

## Synthesis of Innovative Thiolated Red Toon Lignin for the Removal of Fe(III) from Aqueous System

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**ABSTRACT:** In the present work, thiomers have been synthesized via thiourea reactions in high degree of modification and degree of substitution is 2.1. Preparation of polymer follows green chemistry protocol with respect to green solvent utilization and zero waste generation. The thiol products are responsive for further derivatization and were modified to a sulphide. The above mentioned reactions were also carried out using microwave heating to achieve maximum yet uniform modification of red toon lignin. The extent of the derivatization processes was confirmed by iodine titration and precipitation titration. The prepared material have been characterised by some physical and chemical methods such as analytical determination, FTIR, SEM and EDX analysis. The analytical results supported highest sulphur content of 47.93% in thiomers. Synthesised green thiomers have been explored as arsenic ion sorbent at 60ppm. The result showed maximum sorption efficiency 86-90% for Fe(III) in aqueous system.

**Keywords:** Thiol; adsorption; biopolymer and aqueous.

**INTRODUCTION:** Recently, water pollution is a serious problem due to the heavy metals that threaten human health and environmental value. Methods of minimizing heavy metal concentrations in surface waters and waste water are therefore crucial for environmental safety. The result of human activity leads to facing serious threats of air land and water pollution. Water pollution has raised severe environmental impact. In addition to the deficiency of the resources of water due to drought and misuse, the production of large volume of waste water has put a lot of pressure on the humankind. A variety of industries are responsible for the release of heavy metal into the environment through their waste water i.e. steel industry, the non-ferrous industry, mining mineral processing etc (Sarkanen *et al.*, 1971).

Also, many industries are operated at small medium and generate a considerable pollution load as they have no facilities for waste water treatment. Heavy metals are elements having atomic weight between 63.5 to 200.6 and a specific gravity greater than 5. Heavy metals can stance health post risks if their concentration exceeds tolerable limits. The main threats to human health from heavy metals includes (Cd, Pb, Cu, Zn, Ni, Cr, As, Fe etc.) may damage central nerv-

ous function, the cardiovascular and gastrointestinal system, lungs, kidney, endocrine glands, and bones. These metals have been widely studied and their effects on human health regularly reviewed by international bodies such as the WHO. According to the World Health Organization almost 1 billion people do not have access to clean drinking water, and that number is predictable to rise with climate change. Meanwhile, our endlessly rising energy necessities and use of heavy metals in industrial processes have maximized our exposure to toxic materials in water. Industrial activities and mining operation have exposed man to the toxic effects of metals. Heavy metals are reported to inhibit nitrification and denitrification process which harmfully affecting biological waste water treatment and reduced microbial oxidation of organic compounds. The toxicity of heavy metals in waste water rest on the factors like metal species concentration, pH, Sludge concentration and solubility of the metal ions (Bhattacharya *et al.*, 2006).

**Removal of Heavy Metals by Agricultural Wastes:** Several agricultural wastes such as wool, rice, straw, coconut husks, peat moss, exhausted coffee (Orhan *et al.*, 1993 ) waste tea (Ahluwalia *et al.*, 2005) rice hulls (Ajmal *et al.*, 2003) cork biomass (Chubar *et al.*,

2003) seeds of *Ocimum basilicum* (Melo *et al.*, 2004) coconut shells (Babel *et al.*, 2004) soybean hulls and cotton seed hulls saw dust of walnut (Bulut *et al.*, 2003) untreated coffee dust (Oliveira *et al.*, 2008) papaya wood (Saeed *et al.*, 2005) peanut hulls (Johnson *et al.*, 2002) citrus peel were recycled as sorbents for metal removal. However, sea weeds, molds, yeasts, bacteria have been tested for metal biosorption with positive results (Ahluwalia *et al.*, 2007; Mane *et al.*, 2011; Moustafa *et al.*, 2003) Table 1 shows various agricultural sorbents and their removed (Wu *et al.*, 2004; Kumar *et al.*, 2006; Malkoc *et al.*, 2005; Malkoc *et al.*, 2007; Ozer A *et al.*, 2004; Villaescusa *et al.*, 2004). The parameters which have been studied for improving the use of adsorbent in wastewater treatment include nature of adsorbent and adsorbate, metal concentration, contact time, temperature, kinetics of adsorption, adsorption isotherm and pH of the aqueous solution have revised the literature on lignin as a bio-sorbent. Srivastava *et al.* 1994 reported an extreme 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 improved by alkaline glycerol delignification. From the above data and the review by we find that there are significant transformations in the metal sorption capabilities of different types of lignin. Also, the related mechanisms of metal sorption through lignin are still matter to deliberation. Some studies have found that ion-exchange mechanisms may be responsible for the sorption of metal ions on lignin (Wiltowski *et al.*, 1997; Crist *et al.*, 2004; Martin *et al.*, 2002). Most of these wastes were used without chemical variation. Thus they indicate poor metal removal in addition to their non-metal selectivity. Current commercial processes to remove heavy metals including lead, mercury, iron etc, from community drinking water tend to be high and energy-consuming, without being necessarily efficient (Table 1). Less conventional methods for be more efficient, but are single-use, difficult to regenerate, or produce important toxic waste as a side-product.

**Low Cost Adsorbents:** There are numerous nearby existing materials that can be recycled for the elimination of heavy metals. Low cost adsorbents such as natural materials, agricultural wastes, modified biopolymers, or industrial by-products are initiate to be more positive in heavy metal removal (Atkinson *et al.*, 1998; Lalvani *et al.*, 1997). Recently, research for the removal of heavy metals from industrial waste has been absorbed on the use of agricultural by-products as adsorbents over biosorption process. Additionally, biopolymers possess a number of altered functional groups, such as hydroxyls and amines, which surge

the efficiency of metal ion uptake. The source of the biomass must be taken into account while selecting the biomass for metal removal. Classic biosorbents can be derived from three sources such as microbial biomass, e.g. bacteria, fungi, and yeast (Crist *et al.*, 2004), algal biomass, non-living biomass such as bark, lignin, shrimp, krill, squid, crab shell, etc. and gricultural products (Demirbas *et al.*, 2004).

**Lignin as Adsorbent:** 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; Wang *et al.*, 2004) lignite (Mohan *et al.*, 2006) pine bark (Al-Asheh *et al.*, 1997; Goheen *et al.*, 1978) peat (McKay *et al.*, 1997) have studied the presentation of low-cost adsorbents for heavy metal removal from polluted waters and analyzed for many years and still continues (Gabaldon *et al.*, 1996; 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 *et al.* 1963; King *et al.*, 1960; 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 we find that there are significant variations in the metal sorption capability of different types of lig-

nin. Also, the interconnected mechanisms of metal sorption by lignin are still subject to debate. Several studies have originate 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).

**Table 1: Different techniques commonly used for removal of heavy metal from aqueous environment.**

Sr. no.	Experiment	Adsorbent	Adsorbate	Conclusion/Result	Reference
1	Biopolymer adsorption	Chitosan	Cd, Cu, Pb, U, Hg and Cr	Chitosan is a renewable polymer and has the potential for creating greener environment. It has attractive properties like natural decomposition, non-toxic to both environment and humans with no side-effects or allergic effects if implanted in the body.	(Bailey <i>et al.</i> , 1999; Pavlidou <i>et al.</i> , 2008)
2	Adsorption	Activated carbon Clay Surface Calcite Coffee Egg shells Rice straw	Pb Pb <sup>2+</sup> Pb, Cu, Hg, Cd, Pb <sup>2+</sup> Zn, Mn <sup>2+</sup>	Adsorption is a good tool for controlling the level of aqueous Pb pollution. The utilization of low cost adsorbents is helpful as it is simple effective and economical.	(Rether <i>et al.</i> , 2003; (Schneider <i>et al.</i> , 1999)
3	Biosorption	Syzygium-cuminiL. (jamun) Tridaxprocumbens (Asteraceae)	Pb <sup>2+</sup> Pb <sup>2+</sup>	Natural adsorbents are cheaper and environmentally safe, low cost adsorbents for treatment of polluted water from heavy metals	(Walsh <i>et al.</i> , 1994)
4	Biological adsorption methods by microalgae	M. spicatum P.lucens S.herzegov E. crassipes	Pb, Zn, Cu Pb, Zn, Cu Pb, Zn, Cu	Microalgae are used in bioremediation of metal contaminated sites due to their ability to tolerate heavy metals, their high yield of recovery per unit mass and their high specific outer area coupled with a cell wall loaded with ionisable groups.	(Wang <i>et al.</i> , 1996)
6	Complexation-ultrafiltration techniques	Carboxymethyl cellulose (CMC)	Cu(II), Ni(II) and Cr(III)	The use of water soluble metal binding polymers in combination with ultrafiltration is a hybrid approach to concentrate selectively and to recover valuable elements as heavy metals. The advantage of this process is high separation selectivity due to the use of a selective binding and low energy requirements.	(Wang <i>et al.</i> , 2005; Xing <i>et al.</i> , 2007)
7	Electrochemical techniques	Titanium as working electrode	Pb(II), Ni(II), Cr(II), Cd(II), Hg(II)	Titanium as a working electrode is stable, energy efficient and involves control and minimization of environmental pollution through remediation of toxic metal ions from aqueous solution.	(Kobyas <i>et al.</i> , 2005)
8	Ion Exchange method	Cation Exchange resins macroporous AMBERJET 1200 Na	Ni(II), Pb(II)	Ion exchange is a mass transfer process. There are two main rate-determining steps which are considered in most of the ion exchange reactions.	(Zhao <i>et al.</i> , 2010; 11)

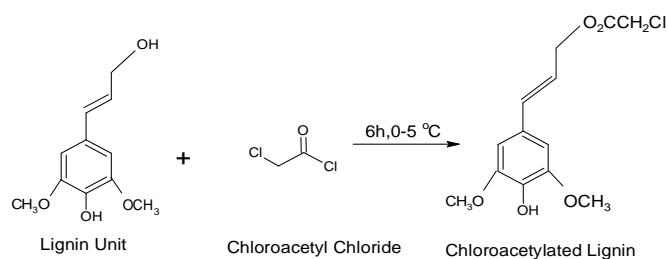
Now, heavy metals are the most serious pollutants, flatter an tremendous public health problem. Processes such as chemical precipitation, solvent extraction, ion exchange, reverse osmosis or adsorption are frequently conceded for removing heavy metals. Among these processes, the adsorption process is a simple and effective technique for the removal of heavy metals from wastewater. (Lalvani *et al.*, 1997). Various chemical used for conversion of rice husk such as Hydrochloric acid ((Rahman & Ismail *et al.*, 1993, Bandyopadhyay *et al.*, 2006), sodium hydroxide (Guo *et al.*, 2011). However, has found that adsorption of Cd raised twice when rice husk was treated with NaOH. The order of maximum removal of the potential to bind with heavy metal ions. The maximum adsorption capacity of Ni<sup>2+</sup> ions was found to be 10.47 mg/g above three metals follows: Cd(II) >Pb(II) > Cu(II). So, So, we have chosen red toon tree and extract the lignin as a bio-polymer and functionalizes it with sulfur which has been successfully prepared for the adsorption of Fe(III) with maximum adsorption capacity as compared to the previous literature.

**MATERIAL AND METHODS:** Lignin, chloroacetylchloride, pyridine, Dimethyl-formamid (DMF), dimethylsulfoxide (DMSO), Thiourea, Sodium hydroxide (NaOH), Colouring reagent and all other reagent used in this study, were of analytical grade and the weights were taken on weighing machine having minimum readability of 0.01mg.

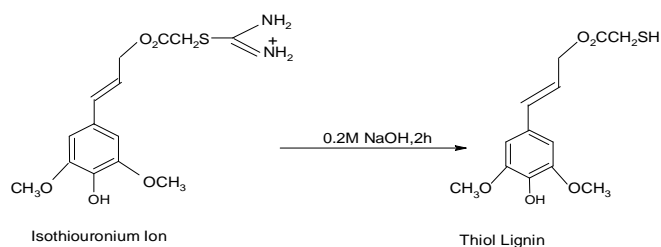
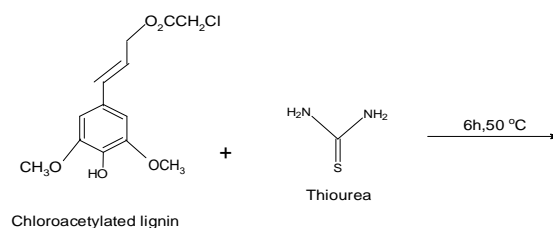
**Synthesis Chloroacetylation of Lignin:** Lignin was dissolved in LiCl /DMF homogenous system in 1:5 equivalent molar ratio. The solution was then cooled down to 0-8°C temperature, dropping funnel, magnetic stirrer and thermometer was added to the flask as an acid acceptor. N,N dimethylformamide solution containing chloroacetyl chloride was then added dropwise and then stirring (Babel *et al.*, 2004).The reaction mixture was cooled then to for 8 hour and subsequently the solution was poured into 200ml of cold 2M aqueous HCl to precipitate the product. The precipitated product was filtered and washed several time with cold distilled water. It was filtered by the reprecipitation using DMSO as solvent and cold distilled water as precipitant and then dried under electrical oven at 40-500 °C temperature.

**Thiolation of lignin:** The above synthesized chlorinated lignin was reacted with thiourea in a 1:5 equivalent molar ratio in a two necked flask equipped. The mixture stirred for 6 hours at 50°C. The mixture homogenous after 30 minute and additional heating ensured completion of the reaction. The solution mixture i.e. (thiuronium salt) was immersed in 0.2 M NaOH

aqueous solution at 40 °C for 2 hours. The solid product was separated by filtration and washed minimum 3 times with dilute HCl and distilled water until pH of the solution was neutral. The product 50-55 °C for use.

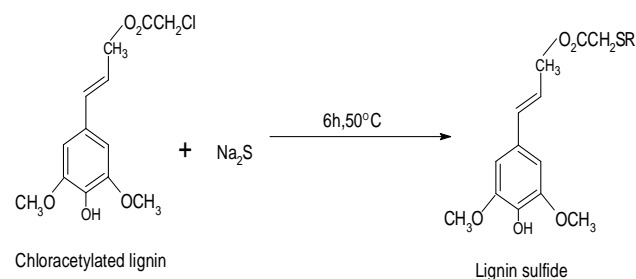


**Scheme 1: Chloroacetylation reaction of lignin.**



**Scheme 2: Thiolation reaction of lignin.**

**Sulfonation of lignin:** Chlorinated lignin solution was added slowly to boiling mixture of Na<sub>2</sub>S (1:5 molar equivalent ratio) in 25.0 ml ethanol and refluxed for 6 hours at 50°C under stirring. The separated solid was product filtered and washed 4 time, separately, with each of 5% NaOH, water and acetone. The product was dried at 50 °C.



**Scheme 3: Sulfonation reaction of lignin.**

**Analytical Determination:** The synthesized product were characterized for the assessment of chloride and sulphur atom content by iodometric titration. The chlorine content atom content was calculated by the following equation (1)

$$\%Cl = \frac{35.5}{2} \times \frac{(V_{cl}-V_0) \times 10^{-3} \times 0.01}{W_{cl}} \times 100 \dots (1)$$

Where,  $V_{Cl}$  is the volume consumed during sodium thiosulfate titration for chloroacetyl lignin,  $V_0$  is the volume consumed by non-chlorinated lignin during sodium thiosulfate titration and  $W_{Cl}$  is the weight chlorinated lignin.

The sulphur atom content was calculated by following equation (2)

$$\%S = \frac{(V_1 \times N_1) \times 33.07 \times 100}{W \times 1000} \dots (2)$$

Where,  $V_1$  is the volume pf sodium thiosulfate solution use for thiolation,  $N_1$  is the normality of sodium thiosulfate,  $W$  is the weight of thiolated lignin.

The degree of substitution is the average number of hydroxyl group that have been substituted in one anhydrous glucose unit of lignin. The DS is the parameter that indicates the molar % of new atom or group introduced in to monomer unit of the synthesized percent (Otto, 1994).

The DS of chlorinated lignin derivative was calculated by following equation (3)

$$DS = \frac{162 \times \%Cl}{(B \times 100) - (C-1) \%Cl} \dots (3)$$

Where %Cl is the percentage of chlorine, 162 is the molar weight of the anhydrous glucose repeating unit, B is the atomic weight of chlorine, C is the molecular weight of the ester substituent (-COCH<sub>2</sub>Cl)-1 76.5, and %Cl is the chloride percent.

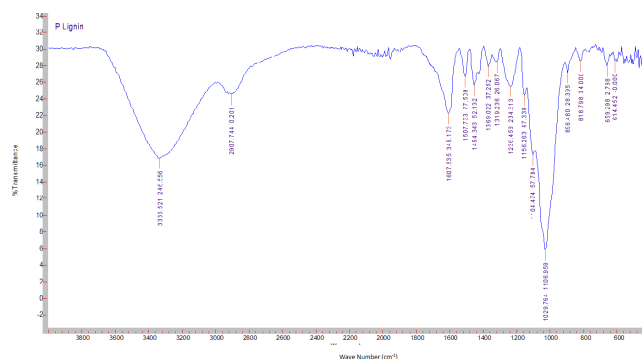
**Characterization Techniques:** In analytical estimation, Iodometric titration confirmed the content of chlorine atom 60.21% for lignin. Moreover, Iodometric also used for determined the content of thiol atom and sulfur atom is 47.93% and 20.84% respectively.

**Table 2: The percentage yield result for chlorine and sulfur atom content.**

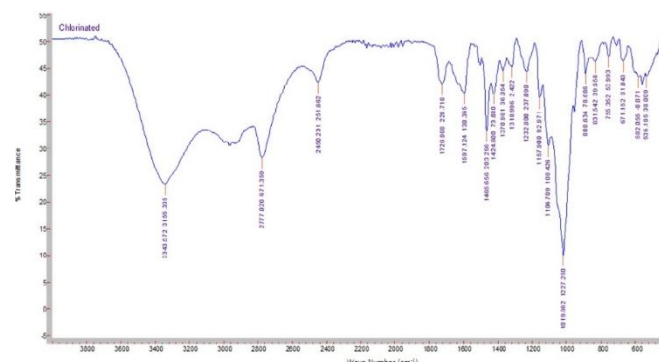
Polymer	%Yield	DS
Chlorinated lignin	70	0.75
Thiolated lignin	44	2.1
Sulfonated lignin	33	0.87

**Characterization by FTIR:** The FTIR (Fourier-transform infrared spectroscopy) spectrum of Lignin shows broad peaks at 324 cm<sup>-1</sup> and 2777 cm<sup>-1</sup> due to -OH and -CH stretching vibrations respectively (figure 1). The absorption band at 1157 cm<sup>-1</sup> and 1080 cm<sup>-1</sup> are due to -CO stretching. However, those around to 1000 cm<sup>-1</sup> like 1019 cm<sup>-1</sup> 888.634 per cm belongs to -C-OH bonding, -C-C stretching and

-CH<sub>2</sub> respectively. The modifications of the chlorinated Lignin was supported by the appearance of an additional peak arises at 1726.98 cm<sup>-1</sup> due to the -C=O stretching of ester linkage (figure 2) in the chloroacetylated group attached in the chloroacetylated Lignin (Fengel *et al.*, 1989; Fengel *et al.*, 2011). The increase in intensity of the -C-CH symmetrical and asymmetrical bonding and decrease in the broadening of the -OH stretching with increase in its wavelength to some extent, from 3343 cm<sup>-1</sup> to 3155 cm<sup>-1</sup>, i.e chloroacetylated Lignin. This provides an additional evidence to confirm the acetyl chloride group, i.e -COCH<sub>2</sub>Cl and hence functions as Lignin's backbone. The small peak at 2492 cm<sup>-1</sup> and 2803 cm<sup>-1</sup> arises due to -SH and -S stretching confirms the conversion the chloroacetylated Lignin into thiolated and sulfonated Lignin (figure 3 and 4) (Rahul *et al.*, 2017). The detection of -SH group i.e. thiol group is almost impossible or we can say that it is difficult to detect, because of its weak signal and poor extent of thiol incorporation into a macromolecular formation (Kalpana *et al.*, 2016). From this, we also conclude the extent of modification in the Lignin infrastructure resulted in an increment in the absorption intensity due to -CS stretching between 1225 cm<sup>-1</sup> to 1423 cm<sup>-1</sup> which accounted for the successful modification of Lignin. In addition to this, the peak at 1335 cm<sup>-1</sup> can be seen, due to -CH<sub>3</sub>.



**Figure 1: FTIR spectrum of Pure lignin.**



**Figure 2: FTIR spectrum of Chlorinated lignin.**

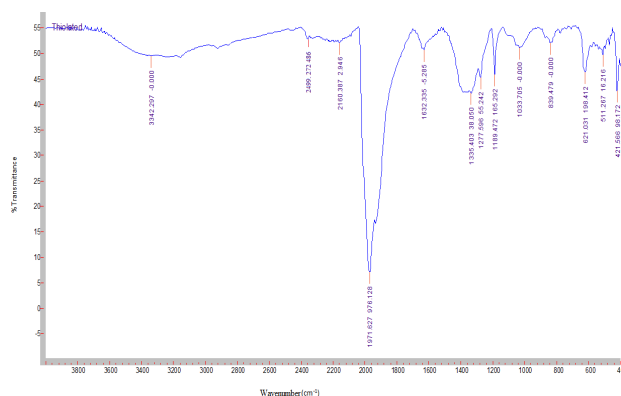


Figure 3: FTIR spectrum of Thiolated lignin.

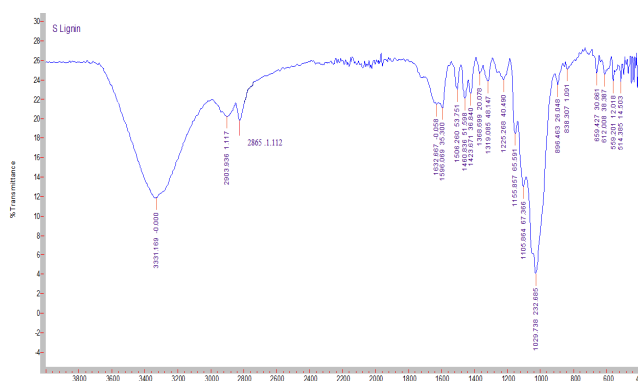


Figure 4: FTIR spectrum of Sulfonated lignin.

**SEM Analysis:** From the figure, we have here Lignin is raw, i.e. untreated and in pure form and is somewhat granular cylindrical, with minute outgrowths in shape having magnification of 1000X to 10 $\mu$ m. Followed by the second step, is chloroacetylation of Lignin occurs, where raw lignin is converted into chloroacetylated lignin. Due to the reaction, cylindrical lignin turns into distorted form i.e. dissociates into smaller fragments of the corresponding material as shown in figures 5(a, b, c and d) having magnification 6500X to 10 $\mu$ m.

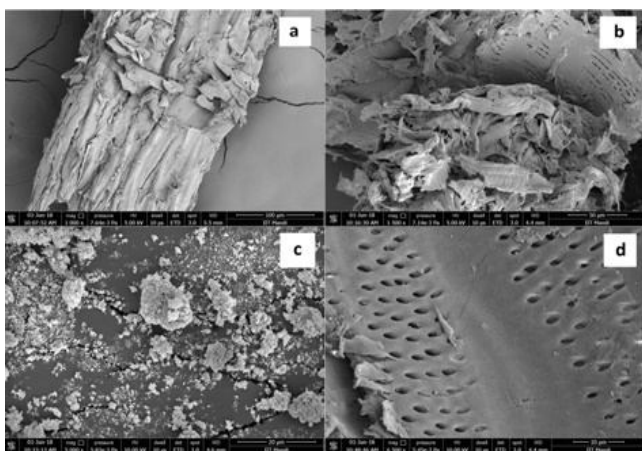


Figure 5: (a) Pure lignin (b) Chlorinated lignin (c) Thiolated lignin and (d) Sulfonated lignin.

Third step involves the thiolation of lignin which to smooth structure and a kind of powdery mass with unsymmetrical outgrowth came with thiol group modification which may be due to weak inter and intra hydrogen bonding. Thereby, formation of thiolated lignin, having outgrowths on its surface, as detected by SEM analysis to magnification 5000X to 20 $\mu$ m 5(c). In addition to this, there are also some independent outgrowths can be visualized in thiol structure, attributed to high extent of derivatisation i.e. chloroacetylated and thiolated complex of lignin and due to this, the complex nature of the lignin molecule comprises of inter and intra molecular H-bonding. Last step involves, surface modification of sulphur lignin. The sulfide lignin shows porous structure with large magnification of 6500X to 10 $\mu$ m enables us to determine the uniform structure formation in figure 5(d) (Kalpana *et al.*, 2015). With the mentioned evidences, we find out that there are minute pores on the surface modification analysis of lignin.

**Characterization by EDX:** EDX results suggested 60.21% of chlorine atoms in chloroacetylated lignin, supported the modification of lignin in figure 6(a). The same evidence could be obtained from the direct correlation molar ratio of carbon and oxygen in the complex derivatives of lignin. EDX results confirm the presence of C and O molecule in the corresponding lignin derivative. The chloroacetylated lignin had an increased C/O ratio due to addition of two carbon. In further step, EDX data supported high percentage of sulphur i.e. 47.48% figure 6(c). However, sulphur content decreased from thiol derivatives to sulfonium structure. The 20.74% decrease in sulphur percentage was due to addition of more than two ethyl units in sulphide lignin figure 6(d) of atomic percentage for sulphur lignin derivative (Prem *et al.*, 2016). Also decrease in C/H ratio shows a lignin shows for EDX characterization as shown in figure 6.

#### Binding Interaction Analysis:

**Concentration, pH and Time Parameters:** Concentration and time parameters had been observed by preparing different concentration in ppm from 10-100ppm corresponds with the 8h time period. The adsorption capacities on Fe-(III) by lignin and its derivatives were 40%, 95% & 84% at 10 ppm, 50ppm and 100ppm along with time period of 8h had been observed. At 100 ppm Fe-(III) concentration in solution is calculated with the % uptake of 95% for Fe(III) after 8h (figure 7). The maximum uptake of Fe-(III) with concentration may be due to the availability of more quaternary sites on the surface of anionic exchanger in general and increase the concentration of

salt solution causes decrease in hydrophilicity of the adsorbent which increase the saturation for better adsorbent with concentration.

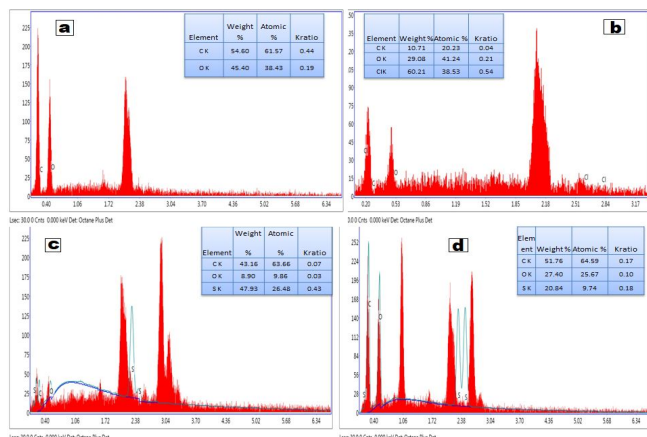


Figure 6: (a) Pure lignin (b) Chlorinated lignin (c) Thiolated lignin (d) Sulfonated lignin.

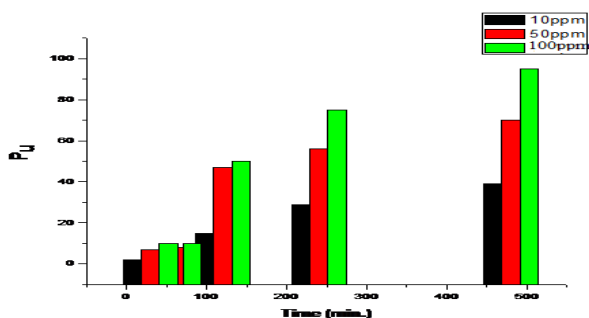


Figure 7: Percentage uptake of Iron with Time.

pH had been observed by preparing different concentration in ppm from 10-100ppm corresponds with 8h time period. The adsorption capacities on Fe-(III) by pectin and its derivatives were 65%, 96% & 85% at 10 ppm, 50ppm and 100ppm along with time period of 8 h had been observed. The pH of the solution was maintained at different pH (1-9) upto 100 ppm concentration it is visible that Fe-(III) adsorption capacity increase as the pH decrease and adsorption was found maximum in the pH range of 2.0 (figure 8).

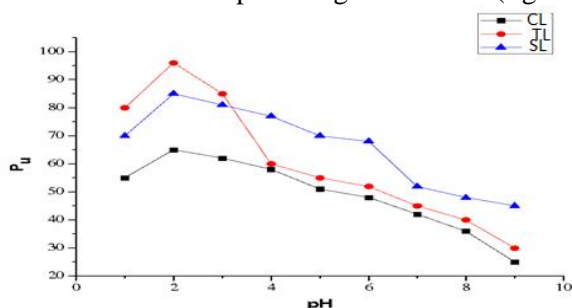


Figure 8: Percentage Uptake Results of Iron with (a), Chlorinated lignin (CL) (b) Thiolated lignin (TL) and (c) Sulfonated Lignin (SL).

**Characterisation by SEM:** The morphology of the adsorbent was characterised by using SEM technique. It is clear from Figure 9 (a), the thiolated lignin have less outgrowth on the surface but after adsorption with Fe(III) is binded with -SH group and more outgrowth on the surface (Zang *et al.*, 2003) in figure 9 (c), sulfide-lignin had smooth surface but after adsorption on it showed outgrowth in figure 9(d).

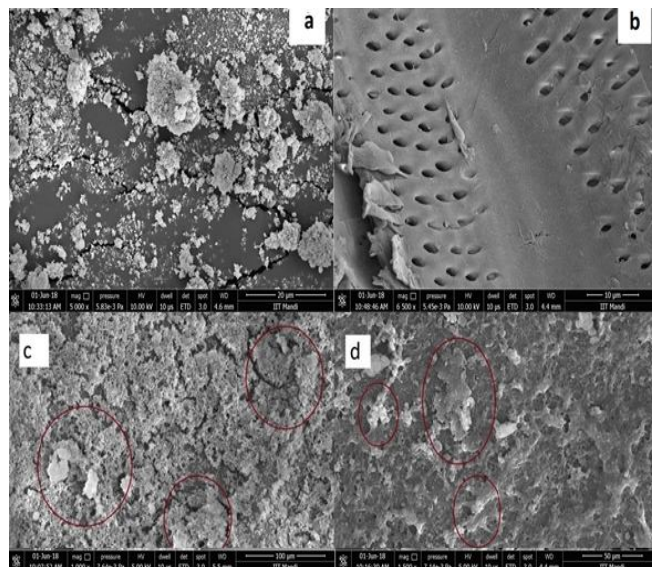


Figure 9: SEM Images (a) Thiolated-lignin (b) Sulfide-lignin (c) Fe(III)-Thiolated lignin (d) Fe(III)-Sulfide lignin.

**Characterisation by EDX:** The EDX analysis of Thiolated lignin showed C(24.01), N(10.62), O(45.51) and S(20.87)., But after adsorption on Fe(III) the weight % of C(24.70), O(29.43), S(5.24) and Fe(40.62) showed in figure 9. The binding ratio is clearly shown in figure 10 in which active site binded with sulphur and complete interference of iron is shown. This weight percentage removal of iron showed thiolated lignin is efficient adsorbent for maximum adsorption which is also has been proved through idomrtic and precipitation titrations in the previous study (kalpana *et al.*, 2017).

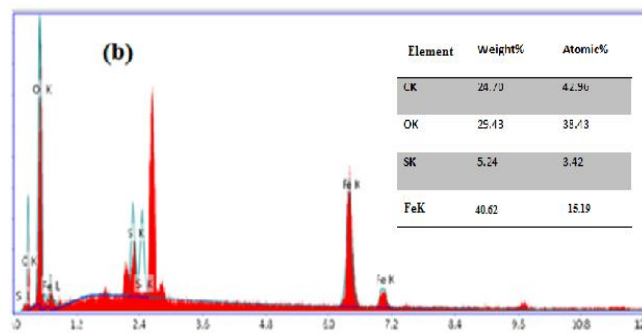


Figure 10: EDX Spectra for Fe(III) Thiolated-lignin.

**CONCLUSION:** Lignin acetylation was taken in a DMF/LiCl homogeneous solution. Synthesized Lignin was then treated with thiourea to generate thiol groups under conventional heating method. Thiourea works as good organic nucleophile which displaces the chloride ion through a nucleophilic substitution reaction. Chloride ion is common leaving group in nucleophilic substitution reactions, to introduce thiourea into chlorinated lignin. As the reaction proceeds involves also an intermediate i.e isothiuronium ion as the sulphur is an efficient nucleophilic centre in various protic solvents. The thiol yield was improved by microwave assisted synthesis up to 85-90 % with the comparison to the previous literature. The thiolated lignin synthesized via heating process had 40.5%-10.25% of sulphur content was confirmed by idiometric titrations. In EDX Characterisation, the high percentage of sulphur i.e. 47.28%- 20.87% of sulphur content is observed, on comparing via analytical determination. The chlorinated lignin was also functionalized to sulphur derivative by conventional heating. This also shows that reactions were more uniformly performed under convention methods in cool conditions. The modification of Lignin via chloroacetylation open up the polymer structure to more extensive reaction as the hydrogen bonding b/w different chain is breaking out. FTIR characterization also confirmed the function group addition after the modification of lignin through -SH and -S group SEM has been showed different morphology of raw lignin after the interference of different functional groups confirmed the modifications. Thus, red toon lignin has been proved an innovative biosorbent in this study. Further this sorbent can be used to calculate different isotherms and kinetics parameter. The thermodynamics can be also calculated and its assortment of quality geographically and wide application attract biomass researchers worldwide.

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