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Preparation, Characterization and Application of Soda Lignin and its Ester Derivatives as Adsorbents in the Adsorption of Pb^{2+} and Cd^{2+} from wastewater

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Abstract: Lignin is an amorphous polymer which is usually discarded as a waste material in pulp and paper industries. It is composed of three phenolic monomeric units which are coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol. These monomeric units have several functional groups which can be modified into useful industrial products. In this present study lignin was extracted from *Gmelina arborea* wood using soda pulping process, it was converted into lignin esters using succinic and maleic anhydrides as esterifying reagents. The Physicochemical properties of soda lignin (SL), succinilyted soda lignin (SSL), maleated soda lignin (MSL) were evaluated using FTIR, SEM, and UV spectroscopy. Soda lignin and its ester derivatives were applied as adsorbents in the adsorption of Cd^{2+} and Pb^{2+} from simulated waste water. The results revealed that lignin ester contains certain functional groups which are not present in soda lignin this led to the difference in their absorbance and λ_{max}. The presence of alcohol (O-H). carbonyl (C=O) and other functional groups as revealed by FTIR, enhanced their adsorption potentials. Their surfaces were rough and the particle sizes unevenly distributed. The results of the adsorption studies revealed the adsorption efficiency increase with increase in adsorbent dosage, contact time, pH and decrease in metal ions concentrations. There was also a disappearance and shift in some adsorbent surface functional groups after the adsorption process. The adsorption efficiencies of lignin esters were higher than that of the resultant soda lignin. Hence lignin which are presently discarded as waste material in paper industries can be modified into lignin esters and use as adsorbent in the removal of heavy metals from wastewater.

1. Introduction

Environmental pollution caused by heavy metals and minerals in the wastewater is the most serious problem in our society as it affects both terrestrial and aquatic animals. Due to the extensive anthropogenic activities such as mining, agricultural processes and disposal of industrial waste materials into the environment; the concentration of heavy metals in the environment keeps on increasing (Bayuo *et al*., 2022). Heavy metals usually present in industrial effluents include chromium, zinc, cadmium, lead, selenium, nickel, arsenic, and gold (Lakherwal, 2014). The release of large amount of industrial effluents into the natural environment has resulted in a number of environmental degradations due to the non-biodegradability and persistence of these materials in the environment. These heavy metals can accumulate in the environmental elements such as food chain, and thus may pose a significant danger to human health (Lakherwal, 2014).

Heavy metals are carcinogenic and even their trace amounts can cause several health problems in humans (Karimi *et al*., 2022). Several acute and chronic toxic effects of heavy metals affect different part of the body. Gastrointestinal, kidney dysfunction, vascular damage, immune system dysfunction, nervous system disorders, birth defects, skin lesions, and cancer are some examples of the complications caused by exposure to heavy metals. Exposure to two or more heavy metals may have cumulative effects in human (Wang *et al*., 2022; Fernandes Azevedo *et al*., 2012; Costa, 2019; Gazwi *et al*., 2020; Cobbina *et al*., 2015). High-dose of heavy metals exposure, particularly mercury and lead, may induce severe complications such as abdominal colic pain, diarrhea, and kidney failure (Bernhoft, 2012; Tsai *et al*., 2017). While low-dosage exposure to heavy metals hidden threat, unless repeated regularly, which may then be diagnosed by its complications, such fatigue, anxiety, and detrimental impacts on intelligence quotient (IQ) and intellectual function in children (Mazumdar *et al*., 2011).

To avoid health hazards associated with heavy metal exposure in the environment, it is essential to remove these toxic heavy metals from industrial effluents before its disposal into the environment. Several methods such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis, ultrafiltration, nanofiltration, coagulation, flocculation, have been used for the removal of heavy metals from industrial effluents. However, most of these methods have disadvantages such as high reagent requirement, high cost, unpredictable metal ion removal and generation of toxic sludge etc. (Jain *et al*., 2010; Adebowale, *et al*., 2015).

Adsorption process being very simple, cheap and effective has become the most preferred methods for the removal of toxic contaminants such as heavy metals from wastewater (Gottipati *et al*. 2012). The adsorbent used should be cheap, sustainable and biodegradable. The removal of Cd^{2+} can be also conducted by using adsorption into *Algerian Luffa Cylindrica*. The biosorption process was studied with respect to contact time, particle size, pH and temperature (Ad *et al*., 2016). The use of hydroxyapatite and hydroxyethyl cellulose modified with a new Gum Arabic or a porous phospho-calcic hydroxyapatite are promised (Errich *et al*., 2021; El Hammari *et al*. 2022).

Lignin which is usually discarded as a waste material from pulp and paper industries can be modified to be more reactive and to enhance many industrial applications and could be converted to many value-added products through chemical modifications. These chemical modifications usually alter its hydrophobic/hydrophilic properties, along with other properties, and thus its applications (Chen *et al*., 2014). The physicochemical properties of lignin vary depending on the plant source and method of extraction. Chemical oxidation of lignin results in the formation of certain functional groups on lignin moieties (Chen, 1992). Lignin has been studied for a wide range of industrial applications such as composites, surfactants, adsorbents and dispersants (Miros-Kudra *et al*., 2022; Hazarika and Gogoi, 2014). Agustin *et al*., 2020, reported the application of lignin nano particles (LNPs) and nano celluloses in the adsorption of pollutants from pharmaceutical wastewater, and reported that LNPs, adsorbed a wider range of pharmaceuticals pollutants than the nano celluloses. Adsorption of emerging pollutants (acetaminophen and acetamiprid) on lignin-based activated carbon was reported by Sellaoui, *et al*., (2023). The maximum adsorption capacity of 665 mg/g and 765 mg/g was reported for acetaminophen and acetamiprid respectively.

The application of Soda lignin and its ester derivatives as adsorbents in the removal of Pb^{2+} and Cd^{2+} from wastewater have not been reported. Hence this present work aimed at extracting lignin from *Gmelina arborea* wood using Soda pulping process, modifying the lignin into lignin esters using maleic and succinic anhydrides, and applying both the lignin and its ester derivatives as adsorbent in the adsorption of Pb^{2+} and Cd^{2+} from simulated wastewater.

2. Methodology

2.1 Extraction of lignin

Soda lignin was extracted from *Gmelina arborea* wood by pulping 100 g of the wood chips with 1000 mL of 20 % sodium hydroxide (NaOH) solution in a 10 L laboratory digester. The pulping was done for three hours at the pulping temperature of 130 °C. After the pulping, the pulps were separated from the black liquor and beaten using mortar and pistil. It was quantitatively transferred to the digester and pulp again for another 3 hours using the same quantity and concentration of the soda liquor in order to extract greater quantity of lignin. Thereafter, the pulps were separated from black liquor and washed with tap water. The black liquor was precipitated using 3 M H_2SO_4, and lignin was obtained as a precipitate at a pH of 2. The precipitate was filtered, washed with distilled water to remove excess acid and dried in the oven at 70 °C for 24.

Percentage yield of the lignin was calculated as follows:

$$\text{Percentage yield (\%)} = \frac{w_2}{w_1} \text{ X } 100 \qquad \text{Equation 1}$$

Where w_1= weight of the sample (g)

w_2 = weight of the lignin (g)

2.2 Esterification of lignin

Soda lignin was esterified separately with succinic anhydride and maleic anhydride. The esterification reaction was carried out by immersing 10 g of soda lignin in 10 % solution of anhydrides in acetone at the ratio of 1:20 (w/v) (Chen, 2014). Thereafter, it was heated at a reflux temperature of (60 ± 5 °C) for 6 h in a reactor vessel provided with an agitator. At the end of the reaction, the reaction mixture was kept for 24 h at room temperature, it was then evaporated to remove most of the acetone. It was filtered and washed with hot distilled water to remove unreacted anhydrides and by-products. The succinylated soda lignin (SSL) and maleated soda lignin (MSL) obtained were oven dried at 70 °C to constant weight. The esterification process was performed in triplicate under the same conditions in order to obtained greater quantity of the lignin esters.

2.3 Characterization of lignin and lignin esters

2.3.1 Determination specific surface area

Saers' method was used for the determination of the specific surface area. A sample containing 0.5 g of soda lignin or soda lignin ester was acidified with 0.1M HCl to pH 3 – 3.5, the volume was made up to 50 mL with de-ionized water after addition of 10.0 g of NaCl. The titration was carried out with standard 0.1M NaOH to pH 4.0, and then to pH 9.0. The volume V required to raise the pH from 4.0 to 9.0 was noted and used to compute for the specific surface area (Sears, 1956).

Specific surface area (S) (m^2/g) = 32V – 25 Equation 2

2.3.2 Determination of functional groups

The functional group on lignin and lignin esters before and after adsorption studies were determined using Fourier Transformed Infrared spectroscopy (FTIR) Cary 630, in the range of 4000 – 1000 cm^{-1} using a KBr disks containing 1 % finely ground sample. The spectrum recorded over 30 scans with a resolution of 4 cm^{-1}.

2.3.3 Determination of wavelength of maximum absorption (λ_{max}) and absorbance

The wavelength of maximum absorption (λ_{max}) and absorbance of the lignin and lignin esters were determined using Ultra Violet/ visible spectroscopy following the literature work reported by Surina *et al*. (2015). Stock solutions were prepared by dissolving 4 mg of lignin or lignin ester in 50 ml of 0.2 M NaOH, the mixture was shaken in a mechanical shaker for 30 min to achieve complete dissolution. The UV/vision absorption spectra were registered on Genesys spectrophotometer in the absorption region from 190 to 450 nm, scan speed 5 nm/s and 1nm resolution.

2.3.4 Determination of surface morphology

Surface morphology of lignin and lignin esters were determined using scanning electrons microscope (SEM) phenom prox.

2.3.5 Determination of zero-point charge (pH_{zpc})

Determination of pH_{zpc} was done to investigate how the surface charge of the lignin and its ester derivatives depended on the pH. A solution of 0.01M NaCl was prepared, and its initial pH was adjusted between 2.0 to 12.0 by using 0.2M NaOH or HCl in each batch. Then 50 mL of 0.01 M NaCl was taken in 250 mL Erylenmeyer flasks and 0.20 g of lignin or lignin ester was added to each solution. These flasks were kept for 48 h, and the final pH of the solutions was measured using pH meter. Graphs were plotted between pH_{final} versus $pH_{initial}$. The point of intersection of the curves were taken as zero-point charge (pHzpc).

2.3.6 Preparation of simulated wastewater

Simulated wastewater solutions of Pb^{2+} and Cd^{2+} ions were prepared from analytical grade $Pb(NO_3)$ and $Cd(NO_3)_2.4H_2O$, respectively. Stock solution (100 mg L^{-1}) of Pb^{2+} and Cd^{2+}, were prepared by dissolving appropriate amount of $PbNO_3$ or $Cd(NO_3)_2.4H_2O$, in distilled water and made up to 1000 ml in standard volumetric flasks. The working solutions were prepared from the stock solution by serial dilutions.

2.4 Adsorption Studies

Adsorption of Pb^{2+} and Cd^{2+} from simulated wastewater was carried out using batch adsorption process. The adsorbents used were of particle size of 0.05- 0.1mm of soda lignin (SL), succinylated soda lignin (SSL) and maleated soda lignin (MSL). Batch experiments were conducted in order to study the effects of adsorbent dosage (0.05 -0.25g), initial adsorbate concentration (10 – 50 mg/L), contact time (30 – 150 min) and adsorbate pH (2 -6) on the adsorption process. The mixtures were agitating at 200 rpm using mechanical shaker. After each adsorption study, the adsorbent was filtered from adsorbate solution. The post adsorption concentration of the adsorbate was determined using Atomic Absorption Spectrometer (AAS). The adsorption efficiency was calculated using Equation 3, and the quantity of heavy metal adsorbed per unit time was calculated using equation 4.

$$\text{Adsorption efficiency (\%)} = \frac{C_{0-}C_e}{C_o}\ X\ 100 \qquad \text{Equation 3}$$

$$q_e = \frac{(C_{0-}C_e)v}{m}\ X\ 100 \qquad \text{Equation 4}$$

q_e = quantity of heavy metal adsorbed per unit time

C_o (mg/L) = concentration of the adsorbate before adsorption studies

C_e (mg/L) = concentration of the adsorbate after adsorption studies

m (g) = mass of the adsorbent

v (L) = volume of the adsorbate solution

3.0 Results and Discussions

3.1 Physicochemical properties of soda lignin and its ester derivatives

Lignin yield depends on the lignin content of the raw material and the pulping process used. As presented in Table 1, the yield of soda lignin from *Gmelina arborea* wood was 25.04 %. While that of the resultant lignin esters were 72.72 % and 67.43 % for SSL and MSL respectively. The high yield of lignin esters is due to the fact that during lignin esterification, the esterifying agent is added to the lignin resulting in the increase in the mass of the product.

Table 1: Physicochemical properties of lignin and lignin esters

Parameters	SL	SSL	MSL
Yield (%)	25.04	72.72	67.43
bulk density	0.89	1.02	0.95
Specific surface area (m^2/g)	77.4	256.6	211.8

SL = Soda lignin; SSL= succilylated soda lignin; MSL = maleated soda lignin

Table 2: Interpretation of FTIR Spectra of soda lignin and lignin esters

Band (cm^{-1})	Assignment	Sample present
337 - 3300	O-H stretching alcohol	All samples
3000 – 2840	C-H stretching alkane	All samples
2850 - 2815	C-H stretch (methoxy, methyl ether)	All samples
1982 - 1833	C-H bending aromatic	All samples
1688 - 1632	C-O carboxyl	SSL and MSL
1648 - 1630	C=C stretching alkene	MSL
1595 – 1510	C-C stretching aromatic	All samples
1465 – 1450	C-H bending methylene and methyl group	All samples
1427 - 1423	O-H bending alcohol	SL
1310- 1250	C-O stretching aromatic ester	SSL
1210 -1163	C-O stretching ester	SSL, MSL
1215 – 1200	C-O stretching phenol	All samples
1160- 1085	C-O-C stretching ether	All samples

SL = Soda lignin; SSL= Succinilyted soda lignin; MSL = Maleated soda lignin

Results from FTIR spectra revealed the changes in the major functional groups that occurred as a result of esterification of soda lignin into lignin esters (succilylated soda lignin and maleated soda lignin). The FTIR spectra before and after metals adsorption are presented in Figure 1 (A, C, E). The information derived from the spectra are presented in Table 2. The spectra showed a broad intense absorption band at 3000 – 3500 cm^{-1} corresponding to the stretching vibration of the free aliphatic and aromatic hydroxyl group, and bonded hydroxyl of carboxylic acids (Faix, 1992). The intensity of this band has been reduced in succinilyted soda lignin (SSL) indicating high level of conversion of hydroxyl groups into esters functional groups. The stretching vibration at 1636 cm^{-1} in MSL and 1688cm^{-1} in SSL are assigned to C-O from carboxyl group with intermolecular hydrogen bonding (Faix, 1992). This band was absent in soda lignin. These adsorption bands in lignin esters are due to the esterification reactions. There were C-O vibration bands of phenol around 1200 – 1215 cm^{-1}, in soda lignin samples and its ester derivatives. The peaks around 1595 – 1510 cm^{-1} found in all the samples are attributed to the presence of the C-C stretching of aromatic ring (Han *et al*., 2010). The C=C aliphatic vibration found at 1648 – 1630 cm^{-1} in MSL is as the results of the introduction of carbon – carbon double bond by Maleic anhydride. There was a little increase in the absorption peak at 2918 cm^{-1} in both lignin esters. This is predominantly arising from C-H stretching of aromatic methoxyl groups, methyl and methylene groups of the side chains (Namasivayam and Kavitha, 2006).

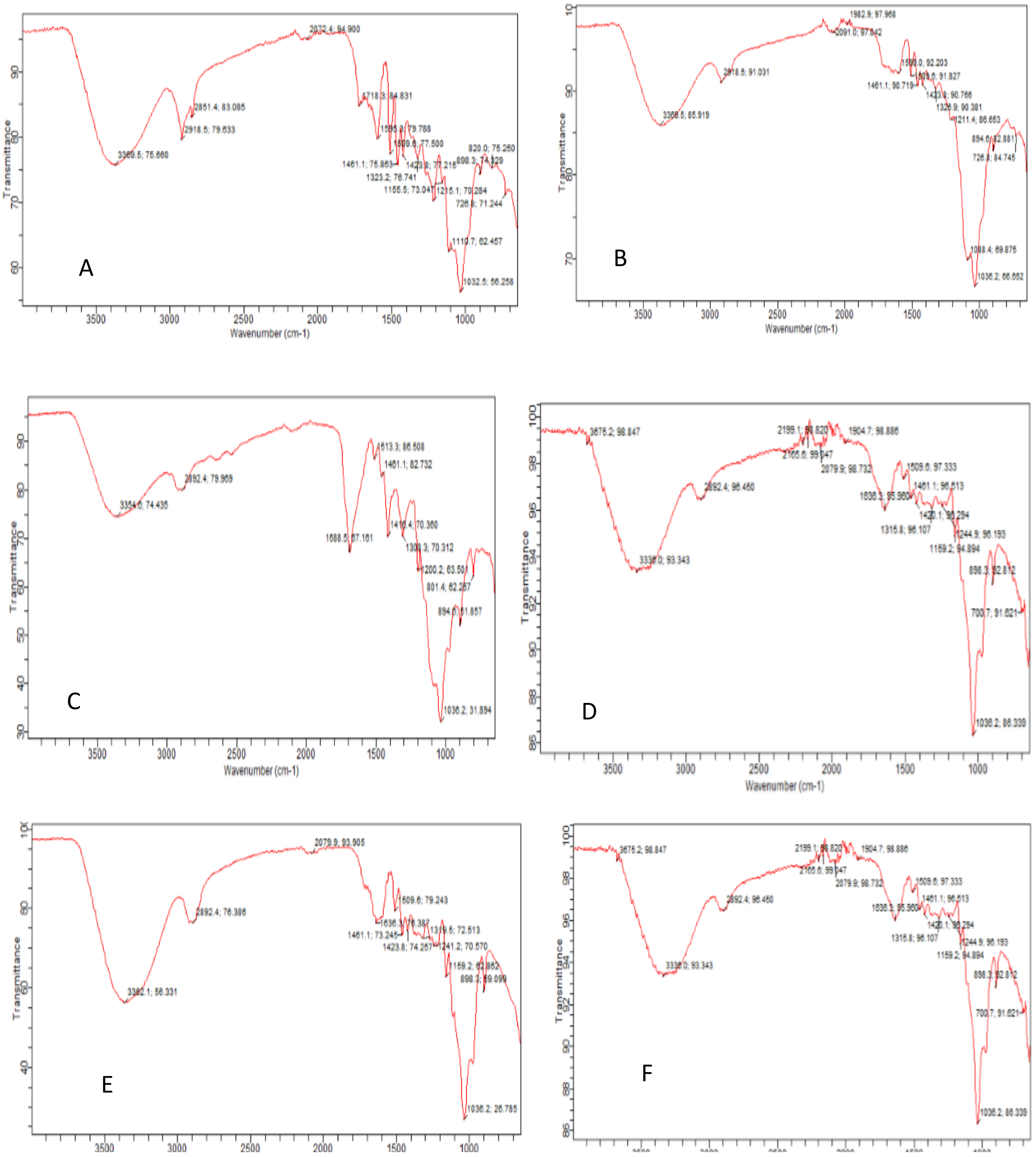

Figure 1: FTIR spectra of SL, SSL and MSL before and after Pb^{2+} adsorption studies

A = SL before Pb adsorption
B = SL after Pb adsorption
C =SSL before Pb adsorption
D = SSL after Pb adsorption
E= MSL before Pb adsorption
F = MSL after Pb adsorption

The absorption peak occurring at 1595cm^{-1} in SL is characteristics of aromatic C-O stretching of phenolic hydroxyl groups. This peak was reduced in the corresponding lignin esters to 1513 and 1509 cm^{-1} in SSL and MSL respectively. This was due to the esterification of the aromatic OH group. There was also an increase in the aliphatic OH bending at 1036 and 1088 cm^{-1} in SL to 1159 and 1100 cm^{-1} in MSL and SSL respectively. This increase is due to the conversion of aliphatic primary –OH to esters (Chen, 2014). The bands around 1300 cm$^{−1}$ (syringyl) and 1200 cm$^{−1}$ (guaiacyl) indicate presence of both syringyl and guaiacyl groups in lignin chemical structure (Chen, 2014). At 1600 and 1510 cm$^{−1}$, aromatic skeletal vibration bands were seen for SL. The presence of carbonyl, carboxyl, alcohol, phenol and alkene functional group in these adsorbents will enhance its adsorption potentials in the removal of heavy metal from waste water (Cheraghi *et al.,* 2001).

The FTIR spectra before adsorption Figure 1 (A, C, E) were compared with the spectra after adsorption studies Figure 1. (B, D, F). Results obtained from UV spectra are presented in Table 3. The esterification of soda lignin with both maleic and succinic anhydrides resulted in shift in λmax to a shorter wavelength (hypsochromic shift,) this is due to the blocking of phenolic hydroxyl groups (Lin and Dence,1992). This decrease in λmax is due to the conversion of phenolic hydroxyl groups to unsaturated carbonyl groups. Moreover, the esterification of both phenolic hydroxyl groups, and aliphatic hydroxyl groups in lignin, results in the decrease in the absorptivity of phenolic hydroxyl groups, as it is seen in SSL (Surina *et al*., 2015). The increase in the absorbance of MSL with corresponding decrease in λmax is due to the introduction of alkene group to lignin moiety.

Table 3. Absorbance and (λmax) of lignin and lignin esters

Sample name	Absorbance	λmax (nm)
SL	3.758	280
SSL	3.498	274
MSL	5.004	256

Surface morphology of lignin and lignin esters revealed that the surface of the adsorbents are rough and the particle size unevenly distributed (Figure 2). The zero-point charge of the adsorbent is the point in which the surface charge of the adsorbent becomes neutral. The zero-point charge of lignin and their esters derivatives (Table 4) ranges from to 2.2. At pH below the zero-point charge the surface of the adsorbent becomes positively charge thereby repelling the heavy metals from adsorbing unto the adsorbent. At pH above zero-point charge the adsorbent surface become negatively charged thereby enhancing the adsorption of heavy metals unto the adsorbent (Sharma and Upadhyag, 2009).

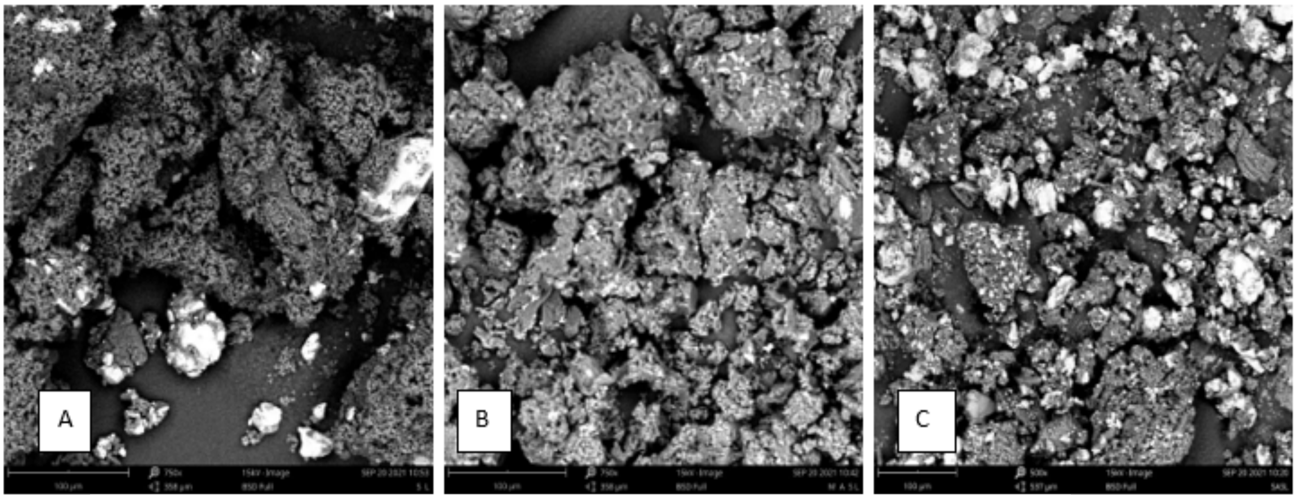

Figure 2: Surface morphology of SA (A), MSL (B), SSL (C)

Table 4: Zero-point charge of lignin and lignin esters

Adsorbents	SL	SSL	MSL
Zero-point charge	2.20	2.20	2.00

4.2 Adsorption Studies

The adsorption studies of lignin and lignin esters were carried out to evaluate their potentials as adsorbent in the removal of heavy metals (Pb^{2+} and Cd^{2+}) from simulated wastewater. As presented in Figure 3, The adsorption efficiency of these adsorbents increased with increase in the mass of the adsorbents, increase in the contact time, decreased in the concentration of the metal ions and increase in the adsorbate pH. The increase in adsorption efficiency with increase in the adsorbent dosages is due to the fact that at the higher mass of the adsorbent, there is an increase in the adsorption binding sites, increase in the surface area and surface functional groups such as hydroxyl and carbonyl groups (Yang *et al*., 2015; Danish *et al*., 2013). These properties enhanced higher adsorption efficiency. However, adsorption efficiency gradually decreases with more increase in the adsorbent dosage (Figure 3), because adsorbent particles begin to agglomerate together and block the binding site of the adsorbent (Bhatti *et al*., 2015; Santander, 2021).

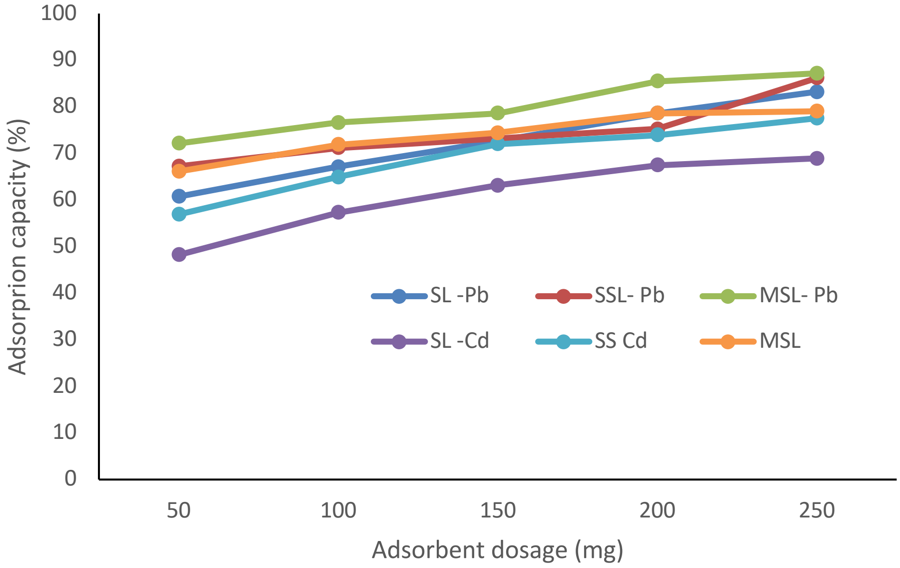

Figure 3: Effect of adsorbent dosage on the adsorption of Pb^{2+} and Cd^{2+} using soda lignin and its ester derivatives

Figure 4, present the results of the effect of contact time on the adsorption of Pb^{2+} and Cd^{2+}. The results revealed that the adsorption efficiency increase with an increase in the contact time and gradually decrease at higher contact time. This is due to the fact that at initial contact time, greater number of vacant binding sites were available for metal adsorption, but these binding sites become gradually saturated by the metal ions as the contact time increases and the remaining vacant surface binding sites are difficult to occupied by the metal ions due to the repulsive forces of the metal ions occupying the adsorbent sites and the metal ions in the bulk liquid phase (Gulipalli *et al*., 2011).

The results of effect of initial adsorbate concentration (Figure 5), revealed that the adsorption efficiency decreases with an increase in adsorbate concentration from 10 – 50 mg/L. This is because at lower adsorbate concentrations, there are fewer molecules of the adsorbate ions, and there are sufficient binding sites on the adsorbent surface that the metal ions can easily occupy. But at higher adsorbate concentrations the binding sites become saturated by the metal ions, hence, the active sorbent site is not available for more metal to accommodate, resulting in less adsorption of the metal ions also the adsorbed metal ions on the adsorbent surface electrostatically repel the incoming metal ions resulting in the decrease in the adsorption efficiency (Mekonnen *et al*., 2015).

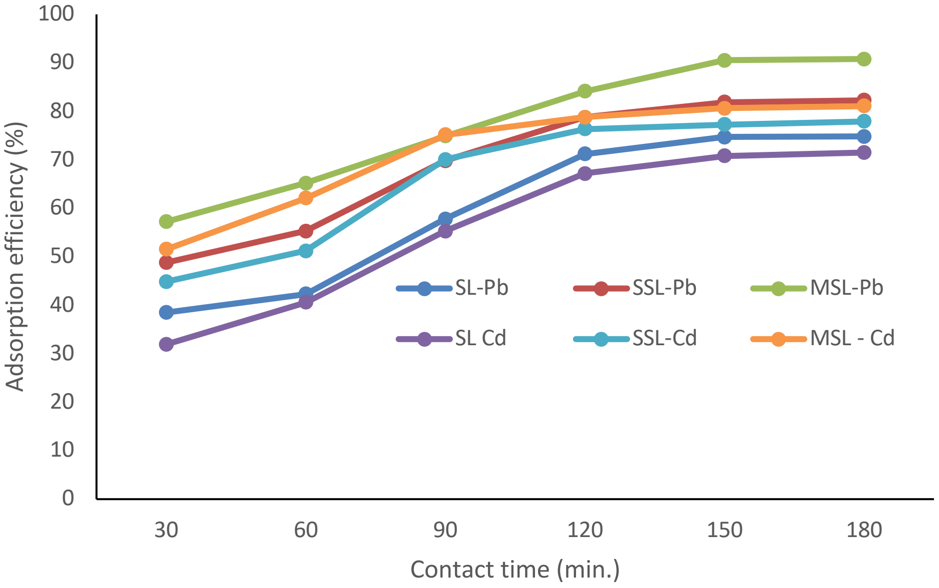

Figure 4: Effect of contact time on the adsorption of Pb^{2+} and Cd^{2+} using soda lignin and its ester derivatives

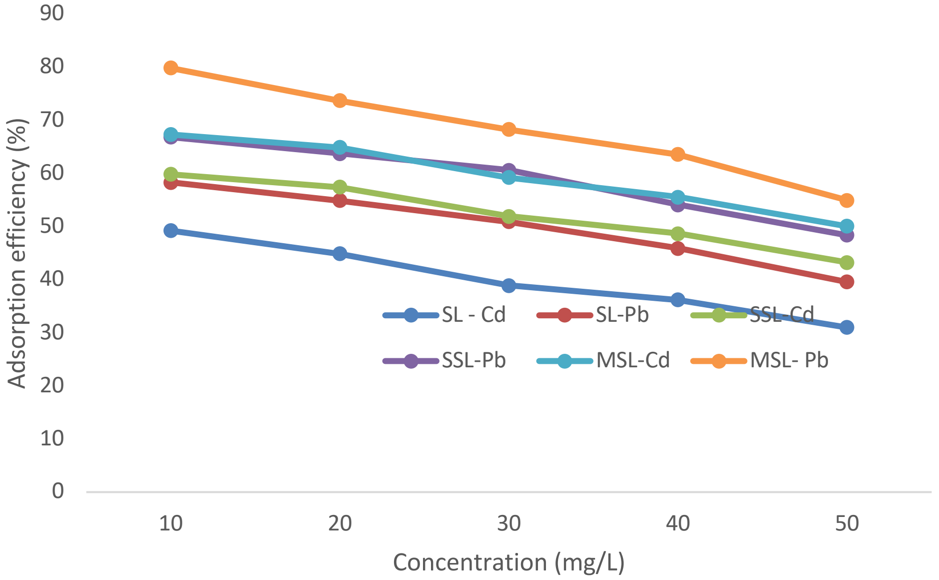

Figure 5: Effect of concentration on the adsorption of Pb^{2+} and Cd^{2+} using soda lignin and its ester derivatives

Adsorbate pH is one of the most important parameters that affects the adsorption of heavy metal ions from waste water by influencing both the surface properties of the adsorbents and the ionic form of the metal ions in solution (Radovic, 2000). Metal ions in aqueous solution usually converted into different insoluble hydrolysis products on account of pH change. As presented in Figure 6, the adsorption efficiency of Pb^{2+} and Cd^{2+}increase remarkably by increasing the adsorbate pH. The maximum adsorption efficiency of Cd^{2+} adsorption using soda lignin occurred at a pH of 4.0, and that of its ester derivatives occurred at a pH of 4.5. While the maximum adsorption efficiency of Pb^{2+} occurred at a pH of 3.5 and 4.0 for its ester derivatives. The reasons of the low pH of maximum adsorption of soda lignin are due to the fact that lignin is acid insoluble, as the adsorbate pH gradually increase, the solubility of soda lignin in adsorbate solution gradually increase thereby decreasing the adsorption efficiency. According to Zhang *et al*. (2020), a good adsorbent should be that one that is insoluble in the adsorbate solution.

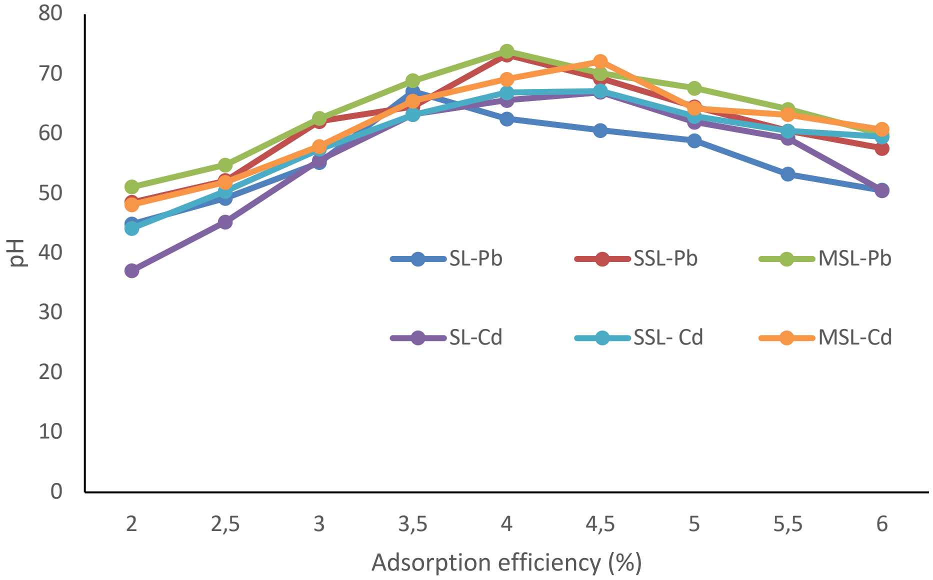

Figure 6: Effect of pH on the adsorption of Pb^{2+} and Cd^{2+} using soda lignin and its ester derivatives

Adsorption efficiency of Pb^{2+} gradually decreases after pH of 4.0 while a decrease in Cd^{2+}adsorption occurred after adsorbate pH of 4.5. The effect of pH on the adsorption efficiency of Pb^{2+} and Cd^{2+} is due to the chemical form of these metal ions in the solution at different pH and the charge of the adsorbent surface properties at a particular pH. In aqueous solution at pH 2, the adsorbent surface becomes positively charged, causing an electrostatic repulsion between the adsorbent surface and the metal ions. Also, at lower pH, there is greater competition between the hydrogen ions (H^+) and the heavy metals (M^{2+}). More hydrogen ions are present in the adsorbate solution at low pH and thereby took up more active site of the adsorbent, and the adsorption of the metal ions reduced (Zhang *et al*., 2020). At pH higher than 6, divalent metals such as Cadmium and Lead exist as $M(OH)_2$, $M(OH)_3^-$ and $M(OH)_4^{2-}$depending on the pH range of the solution.

At moderate pH, the positively charged M^{2+} and $M(OH)^+$ species present in the solution usually exchanged with H^+ from carboxylic (– COOH) or hydroxyl (-OH) groups of the adsorbent surface according to the mechanism of cation exchange (Wang *et al*., 2021), and the rate of adsorption increases because electrostatic repulsions are reduced due to deprotonation of the active sites (Gupta *et al*., 2021). When pH is higher than 4, metal hydroxylated species, particularly the solid hydroxide, participates in the adsorption process (Giraldo and Moreno-Pirajan, 2008). For pH values higher that 6 the species began to diminish and hydroxylated species, such as $M(OH)_2$, $M(OH)_3^-$, $M(OH)_4^{2-}$, precipitated on the surface of the adsorbent thereby blocking the active sites of the adsorbent and hence resulting in lower adsorption capacity (Harter and Naidu, 2001).

The quantity of Cd^{2+} and Pb^{2+} adsorbed (q_t) per unit time was evaluated and presented in Figures 7 and 8. The results revealed that the quantity of metal adsorbed increase with increase in adsorbent/

adsorbation contact time from 30 min and stated decreasing after 150 min. This is because at longer contact time most of the adsorbent binding sites have been saturated by the metal ions, hence the tendency of the adsorbent to adsorb more metal ions from the solution decreased. In all the adsorption processes, soda lignin ester derivatives adsorbed heavy metals more than soda lignin. This is mainly due to the fact that more oxygen atoms in the form of esters and carboxylic acid have been introduced into these derivatives during lignin modifications. These oxygens aid in the adsorption of heavy metal from waste water. The participation of the carbonyl functional group in the adsorption of Pb^{2+} and Cd^{2+} was confirmed by the FTIR spectra before and after the adsorption studies (Figure 1), (Chand *et al.*, 2014). After adsorption studies, there was a disappearance of the carbonyl absorption band 1684 cm^{-1} in SSL and 1707 cm^{-1} in MSL, and This indicates that there was an interaction between the metal ions with carbonyl functional group during adsorption (Paduraru *et al.*, 2015; Simonescu, 2012; Fadhil *et al.*, 2021).

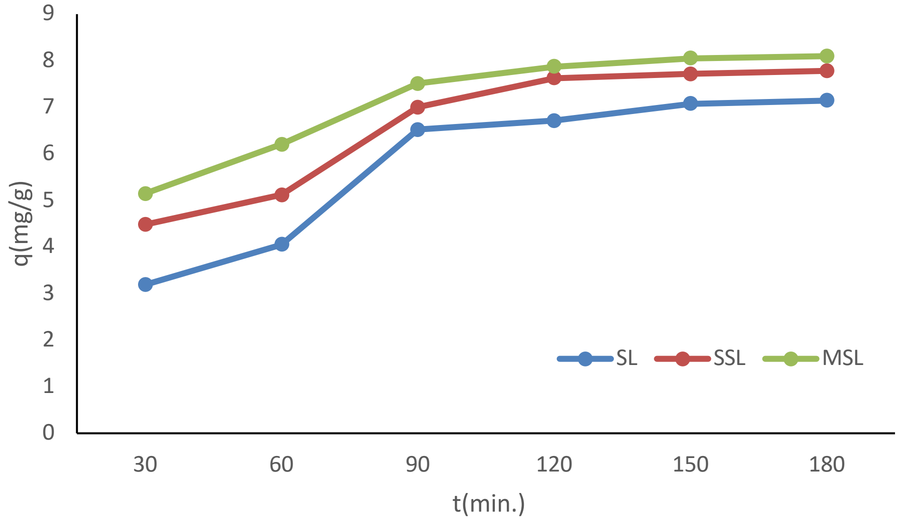

Figure 7: Quantity of Cd^{2+} adsorbed using soda lignin and its ester derivatives

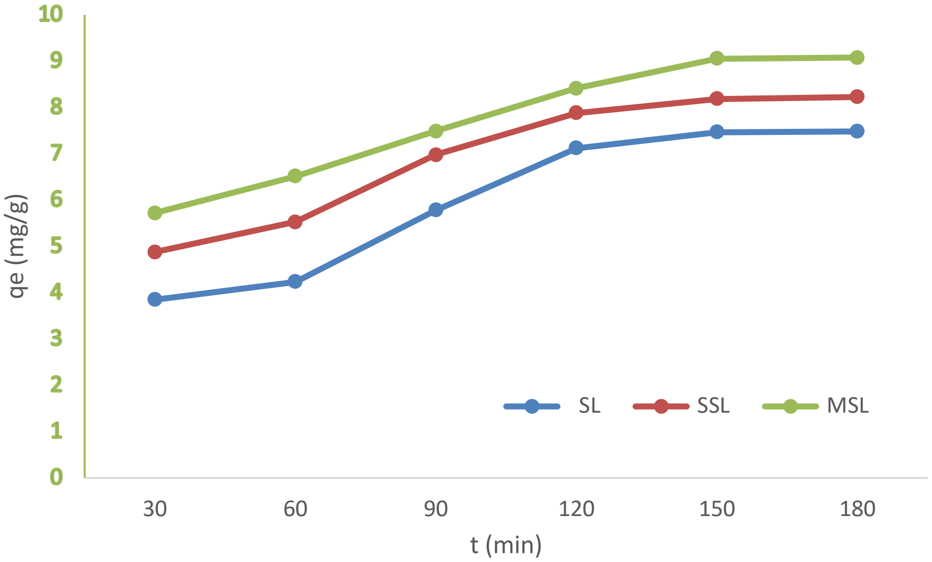

Figure 8: Quantity of Pb^{2+} adsorbed using soda lignin and its ester derivatives

The shift in vibrations frequency of some of the functional groups after metal ion adsorption was also observed. This can be explained based on the change in coordination sites of the functional groups due to the interactions of the Cd $^{2+}$ or Pb^{2+}ions with the functional group of the adsorbent (Thirumavalavan *et al*., 2011). However, there was an abnormal increase in hydroxyl absorption intensity of soda lignin after adsorption, this may be due to the formation of lead (II) hydroxide and cadmium (II) hydroxide on the surface of the adsorbents during adsorption (Chand *et al*., 2014).

Conclusion

Soda lignin extracted from Gm*elina arborea* wood was successfully modified into lignin esters. The physicochemical properties of lignin such as functional groups, absorbance, wavelength of maximum absorption, surface morphology and zero-point charge were different from that of its ester derivatives. At optimum contact time and adsorbent dosage, lignin esters adsorbed over 80% of the heavy metals form the simulated wastewater.

Hence lignin which is usually discarded as waste material in pulp and paper industries can be modified into lignin esters and use as adsorbent in the adsorption of heavy metals from industrial wastewater such as mining effluents and allied wastewater.

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References

Adebowale, K.O., Unuabonah, I.E., Olu-Owolabi, B.I. (2015). Adsorption of some heavy metal ions on sulphate- and phosphate-modified kaolin. *Appl. Clay Sci.,* 29:145–148.

Ad C., Benalia M., Laidani Y., Elmsellem H., Ben Saffedine F., Nouacer I., Djedid M., El Mahi B., Hammouti B. (2015). Adsorptive removal of cadmium from aqueous solution by Luffa Cylindrica: Equilibrium, dynamic and thermodynamic, *Der Pharma Chemica*, 7N°12: 388-397

Agustin, M. B., Mikkonen, Kirsi S., Marianna Kemell, Lahtinend, P. and Lehtonen,M. (2022). Systematic investigation of the adsorption potential of lignin- and cellulose-based nanomaterials towards pharmaceuticals. *Environ. Sci. Nano*, 9: 2006

Bernhoft, R. A. (2012). Mercury toxicity and treatment: a review of the literature. *J. Environ. Public Health*, 460508

Bhatti, H. N., Sadaf, S. and Aleem, A. (2015). Treatment of textile effluents by low-cost agricultural wastes; batch biosorption study. *J. Animal plant science,* 25: 284 – 289.

Bayuo, J., Rwiza, M. and Mtei , K. (2022). A comprehensive review on the decontamination of lead (II) from water and wastewater by low-cost biosorbents. *RSC Adv.*, 12 **:** 11233-11254

Chand, P., Shil, A. K., Sharma, M. and Pakade, Y. B. (2014). Improved adsorption of cadmium ions from aqueous solution using chemically modified apple pomace: mechanism, kinetics and thermodynamics. *International Biodeterioriation and Biodegradation*, 90:8-16.

Chen, C.L. (1992). Nitrobenzene and Cupric Oxide Oxidations. In: *Methods in Lignin Chemistry*; Lin, S., Dence, C., Eds., Springer: Berlin/Heidelberg, Germany, 301–321

Chen, Y., Stark, M. N, Cai, Z, Frihart, C. R. Lorenz, L. F. and. Ibac, R. E. (2014). Chemical Modification of Kraft Lignin: Effect on Chemical and Thermal Properties. *BioResources* 9(3):5488-5500.

Cheraghi E, Ameri E. and Moheb, A. (2015). Continuous biosorption of Cd (II) ions from aqueous solutions by sesame waste; thermodynamics and fixed – bed column studies. *Desalin Water Treat.,* 57: 6936-6949. https://doi.org/10.1080/19443994.2015.1012744

Cobbina, S. J., Chen, Y., Zhou, Z.,Wu, X., Zhao, T., Zhang, Z., et al. (2015). Toxicity assessment due to sub-chronic exposure to individual and mixtures of four toxic heavy metals. *J. Hazard. Mater.* 294, 109–120.

Costa, M. (2019). Review of arsenic toxicity, speciation and polyadenylation of canonical histones. *Toxicol. Appl. Pharmacol*. 375, 1–4.

Danish, M., Hashim, R., Ibrahim, M. N. M., & Sulaiman, O. (2013). Effect of acidic activating agents on surface area and surface functional groups of activated carbons produced from Acacia mangium wood. *Journal of Analytical and Applied Pyrolysis*, 104, 418–425.

El Hammari L., Latifi S., Saoiabi S., Saoiabi A., Azzaoui K., Hammouti B., Chetouani A., Sabbahi R., (2022). Toxic heavy metals removal from river water using a porous phospho-calcic hydroxyapatite, *Mor. J. Chem.* 10(1): 62-72

Errich A., Azzaoui K., Mejdoubi E., Hammouti B., Abidi N., Akartasse N., Benidire L., EL Hajjaji S., Sabbahi R., Lamhamdi A*.,* (2021). Toxic heavy metals removal using a hydroxyapatite and hydroxyethyl cellulose modified with a new Gum Arabic, *Indonesian Journal of Science & Technology* 6(1): 41-64

Fadhil, Z., Zageer, D. S. Faris, A. H. and Al-Mashhadani, M. H. (2021). The usage of lignin in two significant applications: As adsorbent surface of water pollutants and antioxidant of plastic polymers: short review. *GSC Advanced Research and Reviews*, 08(03):108–118.

Faix, O., Grünwald, C. and Beinhoff, O. (1992). Determination of phenolic hydroxyl group Content of milled wood lignins from different botanical origins using selective aminolysis, FTIR, ^{1}H-NMR and UV - Spectroscopy. *Holzforschung*, 46 (5): 425 – 431.

Fernandes Azevedo, B., Barros Furieri, L., Peçanha, F. M., Wiggers, G. A., Frizera Vassallo, P., Ronacher Simões, M.,. (2012). Toxic effects of mercury on the cardiovascular and central nervous systems. *Biomed. Res. Int*., 949048.

Gazwi, H. S. S., Yassien, E. E., and Hassan, H. M. (2020). Mitigation of lead neurotoxicity by the ethanolic extract of Laurus leaf in rats. *Ecotoxicol. Environ. Safe* 192, 110297.

Giraldo, L. and Moreno-Pirajan, J. C. (2008). Pb^{2+} Adsorption from aqueous solutions on activated carbons obtained from lignocellulosic residues. *Brazilian Journal of Chemical Engineering.* 25 (1): 143 – 151.

Gottipati, R. and Mishra, S. (2012). Application of response surface methodology for optimization of Cr (III) and Cr(VI) adsorption on commercial activated carbons, *Research Journal of Chemical Sciences,* 2(2): 40-48.

Gulipalli, C, H., Sekharao, Prasad, B. and Wasewar, K. L. (2011). Batch study, equilibrium and kinetics of adsorption of selenium using rice husk ash. *Journal of Engineering Science and Technology* 6 (5): 586 – 605.

Gupta, A., Sharma, V., Sharma, K., Kumar, V., Choudhary, S., Mankotia, P., Kumar, B., Mishra, H., Moulick, A. and Ekielski, A. (2021). A Review of Adsorbents for Heavy Metal Decontamination: Growing Approach to Wastewater Treatment. *Materials,* 14: 4702.

Han, R., Zhung, L., Song C., Zhang, M, Zhu, H, M. and Zhang L. (2010). Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode. *Carbohydrate polymer*,79: 1140 – 1149

Harter, R. and Naidu, R. (2001). An assessment of environmental and solution parameter impact on trace-metal sorption by soils. *Soil Sci Soc. Am. J.*, 65: 597-612

Hazarika, K. and Gogoi, S. (2014). Comparative study of an enhanced oil recovery process with various chemicals for Naharkatiya oil field. *International Journal of Applied Sciences and Biotechnology*, 2(4):432-436.

Jain, M., Garg, V.K. and Kadirvelu, K. (2010). Adsorption of hexavalent chromium from aqueous medium onto carbonaceous adsorbents prepared from waste biomass, *Journal of Environmental Management*, 91(4): 949 – 957.

Karimi F, Ayati A, Tanhaei B, Sanati AL, Afshar S, Kardan A, Dabirifar Z, Karaman C. (2022). Removal of Metal Ions Using a New Magnetic Chitosan NanoBio-Adsorbent; A Powerful Approach in Water Treatment. *Environmental Research,* 203: 111753.

Lakherwal, D. (2014). Adsorption of Heavy Metals: A review. *International Journal of Environmental Research and Development*, 4 (1): 41-48.

Lin, S. Y. and Dence, C. W. (1992). Methods in Lignin Chemistry; Springer Series in Wood Science; Springer. Berlin, Germany,217–232

Mazumdar, M., Bellinger, D. C., Gregas, M., Abanilla, K., Bacic, J., and Needleman, H. L. (2011). Low-level environmental lead exposure in childhood and adult intellectual function: a follow-up study. *Environ. Health,* 10 (1), 24

Mekonnen, E., Yitbarek, M. and Soreta, T. R. (2015). Kinetic and Thermodynamic Studies of the Adsorption of Cr(VI) onto Some Selected Local Adsorbents. *South African Journal of Chemistry*, 68: 45 – 52

Namasivayam, C. and Kavitha, D. (2006). IR, XRD and SEM studies on the mechanism of adsorption of dyes and phenols by coir pith carbon from aqueous phase. *Microchem J.* 83: 43- 48.

Paduraru, C., Tofan, L., Teodosiu, C., Bunia, I., Tudorachi, N. and Toma, O. (2015). Biosorption of Zinc (II) on rapeseed waste: Equilibrium studies and thermogravimetric investigations. *Process Safety and Environmental Protection*, 94: 18-25.

Patrycja Miros-Kudra, Paulina Sobczak, Ewa Kopania (2022). Removal of Heavy Metals from Aqueous Solutions with the Use of Lignins and Biomass. *Fibres & Textiles in Eastern Europe*, 30 (2) :99 –111

Radovic, L. R., Moreno-Castilla C. and Rivera-Utrilla J. (2000). Carbons materials as adsorbents in aqueous solutions. In: *Chemistry and Physics of Carbon.* A series of Advances. (Ed). Marcel dekker. New York. 267-269.

Santander, P., Butter , B., Oyarce, E., Yanez ,M., Xiao, L., and Sanchez, J. (2021). Lignin-based adsorbent materials for metal ion removal from wastewater: A review. *Industrial Crops and Products, 167: 1-13*

Sears, G.W. (1956). Determination of Specific Surface Area of Colloidal Silica by Titration with Sodium Hydroxide. *Analytical Chemistry*, 28(12): 1981 – 1983.

Sellaoui, L., Gomez-Aviles, A., Dhaouadi, F., Bedia, J., Bonilla-Petriciolet, A., Rtimi, S. and Belver, C. (2023). Adsorption of emerging pollutants on lignin-based activated carbon: Analysis of adsorption mechanism via characterization, kinetics and equilibrium studies. *Chemical Engineering Journal* 452: 139399

Sharma, Y. C., and Upadhyay, S. N. (2009). Removal of a cationic dye from water and wastewater by adsorption on activated carbon developed from coconut coir. *Energy and fuels* 23: 2983 – 2988

Simonescu, M. C. (2012) Application of FTIR Spectroscopy in Environmental Studies. In: Advanced Aspects of Spectroscopy. Farrukh, A. M. (ed). Intech Publishers, New York, 49-84

Surina, I., Jablonsky, M., Haz, A., Sladkova, A., Briskarova, A., Kacik, F., and Sima, J. (2015). "Characterization of non-wood lignin precipitated with sulphuric acid of various concentrations," BioResources, 10 (1), 1408-1423

Thirumavalavan, M., Lai, Y. L. and Lee, J. F. (2011). Fourier transform infrared spectroscopic analysis of fruit peels before and after the adsorption of heavy metal ions from aqueous solution. *Journal of Chemical Engineering Data,* 56:2249-2255.

Wang, X., Li, X., Peng, L., Han, S., Hao, C., Jiang, C. and Fan, X. (2021). Effective removal of heavy metals from water using porous lignin-based adsorbents. *Chemosphere,* 279:1- 10

Wang, C., Wang, X., Li, N., Tao, J., Yan, B., Cui, X., Chen, G. (2022). Adsorption of Lead from Aqueous Solution by Biochar: A Review. *Clean Technol*. 4, 629 – 652.

Yang, S., Wang, L, Zhang, X., Yang, W. and Song, G. (2015). Enhanced adsorption of congo red dye by functionalized carbon nanotube/mixed metal oxides nanocomposite derived from layered double hydroxide precursor. *Chem. Eng. J.*, 275: 315 - 321

Zhang, M., Yin, Q., Ji, X., Wang, F., Gao, X. and Zhao, M. (2020). High and fast adsorption of Cd (II) and Pb (II) ions from aqueous Solutions by waste biomass-based hydrogel. *Scientific report, nature research,*10:3285

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