

SYNTHESIS AND CHARACTERIZATION OF MODIFIED LIGNIN TO BE USED IN THE REMOVAL OF SOME HEAVY METALS FROM INDUSTRIAL WASTE WATER IN POWER PLANTS

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ABSTRACT

A soluble lignin derivative having an amino group was synthesized by a technique based on dry method by the reaction of isolated lignin from guava leaves with thiourea. The factors affecting the nitrogen content of the produced modified lignin mainly: reaction temperature, time and sodium hydroxide concentration besides the concentration of thiourea were studied and discussed briefly.

It was concluded that higher nitrogen content of lignin derivative is obtained at reaction temperature 90°C for reaction time 90 minute. Moreover increasing the amount of thiourea was accompanied by an increase in nitrogen content until a certain ratio. Product obtained was characterized by FT-IR, Thermo gravimetric analysis TGA, elemental analysis (C, H, N, and S). Nevertheless, the adsorption efficiency of metal ions as Zn, Cu, Ni, Cd, Co, V and Fe was determined using atomic absorption spectrometry (AAS). The flocculation performance of the obtained modified lignin was evaluated in terms of turbidity, organic matter, total hardness and total silica. It was observed that the best clarification doses were at 26 ppm ferric chloride and 4ppm modified lignin. This combined dose gives the lowest values of turbidity, total alkalinity, organic matter and total silica which changed from (18.2 NTU, 121ppm, 17.3ppm and 21.8ppm) to (0.97 NTU, 107ppm, 10.89ppm and 7.15ppm) respectively.

It was found also that the modified lignin has high efficiency for removal of elements. For instance, as much as 75% of (Ni^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} , Mn^{2+}) were removed by using (8 ppm) of modified lignin, and 95% removal of (Fe and Cu).

Key words: lignin, flocculants, heavy metal removal, water treatment.

INTRODUCTION

The nature and characteristics of pollutants in water are important in determining the type of the treatment process required for their removal. The size of the particles is another very important characteristic because size determines to a large extent the type of treatment process that can be applied (Fanta *et al.*, 1970).

Flocculants are the materials, which are used in fast solid liquid separations by an aggregation process of colloidal particles; the process is termed as flocculation. Commercial forms of synthetic flocculants may contain toxic monomers from the synthesis and additives. In many countries, the disposal of flocculated sludge with polyacrylamide derivatives has been limited and will be strictly prohibited (Guo *et al.*, 2006 and Hao *et al.*, 2007). An important member of renewable primary products such as cellulose, starch and chitosan, especially low-cost starch, are alternatives to synthetic flocculants (Hafez, 2014; Alkadi, 2015; El-Kareish, 2018). In recent years, considerable attention has been paid on natural materials as flocculants and chelating agents to remove heavy metals (Heinze *et al.*, 2004; Jacrnstrocm *et al.*, 1995 and Pal *et al.*, 2005).

Treatment of industrial wastewater is challenging due to the variation of contaminants. A careful assessment for the types of contaminants can help in an efficient treatment. Industrial wastewater is classified according to their physical, chemical and biological characteristics (Abdel Wahab *et al.* 2018; Ismail *et al.* 2019 and El Sayed *et al.*, 2016). More often, a complex industrial waste is introduced that is hard to be treated by simple methods. Yet, the most hazardous industrial contaminants are heavy metals. Once heavy metals enter food chain they accumulate causing serious diseases (Babel and Kurniawan, 2003). Not only heavy metals but also oil and greases act as a source of water pollution. Although it may be assumed that using water for heating or cooling may not affect water quality, water coming out of cooling or heating cycle damage the aquatic life and water quality. Oil and grease (organic matters) come out with cooling or heating wastewater. The oil and grease cause oxygen depletion. Oil and grease form a thin layer that prevents oxygen from getting to water plants and animals thus killing them. Phosphorus and nitrogen both also participate in water contamination. The increase of phosphorous and nitrogen levels lead to increase in nutrients. Increasing level of nutrients speeds up the growth rate of water plants such as algae. The large quantities of algae consume the oxygen in water causing a devastating effect on fish and other living organisms. Although in many countries, the regulation enforces the treatment of industrial wastewater, most methods used are either inefficient or expensive (Ali and Gupta, 2006). Scientists investigated more economical and efficient methods. They stated that the

combined treatment components can offer better and more efficient pathways in water treatment. Scientists search for natural materials that cost effective and ecofriendly (Crini, 2006). Natural materials such as chitosan, mineral silicate and clay have been introduced as effective materials in the treatment of industrial wastewater (Sanchez *et al.*, 1999). Natural clay showed to be effective in the removal of some contaminants such as many heavy metals (Veli and Alyuz, 2007). Biopolymers or renewable polymers such as cellulose, lignin, starch, pectin and chitin are the abundantly available polymers in environment in the form of plant biomass or other biological sources. Serious studies have been therefore accepted to develop more effective and low-cost metal adsorbents. Materials include industrial or agricultural waste products such as unwanted slurry fly ash (Gupta *et al.*, 1999 and Wang *et al.*, 2004) lignite (Mohan *et al.*, 2006) pine bark (Al-Asheh *et al.*, 1997 and Goheen *et al.*, 1978) peat (McKay *et al.*, 1997) have studied the presentation of low-cost adsorbents for heavy metal removal from polluted water and analyzed for many years and still continues (Gabaldon *et al.*, 1996 and Kadirvelu *et al.*, 2000). Quiet, there are experiments to cultivate new organizations or improved processes for well-organized economic utilization as well as transformation of these biopolymers. Lignin sulfonation is the most deliberate reaction in lignin chemistry since it was the initial and cheapest way to make commodity (Suhas *et al.*, 2010). The lignosulfonates are the most extensively used lignin product in industries for well drilling; cement manufacture, formulation, and pouring; ceramics manufacturing; and

construction materials. Both lignins and lignosulfonates are used to organize oil (Rogers, 1963; King *et al.*, 1960 and Morton *et al.*, 1996). In a biodegradation study, the particular lignocellulosics illustrate highest lignin content in coir pith (37%) followed by *P. juliflora* (23%) and *L. camara* (22%). Though, *Oscillatoria* treated lignocellulosics confirm maximum reduction of lignin content in *L. camara* (18.2%) followed by *P. juliflora* (17.4%) and coir pith (16.9%) after 30 days of incubation was re-evaluate the literature on lignin as a biosorbent. (Srivastava., 1994) obtained extremely high uptake of Pb (II) and Zn(II), up to 1587 and 73 mg/g for Pb (II) and Zn(II), respectively, by using lignin extracted from black liquor. (Demirbas *et al.*, 2004) reported a maximum adsorption competence of 8.2–9.0 mg/g for Pb (II) and 6.7–7.5 mg/g for Cd (II) on lignin from beech and poplar wood personalized by alkaline glycerol delignification (Moreno-Castilla *et al.*, 2004). From the above data and the review, there are significant variations in the metal sorption capability of different types of lignin. Also, the interconnected mechanisms of metal sorption by lignin are still subject to debate. Several studies have originated that ion-exchange mechanisms may be accountable for the sorption of metal ions on lignin (Crist *et al.*, 2003). Mohan *et al.*, 2006 suggested that no single mechanism could explain the Zn(II), respectively, by using lignin extracted from black liquor reported a maximum adsorption capacity of 8.2–9.0 mg/g for Pb (II) and 6.7–7.5 mg/g for Cd(II) on lignin from beech and poplar wood modified by alkaline glycerol delignification (Oubagaranadin *et al.*, 2009).

This investigation was introducing to give some modified agriculture wastes to be used in the treatment of wastewater.

EXPERIMENTAL

Chemicals: Guava leaves as a natural waste product was supplied from local farms, Commercial Thiourea., Sodium hydroxide was supplied by Spectrum, Hong Kong. Ethyl Alcohol was supplied by Adwic, German.,The other chemicals used for analysis of water were of analytical grade.

Source of wastewater: Air preheater washing water in power plants is collected in industrial wastewater basin. This wastewater contains many pollutants and used as source of industrial wastewater in this work.

Table (1): Specifications of the industrial wastewater

Parameters	Specifications
pH	2.5
Conductivity (μ S)	1357
Turbidity (NTU)	40.5
Total dissolved solids (mg/l)	10610
Total hardness (mg/l) as CaCO_3	1097.5
Partial alkalinity (mg/l) as CaCO_3	0
Total alkalinity (mg/l) as CaCO_3	167
Calcium hardness (mg/l) as CaCO_3	551.5
Magnesium hardness (mg/l) as CaCO_3	546
Organic matter (mg/l) as KMnO_4	90.2
COD (mg/l)	22
BOD (mg/l)	11
Ammonia, (mg/l) as NH_4	14.78
Oil and Grease (mg/l)	13.55
Colloidal silica (mg/l)	27

Cont. Table (1): Specifications of the industrial wastewater

Parameters	Specifications
Chloride ion (mg/l)	28
Fe (mg/l)	106
Cu (mg/l)	6.6
Zn (mg/l)	40
Ni (mg/l)	40
Cd (mg/l)	17
Mn (mg/l)	12
Co (mg/l)	13
V (mg/l)	105

Testing and analysis: All series of water examination and chemical analysis were carried out according to the standard method of (ASTM Book of Standards, I, II 2001).

Infrared Analyses: A Fourier transform infrared system (FTIR), JASCO FTIR 4110 spectrometer Japan, was used. Samples were prepared using the KBr disc technique. The infra, red absorption spectra were recorded in the region of 4000-400 cm^{-1} .

Jar test: Simulation of clarification applying Jar test method is considered the most applicable way to permit the comparison of various chemicals combination for determining the optimum chemical program was applied. The jar test method contains a set of six beakers (1liter) in conjugation with multiple stirrers. Each beaker was filled with one liter of wastewater and stirred at 100 rpm. The different doses of coagulant were added rapidly and stirred for 3 minutes. The stirring rate was then reduced to 50 and 20 rpm for a time of 5 and 10 minutes respectively to allow complete flock formation,

and then stirring was stopped. The comparative settling rate, flock size and supernatant clarity were recorded. After a settling time of 15 minutes, 250 ml of supernatant water were siphoned-off for further analysis.

Water analysis:

- Turbidity of water was measured in nephelometric turbidity units (NTU) using Helige digital direct reading turbidimeter.
- Organic matter of water was determined by consumption of KMnO_4 in acidic solution.
- Total silica determined spectrophotometry-using spectrophotometer.
- Metal ions in water were quantified using Atomic Absorption Spectrometer, Solaar S-4 S- Series Thermo Electron Corporation UK.
- The pH of solutions were determined using accumet pH meter model 810 Fisher scientific
- Determination of removal efficiency:
 - % Removal of metal ions, were calculated from the following formula:
 - %Removal = $C_0 - C / C_0 \times 100$

Where, C_0 and C = metal ion concentration, organic matter and turbidity of wastewater before and after coagulation treatment by corncobs derivative, respectively.

Thermogravimetric Analysis (TGA): Thermogravimetric analysis of extracted and modified lignin was performed with Thermo gravimetric analyzer Lecco: Mac-500.ST. Joseph. Michigan-USA. This apparatus

provides a continuous measurement of sample weight at a range of temperatures between ambient and 600 °C. The samples were heated in an alumina cell to 600°C at heating rate of 10°C/mm with nitrogen as the circulating gas.

Elemental analysis (C.H.N, and S): The elemental analysis of lignin and modified lignin (C, H, N, and S) determined by Leco Truspect (CHN) Analyzer, Leco Corporation 3000 LAKE View AVE.ST. Joseph, MI- USA.

lignin isolation by the (NaOH) method: The NaOH method of (Anwar *et al.*, 2004) was carried out for the isolation of lignin from guava leaves. The guava leaves (20 g) was grinded and sieved in 200- μ m mesh. The grinded guava leaves was mixed for 3 h at 90°C with 8% aq. NaOH (50 mL) and the slurry filtered. The filtrate was centrifuged for 20 min, the supernatant was collected, evaporated and dried. The dried sediment was washed twice with distilled water (50 mL) and centrifuged. The residue was suspended in water and adjusted to pH 7 by adding (1M) hydrochloric acid, and the slurry was centrifuged as lignin. The lignin washed three times with acetone and filtered. The filtrated lignin dried in a convection oven at 40 °C for 48 h. The produced lignin was weighted in an analytical balance with production yield of 2 gm.

Preparation of modified lignin: 10 gram of lignin as obtained from lignin isolation step with different concentration of thiouria mainly (1, 2,3,4,5 and 6 gm.) were grinded. The mixtures were heated to a melt until gas was evolved for with intermittent stirring. These mixtures were mixed with 2ml of

different concentration of sodium hydroxide solutions (2, 4, 6, 8, and 10%). Then left at different temperature from 20-160 for different time for completing the reaction. After that, the reaction was cooled to 20° C. and 20 ml of water were added. It was diluted against 100 parts H₂O to give 98% yield of product having different nitrogen and sulfur content (Yalpani *et al.*, 1995).

RESULTS AND DISCUSSION:

Figure (1) shows the typical photograph of the guava leaves (waste material) that used in this work.



Figure (1): shows the typical photo of the guava leaves

The utilization of these waste cause minimization of potential waste disposal problems. However, agricultural waste represents an effective, cheap, biodegradable and environmentally safe for preparation of ion

exchangers that are valuable for water treatment (Gebbie, 2006; Domard, 1996; Jeon and Höll, 2003; Guibal, 2005 and Hu, 2011).

Any agriculture products contain cellulose, hemicellulose and lignin with different percentages as shown in figure (2).

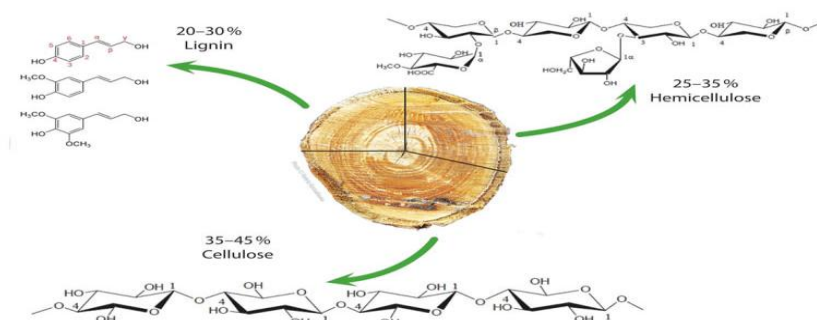


Figure (2): Chemical Structures of Cellulose, Hemicellulose and Lignin

Mechanism of preparing modified lignin: Lignin is quite complex, with different structures and repeat units depending on the plant species, growing location, and growth duration (Zakzeski *et al.*, 2010; Nada *et al.*, 2000).

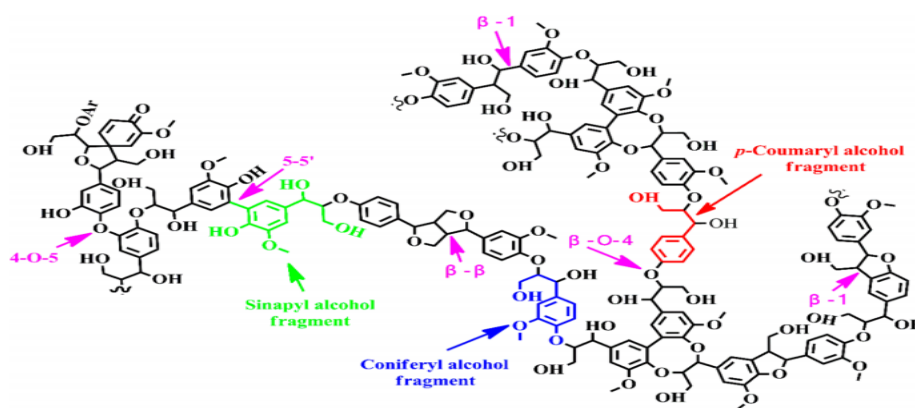


Figure (3): Structure of lignin

Lignin can react with thiourea in alkaline media at high temperature to incorporate amino group and sulfure to the lignin backbone to form (Modified lignin) as the following reaction:

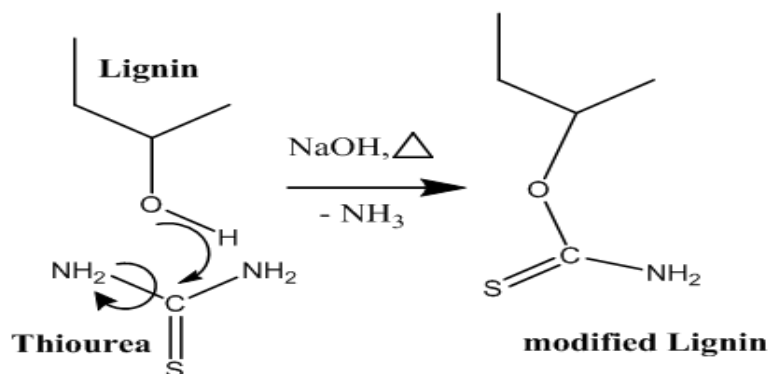


Figure (4)

The produced modified lignin has amino group which imparts the positivity character to the lignin, which acts as ion exchange material and help to remove the turbidity and metal ions from wastewater.

Modified lignin investigation:

Factors affecting reaction of thiourea and lignin: The parameters influencing reaction of thiourea and lignin, for example, time of reaction, temperature of reaction, sodium hydroxide concentration, and additionally, thiourea concentration have been investigated to decide the ideal conditions for reaction yield as nitrogen content.

Effect of temperature: The effect of temperature on the nitrogen content of the lignin derivatives as shown in figure (5) at lignin (2g), 1gm thiourea, 20

min and 2% conc. of NaOH. It is clear that the nitrogen content increases as the temperature is raised up to 120°C. Obviously, the nitrogen content increments as the temperature is raised up to 120°C. This may be ascribed to the fact that, the mobility of the ions and the molecules increased by raising the temperature of the subsequent in an augmentation in the rate of reaction.

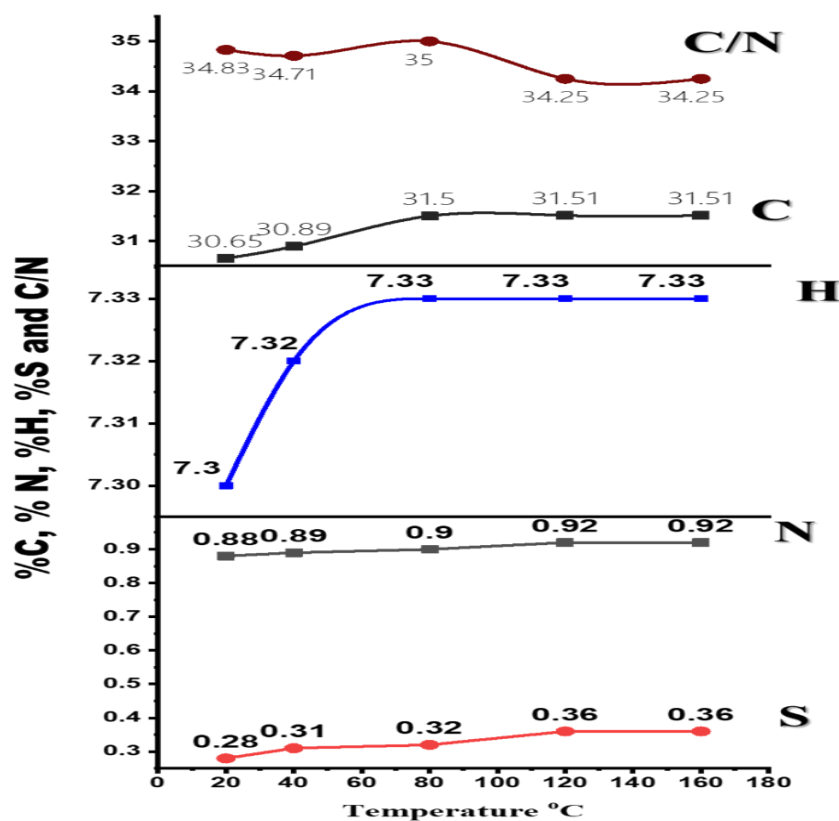


Figure (5): Effect of the temperature on the % (N, C, H, S and C/N) of modified lignin (1gm 20 min. and 2% conc. of NaOH)

Effect of Reaction time: The results represented in Figure (6) shows the effect of the reaction time on the efficiency of the reacting products as nitrogen content at: 1gm thiouria, and 2% conc. of NaOH. It is found that, at the chosen temperature (120 °C), the increase of the reaction time from 20 to 120 min is accompanied by an increment in the reaction rate represented by nitrogen content, and that, after 100 min, the increment does not change. The sulfur values kept constant at 0.36 %.The carbon values are limited from 30.65 to 31.51, Hydrogen values varied between 7.30 to 7.33 % in same time that Nitrogen values varied between 0.88 to 0.92 %, which affect the carbon to nitrogen (C/N) ratio, which varied between 34.25 to 35.01.

It may be concluded that longer reaction time leads to an increase of the reactivity of the ions and molecules in the reacting medium; hence, the activation reaction power is increased leading to greater nitrogen contents in the lignin derivative.

It might be presumed that more drawn out reaction time prompts an increase of the reactivity of the ions and molecules in the reacting medium; consequently, the actuation response control is expanded leading to more noteworthy nitrogen substance in the lignin derivatives.

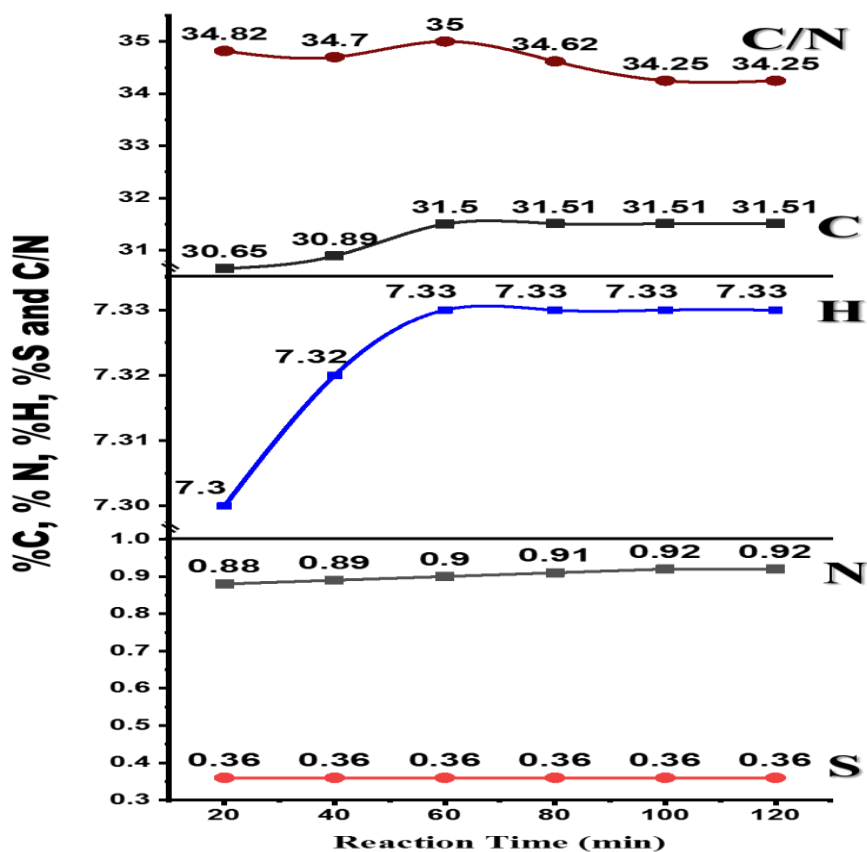


Figure (6): Effect of the reaction time on the on the %(N, C, H, S and C/N) of lignin derivatives

Effect of sodium hydroxide concentration: Figure (7) represents the effect of NaOH concentration on nitrogen content in the modified lignin. For the optimum conditions of temperature (120°C), reaction time (100 min) and 1gm thiouria, different concentrations of NaOH ranging from 2-10% were

examined. It is clear that, by increasing the NaOH concentration until 8%, the nitrogen content increases to a maximum value indicating that this concentration is sufficient for complete neutralization of theuoria and lignin. Further increase of NaOH concentration caused no increase in the nitrogen content.

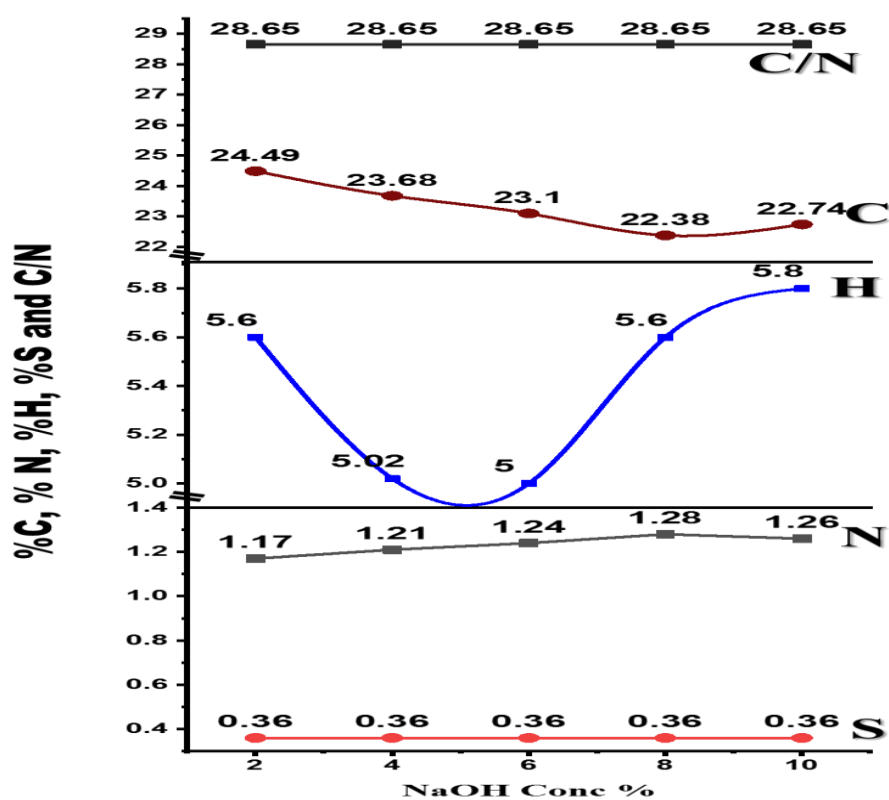


Figure (7): Effect of the NaOH on the nitrogen content (%) of lignin derivatives

Effect of thiourea concentration: Different concentration of thiourea namely (1, 2, 3, 4, 5 and 6 gm) were examined at the aforementioned chosen conditions with lignin. The obtained results are represented in Figure (8) which indicates that by increasing the amount of thiourea, the reaction product increases until (5gm) which is the better (2.48%) then began to decrease by further increment.

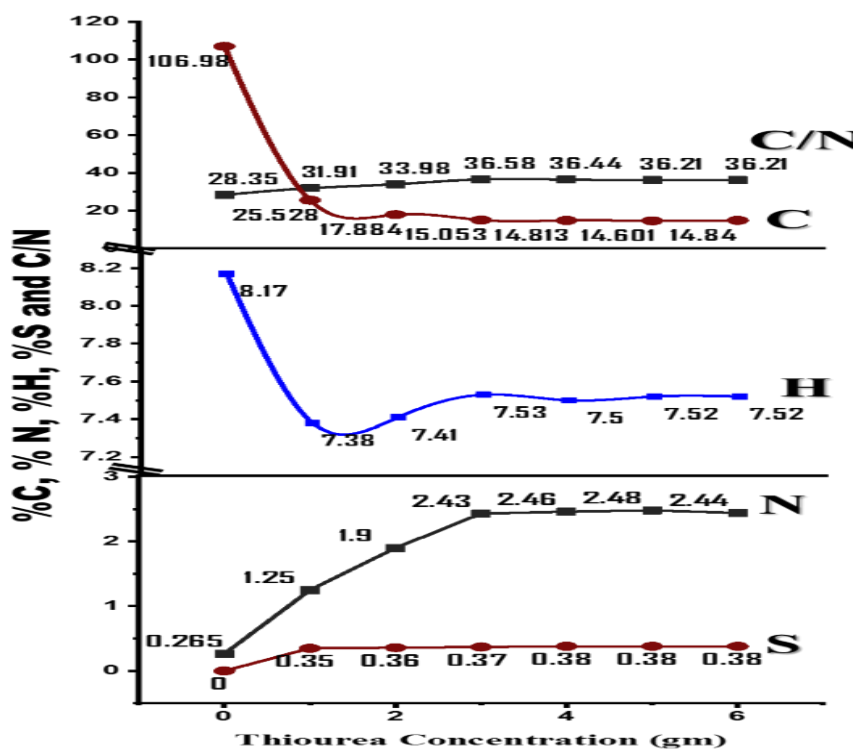


Figure (8): Effect of the thiourea concentration on the % (N, C, H, S and C/N) of modified lignin.

According to nitrogen content of the aforementioned prepared modified lignin. The higher nitrogen content sample was prepared and chosen to make characterization comparison between lignin and modified lignin. In addition to complete the work in the application of water treatment as coagulant especially in the treatment of wastewater produced from washing water of air preheater units in power station by making a comparative study between the prepared lignin derivative and ferric chloride as conventional coagulant materials. The following part shows such results for such application.

Characterization of lignin and modified lignin:

Thermogravimetric analysis (TGA): TGA is a simple and accurate method for studying the decomposition pattern and the thermal stability of the polymers. Figure (9) shows the thermogravimetric analysis (TGA) for lignin (blank), modified lignin, respectively.

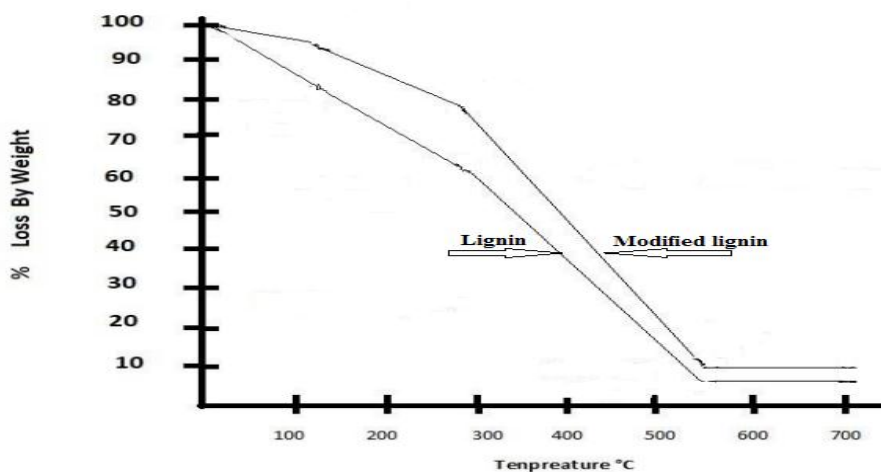


Figure (9): TGA of lignin and modified lignin.

As it obvious, the range for lignin Figure (9) demonstrates four characteristic stages for decomposition. The principal arrange begins at 100 °C and end at 150 °C with a weight reduction of 6 %. This could be perceived as due to the moisture content of lignin. The second stage, which identified with the primary decay of lignin macromolecules happens in one stage of decomposition begin at 150 °C and end at 300 °C with most extreme deterioration temperature of 300 °C and weight reduction of 20%. The third phase of weight loss is identified with the carbonization procedure, which happens up to 550 °C with a weight reduction of 95%. More increasing of temperature leads to for metal oxides with weight loss of 98%. For the considered modified lignin, the primary stage begins at 100 °C and end at 150 °C with weight reduction of 14%. The second phase of decomposition, representing the main decomposition, continues in two stages. The initial step begins at 250 °C and end at 400 °C. The weight reduction in this step for the studied sample was 42 %.

This step of degradation simulates and corresponds to main degradation process recorded for lignin. This degradation, most likely, could be identified with the degradation of modified lignin. The third phase of degradation happens up to 550 °C with weight reduction of 92% for the sample. More increasing of temperature leads to for metal oxides with weight loss of 95%.

Energy dispersive x-ray (EDX): The grinded lignin and lignin derivative were analyzed using energy dispersive x-ray (EDX) and elemental analysis analyzer it has the following specifications:

Figure (10.a) showed the X-ray analysis chart which show that the native lignin contains each of C, Si, K and Ca elements. Figure (10.b) showed the X-ray analysis chart which show that the lignin derivative contains each of C, Si, S, K and Ca elements.

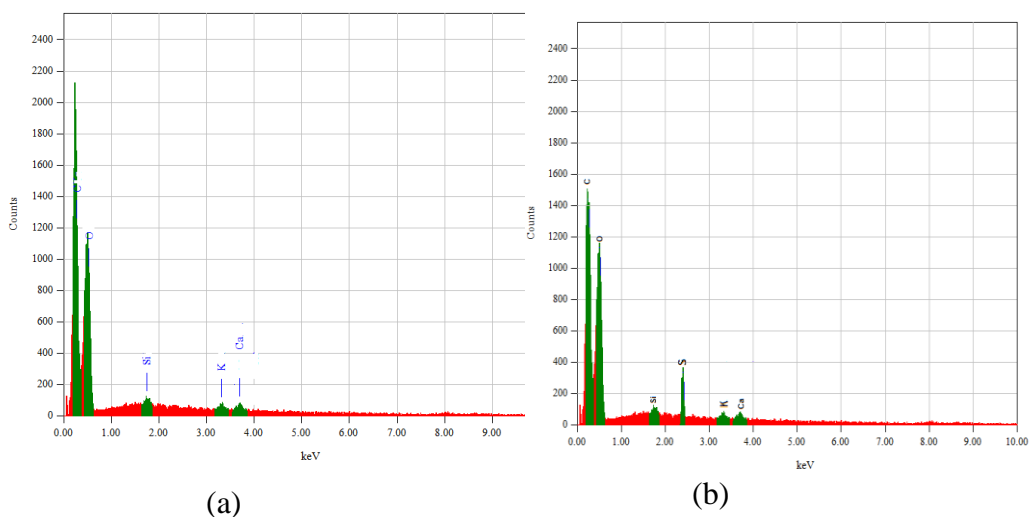


Figure (10): Energy dispersive X-ray (EDX) of lignin (a) and modified lignin (b)

Elemental analysis of raw and modified lignin: The elemental analysis of lignin and modified one are listed in table (2).

Table (2): Elemental analysis of lignin and modified lignin

Element	Lignin					Modified lignin				
	C	H	N	S	C/N	C	H	N	S	C/N
Percentage	28.35	5.19	0.75	Nil	37.8	36.21	7.52	2.44	0.38	14.84

FTIR of raw and modified lignin:

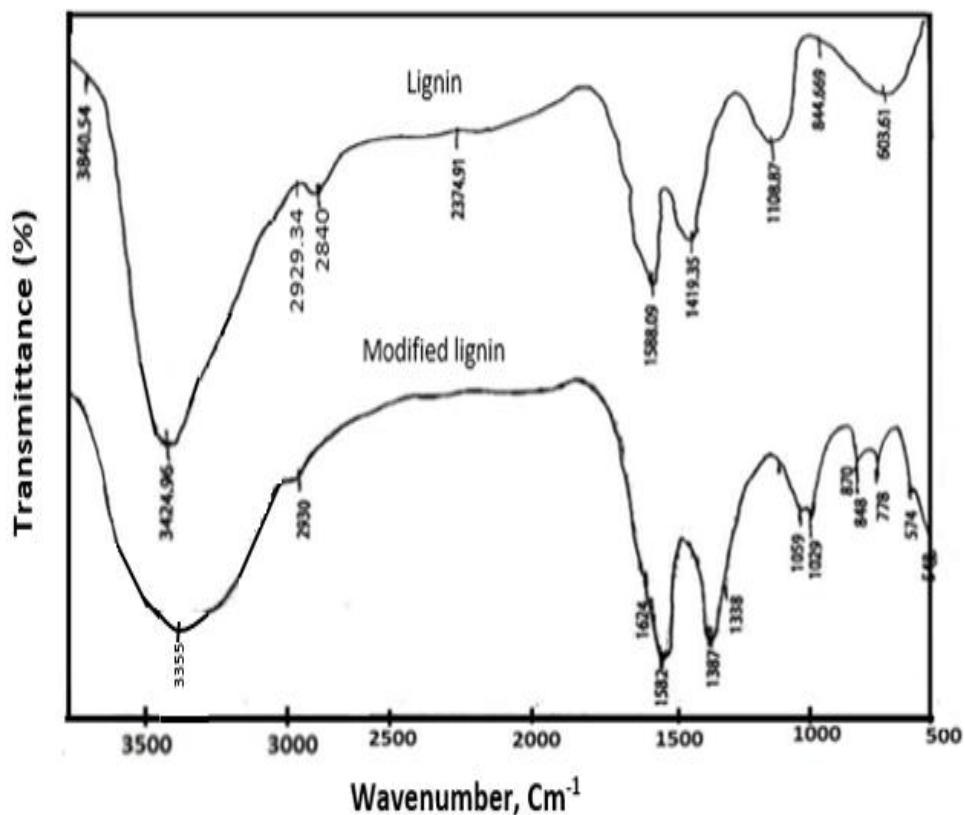


Figure (11): FTIR of raw and modified lignin

The fine powder of isolated lignin from guava leaves was investigated using FTIR technique. The investigation was conducted to identify and characterize the product by comparing the spectra of lignin and modified lignin. Thus, the FTIR spectra of the produced isolated lignin and modified one was studied to show its characteristics. It was concluded from Figure (11)

that all the peaks detected for the isolated lignin are similar to those of modified lignin and related to C-OH, CH, CH₂, CH₃ and C=O groups. Whereas, the FTIR spectra of pure lignin showed a peak at 3424.96 cm⁻¹ which assigned to OH stretching vibration of hydroxyl group of the lignin; this peak in the modified lignin was broadened due to -OH and -NH₂ stretching. A symmetric stretching for CH₃ of methoxyl group appeared at 2840 cm⁻¹. The band detected at 2929.34 cm⁻¹ arises from C-H stretching in methyl and methylene group. A peak at 1713.83 cm⁻¹ assigned to carbonyl stretching-unconjugated ketone and carboxyl groups. The peaks observed at 1588.091cm⁻¹ and 1419.35 cm⁻¹ are corresponding to the aromatic skeletal vibrations, ether bond band. A small peak at 1035 cm⁻¹ may be due to aromatic CH in plane deformation. On the other hand, many peaks are appeared in the modified lignin spectra such as 1624 cm⁻¹, 1338 cm⁻¹, 778 cm⁻¹ and 574 cm⁻¹.

Evaluation of modified lignin as coagulant aid: The modified lignin derivative possessing positively charged groups (amino groups) which acts as ion-exchanger. They can remove organic and inorganic matter carrying negative charge from the water. By using modified lignin for the clarification of raw water in a dose from (2-10 mg/l), the examined parameters revealed that modified lignin is able to remove turbidity, organic matter, colloidal silica, and sulfate gives better water clarity. Table (3) showed that the optimum dose that gave best result was (6 mg/l).

Table (3): Effect of modified lignin dose on the quality of treated water

Parameter	Waste water	Modified lignin dose (mg/l) at 20ppm ferric chloride					
		0	2	4	6	8	10
Turbidity (NTU)	17.4	2.8	1.9	1.1	0.8	0.9	0.9
Sulphates (mg/l)	360	360	140	60	23	23	23
Organic matter (mg/l as KMnO ₄)	19	8.2	14.29	12.23	8.29	8.29	9.29
Total Silica (mg/l as SiO ₂)	19.5	18.9	8.26	7.2	6.1	6.1	6.1

Also it is widely known that natural compounds can build complexes with certain ions such as calcium and magnesium. In addition, the creative amino sites are the main reactive groups for removal of organic matter and total silica removal from water. Therefore, a comparison was made between modified lignin and either ferric chloride as a traditional coagulant. For this purposes a simulation of clarification applying Jar test method which is considered the most applicable way to permit the comparison of various chemicals combination for determining the optimum chemical program was applied. The most important measurements in jar test are coagulation and/or flocculent dosages, flock size, settling characteristics, flock forming time, and finished water clarity.

When comparing the using of modified lignin and ferric chloride in a different dose, the examined parameters revealed that modified lignin is able to remove turbidity, organic matter and gives better water clarity. Table (3) shows that the optimum dose that gave best result was (6 ppm modified linin

+ 20 ppm FeCl₃). While for ferric chloride 35 ppm. It is also seen that the combination of modified lignin gives the best result for removing organic matter, turbidity total hardness, calcium hardness and total silica.

The efficiency of modified lignin is due to protonation of its amino groups in water which makes lignin positively charged, and thereby very attractive for flocculation and different kinds of binding applications. Since most natural colloidal particles, including organic matter, bacteria and macromolecules, are negatively charged attractive electrostatic interactions may lead to flocculation. Besides modified lignin, possess positively charged groups due to the creative amino group. Therefore, the modified lignin can remove organic matter, colloidal silica and some inorganic elements from water.

Table (4): Comparison between modified lignin and ferric chloride doses on the removal of organic matter, turbidity, hardness and total silica of water

Parameters	Raw water	Water clarified by 35 ppm Ferric chloride	Water clarified by 6 ppm Modified lignin + 20 ppm Fe IC ₃
pH	8	7.49	7.67
Turbidity NTU	18.2	2.3	1.1
Total hardness ppm	149	100	90
Ca hardness ppm	81.6	45	41
Organic matter ppm	11.05	7.9	4.14
Total silica ppm	20.92	18.1	17.98

Also figure (11) show the shape and size It is clearly seen that the size of flocs when using modified lignin is much higher than that formed when using ferric chloride or alum. Nevertheless, the time of floc formation and steeling time is better when using modified lignin with ferric chloride.

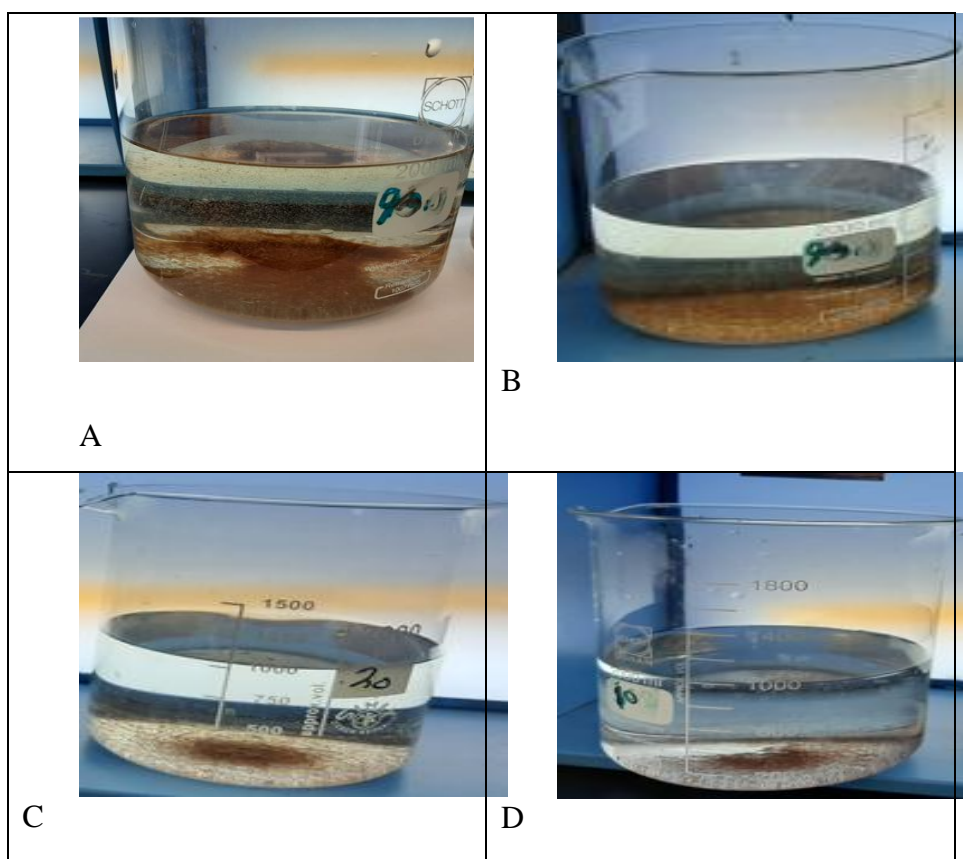


Figure (11): The floc formation at (35 ppm FeCl_3 for A, 20ppm FeCl_3 + 2ppm modified lignin for B, 20ppm FeCl_3 +4ppm modified lignin for C and 20ppm FeCl_3 + 6ppm modified lignin for D)

Table (5) shows the effect of adding combination of ferric chloride and modified lignin to the industrial wastewater with different concentration of ferric chloride and amount of modified lignin injection at 4 ppm.

Table (5): The jar test results of different dose of ferric chloride and modified lignin concentration

FeCl ₃ Injection (ppm)	Industrial waste water	5	10	15	20	25	35
Modified lignin Injection mg/liter		4	4	4	4	4	Zero
Turbidity NTU	18.2	1.32	1.28	1.01	1.1	1.15	2.3
Total Alkalinity ppm	121	119	117	115	112	110	116
Organic Matter ppm	17.3	6.57	6.58	6.75	5.11	5.11	7.9
Total Silica ppm	21.81	17.32	16.52	16.35	15.38	15.39	20.1

It's clearly seen that the best does of ferric chloride is 20 ppm at 4 ppm modified lignin which gives maximum removal of turbidity, organic matter and total silica.

The work was extended to identify the optimum doses of modified lignin by changing the ferric chloride dose in small range (20, 22, 24, 26 and 28ppm). Table (6) shows the results of jar test while changing the FeCl₃ concentration from 20 to 28 ppm and fixing modified lignin injection to 4 ppm. It was observed that the best clarification was at 26 ppm ferric chloride and 4 ppm modified lignin. This combined dose gives the lowest values of turbidity, total alkalinity, organic matter and colloidal silica.

Table (6): The jar test results of different doses of FeCl₃ and modified lignin

Ferric chloride injection (ppm)	Raw water	20	22	24	26	28
Modified lignin Injection mg/liter		4	4	4	4	4
Turbidity NTU	18.2	1.1	1.15	1.19	0.97	0.99
Total Alkalinity ppm	121	112	111	110	107	107
Organic Matter ppm	17.3	5.11	8.68	8.12	7.15	7.18
Total Silica ppm	21.81	15.38	17.84	15.35	10.89	11.16

Heavy metal removal by modified lignin:

Industrial effluents may contain a mixture of heavy metal ions, and therefore, testing of chelation is recommended for the obtained modified lignin as ion chelating agent. Thus, the adsorption of the metal ions Zn, Pb, Fe, Ni, and Cd by the modified lignin was studied by using atomic absorption technique for measuring the examined metals in water. The effect of modified lignin concentrations (2, 4, 6, 8 mg/l) on the removal of such elements from water was studied. Figure (12) show that the modified lignin has high efficiency for removal of elements. For instance, as much as 75% of (Ni²⁺, Zn²⁺, Co²⁺, Cd²⁺, Mn²⁺) were removed by using (8 ppm) of modified lignin, and 95% removal of (Fe and Cu). Also it's clearly seen from Figure (12), that the increment of modified lignin accompanied by decrement of metal ions in water to be examined reaching to complete removal of metals ions at (8 mg/l).

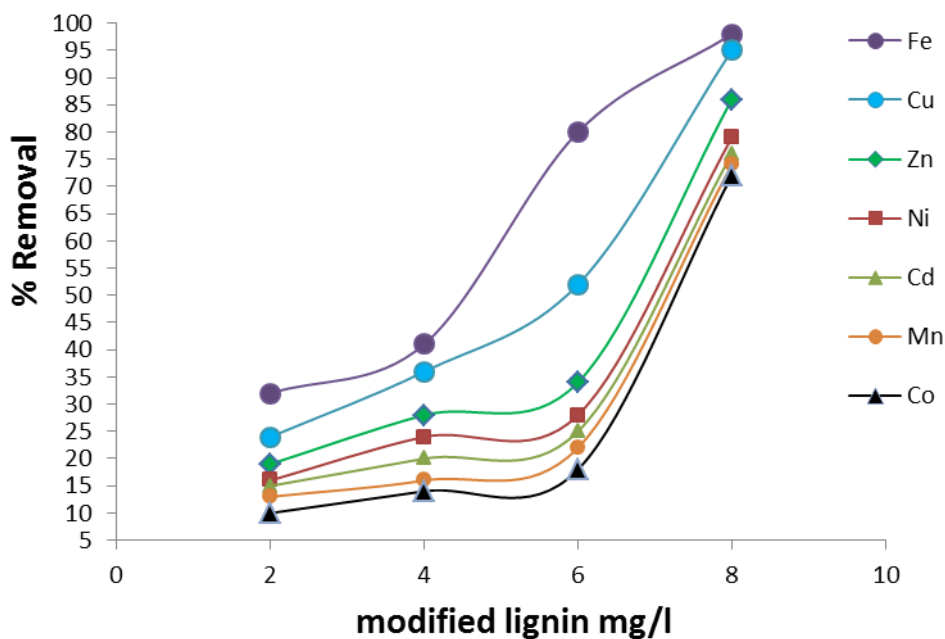


Figure (12): Effect of modified lignin dose on heavy metal removal

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تحضير وتوصيف اللجنين المعدل لاستخدامه في إزالة بعض المعادن الثقيلة من مياه الصرف الصناعي في محطات توليد الطاقة

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المستخلص

في هذا البحث تم تحضير مشتق اللجنين القابل للذوبان الذي يحتوي على مجموعة أمينية بواسطة تقنية تعتمد على الطريقة الجافة عن طريق تفاعل اللجنين المستخلص من أوراق الجوافة مع الثيوريا. تمت دراسة ومناقشة العوامل المؤثرة على محتوى النيتروجين من اللجنين المحور الناتج مثل

درجة حرارة التفاعل - زمن التفاعل - تركيز هيدروكسيد الصوديوم إلى جانب تركيز الثيوريا. حيث أظهرت النتائج أنه يتم الحصول على محتوى النيتروجين العالي من مشتقات اللجنين عند درجة حرارة التفاعل ٩٠ درجة مئوية في زمن قدره ٩٠ دقيقة. علاوة على ذلك فقد صاحب زيادة كمية الثيوريا زيادة في محتوى النيتروجين حتى نسبة معينة. تم توصيف المنتج الذي تم الحصول عليه بواسطة FT-IR، والتحليل الحراري الوزني TGA، وتحليل العناصر (C و H و N و S). وقد تم أيضا تحديد كفاءة امتصاص أيونات المعادن مثل (Zn(II)، Cu(II)، Ni(II)، Cd، Co(II)، V(II) و Fe(III) باستخدام مطياف الامتصاص الذري (AAS). تم أيضا تقييم أداء اللجنين المعدل الذي تم الحصول عليه كمادة تخثر من حيث قياس العكارة والمواد العضوية والاملاح الذائبة والسليكا الكلية. ولوحظ أن أفضل جرعة مشتركة كانت ٢٦ ملجم / لتر من كلوريد الحديدك و ٤ ملجم / لتر من اللجنين المحور تعطي أدنى قيم للعكارة والقلوية الكلية والمواد العضوية والسليكا الكلية التي تغيرت من (١٨,٢ NTU و ١٢١ ملجم / لتر و ١٧,٣ ملجم / لتر و ٢١,٨ ملجم / لتر) إلى (٠,٩٧ NTU و ١٠٧ ملجم / لتر و ١٠,٨٩ ملجم / لتر و ٧,١٥ ملجم / لتر) على التوالي. وقد وجد أيضا أن اللجنين المعدل يتمتع بكفاءة عالية لإزالة العناصر. على سبيل المثال، تمت إزالة ما يصل إلى ٧٥٪ من Zn^{2+} ، Ni^{2+} ، Co^{2+} ، Mn^{2+} باستخدام (٨ ملجم / لتر) من اللجنين المحور، و ٩٥٪ إزالة لكل من Cu^{2+} و Fe^{3+} .

الكلمات الدالة: اللجنين المحور - مواد تخثر - إزالة المعادن الثقيلة - معالجة المياه.