

## Chemically modified local sugarcane bagasse for heavy metal trapping

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### Abstract

Heavy metal contamination of water has become a critical global issue. High costs, complex methods and harmful additives make it difficult to find a feasible solution. Rapidly increasing water pollution demands for a fast and effective water treatment solution. Most of the industries are reluctant to treat dumped water, assuming it is a profitless investment. However, a solution with an additional economical profit and easy access can motivate the industrial sector to think twice on water treatment before dumping waste water to the environment.

The research report herein, reveals the applicability of sugarcane bagasse, an industrial waste, for the removal of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  ions from contaminated water. For this purpose, raw bagasse was treated with cheap chemicals; alkali (4% w/w NaOH) and acid (64% w/w  $\text{H}_2\text{SO}_4$ ) to remove the outer rigid layers of lignocellulose. After ultrasonication and making the pH  $\sim 6$ , crystalline cellulose was isolated. FTIR, XRD and  $^1\text{H}$  NMR techniques were used for structural analysis of isolated cellulose. Isolated cellulose was used for treating water contaminated with  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  and analyzed using AAS and XRF techniques. The percentage removal of  $\text{Cu}^{2+}$  ( $\sim 28\%$ ) and  $\text{Pb}^{2+}$  ( $\sim 55\%$ ) by crystalline cellulose was higher than that of  $\text{Ni}^{2+}$ . Significantly, the percentage removal caused by isolated crystalline cellulose is higher for  $\text{Pb}^{2+}$  (50%) and for  $\text{Cu}^{2+}$  (78%) than that caused by raw bagasse. However, metal adsorption varied with many factors such as pH, temperature, agitation time and initial metal ion concentration. Analysis carried out with  $\text{Pb}^{2+}$  ion solution suggests that maintaining pH  $\sim 6$  is the governing factor compared to the other variables. However, this mechanism would not be applicable with metals such as Ca, Si, Fe, Na and Al which are present in bagasse ash. This work shows that industrial waste can be utilized to treat water polluted with  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  in a reusable manner.

### Introduction

Heavy metal contamination of water has become a critical global issue. High cost, complex methods and harmful additives make it difficult to find a feasible solution. Otherwise, rapid water pollution demands for any fast and effective solution for water treatment. Most of the industries are backward for treating dump water, assuming it is a profitless investment. Anyhow, a solution with an additional economical profit and easy access, will be able to catch the eye of many industrial sectors. Lignocellulosic materials such as bagasse, a by-product of sugar industry have a considerable capacity of trapping metals. The research reported herein, raw bagasse was treated with cheap chemicals; alkali (50 % (w/w) NaOH) and acid (64% (w/w)  $\text{H}_2\text{SO}_4$ ) to remove the outer rigid layers of lignocellulose. After ultrasonication and neutralization (pH  $\sim 6 - 7$ ), the isolated crystalline cellulose, showed an enormous capacity of metal trapping. Column extraction and batch reaction were carried out for trapping metals; Copper, Lead and Nickel. FTIR, XRD and  $^1\text{H}$ NMR techniques were used for characterizing the isolated cellulose

material while AAS and XRF techniques were used for adsorption behaviour analysis. During the research reported herein initially, three metal ion solutions ( $\text{Ni}(\text{CH}_3\text{COO})_2$ ,  $\text{CuSO}_4$  and  $\text{PbCl}_2$ ) were considered. Then, due to the higher trapping capacity, further analysis with variation of pH, agitation time and initial metal ion concentration was taken place with  $\text{PbCl}_2$  solution.

The acidic and basic solutions coming out as the by-product or waste of the crystalline cellulose preparation procedure could be recycled. In addition, dissolved lignocellulosic materials (lignin/hemicellulose) in these solutions may have a potential of providing useful, simpler aromatic formulas such as aromatic alcohols and ethers via electrochemical or catalytic conversion. Moreover, crystalline cellulose consisting of characteristic properties shown in this experiment has a potential of acting as a reinforcement agent in composite preparation.

As the cellulosic structure is usually common for all the plant materials, this mechanism can be applied with many other bio based wastes all over the world. The current research was capable of

addressing a severe global matter through an environmental friendly (naturally digesting), low cost, efficient solution while introducing value added chemicals as by-products of the treatment (no waste; green solution), reusable chemicals and waste utilization of a local industry.

## Materials and Methods

### Materials and Reagents

Bagasse was collected from Pelawatta sugar factory, Sri Lanka, washed several times with distilled water and air dried. NaOH, (extra pure pellets) from LobaChemie Pvt. Ltd. H<sub>2</sub>SO<sub>4</sub> (97-99% wt) and HCl (35.4% wt) from Sigma-Aldrich Chemicals Pvt. Ltd, KBr (extra pure solid) from Loba Chemie Pvt. Ltd, CuSO<sub>4</sub> from E. Merck (India) Ltd, Mumbai and Ni(CH<sub>3</sub>COO)<sub>2</sub>, PbCl<sub>2</sub>, from British Drug Houses Ltd.

### Instrumentation

A Centurion centrifuger was used whenever necessary to centrifuge the mixtures. A drying oven (DHG-9140A, 2050 W, temperature range of 40°C - 280 °C) was used to dry the samples. FS 95 Furnace Auto sample M Series Atomic Absorption Spectrometer (AAS) of Thermo Electron Corporation was used for AAS testing. The qualitative analyses for elements of natural and products were performed from Fisher X-ray Fluorescence (XRF) instrument.

## Methods

### Isolation of cellulose

First, the properly washed, ground and air dried bagasse (RSCB) was refluxed with NaOH ((50% w/w), 20 mL per each gram of solid material) for 2 h with continuous mechanical stirring. Then, the resulting suspension was centrifuged and ultrasonicated for removing soluble salts and further bond breaking. The resultant solid material was treated with H<sub>2</sub>SO<sub>4</sub> ((64%, w/w %), approximately 20 mL per each gram of solid material) for 30 min at (45-55) C under continuous magnetic stirring. Then, the resulting suspension was dialyzed (to achieve the pH value nearly 7), centrifuged and ultrasonicated for removing soluble salts and for further reducing particle size. This isolated crystalline cellulosic (CC) suspension was used for analysing the metal trapping capability.

### Comparison of Metal Trapping Capacity of Raw Bagasse and Isolated Crystalline Cellulose (CC) for Pb and Cu ion solutions

For the comparison the same masses (2 mg) of CC

and RSCB were stirred separately with CuSO<sub>4</sub> (2 ppm), PbCl<sub>2</sub> (9.1 ppm) solutions (20 mL) for 15 minutes at room temperature.

### Trapping of different metals

Ion exchange columns of 2.5 ml volumes were prepared using the CC suspension. Aqueous solutions of Ni(CH<sub>3</sub>COO)<sub>2</sub>, CuSO<sub>4</sub> and PbCl<sub>2</sub> were passed through the separate columns keeping the column dimensions and solution amount (5 ml) constant. Finally, metal ion trapping capacity of cellulosic materials was checked using AAS. The column packed materials for Cu and Pb were dried in air and checked with XRF.

### Effect of initial metal ion concentration and other metals present in the solution

CuSO<sub>4</sub> solutions (5 mL each) in different concentrations (200, 140, 30 ppm) were separately mixed with 1 mL (~1 mg) of CC suspension and stirred continuously for 15 min and initial/final metal ion concentrations were checked using AAS. The same procedure was performed for PbCl<sub>2</sub> with different concentrations (655, 325, 130 ppm). Thereafter, the same experiment was carried out for a mixture of CuSO<sub>4</sub> (78 ppm) and PbCl<sub>2</sub> (78 ppm) solution.

### Effect of agitation time and initial pH of solution

Next, CC suspension (1 mL) was well stirred with Pb<sup>2+</sup> solution (10 mL, 66 ppm) at different pH values and stirring time periods. For pH analysis, pH was adjusted with an aqueous HCl or NaOH solutions of 0.1 mol/L. Minimum contact time and easily achievable pH values were preferred as the optimum conditions. Therefore, study was performed within 5-30 min time durations and 2-12 pH range. The resulting solutions were properly filtered, allowed to settle for a while and AAS analysis was carried out for each supernatant. The percent removal of the metal and the amount of metal adsorbed per gram of adsorbent (q<sub>e</sub>) were calculated using equations (1) and (2).

$$\% \text{ Removal of dye by CC} = \frac{(C_0 - C_e)}{C_0} \times 100 \dots (1)$$

$$q_e = \frac{(C_0 - C_e)}{m} \times V \dots (2)$$

where, C<sub>0</sub> and C<sub>e</sub> are initial and final metal ion concentrations (mgL<sup>-1</sup>) respectively, V is total solution volume (L) and m is the mass of adsorbent (g) used.

**Table 1.** AAS Data for Cu<sup>2+</sup> and Pb<sup>2+</sup> solutions before and after mixing with same mass (2 mg) of untreated bagasse (RSCB) and isolated cellulose (CC).

| Description   | Metal            | Concentration of filtrate after treating with RSCB (mg/L) | Concentration of filtrate after treating with CC (mg/L) |
|---|------------------|---|---|
| Final concentration after running the same initial concentrated metal ion solution (Pb = 9.10 mg/L & Cu = 2.00 mg/L) through both RSCB and CC columns | Pb <sup>2+</sup> | 4.604   | 0   |
|   | Cu <sup>2+</sup> | 1.542   | 0   |

**Results and Discussion**

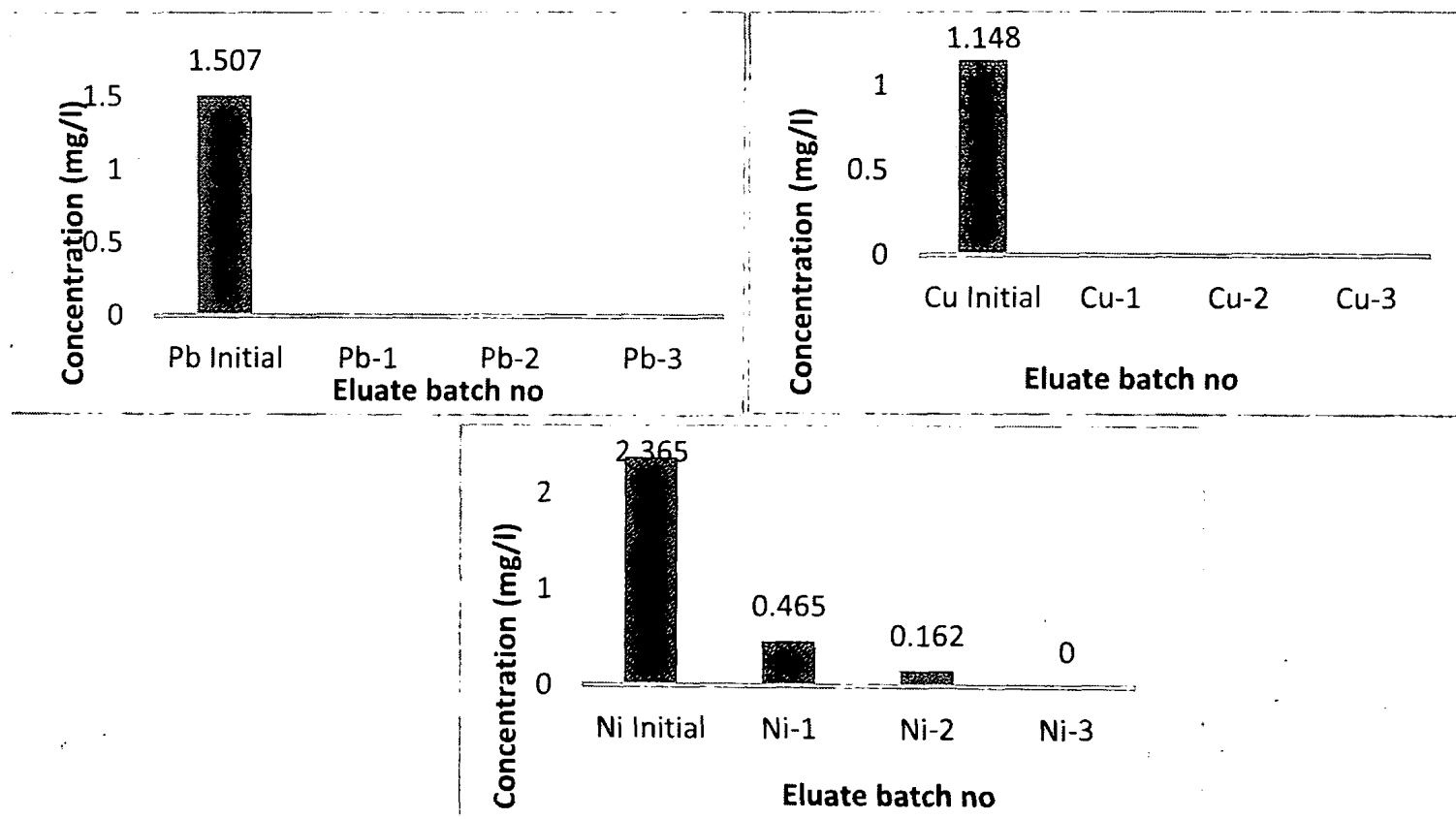
*Comparison of Metal Trapping Capacity of Raw Bagasse and Isolated Crystalline Cellulose (CC) for Pb and Cu ion solutions*

Table 1 describes the metal trapping capability of raw bagasse and isolated crystalline cellulose for two different metal ions. According to the AAS data CC shows a higher removal (50% increase for

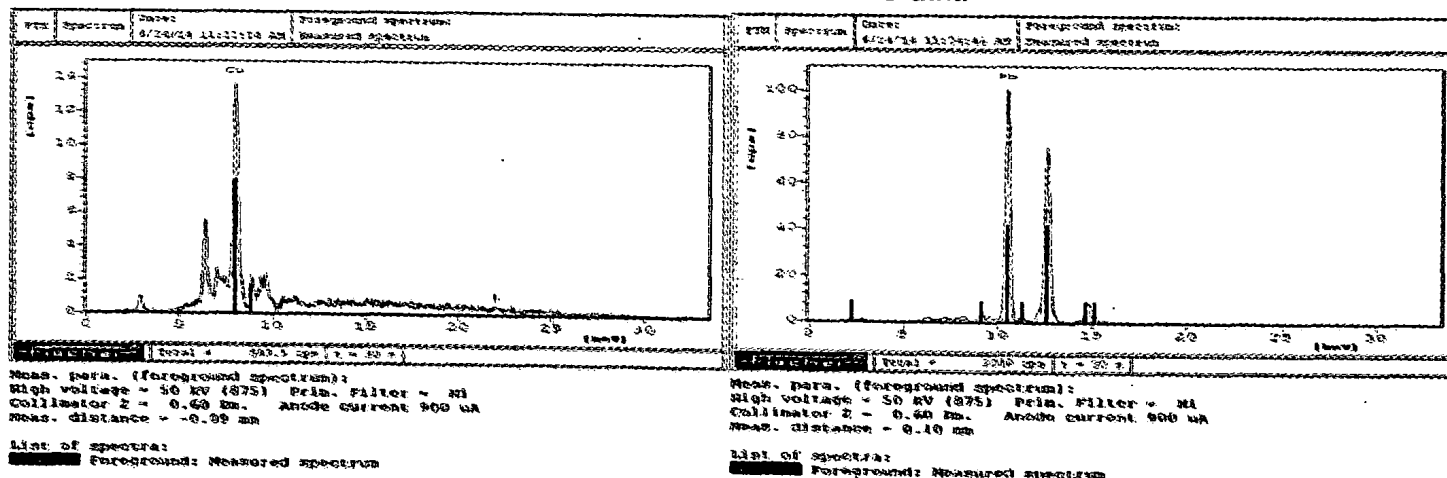
Pb and 78% increase for Cu) than raw bagasse AAS.

Significant removal of Cu, Ni and Pb ions are evident after running through the columns packed with the cellulosic materials isolated from bagasse (Fig. 1). There is a considerable reduction of metal ion percentage after passing through the CC columns but, the highest adsorption can be seen with Pb

*Trapping of different metals*



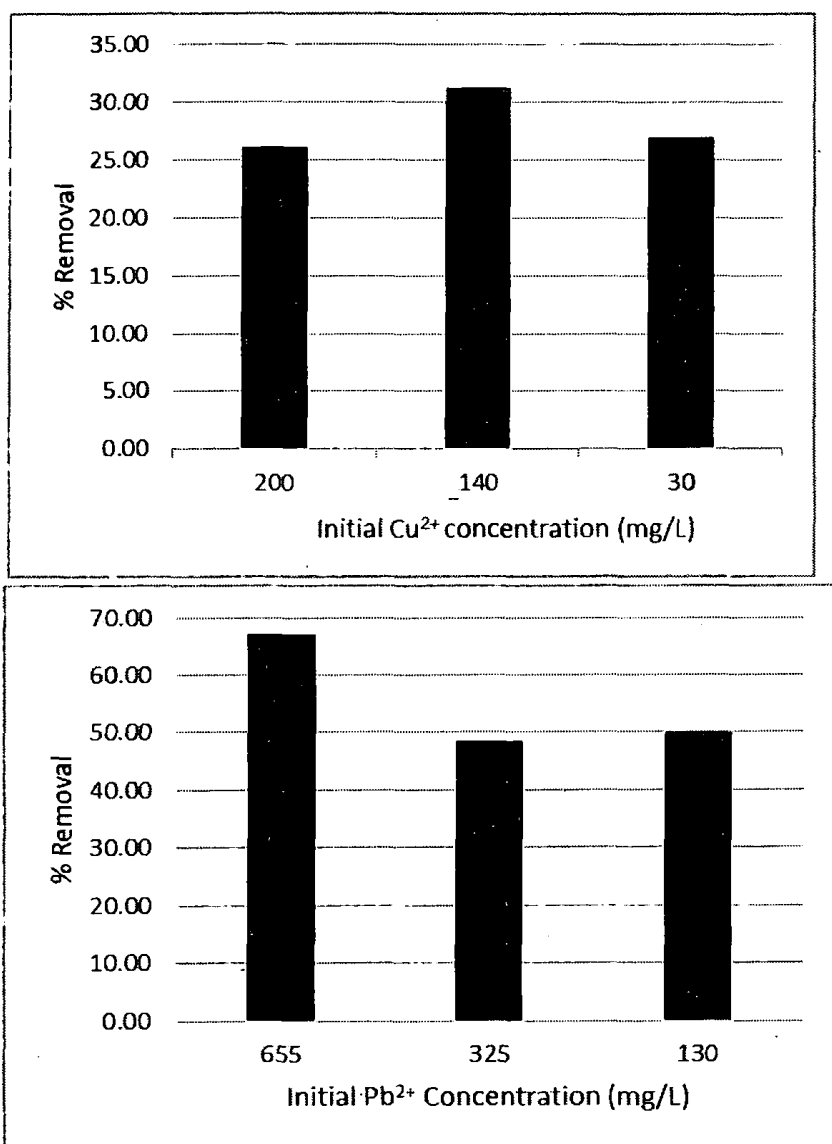
**Fig. 1.** Concentration of Cu<sup>2+</sup>, Ni<sup>2+</sup> and Pb<sup>2+</sup> in initial water samples and in fractions collected after passing through CC columns based on AAS data



**Fig.. 2.** XRF analysis spectra of dried column packed materials after passing a. CuSO<sub>4</sub>, b. PbCl<sub>2</sub> solutions

Fig. 2 shows the  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ion content present in dried column packed material after passing metal ion solutions ( $\text{CuSO}_4$  and  $\text{PbCl}_2$ ). Initially, though there is no presence of these metals in CC, after passing metal solutions some considerable percentages can be seen in the dried solid material. ensuring the trapping

*Effect of initial metal concentration*

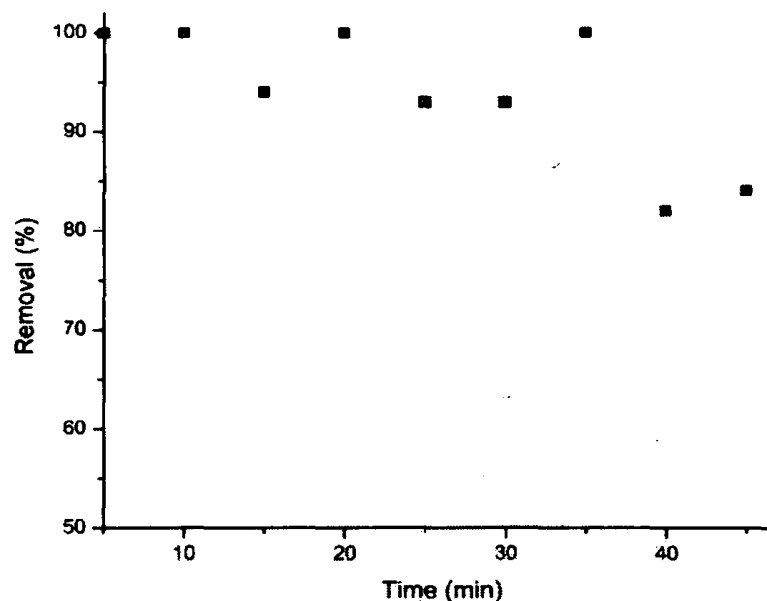


**Fig. 3.** Percentage metal removal of a.  $\text{Cu}^{2+}$  and b.  $\text{Pb}^{2+}$  solutions in different concentrations after mixing with CC

Figure 3 represents the removal of Cu and Pb in different concentrated solutions. According to AAS data average removal of 28% and 55% can be seen for Cu and Pb solutions respectively. Very slight deviation from the average value can be seen at different concentrations for both metals.

*Effect of agitation time*

Percentage removal of  $\text{Pb}^{2+}$  as a function of agitation time was shown in figure 4. During the time periods taken, initially there is a fluctuation of metal removal in between a maxima and a minimal with a gap of about 6%. After 35 min of agitation time, there is a sudden drop of the metal removal by 20%. This phenomena might be due to the desorption occurring under continuous stirring..

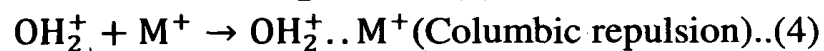
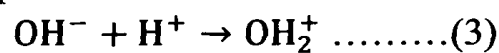


**Fig. 4.** Percentage removal of Pb ion by CC as a function of agitation time

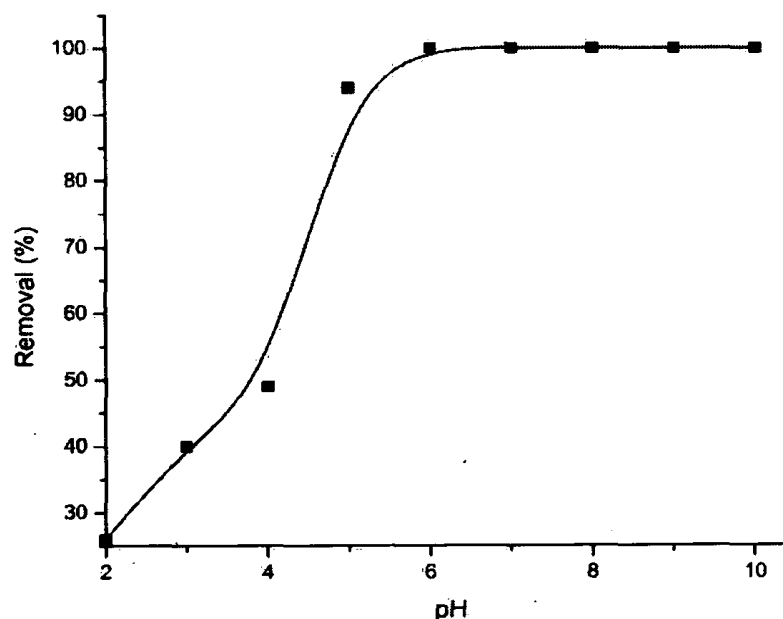
Therefore, first 35 min will be better for metal adsorption and longer agitation periods may release the metal ions back to the solution. Anyhow, percent removal is varying only within 20% gap.

*Effect of pH*

The removal of metal ions from aqueous solutions by adsorption is dependent on the solution's pH and, since it affects adsorbent surface charge, on the degree of ionization, and on the adsorbates species. Figure 5 shows the percent adsorption of Pb onto CC at different pH of the solution. It can be seen that the minimum adsorption was seen at pH 2 and then, percentage removal gradually increased up to the maximum adsorption at pH 6 and then became a constant. Throughout this pH range polymer surface protonation occurs as shown below:



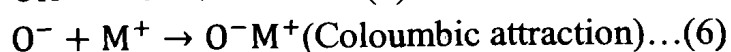
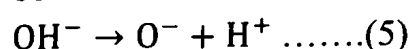
where, M is the metal.



**Fig. 5.** Percentage removal of MB dye by CC as a function of pH

Interaction with the cationic metal ion leads to a decrease of adsorption at lower pH values. However, % removal get increased gradually while increasing the pH and after pH 6.0 % removal

became almost constant. At higher pH values polymer de-protonation and metal ion attraction can be occurred as follows:



Because of the natural acidic nature of cellulose the possibility of the second mechanism (Eq 5 and 6) occurring is higher than that of the first mechanism (Eq 3 and 4) occurring. Therefore, higher percent removal can be seen after pH 5. However, after pH 6 as the removal of H from cellulose and making negative ions comes to equilibrium, percentage removed became constant.

### Conclusions

The current study reveals that the isolated cellulosic material obtained from the treated bagasse has a capability to trap Pb, Ni and Cu ions. Compared to nickel, copper (~28%) and lead (~55%) showed higher percent removals. Further, percentage removal of these ions by isolated cellulose is higher than that by raw bagasse. Anyhow, metal adsorption varies with many factors such as pH,

temperature, agitation time and initial metal ion concentration. According to the analysis done with lead ion solution, pH is a governing factor compared to the other variables and it is 6 for optimum adsorption of Pb. However, this mechanism would not be applicable with the metal ions such as Ca, Si, Fe, Na and Al because they are present in bagasse ash.

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### References:

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2. L. Vinícius, A. Gurgel, R. Pereira, D. Freitas, L. Frederic, Adsorption of Cu ( II ), Cd ( II ), and Pb ( II ) from aqueous single metal solutions by sugarcane bagasse and mercerized sugarcane bagasse chemically modified with succinic anhydride, *Carbohydrate Polymers*, **74**, 922–929.