

Phytoremediation of Banana Leaf - Functionalization of Mercaptan-Cellulose and its Utilization for the Removal of Heavy Metals in Aqueous Environment

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ABSTRACT: Biomass being renewable, cost effective and abundantly available is an attractive feedstock for many competent industrial materials. The most important component in biopolymer class is polysaccharides, an almost inexhaustible polymeric raw material with fascinating structure and properties. However, due to the structural limitations, the metal uptake capacities of these materials of otherwise obvious choice for alternate material, is low and different polymer analogous reactions are needed to affect chemical modification of these materials. In the present isolation of cellulose from banana leaf aim to utilise the waste biomass for the removal of heavy metals in aqueous system. Preparation of polymer follows green chemistry protocol with respect to green solvent utilization and zero waste generation. The dried banana leaf were first cleaned by Soxlet extraction, alkali treatment and bleaching. Extracted cellulose has been functionalized with thiomer via thiourea reactions in high degree of modification. The prepared material have been characterized by some physical and chemical methods such as analytical determination, UV, FTIR, Zeta, SEM and EDX analysis. The analytical results supported highest sulphur content of 20.50% in thiomer. Synthesized green thiomer have been explored as arsenic ion sorbent at 60ppm. The result showed maximum sorption efficiency 70-75% for arsenic in aqueous system.

GRAPHICAL ABSTARCT:



Keywords: Waste-biomass; Water contamination; Sorption; Cellulose and Arsenic.

INTRODUCTION: Adaptation of biomass to renewable and important chemical has paying attention in order to build up sustainable societies. In recent years, renewable resources have been explored as potential adsorbents for the extraction of different contaminants from water. Banana leaf comprises of lignin, hemicelluloses, cellulose, pectin and small quantity of extractives. The abundant functional groups (such as thiol group, amino group, and ester group) on the surface of extracted cellulose makes it a potential low-cost renewable adsorbent for pollutant removal from water (Wang et al. 2016). Water contamination owing to the discarding of heavy metals continues to an enormous unease worldwide. As a result, the treatment of industrial effluents remains a problem of inclusive concern. A multiplicity of industries are accountable for the liberation of heavy metals in to the environment through their waste water i.e., steel industry, the nonferrous metal industry, mining and mineral processing etc. Furthermore, many industries are operated at small or medium scale and generate a considerable pollution load as they have no facilities for waste water treatment. The main threats to human health from heavy metals includes (Cd, Pb, Cu, Zn, Ni, Cr, As, Fe etc.) may damage central nervous function, the cardio vascular and gastrointestinal system, lungs, kidneys, liver, endocrine glands, and bones .These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO.

Heavy metals are the elements having atomic weights between 63.5 and 200.6 and a specific gravity greater than 5. They can pose health hazards if their concentration exceeds allowable limits. These heavy metals are reported to inhibit nitrification and denitrification process which adversely affecting biological waste water treatment and reduced microbial oxidation of organic compound. The toxicity of heavy metals in waste water depends on the factors like metal species concentration, pH, sludge concentration and solubility of the metal ion (Alexander et al. 2018). In this study, readily available banana leaf wastes were pre-treated with bleaching solutions to extract the cellulose fibers as low-cost adsorbents for the removal of arsenic from aqueous solutions. Pre-treatment with bleaching solution is a appropriate method, which separate the hemicelluloses, lignin and other soluble compounds from waste biomass of banana to obtain cellulosic fibers as adsorbent. Modifications of cellulose followed by synthetic and natural methodologies are interesting to obtained efficient adsorbents due to their, large number of hydroxyl groups on the surface and high specific surface area incomparable mechanical properties such as low density, regeneration and low cost.

Chemistry of Arsenic and its geographical distribution: However almost 60% of the United States Public Health Service had a drinking water standard of arsenic up to 50ppb (parts per billion). In 1993, World Health Organization (WHO) lowered the arsenic standard for drinking water to 10ppb in 2006. Wide spread contamination of arsenic in ground is due to the presence of volcanic rock in North Carolina. The sedimentary rocks in Bangladesh are highly prone to arsenic contamination in drinking water. Population is still at risk (Sanca et al. 2000). The cultivated with arsenic contaminated ground water cultivation purpose. A recent statistical review of reveals that only about 5 million wells are regularly checked for arsenic contamination about 30% of population has switched from safe area to a safe. Arsenic is found naturally in deposits of earth's crust worldwide. Arsenic is a most abundant element in the periodic table having atomic number 33. Arsenic occurs in many minerals, usually in combination with sulphur and metals, but also as a pure elemental crystal.

Table 1: Permissible limits of heavy metals indrinking water and their hazardous effect. (WHO,2008)

Metal ion	Guideline value (mg/L)	Remarks
Arsenic	0.010	Skin manifestations, vascu- lar disease.
Cadmium	0.003	Kidney damage, renal dis- order, human carcinogen
Uranium	0.015	Nephrotoxicity, genotoxici- ty, and developmental de- fects
Mercury	0.006	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system
Copper	2.000	Liver damage, Wilson dis- ease, insomnia
Lead	0.010	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system
Nickel	0.070	Dermatitis, nausea, chronic asthma, coughing, human carcinogen
Chromium	0.050	Headache, diarrhea, nausea, vomiting, carcinogenic
Zinc	0.800	Depression, lethargy, neuro- logical signs, and increased thirst
Manganese	0.400	Symptoms of manganese poisoning are hallucinations, forgetfulness and nerve damage

The inorganic arsenic is more toxic then the organic form and is predominantly seen in drinking water, whereas organic is seen in sea foods. Inorganic arsenic are the components of geological formation and extracted into ground water, the contamination can also be due to mining, human activities and natural well waters with high concentration of arsenic. These contaminations extort into drinking water and make it more toxic organic arsenic. Arsenic is known to occur in several oxidation states as -5, -3, 0, +3, +5. Inorganic and organic form of arsenic are responsible for carcinogenic and non-carcinogenic effects. The carcinogenic effects are associated with breast, stomach, colon, head and neck leukemia and lymphoma oncarcinogenic effects are keratosis, cardiovascular effects, diabetes mellitus and adverse birth outcomes (Loukidou et al. 2003).



Figure 1: India's affected districts are also crossing the permissive limit of metal contamination.

During the last years, the attention has been shifted towards adsorption technique which has emerged as one of the widely accepted methods for the removal of all such contaminants. Activated carbon and many more has been recognized as a highly effective adsorbent for the treatment of heavy metals in waste water. Therefore, there is increasing research interest in using alternative low cost adsorbents, which has wide range of application spectrum. The necessity of economical, effective and safe methods for removing heavy metals from waste water has resulted in search for unconventional material that may be useful in the removal of heavy metals from the environment at ppm level. Biomass being environment friendly and biodegradable are finding applications in enrichment, separation and water management technologies shown in Table 2. The use of bio-sorbent is effective due to its excellent adsorption, low cost purification and its environmental friendly nature. Remediation of heavy metal ions from the aqueous systems and treatment of waste water using bio-polymeric supports is an area of current interest (Lesmana *et al.* 2009). 4 crore rural Indians drink metal contaminated water (Mohan, V. 2018). Many more affected districts in India are also crossing the permissive limit of metal contamination as shown in Figure 1 and Table 1.

Table 2: Arsenic removal techniques	(conventional
methods).	

Process	Advantages	Disadvantages			
Adsorption using activated carbon	High efficiency (99%)	Costly, no regene- ration, performance depends on adsor- bent			
Adsorption using industrial by -products or mineral sub- stances	Low-cost, high efficiency	Production, reser- vation and regene- ration of the adsor- bent still cause much attention			
Bio-adsorption using modified biopolymers	Good adsorption capacity, selec- tivity	Challenges con- cerning the proper synthetic methods and optimizing the operating condi- tions			
Chemical coa- gulation	Ease of sludge settling, dewa- tering	Costly, high con- sumption of chem- icals			
Chemical pre- cipitation	Ease of opera- tion, cheap	Large quantity of sludge, sludge disposal problems			
Electrochemical methods	Selectivity for metal ions, no chemical con- sumption, most of the metals can be removed	High capital and operational cost			
Electro dialysis	High selectivity	High operation cost due to membrane fouling and energy consumption			
Ion-exchange	Selective for metal ions, re- generation of materials	Costly, available for less number of metal ions			

Biosorption: Many methods has been developed for heavy metal removal but due to high cost and incomplete removal efficiency these method are Biosorption is a property of certain types of inactive/active organisms to bind and concentrate heavy metals from even very dilute aqueous solutions. Biomass exhibits this property, acting just as a chemical substance, as an ion exchanger of biological origin. It is particularly the cell wall structure of certain algae, fungi and bacteria which was found responsible for this phenomenon. Ahalya *et al.* (2004) has been used dewatered waste activated sludge from a sewage treatment plant for the bio- sorption of zinc from aqueous solution (Muralee dharan *et al.* 1991). Advantages of low lost adsorbent shown in Figure 2.



Figure 2: Low cost adsorbents.

Factors affecting bio-sorption process: Temperature seems not to influence the biosorption performances in the range of 20-35. pH seems to be the most important parameter in the biosorptive process: it affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions(Alluri et al. 2007).Biomass concentration in solution seems to influence the specific uptake: for lower values of biomass concentrations there is an increase in the specific uptake Anon (1978) has been suggested an increase in biomass concentration leads to interference between the binding sites. Hence this factor needs to be taken into consideration in any application of microbial biomass as bio sorbent. Biosorption is mainly used to treat wastewater where more than one type of metal ions would be present; the removal of one metal ion may be influenced by the presence of other metal ions. For example: Uranium uptake by biomass of bacteria, fungi and yeasts was not affected by the presence of Mn, Co, Cu, Cd, Hg and Pb in solution (Aziz et al. 2005).

Cellulose used as Bio-sorbent:

Banana fibers: The banana plant is vastly valued for its fruit, but it also yields vast quantities of bio-mass residues from the trunk and fruit bunch which are discarded on the field or at the site of fruit processing (packing for exports). From these residues, good quality of fibers can be extracted along with numerous other plant components (juice) with bioconversion potential. Demonstration of its utility as a renewable resource for industrial applications would increase the profitability for farmers as well as for new industrial agro industrial economic activities, generating innovative outlets for sustainable development. In the current production chain, the waste management is not addressed to a large extent. Examples of banana paper use in India are indicative of its potential for making pulp without use of wood. Adsorbents shaped through functionalization of cellulose. Raw cellulose has a low heavy metal adsorption capacity as well as inconsistent physical stability. Therefore, chemical modification of cellulose can be carried out to achieve adequate structural durability and proficient adsorption competence for heavy metal ions chemical modification can be used to vary certain properties of cellulose such as its hydrophilic or hydrophobic character, elasticity, water sorption, adsorptive or ion exchange capability, resistance to microbiological attack and thermal resistance (Saravanan et al. 2015) The structure of cellulose contains Carbon (44 to 45%), hydrogen (60 to 65%) and oxygen with the empirical formula $C_6H_{12}O_5$. Cellulose is a natural polymer with the molecular weight ranges in millions. Cellulose is insoluble in water and can be separated easily from other plant constituents but soluble in some organic solvents and ionic liquids such as DMAc/LiCl, Schweizer's Reagent Tetra amine diaquacopper dihydroxide [Cu(NH₃)₄(H₂O)₂(OH)₂] and NMMO. It contains beta-1, 4 linkage, which makes it impossible for human to digest due to lack of enzymes which break down the cellulose into simpler units. (Ahluwalia et al., 2007; Annadurai et al. 2002). It is biodegradable, straight chain polymer and much more crystalline and requires a high temperature (320°C) and pressure (25Mpas) to become amorphous. Functional groups may be attached to these hydroxyl groups through a variety of chemistries. Biomass has components those contain metal active species. The leaves may have different types of metal binding compounds as compared to the stems and roots. The leaves may contain higher protein levels that will supply sulfhydryl, amino and carboxyl groups (Chand et al. 2014). The cellulose content of cotton fibre is 90%, while that of wood is 40-50% and major constituents of paper, paperboard, and card stock. It is the main ingredient of textiles made from cotton and other plant fibers. It can be turned into rayon, and important fibers that has been used for textiles since the beginning of 20th century. Cellulose in our body comes from plant materials such as fruits, and vegetables are excellent source of cellulose. Whole grains, which include the protective seed coating, are also source of cellulose (Ashutosh et al. 2015).

The standard and main routes of direct cellulose modification in the preparation of adsorbent materials are esterification, etherification, halogenation and oxidation. It also provides excellent properties to hybrid materials like the networks/hydrogels due to its linear constitution. Randall *et al.* (1974) has been studied that chloroacetyl cellulose efficiently made in dimethylacetamide (DMA)-LiCl solvent system. Lignocelluloses have ion exchange capacity and general sportive characteristics, which are derived from their constituent biopolymer, extractive, cellulose, hemicelluloses, lignin, protein and structures. The cellulose resources also contain polyphenolic compounds such as tannins and lignin, which are believed to be the active sites for attachments of heavy metal cations (Bhattacharya et al. 1984). Further, the utilization of brown algae for heavy metal removal has been reported by Davis *et al.*, (2003).

Table 3: The main functional groups found in nat-
ural bio-adsorbent.

Formula of func- tional group	Name	Li- gand atom	Class of compound	
ОН	Hydroxyl	0	Alcohols, carbohy- drates, phenols	
$\square \land \square \land$	Etheric	0	Polysaccharides, Ethers	
носо	Carbox- ylic	0	Fatty acids, pro- teins, organic acids	
•нс—о	Carbonyl group	0	Aldehydes, Carbohydrates	
-NH	Amide	N	Proteins	
SH•	Thiols	S	Cysteine, amino acids	

The Cd(II) binding capacity of the modified sawdust was directly related to the acid value estimated by titration and could reach uptakes of up to169 mg g⁻¹ (Marchetti *et al.* 2000).

Low et al. (2004) reported that esterification process increases the carboxylic content of the wood fibre surface leading to a corresponding increase in the sorption of divalent metal ions. This modified wood pulp had Cu(II) and Pb(II) binding capacities of 24 mg g⁻¹and 83 mg g⁻¹, respectively. Through a similar esterification reaction, chemically modified wood pulp using succinic anhydride, in the presence of a number of catalysts, leading to the introduction of carboxyl groups. Removal of arsenic from contaminated drinking water was also studied on a chitosan/chitin mixture. The capacity of the mixture at pH 7.0 was 0.13 equiv. As/g. Chitosan powder derived from shrimp shells, was converted into bead form and used to remove As(III) and As(V) from water Fig. 5. Structure of chitin, chitosan and cellulose in both batch and continuous operations (Chen et al. 2006). Furthermore, wastewater containing arsenic discharged from the manufacturing of GaAs supports was also treated in a continuous operation. The optimal pH value for As(III) and As(V) removal was ~ 5 . Adsorption capacities of 1.83 and 1.94 mg As/g bead for As(III) and As(V), respectively, were obtained. Ion coexistence below 50 mg/L did not affect arsenic removal. Chauhan et al. (2016) has been studied that chitosan thiomer synthesized under microwave irradiation shows efficient removal capability of 85.4% for As (III) and 87% for As (V) from arsenic contaminated water without the need of any pre-treatment and pH adjustment. Interestingly, the pH of drinking water normally exists between 6.0 and 8.0, therefore, the chitosan thiomer can be used as capable sorbent for the removal of As(III) and As(V) from drinking water without imparting any change in pH of the medium. Many more bio- adsorbents have shown abundance of carboxylic groups which are considered as good binder with the ions. Table 3 shows the main functional groups found in natural bio-sorbents. The most active functional groups include the hydroxyl, carboxylic, carbonyl and amino groups. In demanding, one approach has been tried in the functionalization of cellulose into compounds competent of adsorbing heavy metal ions from aqueous solutions. The method involves a direct modification of the cellulose backbone with the introduction of chelating or metal binding functionalities producing a range of heavy metal adsorbents.

MATERIALS AND METHOD: Raw banana leaf, collected from Agricultural University Palampur H.P., caustic soda, sodium Lauryl sulfate, Acetic Anhydride, Pyridine. Dimethylformamide/acetamide (DMF/DMA), Thiourea, Sodium Hydroxide (NaOH), Sodium Arsenate, Colouring reagent and all other reagents used in this study were of analytical grade and the weights were taken on weighing machine having minimum readability of 0.01 mg.

Pre-treatment and extraction of cellulose Banana leaf waste biomass:

Experimental methods: Obtained waste was cleaned by soxlet extraction method and exposed to alkali treatment with 5% caustic soda solution along with 2% sodium Lauryl sulfate. Alkali treatment was carried out at 90°C for 1.5 h on a gas burner further banana fibers were washed with water constantly. Additionally the bleaching treatment was carried out in two steps as per following formulation. Lastly banana fibers which finally turned into cellulose and other contents (Table 4) were washed carefully with water, neutralized using dilute hydrochloric acid (1%) and dried under ambient condition. Then, cellulose (undissolved portion) filtered, washed and dried for bleaching. Several steps of bleaching were performed in order to get white cellulose and other contents also determined the chemical composition of the sample with 0.5% EDTA solution HCl and sulfuric acid (Monika *et al.* 2017).

Step 1:

NaOCl (4% w/v)	Na ₂ CO ₃	pН	Tempera- ture	Time
10 gpl	10 gpl	9.8	90 °C	1h

Step 2:

H ₂ O ₂ (50% w/v)	NaSiO _{3.} 9H ₂ O	Na ₂ CO ₃	pН	Temperature	Time
10gpl	10gpl	10gpl	9.8	90 °C	1h

Table 4: Cellulosic content of banana leaf plant.

Content	Weight (%)
Pectin	5
Hemicellulose	23
Lignin	10
Cellulose	55

Functionalization of extracted Cellulose from Banana leaf waste biomass by Reflux method (two step method):

Synthesis of Cellulose ester (Reflux method): Esterification of cellulose was achieved by following an earlier reported procedure with some modification (Roman et al., 2007). Briefly, extracted cellulose was dissolved in LiCl/DMF homogenous system in 1:5 equivalent molar ratio. The solution was then cooled down to room temperature and charged into a threenecked flask equipped with a nitrogen inlet and outlet, dropping funnel, magnetic stirrer and thermometer probe. To this mixture, 5 molar equivalents of chloroacetyl chloride (dissolved in 60 ml DMF) was added drop-wise with continuous stirring at 0–5 °C. Pyridine was added to the reaction flask in 2 molar equivalent ratio as an acid acceptor. The reaction mixture was stirred for 6 h. The obtained precipitate was collected and washed thoroughly with water and ethanol. Finally, 1:5 molar ratio were prepared by reprecipitation using DMSO as solvent and cold distilled water as precipitant and then dried under electric oven at 40-50 ^oC. (Bhatia *et al*, 2008).

Synthesis of Mercaptan Cellulose (Microwave Assisted): The above prepared thiouronium salt was immersed in a 0.2 M NaOH aqueous solution at 40° C for 2 h.). The solid product was separated by filtration and washed three times with dilute HCl and distilled

water, separately, until the pH of the solution was neutral. Ina 500 ml two neck flask, equipped with a sealed stirrer unit and a reflux condenser place chlorinated starch 0.1g and solution (Smith et al. 2001). Connect tube from the top of the condenser leading an inverted funnel just immersed into KMnO₄ solution in order to prevent the escape of unpleasant odors. Stir the mixture vigorously and heat under reflux for 2 hrs at 40-50 °C. The mixture become homogeneous after about 30 min. and the additional heating ensures the completeness of the reaction. Add a solution of NaOH (10g in 100 ml H₂O) and reflux with stirring for further 2 hrs, during this period thiols separated the upper layer of pure compound. Now allow to cool the solution and separate the upper layer of thiols. Acidified the aqueous layer with cold solution of 5ml concentrated H₂SO₄ and 50 mL H₂O now extract it with 75 mL of ether. Combine the ethereal extract with crude thiol and remove the ether on a water bath. Distill the residue using air bath and filter and dried at 50°C.The mechanism of synthesized products were physical examined as shown in Figure 3 (Frank et al, 1946).



Figure 3: Pictorial graphics of synthesis of extraction of cellulose and derivatives (a) EBC (Extracted Banana Cellulose) (b) EC (Esterified Cellulose) (c) MC (Mercaptan Cellulose).

The thiol yield was recorded as %. The reaction details are presented in below structures of cellulose and its derivatives (Acetylated cellulose and Mercaptan cellulose).



Analytical Determination: The synthesized products were characterized for the quantification of chloride and sulfur atom content by Iodometric Titration. The chlorine content atom content was calculated by the following equation1:

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

where, V_{cl} is the volume consumed during sodium thiosulfate titration for chloroacetyl cellulose, V_0 is the volume consumed by non-chlorinated Cellulose during sodium thiosulfate titration and W_{cl} is the weight of chlorinated cellulose.

The sulfur atom content was calculated by following equation 2:

$$\% SH = \frac{V_1 \times N_1 \times 33.07}{W \times 1000} \times 100$$
......2

where, V_I is the volume of sodium thiosulfate solution use for thiolation, N_I is the normality of sodium thiosulfate, W is the weight of mercaptan ellulose.

Degree of Substitution: The degree of substitution is the average number of hydroxyl groups that have been substituted in one anhydrous glucose unit of cellulose. The DS is the parameter that indicates the molar % of new atom or group introduced in to monomer unit of the synthesized derivatives percent (Otto, 1994).The DS of chlorinated cellulose derivative was calculated by following formula 3:

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

Where, % Cl is the percentage of chlorine, 162 is the molecular weight of the anhydroglucose repeating unit, B is the atomic weight of chloride, C is the molecular weight of the ester substituent (-COCH₂Cl) - 1 = 76.5, and % Cl is the chloride percent. The DS of thiolated Cellulose derivative was calculated by following formula 4:

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

.....4

where, 162 is molecular weight of anhydroglucose unit, *B* is the atomic weight of sulfur, *C* is the molecular weight of thiol group (-SH)-1 = 32, and %S is the sulfur percent in product. Sulfur percent was calculated by iodometric titration and was performed in triplicate experiments. Cellulose was modified via general organic reactions to integrate new functionality of competence. The incorporation of new functionalities will provide a better compatibility and potential for intended applications. **FTIR Analysis:** Functional groups in Infrared (IR) spectroscopy is one of most common spectroscopic techniques used by organic and inorganic chemists. IR spectroscopic analysis is to determine the chemical functionality in the sample. FTIR spectrum of cellulose shows characteristic peaks at 3391cm⁻¹ (-O-H stretching), 2928 cm⁻¹ (C-H stretching) at 986 cm⁻¹ and 1011 cm⁻¹ (-C-O stretching) (Fig. 4a and 4b). Chlorinated Cellulose shows additional peak of ester linkage at 1704 cm⁻¹ (-CO stretching) which confirms the chloroacetylation reaction in Fig. 4b, also in Figure 4c thiolated cellulose shows additional peaks a 2502 cm⁻¹ due to -SH group(Singh *et al.* 2018).



Figure 4: (a) FTIR spectrum of extracted cellulose (b chlorinated cellulose (c) mercaptan cellulose.

SEM, EDX and Zeta Potential Analysis: SEM images were recorded to observe differences in the surface morphology of the synthesized products at each stage of the synthetic scheme. The shapes of native cellulose granules were cylindrical (Fig. 5a) The SEM images of chloroacetyl Cellulose was distorted (Fig. 5b). Outer growth on surface of thiolated cellulose was obtained .The cubes increased in thiol structure.(Fig.5c) The derivatized cellulose (chlorinated cellulose and thiolated cellulose)appeared to have smooth structure with irregular shapes, which may be due to weak inter and intra – hydrogen bonding.



Figure 5: SEM images for (a) cellulose, (b) chloroacetylated cellulose with small outgrowth as surface modification, (c) mercaptan cellulose at 15000X magnification with outgrowth modification on the surface.

				% of thiol contents	
S. No	Polymer	% Yield	DS	Theoretical (EDX)	Experi- mental (Titrime- try)
1.	Chlori- nated Cellulose (1:5)	63	0.69	1.52	4.11
2.	Thiolated Cellulose (1:5)	89	1.95	20.50	16.71

Table 5: The high extent modification percentage observed by iodometric titration of banana leaf derivatives.

The EDX analysis of the extracted cellulose, choroacetylated cellulose, mercaptan cellulose are displayed an intense signal of chloride and sulfur (Fig. 6 (a) – (c). The incorporation of sulfur into the support material was quantified and thus verified by titrimetric method. The theoretical percentage of modified cellulose and its derivatives i.e. for chloroacetylated cellulose in Fig 6(b) was 1.52 % and for mercaptan group it was calculated 14.72% which has sulfur contents where as in experimentally it was more i.e. 1 as shown in Table 5. By titrimetry the % of thiols content were 16.71% and chlorine were 4.11. The high extent modification percentage had been observed similar when analyzed by iodometric titration (Anjali *et al.* 2013).



Figure 6: EDX spectra for (a) chlorinated cellulose, (b) mercaptan cellulose and Particle size distribution results for (a) cellulose, (b) chloroacetylated cellulose, (c) mercaptan cellulose

Zeta potential (ζ – potential) is an important parameter providing information on the charge state of particle

surfaces, which could essentially influence the adsorption process. The value of this parameter is often used as a measure of attractive/repulsive electrostatic interaction forces between particles in a suspension. The zeta potential values of the different sulfur derivatives are presented in Table 2. The zeta potential is a measure of the average surface charge of the particles in a colloidal suspension. The magnitude of the zeta potential is related to the DS of the anionic cellulose. The presented values were recorded as an average of 12 measurements. The correlation shows an increase in zeta potential value with the change of the structural unit from Cellulose to mercaptan derivative (Linlin et al).Cellulose exhibited low negative values of the ζ – potential due to the anionic groups located on the surface of the particles. The cellulose derivatives also demonstrated negative values of the ζ -potential, confirming the anionic surface charge of their surface. In the low pH range. The thiol functional group matrix resulted in an essential decrease in the ζ – potential value, as compared with pure cellulose and this can have a positive effect on the cationic metal adsorption (Table 6). The negative charge on the surface of cellulose derivatives benefited the adsorption of As(V) ions in solution.

Table 6: Average zeta potential or surface chargedensity values with standard deviations for theproducts synthesized at pH 7.0.

Polymer	Zeta poten- tial(mV)	Standard deviation
Cellulose	-43.4	8.61
Chloroacetylated Cellulose	-2.15	6.23
Mercaptan Celluose	-24.0	3.63

Thermal (TGA) Studies: A calibration curve of TGA was used to calculate the amount of free thiol groups immobilized on the polymer. The thermo-gravimetric analysis curve of extracted cellulose and thiolated cellulose material (Fig. 5a, b) revealed that functionalized cellulose is more thermally stable than extracted cellulose. The initial weight loss has been observed from 100 °C - 300°C with 12.19 % and 9.902 % for extracted cellulose and ester cellulose, respectively. The primary decomposition reaction was observed due to dehydration upto 200 .The total weight loss was 84.2 % upto 580 °C for chlorinated cellulose sample as compared to 66.07 % weight loss for extracted cellulose upto 500 °C and in case of thiolated cellulose for mercaptan group weight loss was 10.65 % at 175 °C, 5.3% at 895 °C temperature showed that thiolated cellulose with raising degrees of conjugated thiol groups could be received (Figure 7).



Figure 7: TGA curves (a) Extracted cellulose (b) chloroacetylated Cellulose (c) mercaptan Cellulose.

Batch adsorption Analysis: Batch sorption experiments were performed with 100mg of synthesized sorbents in 25ml Arsenic solution (10ppm) at ambient temperature till the completion of equilibrium (Thirunavukkarasu et al. 2001). The solution pH was adjusted for each experiment using 0.1M NaOH and 0.1M HCl. Aliquots of 0.1ml were tested from each test set at different contact time. The coloring reagents were used to quantify the extent of arsenic removal capacity of the synthesized cellulose derivatives at 220nm wavelength in UV-visible spectrophotometer. The unknown concentration of the rejected filtrate was detected by using a standard curve, which was generated by taking 10 standard concentrations has been shown in Fig. 8 (Singh et al., 2015). The results of the adsorption were calculated by using the following equation 5:



Figure 8: Standard curve of Arsenic.

Effect of concentration and time: The adsorption capacity on synthesized mercaptan cellulose was evaluated for arsenic ion sorption with time at 10 ppm, 30ppm, 60ppm as shown in Fig. 9. It is clear that the newly synthesized sorbent is capable of removing arsenic from water even in low initial concentration at

10ppm. After 12h, the mercaptan cellulose shows 70-75% removal for arsenic from the aqueous system. Variations in concentration and time had been observed by preparing different concentration in ppm for arsenic stock solution from 10-60 ppm parallel with respect to the time period of 12h. The adsorption capacities on As(V) by cellulose and its derivatives were 40%, 60% & 75% at 10 ppm ,30ppm and 60ppm along with time period of 12h had been observed as shown in Fig.7. At 60 ppm As(V) concentration in solution is calculated with the % uptake of 70-75% for As(V) after 12h. The maximum uptake of As(V) 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 hydrophobicity of the adsorbent which increase the saturation for better adsorbent with concentration (Andreae et al., 1977). The batch experiments were carried out at constant temperature in a shaking water thermostat maintained at 25 °C. The equilibration time was 12 h at an agitation speed of 110 rpm. The filtrate was analyzed for arsenic. The amount of the arsenic adsorbed (mg) per unit mass of cellulose (g), was obtained by mass balance using equation 6:

$$qe = \frac{Ci - Ce}{m}V$$

Where, c_i and c_e are initial and equilibrium concentrations of the metal ion (mg/L), respectively, *m* is dry mass of cellulose (g), and *V* is the volume of the solution.



Figure 9: Percentage uptake on As(V) removal by mercaptan cellulose.

Effect of pH: The solution pH is a significant cause for all water and wastewater management routes because it marks the speciation of metal in water. To study the effect of initial pH (4–9) on arsenic uptake, experiments were performed with initial arsenic concentrations of 1000 μ g/L at a fixed contact time of 12 h (Figure 8). The effect of contact time was studied with an initial arsenic concentration of 500 μ g/L and adsorbent dose of 2.5 g/L; pH was kept at 5.0 - 6.5 and contact time was varied from 15 to 720 min. The pH of the solution was adjusted to 5.0 - 6.5 by adding 1.0 M sodium hydroxide or 1.0 M hydrochloric acid solutions. As (V) adsorption capacity decrease as pH increases and adsorption was found maximum in pH range (5.0 - 6.5). It is evident from Fig. 8 that adsorption increases with increase in pH and reaches a maximum, and further increase in pH above 7.5 results in decreased adsorption. Maximum adsorption is found to be at pH 6.5 for As(V) using respectively. The observed difference could be due to the pH-dependent As speciation or the surface charge (Schiewer *et al.* 2008; Saravanan *et al.* 2015).





FTIR Sorption Analysis: The interaction and binding behavior between Mercaptan-cellulose and As(V) was investigated with FTIR as shown in Fig11. The FTIR spectroscopy was evaluated to investigate the interaction and binding behaviour between mercaptan cellulose on As(V) as shown in Fig.11(b). IR spectrum of the mercaptan-arsenic complex in contrast to mercaptan-cellulose S-H peak at 2502 cm⁻¹ suggesting the formation of complex through the -SH group of the mercaptan-cellulose which has been disappear. Similarly, the additional peak at 765, 864, 900 and 1081 cm⁻¹ of As(V)–O bond gets enhanced in intensity, which demonstrate the complex formation between mercaptan-cellulose As(V) (Figure 11b). After adsorption of As(V), broadening of the peak at 3430 cm-1 corresponding to -OH group is observed. Shifting of carbonyl stretching frequencies from 1636 cm⁻¹to higher frequency 1642 cm⁻¹after arsenic loading. A sharp doublet at 1070 cm⁻¹ (-C-O stretching) after arsenic adsorption. Appearance of doublet at 1500 and 1392 cm⁻¹ (-CH stretching) after arsenic loading. Intense peak at 864cm⁻¹after arsenic loading could be attributed to As-O stretching vibration. Appearance of strong stretching vibration of As-O at 686 and

769cm⁻¹after arsenic adsorption (Singh *et al.*, 2016). Therefore, the FTIR study results support the complexation mechanism for the arsenic sorption (Figure 11).



Figure 11: FTIR spectrum (a) mercaptan cellulose and (b) As-mercaptan cellulose complex.



Figure 12: As-mercaptan cellulose complex sorption mechanism.

Binding Interaction Analysis:

SEM and EDX Analysis: The morphology of the adsorbent was characterized by using SEM technique. As-Mercaptan cellulose complex were observed through SEM images and mechanism shown as shown in Fig. 12 and 13. It is evident from Fig. 12a, that mercaptan cellulose processes heterogeneous surface. After modification to composite, SEM image reveals clear conversion in the morphology of mercaptan cellulose and confirms many minute particles attached on the surface of mercaptan cellulose (Fig.13b). Moreover, the SEM image of functionalized-As (V) complex shows uniformity on the surface. As element is confirmed in EDX analysis. Fig. 13 presented As(V) adsorbed on the surface of thiolated cellulose. The wt% content is as high as 23.40% for As(V) (Figure 13a) (Anjali et al. 2013).



Figure 13: SEM images for (a) Mercaptancellulose (b) As- Mercaptan cellulose complex at 150000X magnification.



Figure 14: EDX spectra As(V)-Mercaptan cellulose complex.

CONCLUSION: This study presented a unique approach with tremendous potential for rapid in-field analysis and a superior sorbent for excellent sorption of arsenic in water sample. This study shows that mercaptan cellulose with DS 1.95 is highly effective adsorbent for the removal of arsenic from dilute solutions. SEM, EDX, UV & FTIR data also supported the high adsorption in arsenic removal with the thiol group. Adsorption was found maximum in pH range of (6.0-7.0) and at concentration 60 ppm. In conclusion, the attempt to synthesize environment friendly thiomer as proficient alternative is successful as it integrate thiol group to the matrix in high degree of content. The thiol functional groups are responsible for the enhanced potential in arsenic ion sorption. Mercaptan cellulose has been proved an innovative bio sorbent in this study. Further this sorbent can be used to calculate different isotherms and kinetics parameter. The thermodynamics can be also calculated. Mercaptan cellulose functionalization can be used for the textile industries for making fabric by using green method and become a noble application.

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