# CHEMICAL MODIFICATION, CHARACTERIZATION, AND HEAVY METAL ADSORPTION OF CELLULOSE-BASED NATURAL FIBERS

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**Abstract:** The introduction of heavy metal ions into aquatic environment by industrial waste, agricultural waste, and natural disposals is a major environmental concern. Several methods such as precipitation, reverse osmosis, and bioremediation have been used for removal of heavy metals from wastewater and environmental samples but such techniques are expensive, time-consuming, or results in yielding toxic chemicals. Alternatively, adsorption is a preferred method as it combines both environmental and economic advantages. This paper presents the development of adsorbents by chemical modification of cellulose-based natural fibers. Cotton fibers, which are rich in cellulose, were modified by tethering different ligands (including cystamine and polyamines) and measured their efficacy in removing heavy metals (such as Cd(II), Cu(II), Hg(II), Pb(II), and Zn(II) ions) from stimulated contaminated water. The fibers were characterized by FTIR, SEM, EDS, and TGA and their efficacy for removal of heavy metals was investigated using stimulated polluted water with either Cd(II), Hg(II), or Pb(II) metal ions. The results show that the metal-removal capacity of cystamine-modified cotton increased by ~200% and of polyamines-modified cotton by ~400% for Cd(II), and Pb(II) metal ions.

**Keywords:** Heavy Metals, Cotton, Wastewater, Adsorbent, Natural Fibers, Cellulose.

## Introduction

The introduction of heavy metal ions (such as Pb, Hg, Cd, Cu, Zn, Ni, Co, Fe) into the aquatic environment from industrial, agricultural, and natural disposals is a major environmental and health concern. Each year, millions of tons of these metals are released into the environment by one or the other of the abovementioned artificial processes alone (Hubicki & Kołodyńska, 2012). Although most of these metals are required by the plant and animal bodies in low amounts, they can become harmful if present in increased amounts. Lead exposure, for example, can severely damage internal body organs and cause health issues such as kidney and brain damage, and anemia (Pagliuca & Mufti, 1990). Exposure to mercury can lead to health issues such as kidney damage, pneumonia and lung damage, and disorders such as dyslexia and attention deficit hyperactivity disorder (ADHD) (Weiss & Landrigan, 2000), while exposure to cadmium released into the atmosphere by industries causes cadmium(II) to accumulate in the digestive organs in the body and harm the kidneys and respiratory tract (Friberg, 1985). The recommended limits for lead(II), mercury(II), and cadmium(II) in drinking water are 0.005 ppm, 0.0005 ppm and 0.003 ppm, respectively (Dabrowski, Hubicki, Podkoscielny, & Robens, 2004; Hubicki & Kołodyńska, 2012; O'Connell, Birkinshaw, & O'Dwyer, 2008).

Over the years, several techniques have been developed to remove heavy metals from the environment, such as ion exchange, adsorption, reverse osmosis, electrolytic reduction, precipitation, and solvent extraction (Hubicki & Kołodyńska, 2012). However, most of these techniques are either expensive or energy-demanding, thus great interest has been focused on using renewable natural fibers as adsorbents of heavy metals (Mosa, El-Ghamry, & Truby, 2011; Qu et al., 2009; Shukla, Pai, & Shendarkar, 2006; Xie, Jing, Zhao, & Zhang, 2011). Ideally, for a fiber to be an efficient adsorbent material, it should be rich in functional groups containing atoms such as oxygen, nitrogen or sulfur, which can coordinate with heavy-metal ions. One good example of such a natural material is cellulose, which is a linear homopolymer solid composed of D-anhydroglucopyranose monomeric units assembled via β-(1,4)-glycosidic bonds. Cellulose is mechanically strong, hydrophilic, biocompatible and biodegradable, and with lignin, it accounts for most agricultural crops (Mosa et al., 2011; Qiu & Hu, 2013). Thus, plant materials such as rice straw, cotton, and maize stalks were found to be good adsorbents of heavy metals, with cotton stalk having the highest binding capacity (Mosa et al., 2011).

Herein, we report on the chemical-modification of cellulose present in natural cotton fibers to enhance the cotton's efficiency in removing heavy metals form water. The cellulose in cotton was chemically tethered to nitrogen- and sulfur-rich ligands which have binding affinity to heavy metals such as lead and mercury; the ligands used were triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, and cystamine. The fibers were then used to remove heavy metals from synthetic polluted water where 100-400% increase in the metal-removal capacity of the modified fibers was observed in comparison to unmodified cotton fibers.

## Materials and Methods

*Materials and Equipment:* The metal solutions used were at 100, 200, and 300 ppm mercury(II), lead(II) and cadmium(II) solutions, which were separately prepared using mercury(II) acetate, lead nitrate and cadmium chloride salts, respectively, with deionized water. Metal salts from BDH and/or Panreac (Barcelona, Spain). Acidic conditions (pH= 6.0 ± 0.1) were maintained for all metal solutions using $HNO_3$ (0.1 M). pH was measured using PerpHecT Basic Benchtop Model Orion 320 pH meter (Thermo- Orion, Loughborough, UK). Infra-red (IR) spectra were recorded using KBr discs on an FTIR spectrometer (from PerkinElmer, USA). Samples were shaken at 25 °C using a ThermoShaker Edmund Buhler KS-15/TH-15, Germany. Thermo-gravimetric measurements were performed on a TGA 4000 Thermogravimetric Analyzer (TGA) from PerkinElmer USA. All measurements were performed under N2 gas, and the temperature ramp was set at 10 °C/ min. Scanning Electron Microscope (SEM) was performed on a Tescan VEGA III LMU (Czech Republic) with Oxford Instruments EDS surface analysis capability. SEM-Resolution: 3 nm in High vacuum Mode (30 kV); Low Vac and BEI Resolution: 5 nm; Magnification 4 x 1,000,000X; EDS Detector Resolution: 127 EV; EDS Detector Size; 10 mm; EDS Detection range: Be to U with low sensitivity for atoms below Na. Metal analysis was carried out on Inductively Coupled Plasma (ICP) instrument.

*Synthesis of Oxidized Cellulose*: Cotton (20.00 g) was soaked in a solution of sodium periodate (10.0 g $NaIO_4$ in 1000 mL of deionized water) and stirred continuously at a temperature ~65 °C for 1 hour. After cooling to room temperature, the cotton was filtered, washed with ice cold deionized water, and dried under vacuum for 12 hours at room temperature.

*Synthesis of Modified Cellulose*: Oxidized cotton (2.000 g) was added to a solution (200 mL) of sodium carbonate (35 mM) and the ligand (45 mM). The mixture was allowed to stir for 24 hours at room temperature before it was filtered, washed with ice cold deionized water, and dried under vacuum for 12 hours. The ligands used were triethylenetetramine, tetraethylenepentamine, pentaethylene-hexamine, and cystamine ligands.

*Adsorption of Metals*: Samples (100 mg) of the modified and the unmodified cotton were incubated with a solution of the metals (5 ml) at different concentrations (5.0 ppm, 20.0 ppm, 50.0 ppm, 100.0 ppm, and 200.0 ppm) at pH=6.0±0.1 for 12 hours at 25 °C while being swirled using a thermoshaker. The sample solutions were then filtered to remove the cotton, and the concentration of the metal in the filtrate was then measure using ICP.

## Results and Discussion

The synthesis (Saravanan & Ravikumar, 2015) of the modified fibers started with the oxidation of the cellulose in the cotton with aqueous sodium periodate ($NaIO_4$) to form the dialdehyde groups which were then reacted with the amino group of the ligands in basic solution to form the imino linkage with the ligands (Figure 1). Physical examination of the modified cotton showed no visible change on the mechanical strength of the fiber. A closer examination of the fibers surface using SEM showed that the fibers of the oxidized cotton and those of the chemical modified cotton had slightly more rough surfaces than that of the unmodified cotton as depicted in Figure 2.

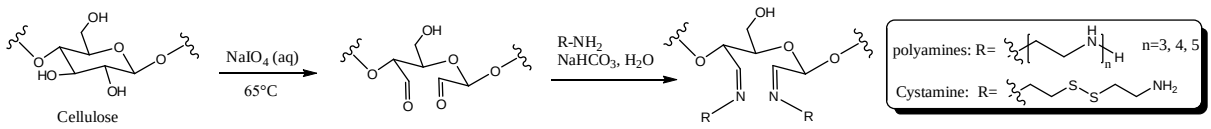



**Figure 1.** Synthetic scheme of the chemical modifications of the cotton fibers

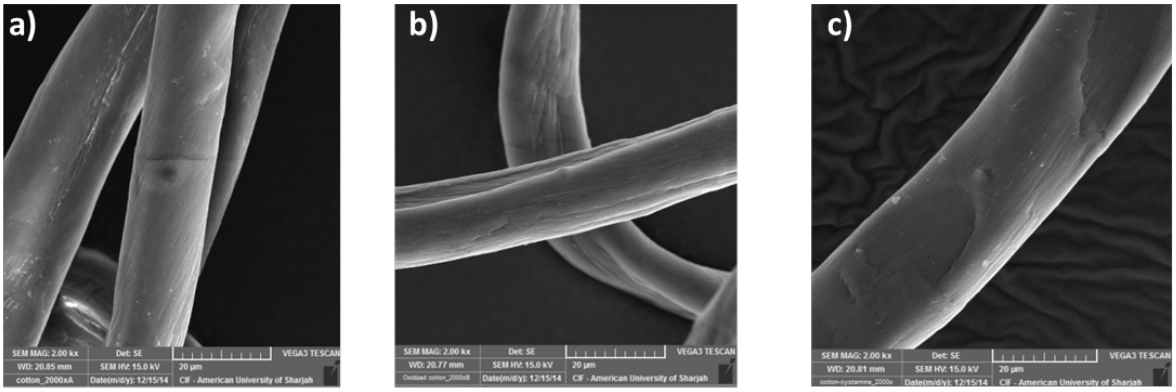



**Figure 2.** SEM images of the fibers' surface (2000x) of (a) unmodified cotton, (b) oxidized cotton and (c) cystamine-modified cotton

The changes in the IR spectra of the modified cotton indicated the attachment of the ligands to cellulose. Figure 3 shows the IR spectra of unmodified cotton, oxidized cotton, and triethylenetetramine-modified cotton fibers. The characteristic peaks of cellulose appear at 3300-3450 $cm^{-1}$ due the stretching of O-H bonds and ~2900 $cm^{-1}$ for the stretching of the non-aromatic C-H bonds. For the oxidized cotton spectra, along with these peaks, a new shoulder peak was observed at around 1737 $cm^{-1}$ (Figure 3) due to the C=O bond stretch of the aldehyde along with peaks at around 1263 $cm^{-1}$ and 810 $cm^{-1}$. These peaks disappeared when the ligand was attached and new peak appeared at ~3445 $cm^{-1}$ (overlapping with that the OH band) corresponding to the stretching of N-H bonds in the ligand.

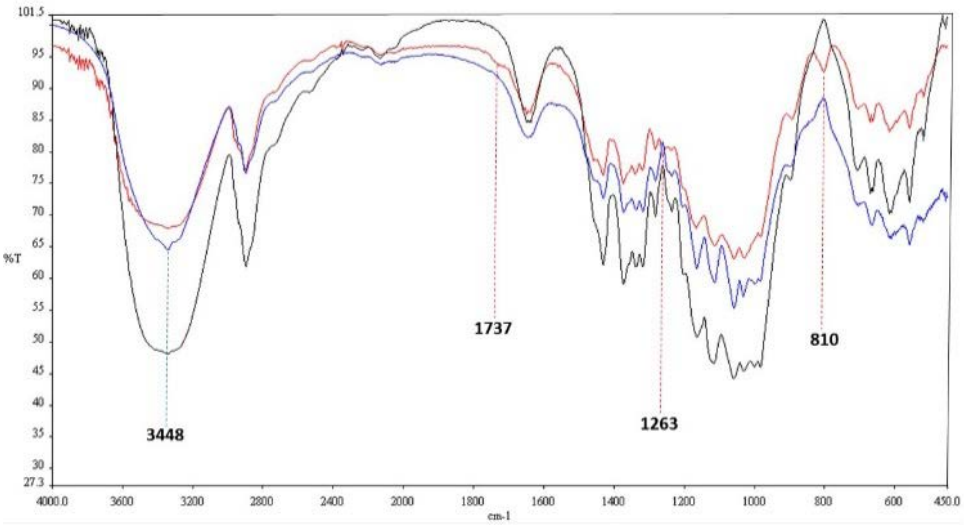



**Figure 3.** IR spectra of unmodified cotton (black), oxidized cotton (red) and triethylenetetramine-modified cotton (blue) fibers.

Furthermore, elemental analysis of the fiber surface using SEM-Energy Dispersive X-ray Spectroscopy (EDS) further supported the attachment of the ligand to the cotton surface. Figure 4 shows EDS spectra of unmodified cotton and cystamine-modified cotton fibers. The top spectra show the main elements present in cellulose fibers: carbon, hydrogen, and oxygen. After oxidation and attachment of the cystamine ligand, a new peak corresponding to sulfur appeared; the appearance of the peak was on the expense of the oxygen peak; the relative intensity of which decreased from 48.4% in the unmodified cotton to 45.7% in the cystamine-modified cotton.

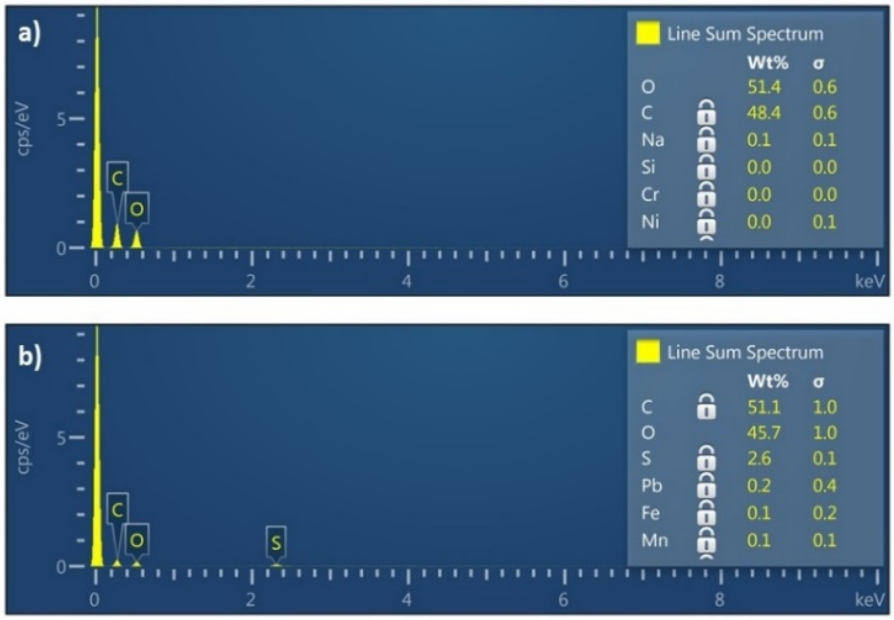



**Figure 4.** EDS spectra for (a) unmodified cotton and (b) cystamine-modified cotton fibers.

Thermal Gravimetric Analysis (TGA) of the ligand-modified cotton fibers showed that these were less thermally stable than the unmodified cotton fibers. The thermograms (Figure 5) of the fibers showed that unmodified cotton was stable up to 290 °C at which it started to decompose. However, all the modified fibers started to decompose at ~ 200°C and lost half their weight at ~365 °C. Cystamine-modified cotton showed a slightly different trend from the polyamine-modified fibers decomposing at a slower rate. The lower thermal stability of the modified fibers can be attributed to the weak imine bond which links the ligands to cellulose versus the C-C and C-O bonds present in the unmodified cotton (Saravanan & Ravikumar, 2015).

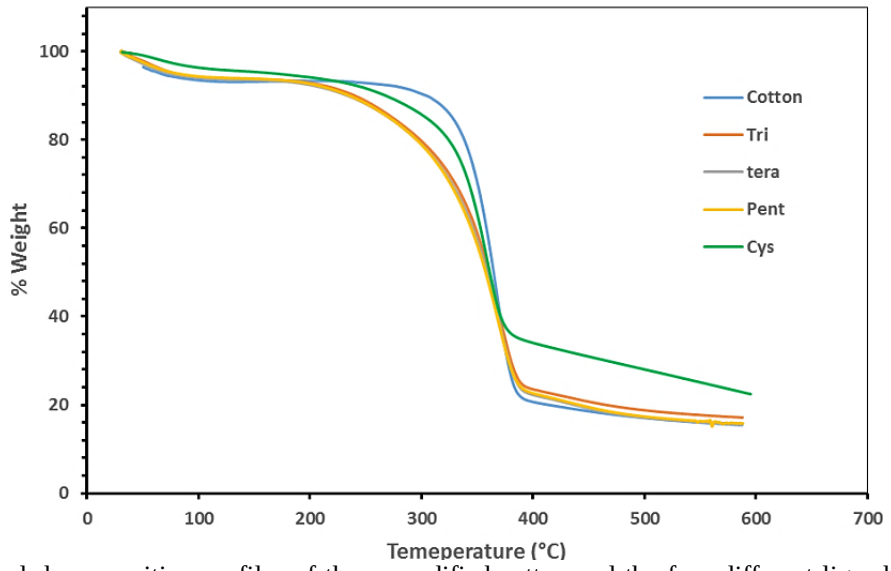



**Figure 5.** Thermal decomposition profiles of the unmodified cotton and the four different ligand-modified cotton fibers.

The ability of the modified fibers to remove metal ions from polluted water was evaluated through batch experiments where modified and non-modified fibers were soaked in solutions of different metals for 12 hours. Figure 6 shows the amount of Cd, Hg and Pb metal ion removed from 100 ppm solution using 20 g of fibers per one litter of solution. The fibers modified with the polyamines ligand removed about 50 % of Cd ions while fibers modified with

triethylenetetramine and cystamine removed around 50% of Hg and about 90% of Pb; however, non-modified cotton removed only 22% of Cd, 45% of Hg and 43% of Pb.

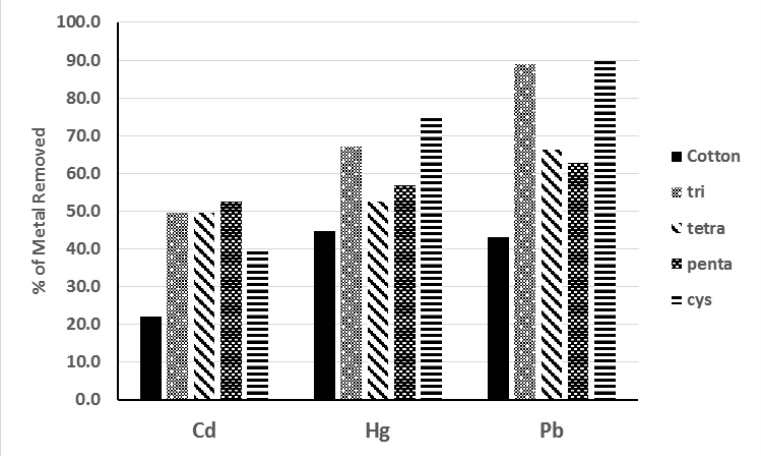
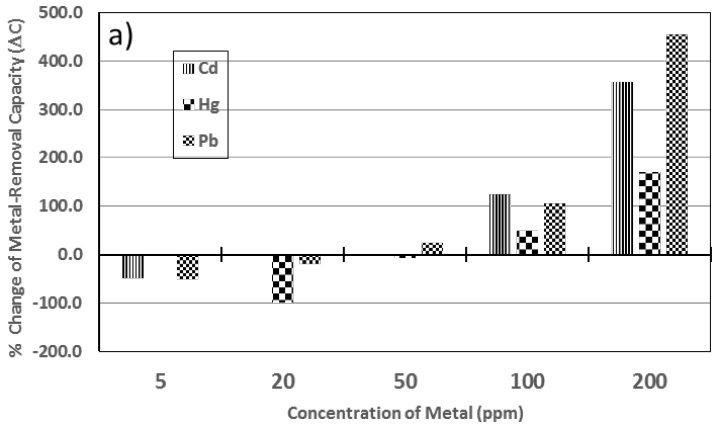



**Figure 6.** The % removal of the metal at 100 ppm concentration using the modified fibers at 20 g/L ratio.

The efficacy of the modified fibers to remove the metals was dependent on the concentration of the metal in solution. Figure 7 shows the relative change in metal-removal capacity (ΔC) of cotton as it was modified with triethylenetetramine and cystamine, respectively. The percentage change of metal-removal capacity was calculated according to (1):

$$\Delta C = [\ (C_f - C_o) / C_o] \times 100 \qquad (1)$$

where $C_f$ is the metal-removal capacity of modified fiber (mg/g of metal/fiber), and $C_o$ is the metal-removal capacity of non-modified fiber (mg/g of metal/fiber). The results showed that the chemical modification of cotton with triethylenetetramine had negative or insignificant effect on the metal-removal capacity at metal concentrations lower that 100 ppm; as metal concentration increased to 200 ppm, the metal-removal capacity increased by 350% for Cd, 150% for Hg and 450 % for Pb. Chemical modification of cotton with cystamine had insignificant effect on the metal-removal at 5 ppm and 20 ppm concentrations. As the concentration increased to 50 ppm, the loading capacity of Cd increased by 200 % and then it decreased to 140% and 110% at 100 ppm and 200 ppm, respectively. An opposite trend, however, was observed of Pb-removal capacity which increased by 30% at 50 ppm, 130% at 100 ppm and 190% at 200 ppm.



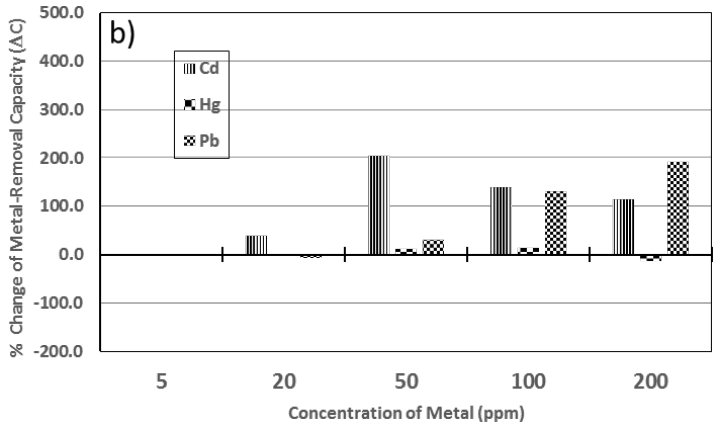



**Figure 7.** The % change of the metal-removing capacity (DC) of the cotton fibers upon modification with (a) triethylenetetramine and (b) cystamine.

## Conclusion

The results of this report showed that chemical modification of cellulose natural fibers would enhance their efficacy as adsorbent for metal ions from polluted water. Further development of the procedures and investigations of other ligands and fibers could provide valuable tool for remediation of wastewater contaminated heavy metals at a relatively low cost.

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