705	0.3741	0.9848	0.4923	Aliased
Adsorption Capacity	Linear	0.0002	0.0050	0.7276	0.5877	
	2FI	0.1015	0.0065	0.8046	0.7341	
	Quadratic	0.0139	0.0171	0.9335	0.7773	Suggested
	Cubic	0.1071	0.0269	0.9799	-0.6086	Aliased

According to analysis of variance, for Ni(II) removal efficiency of TAC, F-value of the model was found to be 68.37 as described in Table 5.25, expressing that the quadratic model was significant with only a 0.01% chance that such large F-value could occur due to noise. Values of “Prob > F” less than 0.0500 indicated that the A, B, C, AB, AC, BC, A², B², C² were significant model terms while other factors which had Prob > F” values greater than 0.1000 were insignificant while the F-value was 2.19 and “Prob > F” for “lack of fit” was 0.3420, indicating that lack of fit was insignificant with 34.20% chance that F- value could occur due to noise.

Table 5.25: ANOVA results for adsorption capacity of Ni(II) by TAC

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4667.66	9	518.63	68.37	< 0.0001	significant
A-Ads. Dosage	7.96	1	7.96	1.05	0.3397	
B-Initial Conc.	347.21	1	347.21	45.78	0.0003	
C-Contact Time	2449.24	1	2449.24	322.90	< 0.0001	
AB	176.61	1	176.61	23.28	0.0019	
AC	102.13	1	102.13	13.46	0.0080	
BC	144.86	1	144.86	19.10	0.0033	
A ²	45.60	1	45.60	6.01	0.0440	
B ²	904.61	1	904.61	119.26	< 0.0001	
C ²	430.70	1	430.70	56.78	0.0001	
Residual	53.10	7	7.59			
Lack of Fit	44.91	5	8.98	2.19	0.3420	not significant
Pure Error	8.19	2	4.09			
Cor Total	4720.76	16				

For adsorption capacity of TAC to adsorb Ni(II) from aqueous medium, the F-value of the model was found to be 25.94 as described in Table 5.26, which implied the model was significant with only a 0.01% chance that such large F-value could occur due to noise. Values of “Prob > F” less than 0.0500 indicated that the A, B, AB, A² were significant model terms. For “lack of fit” of the mode, the F-value was 57.90 and “Prob > F” was 0.0171 respectively, indicated that lack of fit was significant with only 1.71% chances that this lack of fit could occur due to noise. Factors due to which significant lack of fit can occur for adsorption capacity has been discussed in previous chapter.

Table 5.26: ANOVA results for adsorption capacity of Ni(II) by TAC

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	81806.29	9	9089.59	25.94	0.0001	Significant
A-Ads. dosage	33420.11	1	33420.11	95.37	< 0.0001	
B-Initial Conc.	30855.76	1	30855.76	88.05	< 0.0001	
C-Contact Time	1332.13	1	1332.13	3.80	0.0922	
AB	7948.67	1	7948.67	22.68	0.0021	
AC	81.58	1	81.58	0.2328	0.6442	
BC	330.20	1	330.20	0.9423	0.3640	
A ²	6678.32	1	6678.32	19.06	0.0033	
B ²	588.35	1	588.35	1.68	0.2362	
C ²	740.03	1	740.03	2.11	0.1895	
Residual	2453.04	7	350.43			
Lack of Fit	2436.20	5	487.24	57.90	0.0171	significant
Pure Error	16.83	2	8.42			
Cor Total	84259.32	16				

The equations of the quadratic model for Ni(II) removal efficiency of TAC, in coded form, is in equation 5.11 whereas equation 5.12 is for adsorption capacity of TAC to adsorb Ni(II) from aqueous medium.

Removal Efficiency

Equation 5.11

$$\begin{aligned} &= +93.23 + 0.8299A - 5.50B + 14.56C \\ &+ 4.70AB + 3.57AC - 4.26BC - 2.66A^2 \\ &- 11.98B^2 - 8.17C^2 \end{aligned}$$

Adsorption Capacity

Equation 5.12

$$\begin{aligned} &= +68.06 - 53.78A + 51.83B + 10.74C \\ &- 31.52AB - 3.19AC + 6.42BC + 32.16A^2 \\ &- 9.66B^2 - 10.71C^2 \end{aligned}$$

It is evident from equation 5.11 that in Ni(II) adsorption by TAC, adsorbent dosage and contact time had positive impact while initial concentration had negative impact on removal efficiency. According to equation 5.12, both the initial concentration and contact time had positive effect on adsorption capacity while adsorbent dosage had negative impact.

Figure 5.6 depicts the optimum conditions of different factors for both Ni(II) removal efficiency and adsorption capacity by TAC using Three-dimensional response surfaces. The red area/point on the plots shows the highest removal efficiency of Ni(II) ion in certain conditions. Figure 5.6 (a) shows the combined effect of adsorbent dosage and initial concentration on Ni(II) removal at 120 min contact time. Figure 5.6 (b) shows the combined effect of adsorbent dosage and contact time on Ni(II) removal at 175 ppm initial concentration. Figure 5.6 (c) shows the combined effect of initial concentration and contact time on Ni(II) removal at 2.5 gL⁻¹ adsorbent dosage. Figure 5.6 (d) shows the combined effect of adsorbent dosage and initial concentration on Ni(II) adsorption capacity of TAC at 120 min contact time. Figure 5.6 (e) shows the combined effect of adsorbent dosage and

initial concentration on Ni(II) adsorption capacity of TAC, at 175 ppm initial concentration. Figure 5.6 (f) shows the combined effect of initial concentration and contact time on Ni(II) adsorption capacity of TAC at 2.5 gL⁻¹ adsorbent dosage.

According to CCD optimisation analysis, the optimum conditions of 1.834 gL⁻¹ adsorbent dosage, 55.600 ppm initial concentration and 179.893 min contact time for maximum Ni(II) removal of 80.94% along with 15.133 mgg⁻¹ adsorption capacity. The maximum adsorption capacity of 226.855 mgg⁻¹ and removal efficiency of 71.742% was achieved at 1.0 gL⁻¹ adsorbent dosage, 300 ppm initial concentration and 150.335 min contact time, as optimum parameters.

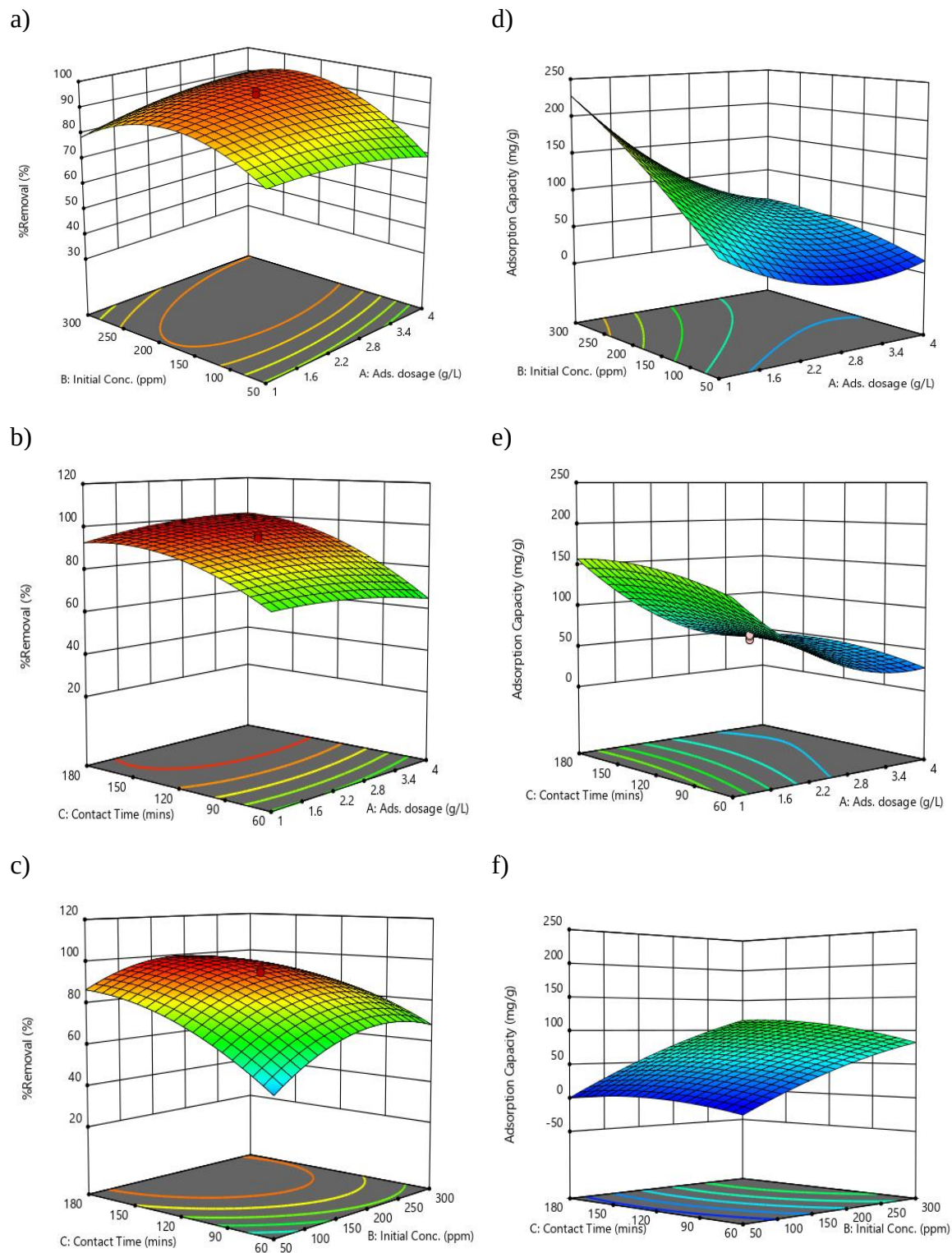


Figure 5.6: 3D response surface graphs illustrating the interlinked effect of adsorbent dosage, initial concentration and contact time on Ni(II) removal efficiency and adsorption capacity of TAC

5.4 Conclusion

Adsorption of Cu(II), Pb(II) and Ni(II) by LAC and TAC was optimised using RSM-CCD, and it was found that adsorbent dosage, initial metal concentration, and contact time all had a significant influence on the adsorption process. The quadratic model well described the heavy metals adsorption process, as predicted and actual coefficient of correlation were found close to each other. The optimised adsorption efficiency of *Melia azedarach* leaves activated carbon for Cu(II), Pb(II), and Ni(II) removal was 98.63%, 99.52% and 88.18%, respectively, while the optimal adsorption capacity for Cu(II), Pb(II), and Ni(II) was 192.12 mgg^{-1} , 170.94 mgg^{-1} , 160.77 mgg^{-1} , respectively. The optimum adsorption efficiency of *Melia azedarach* twigs activated carbon was 99.66%, 95.05% and 97.53% for Cu(II), Pb(II) and Ni(II) removal respectively, while the optimum adsorption capacity for Cu(II), Pb(II), and Ni(II) was 172.32 mgg^{-1} , 254.59 mgg^{-1} and 232.16 mgg^{-1} , respectively. This study is significant as the activated carbon derived from *Melia azedarach* biomass has demonstrated the capacity to be a value-added product as an adsorbent capable of adsorbing heavy metals from aqueous medium and the optimal experimental conditions obtained from RSM-CCD can be applied on a large scale for further insight.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

Based on the overall experimental observations discussed in Chapters 3, 4 and 5, it can be concluded that *Melia azedarach* leaves and twigs are promising feedstock to produce activated carbon through molten salt synthesis. In molten salt synthesis, powdered *Melia azedarach* leaves and twigs were impregnated with 10% ZnCl₂ solution for 2 h at 85 °C, followed by overnight drying, Carbonisation at 500 °C for 2 h, crushing, washing and grinding.

The activation method increased the carbon and ash content of both LAC and TAC, according to EDX, proximate and elemental tests. Furthermore, the surface area of LAC and TAC was found to be 121.592 m²g⁻¹ 91.423 m²g⁻¹ respectively, which is significantly higher than the respective feedstock. According to N₂ adsorption-desorption isotherm, both LAC and TAC are mesoporous in nature. The FESEM analyses of LAC and TAC revealed that a considerable number of irregular pores formed during the activation process. FTIR analyses indicated the presence of several functional groups such as hydroxyl, carboxylate, carbonyl, alkyl and chloride groups on the surfaces of LAC and TAC. The bulk densities of the prepared activated carbon LAC and TAC were 0.365 cm³g⁻¹ and 0.368 cm³g⁻¹, respectively, fulfilling the American Water Works Association's minimum bulk density criteria (>0.25 cm³g⁻¹) for an activated carbon to be practically fit for use.

At constant adsorbent dosage, initial metal concentration, solution pH and temperature, increasing contact time enhanced the adsorption capacity and removal efficiency of the activated carbon LAC and TAC to remove Cu(II), Pb(II) and Ni(II) from aqueous medium. After 120 min, the trend of adsorption capacity and removal efficiency of LAC was Cu(II) > Pb(II) > Ni(II) whereas TAC was Cu(II) > Ni(II) > Pb(II). Furthermore, LAC demonstrated better adsorption performance than TAC for all three heavy metal ions, which might be attributed to the LAC's larger surface area than TAC.

To optimise the influence of adsorbent dosage, initial metal concentration and contact time on heavy metal ions adsorption, CCD in response surface approach was followed. The quadratic model was found to be elaborating the adsorption process by both LAC and TAC, as predicted and actual coefficient of correlation were found close to each other for Cu(II), Pb(II) and Ni(II) adsorption. For adsorption by LAC, The optimised conditions for Cu(II) removal were 3.2 gL⁻¹ adsorbent dosage, 54 ppm initial concentration and 140 min contact time for optimum removal of 98.52%. For Pb(II) removal, 2.3 gL⁻¹ adsorbent dosage, 56 ppm initial concentration and 137 min contact time were optimum factors for 98.58% Pb(II) removal. For Ni(II) removal, 3.903 gL⁻¹ adsorbent dosage, 56 ppm initial concentration and 158 min contact time gave optimum 89.17% removal.

Optimum adsorption capacity of TAC for Cu(II) was found to be 150.05 mgg⁻¹ at adsorbent dosage of 1 gL⁻¹, initial concentration of 300 ppm and contact time of 180 min. For optimum adsorption capacity of 184.93 mgg⁻¹ Pb(II) at 1 gL⁻¹ adsorbent dosage 297 ppm initial concentration and 178 min contact time were found to be the optimum parameters. For Ni(II), maximum adsorption capacity of 158.56 mgg⁻¹, 1 gL⁻¹ adsorbent dosage, 300 ppm initial concentration and 180 min contact time were the optimum conditions.

For adsorption by LAC, The optimised conditions for Cu(II) removal were 3.9 gL⁻¹ adsorbent dosage, 60 ppm initial concentration and 155 min contact time for optimum removal of 98.52%. For Pb(II) removal, 4 gL⁻¹ adsorbent dosage, 50 ppm initial concentration and 168 min contact time were optimum factors for 94.33% Pb(II) removal. For Ni(II) removal, 1.83 gL⁻¹ adsorbent dosage, 56 ppm initial concentration and 179.89 min contact time gave optimum 80.94% removal from aqueous medium.

Optimum adsorption capacity of TAC for Cu(II) was found to be 148.98 mgg⁻¹ at adsorbent dosage of 1 gL⁻¹, initial concentration of 300 ppm and contact time of 180 min. For optimum adsorption capacity of 152.29 mgg⁻¹ Pb(II) at 1 gL⁻¹ adsorbent dosage 300 ppm initial concentration and 180 min contact time were found to be the optimum parameters. For Ni(II), maximum adsorption capacity of 226.855 mgg⁻¹, 1 gL⁻¹ adsorbent dosage, 300 ppm initial concentration and 150 min contact time were the optimum conditions.

The Freundlich isotherm was followed by Pb(II) and Ni(II) adsorption onto LAC and TAC, whereas the Temkin isotherm was followed by Cu(II) adsorption. All heavy metal ions were absorbed by both LAC and TAC using a pseudo second order kinetic model. Desorption by using HNO₃ is shown to be the best possible technique for regenerating the spent activated carbon (LAC and TAC).

This study is significant because activated carbon derived from *Melia azedarach* biomass has demonstrated the capacity to be a value-added product as an adsorbent capable of adsorbing heavy metals from aqueous medium.

Despite the significance of this work, there are a few constraints. Adsorption behavior, including heavy metal ions removal efficiency and adsorption capacity of LAC

and TAC was determined for individual metal ions separately. As the performance of these adsorbents was not evaluated in binary and tertiary metal ions medium, this work cannot be fully applicable to such systems. Moreover, the influence of alkali and alkali-earth metal cations usually found in water on performance of LAC and TAC in the removal of Cu(II), Pb(II) and Ni(II) ions was not studied.

6.2 Recommendations

It is suggested that the adsorption performance of both activated carbons LAC and TAC prepared in this study be further evaluated for removing Cu (II), Pb (II), and Ni (II) ions from waste effluents emitted by various industrial processes. This will offer a better understanding of the performance of activated carbon as well as the adsorption mechanism, which might be impeded by other constituents in the effluents. Evaluation of both LAC and TAC as adsorbent should be evaluated in Fixed bed process. Competitive adsorption of Cu(II), Pb(II), and Ni(II) ions in binary and ternary system should also be explored in batch and fixed bed processes. The influence of dissolved organic compounds on the removal efficiency of the selected metal ions should be studied as well.

The alkali and alkali-earth metal cations of Na^+ , Ca^{++} and Mg^{++} are commonly present in water. The effect of these hard cations on the removal efficiency of the targeted metallic contaminants of Cu(II), Pb(II) and Ni(II) ions should be evaluated. It is also suggested to modify the activated carbon LAC and TAC with appropriate oxidising agents to improve the physical properties and adsorption performance, as the impact of active functional groups on the LAC and TAC's surface has been observed. Both LAC and TAC have the potential to be explored for the removal of additional heavy metal ions as well as other contaminants such as pesticides, dyes and phenolic chemicals.

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APPENDICES

Appendix A: Journal Publications

1. **Imran-Shaukat, M.**, Wahi, R., & Ngaini, Z. (2022). The Application of Agricultural Wastes for Heavy Metals Adsorption : A Meta-Analysis of Recent Studies. *Bioresource Technology Reports*, 17, 100902.
2. **Imran-Shaukat, M.**, Wahi, R., Rosli, N. R., Aziz, S. M. A., & Ngaini, Z. (2021). Chemically Modified Palm Kernel Shell Biochar for the Removal of Heavy Metals From Aqueous Solution. *IOP Conference Series: Earth and Environmental Science*, 765(1), 79–91.
3. **Imran-Shaukat, Muhammad**, binti Rosli, N. R., Wahi, R., Abdullah, S. M. A. A., & Ngaini, Z. (2021). Chemically Modified Coconut Shell Biochar for Removal of Heavy Metals from Aqueous Solution. *Defect and Diffusion Forum*, 411, 79–91.

Appendix B: Proximate Analysis Calculations

Appendix B1: Moisture Content Analysis

Sample	Trial	Weight B/heating	Weight A/heating	Moisture Contents	Mean	Stdv.
RLP	Trail-1	1.107	1.044	5.691	6.121	0.402
	Trail-2	0.938	0.88	6.183		
	Trail-3	1.048	0.98	6.489		
RTP	Trail-1	1.083	1.01	6.741	6.275	0.689
	Trail-2	1.015	0.948	6.601		
	Trail-3	1.003	0.948	5.484		
LAC	Trail-1	0.7	0.691	1.286	1.137	0.502
	Trail-2	0.865	0.86	0.578		
	Trail-3	1.098	1.081	1.548		
TAC	Trail-1	1.009	0.961	4.757	4.757	0.884
	Trail-2	1.046	0.987	5.641		
	Trail-3	1.007	0.968	3.873		

Appendix B2: Ash Content Analysis

Sample	Trial	Weight B/heating	Weight A/heating	Ash Content	Mean	Stdv.
RLP	Trail-1	1.119	0.107	9.562		
	Trail-2	0.945	0.092	9.735	7.985	2.883
	Trail-3	1.052	0.049	4.658		
RTP	Trail-1	1.09	0.071	6.514		
	Trail-2	1.038	0.026	2.505	3.951	2.225
	Trail-3	1.023	0.029	2.835		
LAC	Trail-1	1.002	0.712	71.058		
	Trail-2	0.974	0.614	63.039	66.220	4.259
	Trail-3	0.903	0.583	64.563		
TAC	Trail-1	1.278	0.607	47.496		
	Trail-2	1.252	0.597	47.684	44.590	5.197
	Trail-3	1.205	0.465	38.589		

Appendix B3: Volatile Content Analysis

Sample	Trial	Weight B/heating	Weight A/heating	Volatile matter	Mean	Stdv.
RLP	Trail-1	1.144	0.314	66.861		
	Trail-2	1.048	0.304	64.809	63.960	3.032
	Trail-3	1.048	0.349	60.210		
RTP	Trail-1	1.09	0.253	71.098		
	Trail-2	0.999	0.211	72.696	71.867	1.079
	Trail-3	0.963	0.209	71.808		
LAC	Trail-1	0.996	0.77	17.000		
	Trail-2	1.011	0.775	17.160	15.655	2.175
	Trail-3	1.047	0.845	12.805		
TAC	Trail-1	0.919	0.726	16.244		
	Trail-2	1.048	0.824	15.734	17.383	1.661
	Trail-3	1.048	0.796	20.173		

Appendix B4: Fixed Carbon Content Analysis

Sample	Trial	Moisture content	Ash content	Volatile matter	Fixed carbon	Mean	Stdv.
RLP	Trail-1	5.691	9.562	66.861	17.886		
	Trail-2	6.183	9.735	64.809	19.273	21.934	5.851
	Trail-3	6.489	4.658	60.21	28.643		
RTP	Trail-1	6.74	6.51	71.098	15.65		
	Trail-2	6.60	2.50	72.696	18.20	17.907	2.128
	Trail-3	5.48	2.83	71.808	19.87		
LAC	Trail-1	1.286	71.011	21.41	6.293		
	Trail-2	0.578	63.039	22.77	13.613	12.015	5.114
	Trail-3	1.548	64.563	17.75	16.139		
TAC	Trail-1	4.757	47.496	16.24	31.507		
	Trail-2	5.641	47.684	15.79	30.885	33.067	3.255
	Trail-3	3.873	38.589	20.73	36.808		

Appendix B5: Bulk Density Analysis

Sample	Trial	Volume	Dry Weight	Bulk Density	Mean	Stdv.
RLP	Trail-1	17.800	9.483	0.533		
	Trail-2	17.100	9.721	0.568	0.543	0.022
	Trail-3	17.400	9.192	0.528		
LAC	Trail-1	20.500	7.483	0.365		
	Trail-2	21.000	7.721	0.368	0.365	0.003
	Trail-3	21.000	7.592	0.362		
RTP	Trail-1	19.100	9.124	0.477		
	Trail-2	19.700	9.165	0.465	0.474	0.008
	Trail-3	19.300	9.259	0.479		
TAC	Trail-1	22.000	8.124	0.369		
	Trail-2	22.500	8.165	0.363	0.368	0.004
	Trail-3	22.000	8.159	0.371		

Appendix B6: Summary Proximate Analysis

Material	Moisture content	Ash content	Volatile matter	Fixed Carbon	Bulk Density (cm³g⁻¹)
RLP	6.12 ± 0.40	7.99 ± 2.88	63.96 ± 3.03	21.93 ± 5.85	0.543 ± 0.022
RTP	6.28 ± 0.69	3.95 ± 2.23	71.87 ± 1.08	12.02 ± 5.11	0.474 ± 0.008
LAC	1.14 ± 1.45	71.01 ± 6.43	15.66 ± 2.18	17.91 ± 2.13	0.365 ± 0.003
TAC	4.75 ± 0.88	44.59 ± 5.20	17.38 ± 1.66	33.07 ± 3.26	0.368 ± 0.004

Appendix C: Elemental Analysis

Sample	RLP	LAC	RTP	TAC
C	51.61 $\pm$ 0.20	56.80 $\pm$ 0.53	39.89 $\pm$ 9.83	65.42 $\pm$ 2.44
H	7.00 $\pm$ 0.06	2.11 $\pm$ 0.47	5.12 $\pm$ 1.46	1.38 $\pm$ 0.05
N	4.54 $\pm$ 0.13	4.00 $\pm$ 0.05	2.51 $\pm$ 2.31	3.95 $\pm$ 0.09
S	0.33 $\pm$ 0.02	0.82 $\pm$ 0.04	0.19 $\pm$ 0.19	0.72 $\pm$ 0.02
O	36.52 $\pm$ 0.05	36.27 $\pm$ 0.81	52.28 $\pm$ 13.78	28.54 $\pm$ 2.35
H/C	1.63	0.04	0.13	0.02
N/C	0.08	0.07	0.06	0.06
O/C	0.53	0.64	1.31	0.44

Appendix D: BET (Brunauer-Emmett-Teller) Analysis

Appendix D1: Surface Area of RLP

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Analysis

Operator: 1

Sample ID: J113-SD

Sample Desc: RLP

Sample Weight: 0.099 g

Approx. Outgas Time: 21.2 hrs

Analysis gas: Nitrogen

Analysis Time: 0:45 hr:min

Analysis Mode: Standard

VoidVol. Mode: He Measure

Date: 2022/05/10

Filename: J113-SD.qps

Comment: RLP

Instrument: Autosorb iQ Station 1

Final Outgas Temp.: 300 °C

Non-ideality: 6.58e-05 1/mmHg

Bath temp.: 77.35 K

Report

Operator: 1

Date: 2022/05/11

Extended info: Available

CellType: 6mm

VoidVol Remeasure: off

Warm Zone V: 14.5868 cc

Cold Zone V: 2.21524 cc

Multi-Point BET

Data Reduction Parameters Data

Adsorbate

Thermal Transpiration: on

Nitrogen

Molec. Wt.: 28.013

Eff. mol. diameter (D): 3.54 Å

Temperature 77.350K

Cross Section: 16.200 Å²

Eff. cell stem diam. (d): 4.0000 mm

Liquid Density: 0.808 g/cc

Multi-Point BET Data

Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]	Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]
5.00160e-01	-0.7615	-1.0514e+03	8.01347e-01	1.6797	1.9215e+03
5.99915e-01	0.4772	2.5142e+03	8.99707e-01	3.0211	2.3759e+03
6.99432e-01	0.9637	1.9321e+03			

BET summary

Slope = 6250.583

Intercept = -2.838e+03

Correlation coefficient, r = 0.671956

C constant = -1.203

Surface Area = 1.020 m²/g

Appendix D2: Surface Area of LAC

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Analysis		Report	
Operator:	1	Date:	2022/05/10
Sample ID:	J113-SC	Operator:	1
Sample Desc:	LAC	Filename:	J113-SC.qps
Sample Weight:	0.1341 g	Comment:	LAC
Approx. Outgas Time:	21.2 hrs	Instrument:	Autosorb iQ Station 1
Analysis gas:	Nitrogen	Final Outgas Temp.:	300 °C
Analysis Time:	1:05 hr:min	Non-ideality:	6.58e-05 1/mmHg
Analysis Mode:	Standard	Bath temp.:	77.35 K
VoidVol. Mode:	He Measure	Cold Zone V:	1.77159 cc

Extended info: Available
CellType: 6mm
VoidVol Remeasure: off
Warm Zone V: 14.6487 cc

Multi-Point BET

Data Reduction Parameters Data

<u>Adsorbate</u>	Thermal Transpiration: on	Eff. mol. diameter (D): 3.54 Å	Eff. cell stem diam. (d): 4.0000 mm
	Nitrogen	Temperature 77.350K	
	Molec. Wt.: 28.013	Cross Section: 16.200 Å²	Liquid Density: 0.808 g/cc

Multi-Point BET Data

Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]	Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]
1.02199e-01	38.4441	2.3691e+00	2.49300e-01	41.2548	6.4408e+00
1.49453e-01	39.8282	3.5300e+00	2.99583e-01	41.7729	8.1926e+00
2.00591e-01	40.7116	4.9315e+00			

BET summary

Slope = 29.444
 Intercept = -8.026e-01
 Correlation coefficient, r = 0.997641
 C constant = -35.684

 Surface Area = 121.592 m²/g

Appendix D3: Surface Area of RTP

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Analysis		Report	
Operator:	1	Date:	2022/05/10
Sample ID:	J113-SA	Operator:	1
Sample Desc:	RTP	Filename:	J113-SA.qps
Sample Weight:	0.0861 g	Comment:	RTP
Approx. Outgas Time:	21.2 hrs	Instrument:	Autosorb iQ Station 1
Analysis gas:	Nitrogen	Final Outgas Temp.:	300 °C
Analysis Time:	0:56 hr:min	Non-ideality:	6.58e-05 1/mmHg
Analysis Mode:	Standard	Bath temp.:	77.35 K
VoidVol. Mode:	He Measure	Cold Zone V:	1.79951 cc
		Warm Zone V:	14.7232 cc

Multi-Point BET

Data Reduction Parameters Data

<u>Adsorbate</u>	Thermal Transpiration: on	Eff. mol. diameter (D): 3.54 Å	Eff. cell stem diam. (d): 4.0000 mm
	Nitrogen	Temperature 77.350K	
	Molec. Wt.: 28.013	Cross Section: 16.200 Å ²	Liquid Density: 0.808 g/cc

Multi-Point BET Data

Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]	Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]
5.00672e-01	-0.5397	-1.4866e+03	8.00738e-01	0.4887	6.5791e+03
6.00631e-01	0.5438	2.2128e+03	9.01821e-01	2.3339	3.1491e+03
7.00906e-01	0.3648	5.1402e+03			

BET summary

Slope = 13580.008
Intercept = -6.400e+03
Correlation coefficient, r = 0.697477
C constant = -1.122
Surface Area = 0.485 m²/g

Appendix D4: Surface Area of TAC

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Analysis		Report	
Operator:	1	Operator:	1
Sample ID:	J113-SB	Filename:	J113-SB.qps
Sample Desc:	TAC	Comment:	TAC
Sample Weight:	0.1564 g	Instrument:	Autosorb IQ Station 1
Approx. Outgas Time:	21.2 hrs	Final Outgas Temp.:	300 °C
Analysis gas:	Nitrogen	Non-ideality:	6.58e-05 1/mmHg
Analysis Time:	1:28 hr:min	Bath temp.:	77.35 K
Analysis Mode:	Standard		
VoidVol. Mode:	He Measure	Cold Zone V:	1.69744 cc
		Warm Zone V:	15.0954 cc

Multi-Point BET

Data Reduction Parameters Data

<u>Adsorbate</u>	Thermal Transpiration: on	Eff. mol. diameter (D): 3.54 Å	Eff. cell stem diam. (d): 4.0000 mm
	Nitrogen	Temperature 77.350K	
	Molec. Wt.: 28.013	Cross Section: 16.200 Å²	Liquid Density: 0.808 g/cc

Multi-Point BET Data

Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]	Relative Pressure [P/Po]	Volume @ STP [cc/g]	1 / [W((Po/P) - 1)]
9.94745e-02	22.9847	3.8453e+00	2.50913e-01	28.2574	9.4845e+00
1.50177e-01	25.0417	5.6463e+00	3.00563e-01	29.7893	1.1542e+01
2.00582e-01	26.8179	7.4860e+00			

BET summary

Slope = 38.236
 Intercept = -5.940e-02
 Correlation coefficient, r = 0.999441
 C constant = -642.720
 Surface Area = 91.223 m²/g

Appendix E: Batch Adsorption

Appendix E1: Effect of Initial Concentration

a)	Effect of Initial Concentration on Cu(II) adsorption by LAC							
	1	2	3	Average	% Removal		Adsorption	
							Capacity	
					Mean	Stdv	Mean	Stdv
5	0.150	0.111	0.200	0.154	96.930	0.897	4.847	0.045
10	0.265	0.220	0.155	0.213	97.872	0.553	9.787	0.055
15	0.216	0.261	0.230	0.235	98.431	0.144	14.765	0.023
20	0.527	0.612	0.599	0.579	97.105	0.229	19.421	0.046
25	0.780	0.815	0.873	0.823	96.710	0.188	24.178	0.047
30	2.045	0.218	0.242	0.835	97.217	3.493	29.165	1.048
35	1.167	1.284	1.310	1.254	96.419	0.217	33.747	0.076
40	1.565	1.719	1.711	1.665	95.838	0.216	38.335	0.087
45	2.031	2.276	2.345	2.217	95.073	0.367	42.783	0.165
50	2.778	2.807	3.003	2.863	94.275	0.244	47.137	0.122

b) Effect of Initial Concentration on Pb(II) adsorption by LAC

	1	2	3	Average	% Removal		Adsorption Capacity	
					Mean	Stdv	Mean	Stdv
5	0.792	0.310	0.572	0.558	88.843	4.831	4.442	0.242
10	1.796	1.089	1.352	1.412	85.877	3.571	8.588	0.357
15	2.120	2.077	2.328	2.175	85.500	0.894	12.825	0.134
20	2.409	2.357	3.180	2.649	86.757	2.305	17.351	0.461
25	3.253	4.799	4.539	4.197	83.212	3.312	20.803	0.828
30	5.156	5.465	4.867	5.163	82.791	0.996	24.837	0.299
35	5.656	7.106	5.545	6.102	82.565	2.489	28.898	0.871
40	7.223	7.209	7.286	7.239	81.902	0.103	32.761	0.041
45	7.434	8.112	8.143	7.896	82.453	0.891	37.104	0.401
50	9.263	9.060	9.116	9.146	81.707	0.209	40.854	0.104

c) Effect of Initial Concentration on Ni(II) adsorption by LAC

	1	2	3	Average	% Removal		Adsorption Capacity	
					Mean	Stdv	Mean	Stdv
5	0.967	1.019	0.628	0.871	82.575	4.245	4.129	0.212
10	2.033	2.865	2.977	2.625	73.750	5.161	7.375	0.516
15	4.347	4.500	4.686	4.511	69.927	1.132	10.489	0.170
20	6.729	7.203	7.383	7.105	64.475	1.689	12.895	0.338
25	8.556	8.661	9.177	8.798	64.808	1.330	16.202	0.332
30	11.037	11.079	11.526	11.214	62.620	0.903	18.786	0.271
35	13.851	14.532	14.541	14.308	59.120	1.131	20.692	0.396
40	13.482	13.860	13.635	13.659	65.853	0.475	26.341	0.190
45	15.546	16.233	16.269	16.016	64.409	0.905	28.984	0.407
50	18.468	12.261	17.985	16.238	67.524	6.905	33.762	3.453

d) Effect of Initial Concentration on Cu(II) adsorption by TAC

	1	2	3	Average	% Removal		Adsorption Capacity	
					Mean	Stdv	Mean	Stdv
5	0.0083	0.013	0.0139	0.011733	97.653	0.601	4.883	0.030
10	0.0219	0.026	0.0407	0.029533	98.523	0.494	9.852	0.049
15	0.0446	0.0485	0.0511	0.048067	98.398	0.109	14.760	0.016
20	0.0543	0.0603	0.0627	0.0591	98.523	0.108	19.705	0.022
25	0.0627	0.0684	0.0749	0.068667	98.627	0.122	24.657	0.031
30	0.0774	0.0814	0.0891	0.082633	98.623	0.099	29.587	0.030
35	0.0941	0.0952	0.0974	0.095567	98.635	0.024	34.522	0.008
40	0.1188	0.1223	0.1363	0.1258	98.428	0.116	39.371	0.046
45	0.2151	0.2162	0.2303	0.220533	97.550	0.094	43.897	0.042
50	0.273	0.2733	0.4214	0.322567	96.774	0.856	48.387	0.428

e) Effect of Initial Concentration on Pb(II) adsorption by TAC

	1	2	3	Average	% Removal		Adsorption Capacity	
					Mean	Stdv	Mean	Stdv
5	0.1584	0.0619	0.1144	0.1116	66.530	14.494	3.327	0.725
10	0.3591	0.2178	0.2704	0.2824	57.635	10.712	5.764	1.071
15	0.4239	0.4154	0.4655	0.4349	56.507	2.681	8.476	0.402
20	0.4818	0.4713	0.636	0.5297	60.273	6.916	12.055	1.383
25	0.6505	0.9597	0.9078	0.8393	49.640	9.935	12.410	2.484
30	1.0311	1.0929	0.9734	1.0325	48.377	2.988	14.513	0.896
35	1.1311	1.4212	1.109	1.2204	47.696	7.467	16.694	2.613
40	1.4446	1.4417	1.4572	1.4478	45.706	0.309	18.283	0.124
45	1.4867	1.6224	1.6286	1.5792	47.359	2.673	21.312	1.203
50	1.8525	1.812	1.8236	1.8294	45.119	0.626	22.560	0.313

f) Effect of Initial Concentration on Ni(II) adsorption by TAC

	1	2	3	Average	% Removal		Adsorption Capacity	
					Mean	Stdv	Mean	Stdv
5	0.0619	0.1144	0.1584	0.1116	77.687	9.662	3.884	0.483
10	0.2178	0.2704	0.3591	0.2824	71.757	7.141	7.176	0.714
15	0.4154	0.4239	0.4655	0.4349	71.004	1.787	10.651	0.268
20	0.4713	0.4818	0.636	0.5297	73.515	4.610	14.703	0.922
25	0.6505	0.9078	0.9597	0.8393	66.427	6.623	16.607	1.656
30	0.9734	1.0311	1.0929	1.0325	65.584	1.992	19.675	0.598
35	1.109	1.1311	1.4212	1.2204	65.130	4.978	22.796	1.742
40	1.4417	1.4446	1.4572	1.4478	63.804	0.206	25.522	0.082
45	1.4867	1.6224	1.6286	1.5792	64.906	1.782	29.208	0.802
50	1.812	1.8236	1.8525	1.8294	63.413	0.417	31.706	0.209

Appendix E2: Effect of contact time

a) Effect of Contact Time on Cu(II) adsorption by LAC

Time	1	2	3	Average	% Removal		Adsorption Capacity	
					Mean	Stdv	Mean	Stdv
10	37.920	41.256	37.028	38.735	22.531	4.457	11.265	2.229
20	20.900	24.888	27.54	24.443	51.115	6.685	25.557	3.342
30	10.064	17.384	11.62	13.023	73.955	7.713	36.977	3.856
40	11.924	7.788	7.548	9.0867	81.827	4.920	40.913	2.46
60	3.476	2.600	2.120	2.732	94.536	1.375	47.268	0.688
90	1.996	2.884	1.872	2.2507	95.499	1.104	47.749	0.552
120	1.432	0.056	2.012	1.1667	97.667	2.009	48.633	1.005
150	0.160	3.236	1.960	1.7853	96.429	3.091	48.215	1.545
180	3.028	1.292	1.268	1.8627	96.275	2.019	48.137	1.009
240	0.736	0.148	2.160	1.0147	97.971	2.069	48.985	1.035

b) Effect of Contact Time on Pb(II) adsorption by LAC

Time	1	2	3	Average	% Removal		Capacity	
					Mean	Stdv	Mean	Stdv
10	28.424	22.18	29.72	26.775	46.451	8.063	23.225	4.0315
20	13.497	13.251	11.985	12.911	74.178	16.226	37.089	0.8113
30	8.13	4.998	5.787	6.305	87.39	3.26	43.7	2.6747
40	2.598	2.394	2.376	2.456	95.088	0.2466	47.544	0.1233
60	2.262	2.079	1.9665	2.1025	95.795	0.2983	47.898	0.1491
90	1.947	1.857	1.695	1.833	96.334	0.2554	48.167	0.1277
120	1.572	1.449	1.44	1.487	97.026	0.1475	48.513	0.0737
150	1.422	1.407	1.146	1.325	97.35	0.3104	48.675	0.1552
180	1.372	1.264	1.2	1.2787	97.443	0.1739	48.721	0.0869
240	1.188	1.168	1.1	1.152	97.696	0.0923	48.848	0.0461

c) Effect of Contact Time on Ni(II) adsorption by LAC

Time	1	2	3	Average	% Removal		Capacity	
					Mean	Stdv	Mean	Stdv
10	41.844	37.644	41.220	40.236	19.528	4.533	9.764	2.266
20	38.820	42.110	33.084	38.005	23.991	9.136	11.995	4.568
30	30.636	27.408	32.568	30.204	39.592	5.214	19.796	2.607
40	24.176	22.082	21.188	22.482	55.036	3.067	27.518	1.534
60	19.054	14.320	15.412	16.262	67.476	4.958	33.738	2.479
90	17.256	11.929	17.100	15.428	69.143	6.063	34.572	3.031
120	16.272	12.584	16.749	15.202	69.597	4.559	34.798	2.280
150	12.864	16.260	15.706	14.943	70.113	3.644	35.057	1.822
180	14.816	14.016	17.080	15.304	69.392	3.176	34.696	1.589
240	15.840	12.876	16.964	15.227	69.547	4.224	34.773	2.112

d) Effect of Contact Time on Cu(II) adsorption by TAC

Time	1	2	3	Average	% Removal		Capacity	
					Mean	Stdv	Mean	Stdv
10	14.200	21.070	13.665	14.200	67.377	4.457	33.688	4.13
20	13.650	11.515	10.810	13.650	76.017	6.685	38.008	1.479
30	10.755	6.815	6.115	10.755	84.210	7.713	42.105	2.501
40	5.940	4.870	4.760	5.940	89.620	4.92	44.81	0.652
60	4.545	4.455	4.970	4.545	90.687	1.375	45.343	0.275
90	5.385	5.370	5.310	5.385	89.290	1.104	44.645	0.04
120	5.310	5.300	5.270	5.310	89.413	2.009	44.707	0.021
150	5.256	5.225	5.230	5.256	89.526	3.091	44.763	0.016
180	5.235	5.130	5.145	5.235	89.660	2.019	44.83	0.057
240	5.195	6.500	5.415	5.195	88.593	2.069	44.297	0.699

e) Effect of Contact Time on Pb(II) adsorption by TAC

Time	1	2	3	Average	% Removal		Capacity	
					Mean	Stdv	Mean	Stdv
10	45.0112	45.2144	39.7864	43.337	13.325	6.154	6.663	3.308
20	39.7408	35.28	33.2128	36.078	27.844	3.336	13.922	3.336
30	28.7196	28.7196	30.8178	29.419	41.162	1.211	20.581	1.211
40	25.0872	30.0936	30.5144	28.565	42.870	3.019	21.435	3.019
60	27.6848	29.5264	20.5464	25.919	48.162	4.743	24.081	4.743
90	24.1872	24.4672	25.7528	24.802	50.395	0.835	25.198	0.835
120	22.852	23.512	26.194	24.186	51.628	1.770	25.814	1.770
150	20.671	28.475	22.993	24.046	51.907	4.007	25.954	4.007
180	19.449	26.536	27.52	24.502	50.997	4.403	25.498	4.403
240	20.136	29.859	24.4992	24.831	50.337	4.870	25.169	4.870

f) Effect of Contact Time on Ni(II) adsorption by TAC

Time	1	2	3	Average	% Removal		Adsorption Capacity	
					Mean	Stdv	Mean	Stdv
10	39.040	38.670	37.950	38.553	22.893	1.109	11.447	0.544
20	31.176	31.544	30.440	31.053	37.893	1.124	18.947	0.562
30	23.358	23.058	24.144	23.520	52.960	1.122	26.48	0.561
40	18.735	18.740	18.710	18.728	62.543	0.032	31.272	0.016
60	18.450	18.280	18.075	18.268	63.463	0.376	31.732	0.188
90	18.525	19.930	19.265	19.240	61.520	0.867	31.06	0.434
120	18.930	19.265	19.345	19.180	61.640	0.44	30.82	0.22
150	20.160	20.310	20.800	20.423	59.153	0.669	29.577	0.335
180	20.770	20.445	20.745	20.653	58.693	0.362	29.347	0.181
240	20.060	20.750	21.165	20.658	58.683	1.107	29.345	0.554