ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

A novel Coagulant based on Lignin and Tannin for Bentonite Removal from Rawwater

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Manuscript Info

Manuscript History:

Received: 11 December 2014
Final Accepted: 25 January 2014
Published Online: February 2015

Key words:

Lignin, Tannin, bentinite, adsorption, Rawwater**.**

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Abstract

By using FTIR, UV, GC-Mass, X-ray DSC and TG techniques, polymer based on lignin and tannin have been prepared and characterized. All characterization techniques confirm the existence of lignin and tannin. The study concerned with the effectiveness of lignin-tannin polymer as a coagulant/flocculant in treatment of surface water. The tests of two kinds of water were carried out in laboratory. The first one is synthesis water mixed with high and low concentrations of bentonite, simulating thus turbid water. The second one is raw water from the treatment station of Shatt Al-Arab River. The performance of coagulation/flocculation process has been assessed by measuring the supernatant turbidity for different pH, doses and flocculation time of lignin-tannin polymer . The obtained results show that lignin-tannin polymer effectiveness was strongly dependent on pH and the doses of lignin-tannin polymer, on the initial turbidity and on the water quality.

INTRODUCTION

Coagulation/flocculation has remained the most widely used method for the removal of particles and organic matter in wastewater treatment (1). In this case, a coagulant agent is employed that usually reacts with water and forms hydrophobic hydroxide and polymeric compounds with different charges, depending on the solution's pH. Coagulant agents interact with colloidal materials by charging either neutralization or adsorption, leading towards coagulation/flocculation, usually followed by sedimentation (2). Conventional coagulants in wastewater treatment are alum [$Al_2(SO_4)_3.14H_2O$], ferric chloride [$FeCl_3.6H_2O$], sodium aluminate, aluminum chloride and ferric sulfate. Conventional coagulants are basically salts of a strong acid (e.g. HCl or H_2SO_4) and a weak base (e.g. $Al_2(OH)_3$ or $Fe(OH)_3$); thus they are a mixture of a cation (from a base) and an anion (from an acid). However, recent studies have detected several serious drawbacks, such as the onset of Alzheimer's disease, when aluminum salts are used. There is also the problem of alum reaction to natural alkalinity present in the water which leads to pH reduction. In this context, an environmental friendly coagulant presents a viable alternative for the treatment of wastewater (3). The use of natural coagulants (lignin , tannin. etc) in the coagulation could provide a more suitable sludge for fertilization purposes as these natural coagulants are biodegradable (4)

Lignin is a phenolic, three-dimensional, cross-linked polymer occurring in plant tissues, and whose role is cementing cellulose fibers. It is based on three phenyl propanoid monomers, see Fig. 1, connected with each others through various inter-unit linkages (5), thus resulting in a complex macromolecular structure. In general, lignin is a waste material from the pulp and paper industry, and is most often used as fuel for the energy balance of pulping process (6). Yet, considerable effort has been made in the past for finding high value-added applications to lignin. For instance, it has been proved that glyoxalated lignin can be an effective precursor of adhesive resin for formaldehyde free particle boards (7). In addition, potential health applications of lignin have been explored, and it was shown that lignin possesses high activity as binder of cholic acid sodium salt, and as antitumor and antivirus (8).Although it is not the first time that lignin is used as gel precursor, few works exist about gels based on lignin (6).

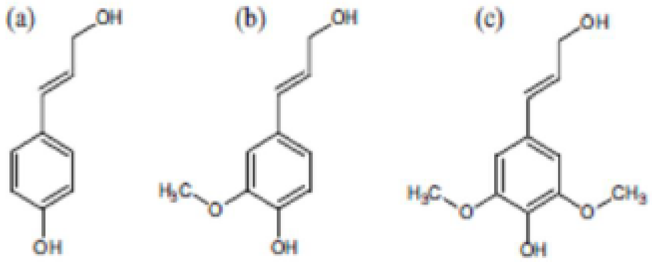


Fig.-1 Schematic representation of structureal unit of lignin: (a) p-coumaryl alcohol (4-hydroxyl phenyl), (b) coniferyl alcohol (guaiacyl), (c) sinapyl alcohol (syringyl)

Tannins are high molecular weight polycyclic aromatic compounds widely distributed through the plant kingdom. Tannins can be classified into two groups (9), the proanthocyanidins (or condensed tannins) and the polyesters of gallic acid and (or) hexahydroxydiphenic acid (hydrolysable tannins, respectively, gallo- and ellagitannins). The co-occurrence of both kinds of tannins in the same plant or plant tissue is often observed. Tannins are found in the leaves, fruits, barks, roots and wood of trees (10). The structure of tannin is presented schematically in Figure 2 . Complex polysaccharide tannin derivatives have been used extensively in potable water, wastewater and industrial effluent treatment applications (11). In addition tannin helps the filtration process (12) . The various studies that have been conducted on water treatment using the tannins as a coagulant have revealed that the effectiveness of tannins depends mainly on the chemical structure of tannins that have been extracted from the plant and the degree of tannin modification (13).

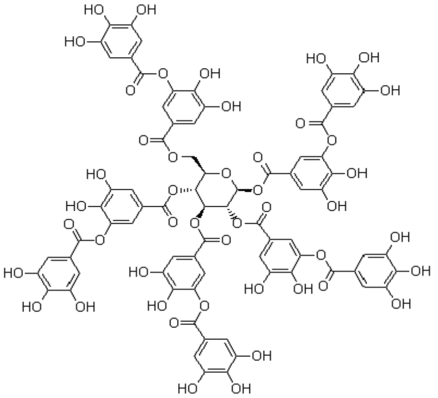


Figure 2 : Structure of Tannin

The idea of using a tannin to purify industrial wastewater, connected to the natural ability of polyphenols to entrapped metal ions with the easy removal system of such a new products (14). The scavenging behaviour of tannins for several kind of metal ions is well-known (15). Today they are also widely used in tannin-modified adhesive formulations (16), as adsorbents for pollution control of industrial effluent (17), and as flocculants (18). Their natural origin is as secondary metabolites of plants (19), occurring in the bark, fruit, leaves, etc. Tannin derivatives have been used extensively in potable water ,wastewater and industrial effluent treatment applications(11).

The aim of this study is to investigate the bentonite turbidity removing from rawwater by adsorption and to evaluate factors affecting on the removal of bentonite turbidity using as a bio-adsorption material.

EXPERIMENTAL

Materials and methods

Materials

All reagents in this work were of analytical grade and were used as received without further purification and then tested and prepared in order to be suitable for real experiments. The prepared reagent consist of: (1) reagent for isolation of lignin i.e. 4% (w/v) NaOH , HCl and 95% ethanol(2) reagents for preparation of Tannin formaldehyde, ie 10% NaOH and Formaline (3) reagents for preparation of Lignin-Tannin polymer, i.e H_3PO_4, HCl, ethanolamine, $NaHCO_3$ and buteraldehyde (4) Stock solution of 500 NTU from bentonite (5) standard solutions for preparing 10, 20, 50, 100, 200, 300 NTU for the determination of turbidities using Turbidity meter(LP2000 HANNA).

Methods

Isolation of Lignin

A 100 ml of black liquor was treated with a sufficient (4%) aqueous sodium hydroxide solution to cover it completely and heated under the reflux condenser at 100°C for 4 hrs. The reaction mixture was filtered and the lignin precipitated by the addition of concentrated hydrochloric acid to the filtrate . The obtained lignin from extraction was purified by dissolving it in 500 ml of (2%) aqueous sodium hydroxide solution and adding to it 1 liter of (95 %) ethanol. The precipitate was filtered off, the filtrate was acidified with hydrochloric acid, and the alcohol was removed by distillation. The lignin was washed with water until the wash water was free of chlorides and dried in oven at 56°C for 3hrs. Yield, 45 gm. An amorphous brown substance was obtained.

Isolation of Tannin

The *Laurus nobilis* leaves was cut into pieces and powdered using grinding machine.The powdered sample was sieved through a pair of 40 and 60 mesh sieve. In order to obtain maximum quantity of tannin , extraction was carried out at elevated temperature. The extraction of 50 gram of sample was carried out with water-ethanol mixture (1:1) in soxhlet apparatus. The tannin extract obtained from different cycles of reflux was collected in a flask and its volume was reduced in rotary evaporator. The concentrated tannin extract was dried at 50°C. The dried tannin extract which contains 64-67% tannin was ground in a morter with a pestle. The powdered sample was sieved (60 mesh) and stored in sample bottle.

Synthesis of Tannin formaldehyde

TF resin was synthesized adopting the following procedure: 10 g tannin was dissolved in 50 ml water, the PH of solution was adjusted to (10-11) by added some drops from 10% NaOH solution, the solution then transferred to a 250 mL 3-necked round-bottom flask equipped with a reflux condenser, a thermometer and a magnetic stirring bar, the temperature of the solution raised to 80°C with stirring for 75 min. Afterwards the solution was allowed to cool to 60°C, then 40 ml from formalin solution was added, the temperature of the mixture was kept at 60°C; the reaction time was about 3 hrs.

Tannin- Lignin Polymer Synthesis

Add 3 drops of O-phosphoric acid in a 250 mL 3-necked round-bottom flask containing 25 ml ethanolamine , the temperature of the solution raised to 60°C with stirring for 30 min. after that an aqueous solution of 1 gm tannin-formaldehyde in 10 ml ethanolamine were added into the reactor by controlling the dropping speed with stirring for 30 min , and then the temperature of the solution raised to 100°C with stirring for 4 hrs . After cooling , solution was neutralized by sodium bicarbonate and then filtered and evaporated in oven. Then a 10 ml of 1% N-methyl-2-pyrroliodine were added , a magnetic stirring bar and mixed for 60 min or until dissolved. After that an aqueous solution of 2 gm lignin in 25 ml distilled water were added, and then 0.5 ml of buteraldehyde was added into the reactor by controlling the dropping speed. The reaction was continued for 3h at room temperature (25°C) . Adjusted the pH to 2 by HCl, the lignin-tannin polymer was obtained (Fig.3).

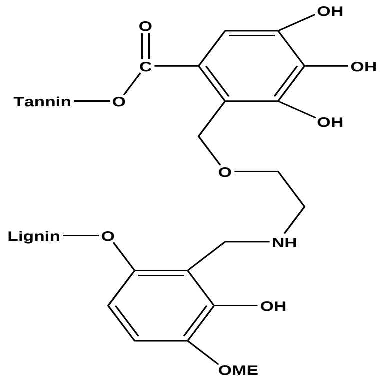


Figure 3: Lignin-Tannin polymer structure

Characterization techniques and instruments

Six methods were used for the characterization of the lignin, tannin and lignin- tannin polymer:

The UV-visible spectra were recorded over the range of 200–700 nm using the T60 U PG Instrument Limited UV-visible spectrophotometer (UK).

Fourier transform infrared (FTIR) spectra were obtained with a FTIR- RX1 spectrometer (Perkim Elmer, USA) with samples incorporated into KBr discs in the range of 400 to 4000 cm^{-1}.

Gas chromatography-mass spectrometry (GC-MS) were performed using an Agilent Technologies 7890 GC with 5975 MSD1µL of reconstituted sample was injected through a 7683B Series Injector using a split mode of 50%. The GC separation was done using a DB5 column at a flow rate of 1mL/min He 99.999%. The oven temperature was programmed as follows: 50 °C (hold 1 min), 25 °C/min to 150 °C, 20 °C/min to 170 °C and 80 °C/min to 250 °C for 3 min. (The total run time was 10 min). Products were detected using a 5975C VLMSD with TripleAxis Detector (m/z 50-250).

Differential scanning calorimetry (DSC) experiments were carried out using a TA Instruments DSC 30 (Mettler Toledo , Switzerland) Differential Scanning Calorimeter. Samples (5–10 mg) were loaded into standard aluminium pans and run using a heat/cool/heat cycle with a heating rate of 10 °C min^{-1} and a cooling rate of 5 °C min^{-1}.

Thermogravimetric analysis (TGA) measurements were performed using a TA Instruments TGA (Mettler Toledo , Switzerland) Thermogravimetric Analyzer. Samples (8–14 mg) were weighed out on platinum pans and heated to 600 °C at 10 °C min^{-1}under a nitrogen atmosphere. All thermal analysis employed duplicate runs for each sample. Working temperature range was 25–800°C with a efficiency of 10°C min^{-1}. Air was used as environmental medium at100 ml min^{-1}flux.

The crystallinity of polymers in powder form was studied by X-ray diffraction method (Empyrean series 2) PAN analytical (Netherland) using Cu Kα radiation generated at 40 kV and 40 mA at scanning speed of 0.3 2θ/ min within a range of 10^0 to 60^0.

Study of Coagulation adsorption experiment by synthesized Lignin – Tannin Polymer

Bentonite has been chosen for this study for its abundance and availability. To prepare water with turbidities (10, 20, 50, 100, 200, and 300) NTU , bentonite was ground and sieved. The sieve fraction below 200 µm was maintained for all the tests. The initial suspensions were mixed with deionized water at 500 rpm for 5 minutes. The suspensions were left thereafter, settling in for 20 minutes. This operation is followed by filtration of the supernatant to remove the large particles not suspended.

A convential jar test apparatus was used for the coagulation experiments . In all the experiments before the best slow stirring velocity and time were determined . The pH of the suspension was adjusted by adding 0.1 M NaOH or 0.1 M HCl. The reactor, which contain turbid water or synthetic water having different pH and turbidity values, was set at 100 rpm paddle speed. Once the polymer was added, then water was fast mixed for 1 min at 200 rpm followed by 15 min of slow mixing (at 15 rpm). The supernatant was the withdrawn for turbidity measurement using pipette with the open end placed 3 cm below the surface of the liquid.The sensitivity of the instrument permits the detection of turbidity as low as 0.02 NTU (Nephlometric Turbidity Units).

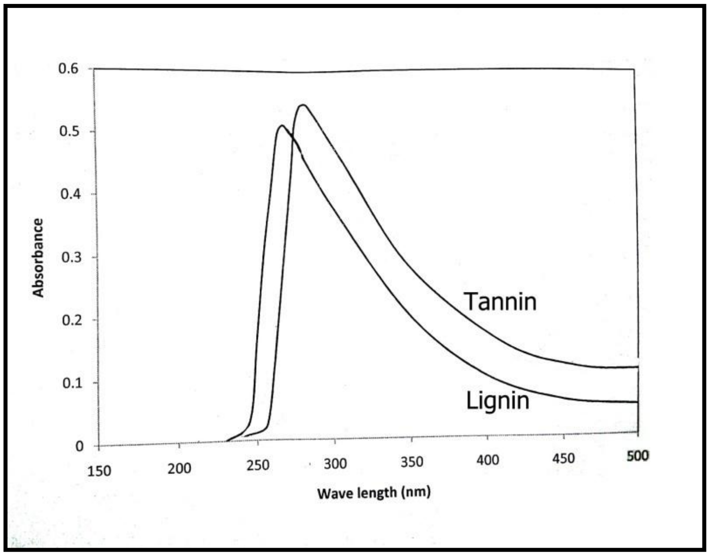
RESULTS AND DISCUSSION

Ultraviolete –visible study of the Compounds

Ultraviolet/visible (UV-Vis) spectroscopy is useful as an analytical technique for two reasons. Firstly, it can be used to identify certain functional groups in molecules, and secondly, it can be used for assaying. UV-Vis spectroscopy involves the absorption of electromagnetic radiation from the 200–800 nm range and the subsequent excitation of electrons to higher energy states. The absorption of ultraviolet/visible light by organic molecules is restricted to certain functional groups (chromophores) that contain valence electrons of low excitation energy . The UV of the studied compounds: chitosan, tannin and lignin was carried out in double beam UV-visible photometer , using dilute solution (3.5×10^{-3}) .

The UV spectra for lignin is show an intense bands at λmax 281 nm as shown in Fig(4) . From the figure could conclude that the conversion of lignin is higher than tannin , this is due to the presence of electron donating group on benzene ring i.e.(-OCH_3) for lignin which increase the electron density on the carbon-carbon double bond of lignin.

The U.V. spectra for tannin, show an intense bands at λmax 270 nm for $\pi\rightarrow\pi^*$ transition due to the high conjugation between the π electrons of the benzene ring and the carbonyl group through the carbon-carbon double bond.



Fig(4): UV-Vissible Spectra of Lignin and Tannin

Gas Chromatography- Mass Spectrmetry

Mass spectrometry (MS) is a destructive analytical technique used for measuring the characteristics of individual molecules. The basic information obtained from mass spectrometric analysis is the molecular mass of a compound, which is determined by measuring the mass to charge ratio (m/z) of its ion. With the ionization method, full particulars about a molecule's chemical structure can be found. MS can analyze chemicals with a wide mass range–from small molecules to complicated biomolecules such as carbohydrates, proteins, peptides or nucleic acids.

The GC-MS analysis detected all organic species quantitatively. Each peak area in the chromatogram was propotional to the amount of the organic compounds forming that peak.

GC-MS provides a rapid and easy alternative to tedious chemical degradation procedures for analyzing the monolignol composition of lignin samples. It requires only a small amount of lignin (<1 mg) . Compounds separated on a GC column can easily by identified from their mass spectra as being derived from p-hydroxyphenyl (H), guaiacyl (G), or syringyl (S) propane units. Figure 5 shows the chromatograms from the lignin . The peaks at m/z 970.1 with retention times under our chromatography conditions around ~6 mins. Lignin consists of a ratio of p-hydroxyphenyl to guaiacyl to syringyl-based units (H/G/S ratio) of approximately 12.4:13.8:1. Therefore this lignin could be considered a p-hydroxyphenyl-guaiacyl lignin. The molecular weight of the obtained lignin was 2818.5 .

Conditions could be found for tannin that giving peaks at 647.2 m/z with retention times under our chromatography conditions around ~15 mins as shown in Fig. 6. Tannin consists of a ratio of gallic acid to glucose units of approximately 12:13. Therefore this tannin could be considered a hydrolysable tannin. The molecular weight of the obtained lignin was 2836.7

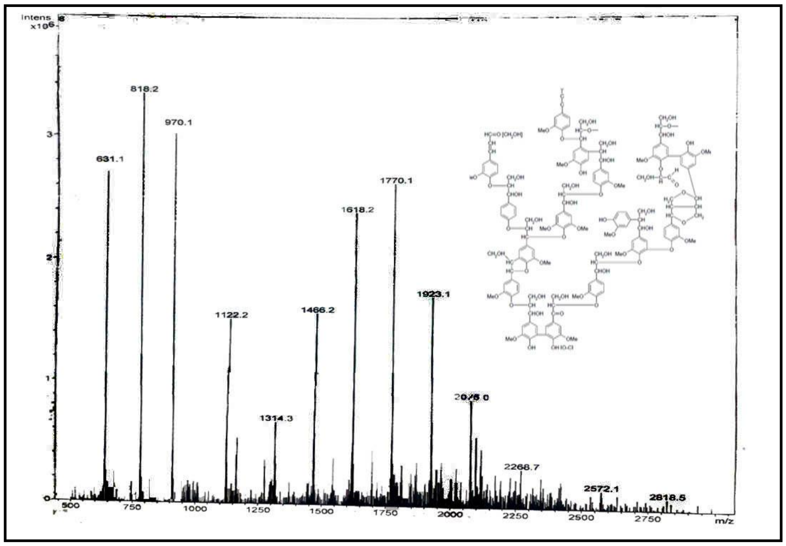


Fig. (5): GC-MS spectra of Lignin

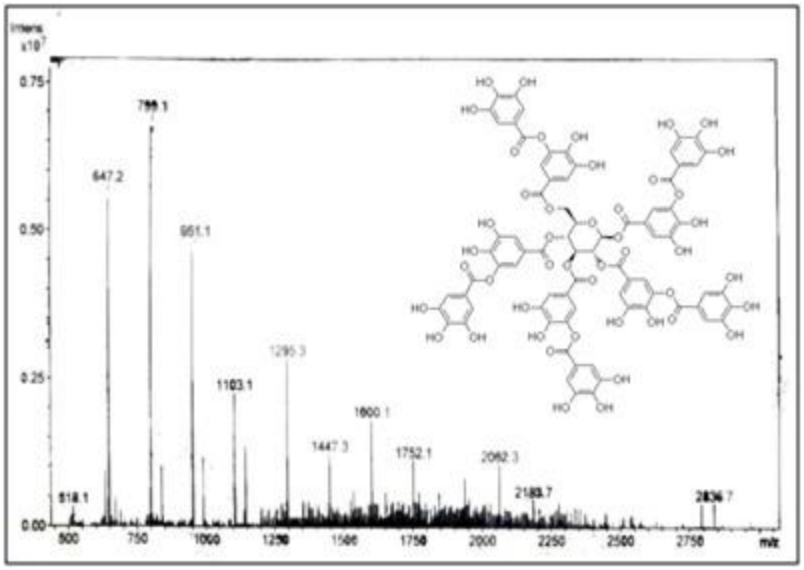


Fig. (6): GC-MS spectra of Tannin.

Forier Transformer Spectroscopy(FTIR)

Fourier transform infrared spectroscopy (FTIR) was used to determine the vibration frequency of the functional groups in the three different polymers. The spectra were measured by an FTIR spectrometer within the range of 400–4000 cm^{-1} wave number. The dry amount of polymers (about 0.1 g) was thoroughly mixed with KBr and pressed into a pellet and the FTIR spectrum was then recorded.

FTIR of Lignin

The FT-IR spectra of lignin are shown in Figure 7 Around 3451 cm $^{-1}$ it can be observed a wide vibration caused by the stretching of the O-H group,the spectra presented band between 2937 and 2875 cm $^{-1}$ that corresponded to the vibration of C-H bond in methyl and methylene groups. Around 1462 cm $^{-1}$ streching vibrations of C-C aromatic groups appear in spectrum. Three typical vibrations appeared in aromatic compounds such as lignin, these bands were exhibited around 1512, 1462 and 1425 cm $^{-1}$. Therefore, phenylpropane units (lignin skeleton) were identified in all extracted lignins The vibration at around 1622 cm $^{-1}$ was associated to the C=O bond stretching. The most significant bands in lignin spectra were those that corresponded to its main substructures : guaiacylpropane (G), syringylpropane (S) and p-hydroxyphenylpropane (H) -such as the peak around 1033 cm $^{-1}$ that was related to the breathing of the syringyl ring with C-O stretching and the bands at around 1215cm-1 (shoulder) that were associated to the breathing of the guaiacyl ring with C-O-C stretching. Around 1112 cm $^{-1}$ a vibration can be distinguished that was caused by the deformation of the bond C-H in guaiacyl substructures and syringyl substructures. The vibration at around 1030 cm $^{-1}$ was due to the deformation or the aromatic C-H linkages in guaiacyl substructures and as well it can be related to the deformation of the bond C-O in primary alcohols. Finally, at 760 cm $^{-1}$ shows the result distortion vibration of C=C in benzene rings.

FTIR of Tannin

The poly phenolic tannin compound have many characteristics bands at certain frequencies. Its FT-IR spectrum is shown in Fig.(7) broad peak at 3412 cm^{-1} is attributed to polymeric O-H group, the frequency at 2935 cm^{-1} corresponds to C-H stretching frequency and the peak at 1614 cm^{-1} has been assigned to C=O , and the wideness of the 1709 cm^{-1} band can be related to the presence of conjugated carbonyl groups . The presence of the functional group C-O-C in tannin is confirmed from the band at 1207 cm^{-1} ,C-H bending frequency is noted at 1340 cm^{-1} . A notable band at 1031 cm^{-1} can be assigned to C-O stretching . At 759 cm^{-1} shows the result distortion vibration of C=C in benzene rings. Around 1449 cm^{-1} streching vibrations of C-C aromatic groups appear in spectrum . The absorption band at 869 cm-1, corresponds to the characteristic absorption of β-D- glucose unit .

FTIR of Tannin-Formaldehyde

The FT-IR spectra of these resins showed new intense bands in the region 2980-2840 cm^{-1} attributed to the C-H stretching vibration of the methylene group, which confirms the occurance of hydroxyl methylation for phenolic tannin. Another proof for the hydroxyl methylation is the intense band in the region 3600-3360 cm^{-1} due to the stretching vibration of –OH group intra and intermolecular hydrogen bonded of the methylol . The C-O stretching vibration of the hydroxyl groups showed very strong band in the region 1040 – 1020 cm^{-1} (Figure 7).

Figure (7) shows the same bands but with different intensities. The absorption intensity of –NH and –OH groups in regions (3200-3700 cm^{-1}) from the obtained compound after the addition of hydroxyl amine to tannin formaldehyde is lower than that of –OH group from tannin formaldehyde which indicates a reaction occurred between hydroxylamine and tannin formaldehyde.

FTIR of Tannin – lignin polymer

As shown in Fig.(7) , the absorption peak 3484 cm^{-1} is affected by extending vibration of –NH and –OH, the frequency at 2935 cm^{-1} corresponds to C-H stretching frequency and the peak at 1617 cm^{-1} has been assigned to C=O and the band at 1706 cm^{-1} can be related to the presence of conjugated carbonyl groups , the extending vibration bands and distortion vibration band of C=C in benzene are observed at 1518cm^{-1}, 1451 cm^{-1} and 759 cm^{-1}. Both characteristic absorption peaks of tannin and lignin can be observed in the FTIR spectrum of tannin/lignin indicating that tannin is modified by lignin successfully.

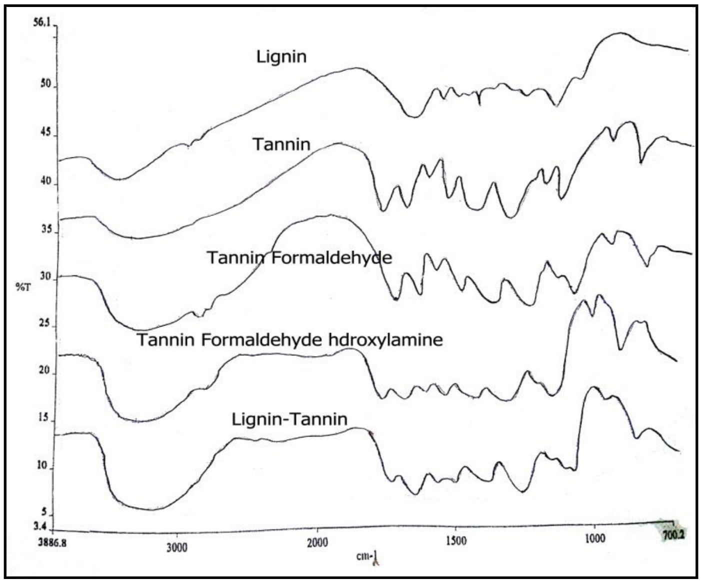


Fig.(7): FTIR of Lignin, Tannin and Lignin-Tannin polymer

The Thermal Stability Study of the compounds

In the present study the thermal stability characteristics of the compounds was investigated by TG and DTG technique. TG is one of the familiar techniques for systematic assessment of polymers thermal stability. It is very useful tool and help to indicate the relative order of stability of various polymers. TG is defined as a continuous measurement of sample weight as a function of time or temperature at a programmed rate of heating. The resulting weight change v.s. temperature (or time) curve gives information about the thermal stability and decomposition of the materials.

The thermogravimetric analysis traces obtained for the polymers heated at a rate of 10°C/ min, which show the dependence of the mass loss of the sample expressed as a percentage of the initial mass and temperature. Also the first derivative is below of them.

The samples of lignin were subjected to thermogravimetric analysis in order to study their thermal behavior. As shown in Fig.(8),the sample showed a weight loss around 4%wt. at 100 ^{o}C that was associated to the moisture present in the lignin samples, that can be attributed to hemicelluloses degradation products. Between 200 and 300 oC another weight loss was observed (39.98%wt.) that can be related to the presence of hemicelluloses. Lignin degradation occurred slowly in a wide range of temperatures with maximal mass loss rate between 350 and 650 ^{o}C which about 14%wt., this fact being associated to the complex structure of lignin with phenolic hydroxyl, carbonyl groups and benzylic hydroxyl, which are connected by straight links . Lignin samples presented high percentage of final residue (41.95%wt.) due to lignin aromatic polycondesations.

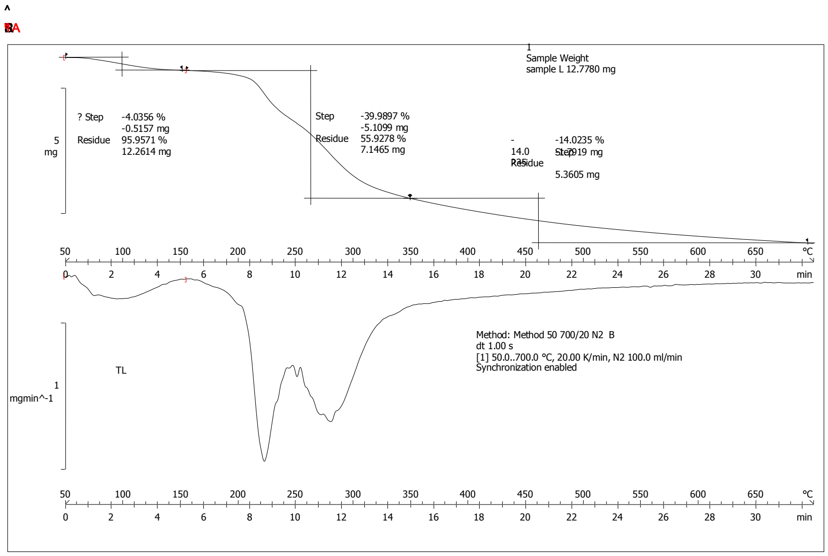


Fig.(8): Thermogravimetric digram of Lignin

From thermogram of the tannin degradation , three distinct mass loss peaks can be seen in Fig.(9), a week peak centered at 150 oC where almost 2.35% of weight due the postcuring, thermal reforming , preliminary oxidation steps and elimination of volatile fractions. The second peak is sharper and more pronounced and it is found at 305 oC which about 63.3% where the degradation tannin begins and it could be the result of partial breakdown of the intermolecular bonding . Third degradation of tannin takes place after 450 oC with remark peak at 580 oC, in this section is seen a mass loss of 6.56% with 27.73% of carbon residue

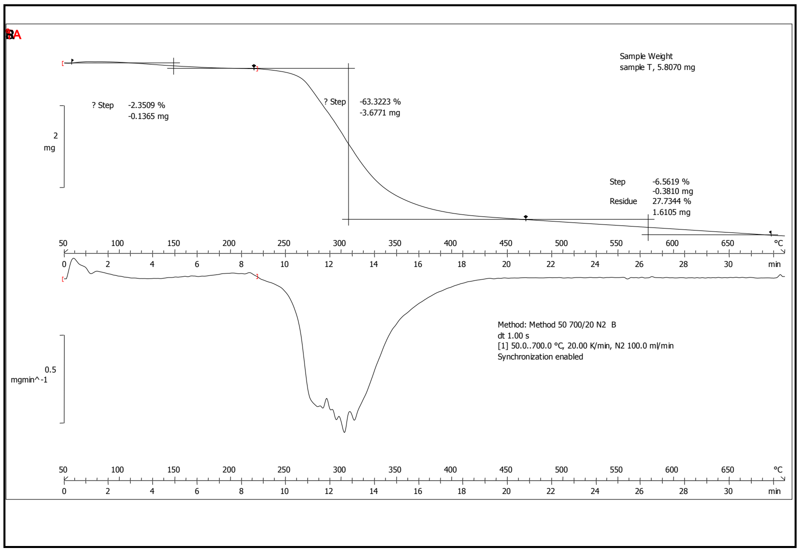


Fig.(9): Thermogravimetric digram of Tannin

Concerning tannin-lignin polymer, three stages of decomposition are shown in Fig.(10). The first stage at 100°C related to the loss of water molecules (4.75%) . The second stage at 280°C can be related to the loss of buteraldehyde molecules (55.85% wt.) from the cleavage of the methylene group .The third stage is eguivalent to 10.63% wt. loss at 500 oC corresponds to the depolymerization of tannin and lignin with remains 28.78% wt. of carbon .

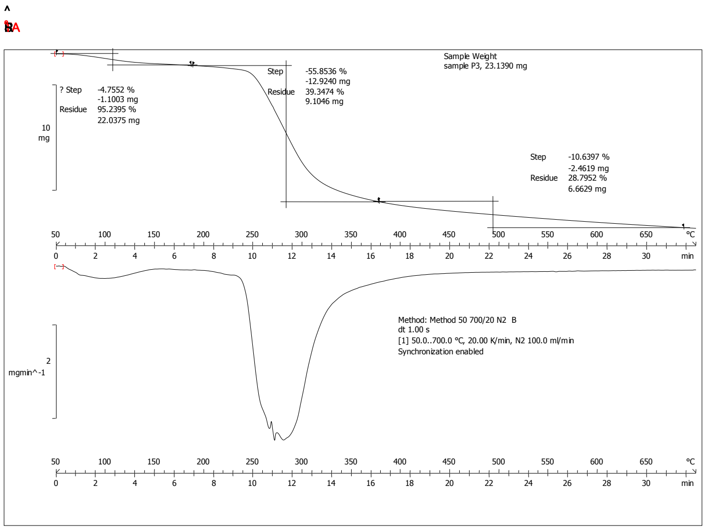


Fig.(10): Thermogravimetric digram of Lignin-Tannin polymer

Differential scanning calorimetry(DSC)

Differential scanning calorimetry can be used to measure a number of characteristic properties of a sample. This technique is used widely for examining polymeric materials to determine their thermal transitions. The sample undergoes a physical transformation such as phase transition which is exothermic or endothermic depending on the type of sample. DSC may also be used to observe more physical change such as glass transition temperature (Tg) , crystallization temperature (Tc) , melting of polymers (Tm) , heat capacity , thermal of expansion and for studying polymer curing. From DSC thermo grams several parameters can also be determined like curing reactions , energy of curing , melting temperature, activation energy of curing , degree of crystallization , charging enthalpy and degree percentage of curing(124).Using it is possible to Glass transitions may occur as the temperature of an amorphous solid is increased. As the temperature increases, an amorphous solid will become less viscous. At some point the molecules may obtain enough freedom of motion to spontaneously arrange themselves into a crystalline form. This is known as the crystallization temperature (Tc). This transition from amorphous solid to crystalline solid is an exothermic process(the cross-linking of polymer molecules that occurs in the curing process), and results in a peak in the DSC signal that usually appears soon after the glass transition. As the temperature increases the sample eventually reaches its melting temperature (Tm). The melting process results in an endothermic peak in the DSC curve.

Lignin displayed a DSC curve (Figure11) with endothermic peak at 100 ºC corresponding to the loss of hydration. When the 386.18 ºC was reached, a sharp exothermic peak corresponding to the melting was apparent.

Figure(11) shows the DSC thermogram of tannin which showed two endothermic peaks , The first one is a wide peak which occur at 114.96 ºC corresponding to a dehydration. The second endothermic peak (232.6ºC) corresponded to the chemical bonds decomposition of tannin chains . At temperatures 364.62 ºC the presence of one exothermic peak corresponding to the melting of tannin.

The DSC thermogram of Lignin-Tannin polymer (Fig. 11) showed an endothermic peak at 104.85 ºC corresponding to the loss of hydration and at about 205.10 ºC the glass transition temperature is appeared in a medium exothermic peak. When the range 205.10- 480 ºC was reached, a broad exothermic peak corresponds to the decomposition of the polymers.

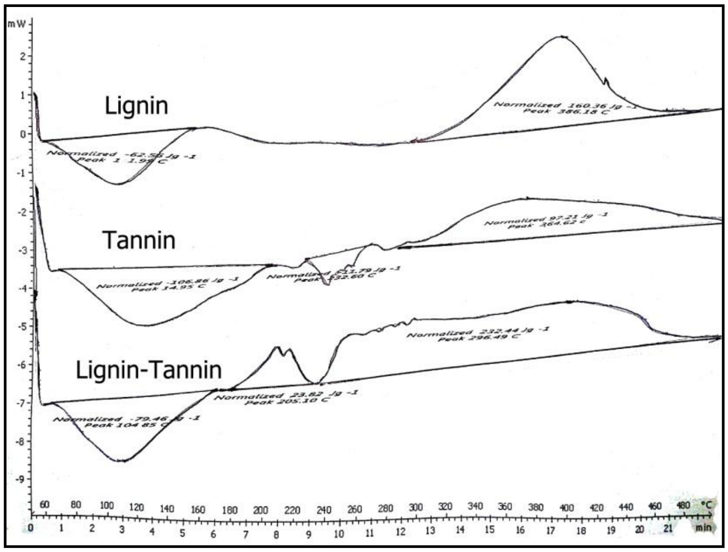


Fig.(11): DSC thermogram of Lignin, Tannin and Lignin-Tannin polymer

X-ray Diffractometry:

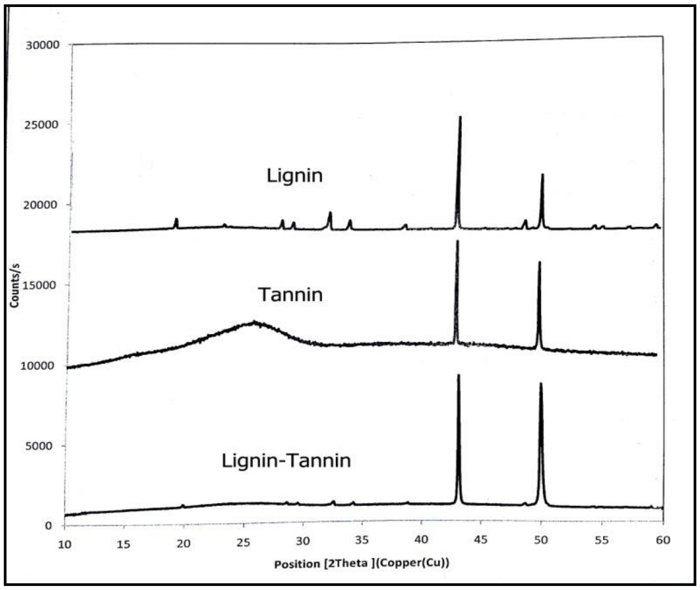
X-ray spectroscopy is unarguably the most versatile and widely used means of characterizing materials of all forms. There are two general types of structural information that can be studied by X-ray spectroscopy: electronic structure (focused on valence and core electrons, which control the chemical and physical properties, among others) and geometric structure (which gives information about the locations of all or a set of atoms in a molecule at an atomic resolution). This method encompasses several spectroscopic techniques for determining the electronic and geometric structures of materials using X-ray excitation: X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), X-ray photoelectron spectroscopy (XPS) and X-ray Auger spectroscopy. Which type of X-ray spectroscopy is employed depends on whether the target information is electronic, geometric or refers to oxidation states . X-ray spectroscopy is thus a powerful and flexible tool and an excellent complement to many structural analysis techniques. The properties of polymers depended mostly on the molecular weight, polydispersity and crystallinity. XRD Commonly used to measure crystallinity,

The crystallinity index (CI) can be calculated on the basis of X-ray diffractograms. Postulating the following equation for determining the crystallinity index (CI):

$$\mathbf{CI\ (\%) = [(Im - Iam)/I110] \times 100}$$

Where: Im (arbitrary units) is the maximum intensity of the crystalline peak at around 2θ = 51°, and Iam (arbitrary units) is the amorphous diffraction at 2θ = 15°. In most cases, CI provides information about the crystal state. crystallinity could also be assigned from an X-ray diffractogram by dividing the area of the crystalline peaks by the total area under the curve (background area). In these calculations, the crystallinity percentage supplied information on relative crystallinity.

It was observed that the X-ray diffractogram (Fig.12) of lignin shows an almost amorphous structure (71%) , the bands at 2θ = 42° and 51°. Figure (12) shows the X-ray diffraction patterns of the tannin sample showed strong reflections at 2θ around 42° and 2θ of 51°. Tannin have crystalline region and non-crystalline region. The crystallizations of tannin were 50% . In turn, the X-ray diffraction patterns of the Lignin-Tannin polymer showed that the bands at 2θ = 42° and 51° decreased significantly after crosslinking (Fig.12), and that this was followed by a dramatic increase in the crystallinity percentage which was found to be (86%). It was therefore concluded that the crystallizations is influenced by components, reaction condition and so on.



Fig(12): X-Ray Spectra of Lignin , Tannin and Lignin-Tannin polymer

Coagulation study

Polymers have been utilized in coagulation/ flocculation processes for water purification for more than three decades. Organic polymers may be used as coagulants as well as in the more traditional flocculation step of binding already formed small flocs into larger particles in water treatment. Coagulation with organic polymers followed by sedimentation can clean up industrial effluent when the flocs formed are dense enough. A major use of organic polymers in water treatment is as a coagulant aid to bridge the coagulated particles formed . The large aggregates formed then settle more rapidly.

The mixture of fine particles of bentonite in water induces a detachment of them due to their strong hydration. The dispersion of bentonite releases very fine colloidal particles. They remain in a state of suspension and cannot be removed from the dispersion by sedimentation or ultracentrifugation. The two mechanisms (strong hydration and dispersion), believed to play an important role in the detachment of bentonite colloidal particles; increase the solubility and the stabilization of colloidal system .

After the coagulant was added to the jars, which contained turbid water , rapid mixing was done for 1 min at 200 rpm and slow stirring for 15 min at 15 rpm. Fifteen minutes were allowed for the settling of the flocs. The turbidity of the supernatant, withdrawn using pipette from a 3 cm depth, was measured by using a Turbidimeter. The sensitivity of the instrument permits the detection of turbidity as low as 0.02 NTU (Nephleometric turbidity units).

The removal efficiency of the studied parameters in these experiments was calculated by applying the following formula:

$$\textbf{Removal efficiency} = \frac{\mathbf{T0-Ti}}{\mathbf{To}} \times \mathbf{100}$$

Where , T^O(NTU) is the initial turbidity of solution, Ti (NTU) is the final turbidity of solution.

Effect of pH on turbidity removal effeciency:

A series of jar tests was conducted to study the coagulation effectiveness of lignin-tannin with turbidities of 10, 20, 50, 100, 200 and 300 NTU under various pH conditions for each turbidity value with pH values of : 2, 3 , 4 , 5 , 6, 7, 8 and 9, respectively. The obtained results in Fig.(13) shows that the removal efficiency of bentonite decreasing with increasing pH. Therefore , the optimal pH was 5 in which high removal efficiency of bentonite was observed , the effect of pH on synthesized polymer was insignificant in terms of bentonite removal in the range pH

5-9. This can attribute to an increase in the number of protonated amine groups in polymer at lower pH. The destabilization of particles was enhanced by the increased number of charged groups followed by charge neutralization. The use of lignin-tannin polymer in water treatment as coagulant is hardly ever preferred.

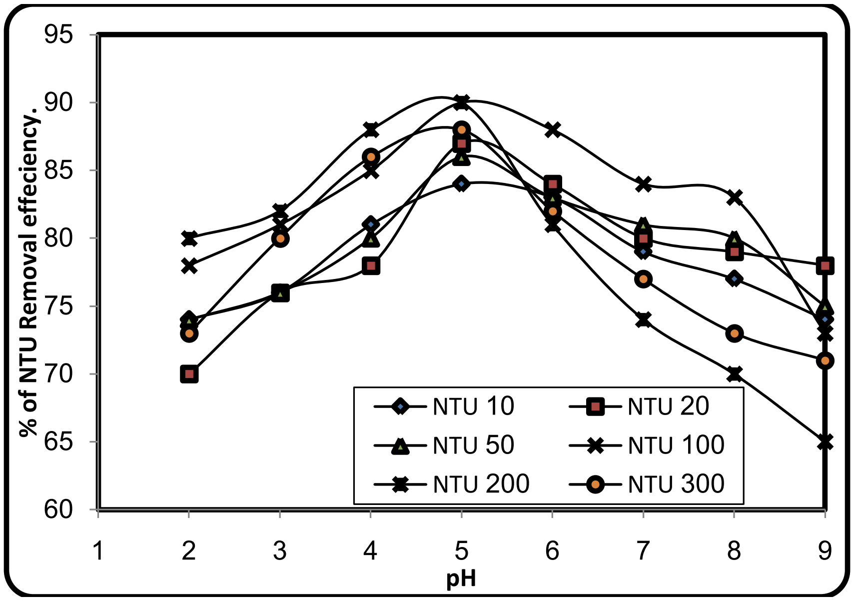


Fig (13) : Turbidity removal efficiency of Lignin-Tannin polymer as a function of pH

Effect of the Lignin-Tannin polymer dosage on turbidity removal effeciency:

To determine the effect of polymer dosage, the jar test experiments with lignin-tannin polymer usingsynthetic water with turbidities of 10, 20, 50, 100, 200 and 300 NTU on turbidity removal at pH 5, were run. We initially conducted tests to determine the optimal dosage of polymer (0.1-1) gm . The results obtained are shown in Figure (14) indicate that the optimum coagulation dosage were 0.1 gm for 10, 20 and 50 NTU turbidities respectively, and it was 0.2 gm for 100, 200 and 300 NTU turbidities. The obtained curves are typical of coagulation flocculation process controlled by the neutralization of charges. Anionic particles of bentonite are electrostatically attracted by the protonated amino groups of lignin-tannin polymer. This reaction facilitates the neutralization of the anionic charges which can bind together and settle rapidly by the effect of gravity. If the increase of the polymer amount added to the solution is in excess, the protonated amino groups (cationic charges) cause a further stabilization of the suspension and reduce the process efficiency.

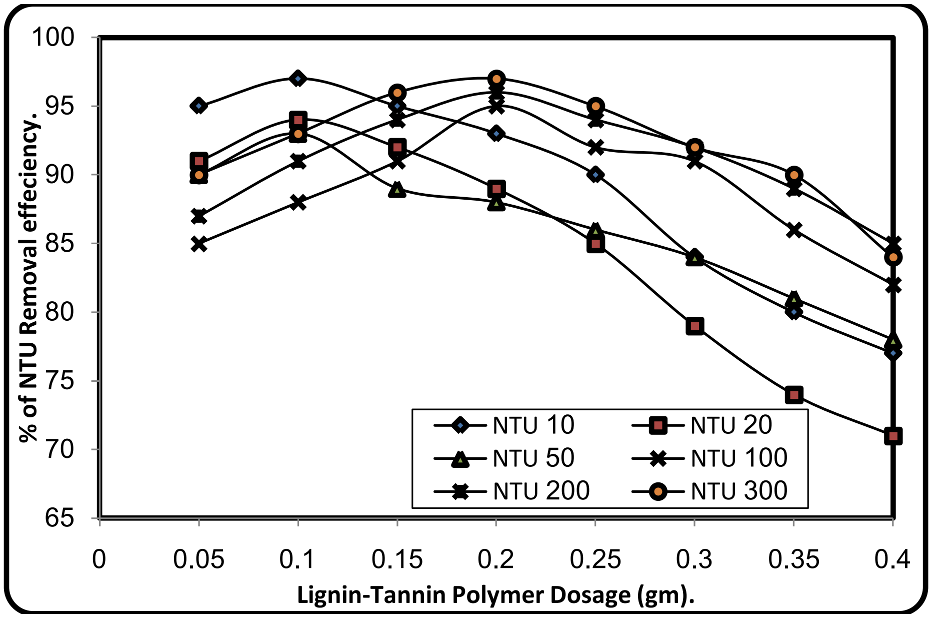


Fig. (14): Turbidity removal efficiency as a function of Lignin-Tannin polymer dosage (gm)

Effect of flocculation time on turbidity removal effeciency

The effect of flocculation time on turbidity removal effeciency was studied by varying the flocculation time from 10 to 60 min, at optimum pH and polymer dose, for 10 , 20 , 50 , 100 , 200 and 300 NTU turbidities. The results obtained are shown in Figure (15), the optimum flocculation time for lignin-tannin polymer is 30 min. The obtained results shows an increase in residual turbidity with flocculation times. This could be due to the redispersion and restabilization of flocs at higher flocculation time. The efficiencies of turbidity removal at the optimum conditions were 98%, 97%, 98.5%, 99%, 99.5% and 99.5%for 10 , 20 , 50 , 100 , 200 and 300 NTU turbidities, respectively.

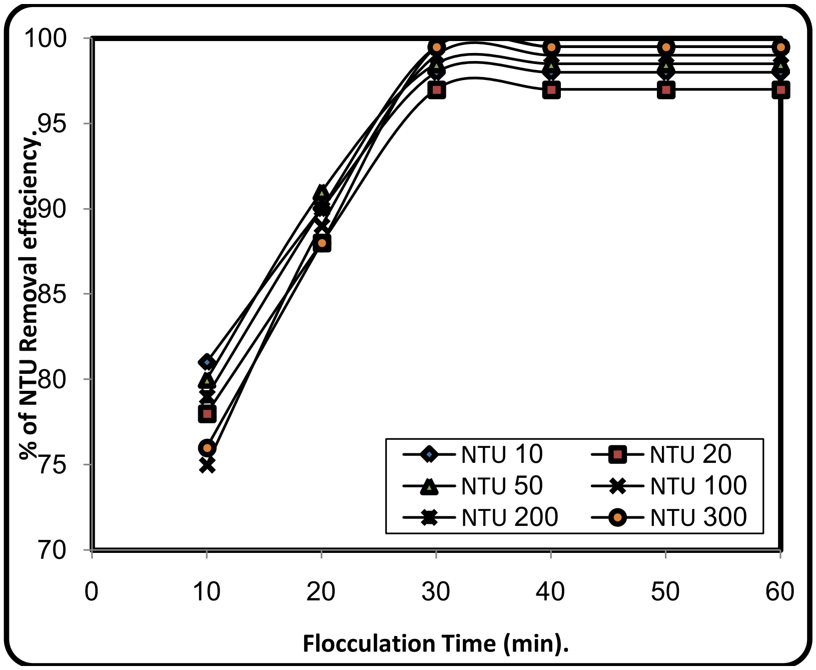
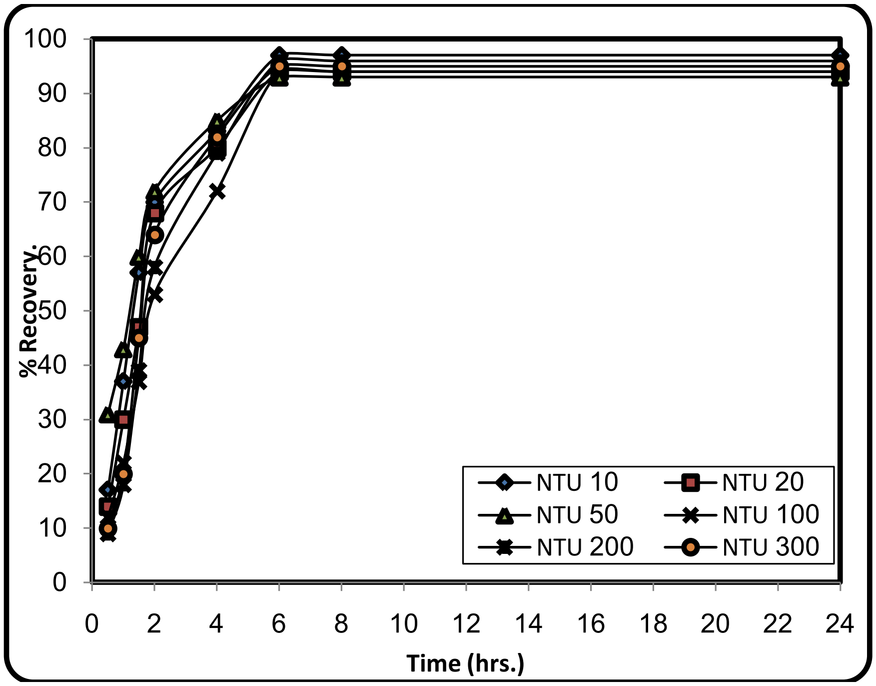


Fig.(15) : Turbidity removal efficiency of Lignin-Tannin polymer as a function of flocculation time

Desorption study for Lignin-Tannin polymer

For the batch desorption experiments of bentonite from Lignin-Tannin polymer were performed by suspending 0.1 gm for 10, 20 and 50 NTU turbidities respectively, and 0.2 gm for 100, 200 and 300 NTU turbidities respectively of synthesized polymer in 10 ml of 3 M HCl and shaking on shaker at 200 rpm at 25°C . After constant time intervals (0.5-24 hrs) the samples were filtered (Whatman filter paper No. 42) and the filterate was analyzed by Turbidimeter for the turbidity contents.

The recovery percentage of bentonite from Lignin-Tannin polymer at different contact time are shown in Figs.(16) .The present results show that recovery percentage of bentonite increased initially with the increasing of the contact time. After six hours, maximum recovery of bentonite were observed.



Fig(16): Effect of contact time on the recovery percentage of bentonite from Lignin-Tannin polymer with (3 M HCl)

Treatment of raw water samples by the Lignin-Tannin polymer

Jar tests were conducted again to test the polymers flocculation ability on initial turbidity for raw water sample near paper production factory with high initial turbidity 155 NTU . The raw water sample was treated with the optimum amount of the polymers for 50 ml from raw water samples and pH , polymer dosage and flocculation time as discussed previously. Fig.(17) shows the water turbidity removal efficiency of the synthesized polymer . A large removal efficiency of polymer has been observed. It was recorded a good removing of turbidity of approximately 98% at 0.2 gm of Lignin-Tannin polymer . At this dose, the settling rate was very fast. These results shows that the synthsized polymer are effective for the turbidity reduction of raw water near the paper production factory with a high initial turbidity (155 NTU), It was observed during the second phase (slow agitation) of coagulation/ flocculation process that flocs appear rapidly with large size. They were fibrous forming cobwebs. This could be attributed to high concentration of colloidal particles , the effect of the concentration of colloidal particles in water is important because they serve as cores to the coagulation. If the concentration of colloids in the water is low, there are too few particles to ensure good flocculation, even though they are neutralized. Another inconvenience of waters that contain few colloids comes because it is easy to add coagulant and to reverse the load of the particles finally instead of neutralizing it. Results obtained indicate the Lignin-Tannin polymer are effectiveness in removing of turbidity of raw water which is highly dependent on initial turbidity and on flocculant dose.

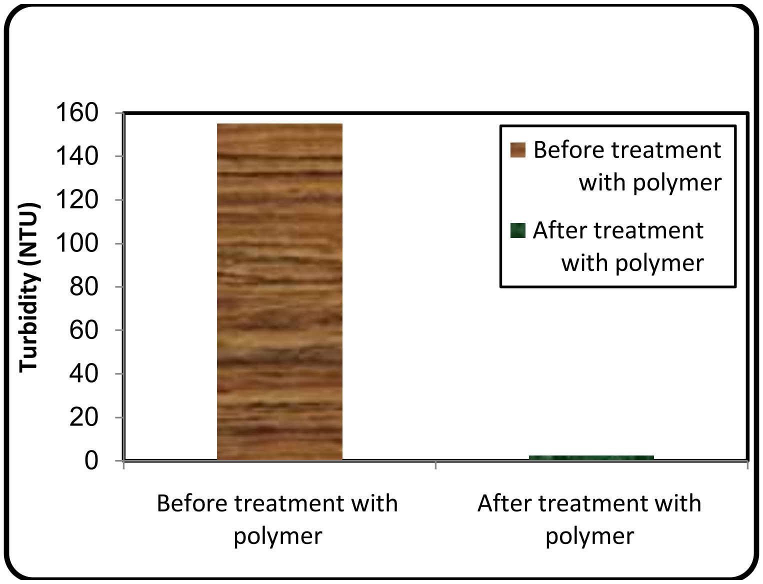


Fig.(17) : Effect of Lignin-Tannin polymer on residual turbidity (at 155 NTU) of raw water at optimum conditions.

ACKNOWLEDGMENT

The authors gratefully acknowledge the contributions of Prof Dr.S.Archibald in the University of Hull, UK, for his benefic contribution of this study.

Conclusion

Natural polymer "Lignin-Tannin polymer" provides axcellant method for bentonite removing. The characterization of material gives information about molecular weight, crystallinity , good chemical and thermal stability which revels applicability towards turbidity removal . This low-cost adsorbents are effective for the removal of bentonite from aqueous solutions . The batch method was employed parameters such as pH, polymer dose and agitation time were studied at an ambient temperature 25°C. The optimum pH corresponding to the maximum adsorption of bentonite removing was pH 3 . Bentonite was adsorbed onto the adsorbents very rapidly within the 0.2 gm of polymer for 30 min.

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