



## SCAVENGING LEAD FROM WATER USING NANO CELLULOSE

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### Abstract

Nano fibrillary cellulose with sodium maleate groups was synthesized by the reaction of cellulose with maleic anhydride followed by sodium exchange of protons. In the present work, we demonstrate that these carboxylic groups act as Chemisorb ants towards toxic heavy metal ions present in contaminated water. The effects of the operating parameters such as resident time, temperature, pH, ion concentration and ion nature on chemisorb ability were estimated for a given cellulose carboxylate. The kinetic results for the chemisorption of  $Pb^{2+}$  ion were indicative of an intra particle diffusion model and pseudo second order reaction. The chemisorption is well explained by a Freundlich isotherm model showing a multilayer chemisorption, heterogeneous surface and interaction between chemisorbed molecules. The chemisorption capability was enhanced upon decreasing the dimension of the cellulose fibril. The efficiency depended also on the nature of metal ions, dictated by the stability of the geometry of the resultant complex. The maximum chemisorption capacities of macro, micro and nano forms of sodium cellulose-maleate for  $Pb^{2+}$  were 20 mg/g, 40 mg/g and 115mg/g, respectively at pH of 5.5. The ion exchanged nano-cellulose maleate could be regenerated by sodium chloride solution without loss of efficiency even after 7 cycles.

**Keywords:** Nano fibrillary cellulose, Chemisorb ants, Heterogeneous surface, Cellulose-maleate.



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### Materials

Jute fibers were procured from M/s William good acre Alappuzha Kerala India. The various chemicals used for the extraction of cellulose Nano whiskers are sodium hydroxide (NaOH), acetic acid (CH<sub>3</sub>COOH), sodium hypochlorite, and oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), purchased from Sigma Aldrich, India. Maleic anhydride (C<sub>4</sub>H<sub>2</sub>O<sub>3</sub>), Itaconic anhydride (C<sub>5</sub>H<sub>4</sub>O<sub>3</sub>), Succinic anhydride (C<sub>4</sub>H<sub>4</sub>O<sub>3</sub>), Nadic anhydride (C<sub>9</sub>H<sub>8</sub>O<sub>3</sub>), Phthalic anhydride (C<sub>6</sub>H<sub>4</sub> (CO)<sub>2</sub>) were purchased from Sigma Aldrich. Lead (II) nitrate, N, N-dimethyl form amide (DMF), acetone, sodium bicarbonate, sodium chloride, pyridine were purchased from Merck India Pvt.Ltd. Mumbai All other chemicals were procured from Sigma Aldrich India. De ionized water (DM) used was doubly distilled and free from all ions. Material used for the Tea bag was

whatmann filter paper with known bio sorption property. All chemicals were used as received without further purification.

### **Experimental methods of preparation**

This part gives a detailed description of the experimental method used for the preparation of Nano cellulose whiskers from jute and followed by the different chemical modification with maleic anhydride, itaconic anhydride, phthalic anhydride, succinic anhydride and nadic anhydride separately.

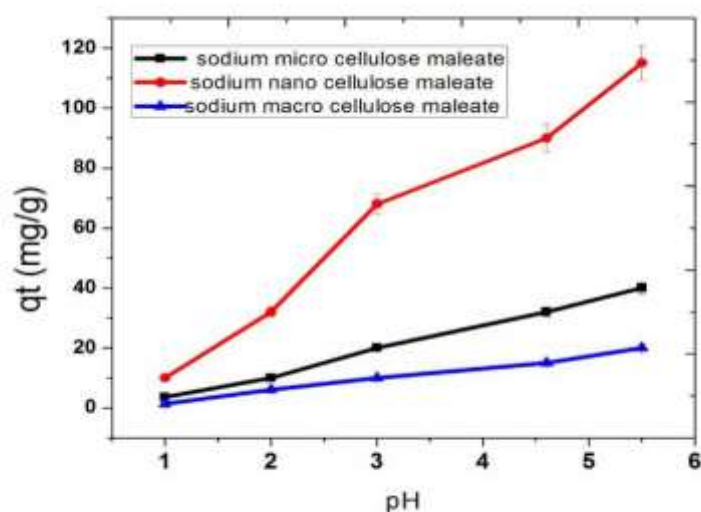
### **Kinetics of chemisorptions**

The chemisorption capacities of macro, micro and nano forms of sodium cellulose maleate at equilibrium were 10 mg/g, 20mg/and 90mg/g respectively at 4.6 pH, normal temperature and pressure. In fact, the high surface to volume ratio of the Nano cellulose accounts for highest chemisorption capacity. Carboxylic acid content formed during the chemical modification was the reason for its variation of the chemisorption capacity. It is evident that the chemisorption equilibrium of the sodium nano, micro and macro cellulose maleates was reached within two minutes. Faster chemisorption rates are always desirable for all chemisorption based separation processes. The typical results from the kinetic chemisorption study with sodium nano, micro and macro cellulose maleates showed that high chemisorption rates for lead ions occurred in the initial stage and the chemisorption process finally reached the equilibrium within two minutes. Metal ion sorption kinetics is influenced by sorption reaction and mass transfer steps that govern the transfer of metal ions from the bulk of the solution to the sorption sites on the surface and inside chemisorb ant particle i.e., external and internal particle diffusion. In turn, these mechanisms depend on the physical form of chemisorb ants, the intrinsic structure, the nature of the metal and the solution as well as process conditions (pH and temperature). A simplified model like intra-particle diffusion model was used to describe the kinetics. The intra-particle diffusion model for sodium nano, micro and macro cellulose maleates showed that the three linear sections on the plot of  $qt$  against  $t^{0.5}$ . This means that the process occurs in more than one-step. The first stage was sharper, as it was caused due to the external surface chemisorption or an instantaneous chemisorptions stage. The second portion was a gradual chemisorption stage, where the intra particle diffusion was the controlling factor. The third portion was final equilibrium stage where intra-particle diffusion started to decelerate due to extremely low solute concentration in the solution. A pseudo second order kinetic was assigned and the related parameters estimated from the experimental data using non-linear curve fitting procedure that showed a

good correlation with fitting requirements. Pseudo first order reaction model was not effectively correlated with successful fitting and hence not presented

### Effect of pH

The chemisorption capacities of  $Pb^{2+}$  on the product was increased with increasing pH and it was evident from Fig.1. This was due to the decrease in proton concentration and hence, chemisorb ant surface charge became negative with increase in pH. Therefore, the electrostatic attraction between the metal ion increases and the sorbent tends to a higher sorption capacity. The chemisorptions capacities of lead ions on the sodium nano, micro and macro cellulose maleate were 115mg/g, 40 mg/g and 20 mg/g respectively at pH=5.5. In order to avoid the formation of insoluble hydroxides, the pH of chemisorption kinetic experiments was kept at 5.5 for  $Pb^{2+}$  ions. Hence 5.5 is the optimum point based on the maximum chemisorption and the safest level for lead ions in solution.



### Dependency on ion concentration

The concentration of lead was an important factor in the analysis. It is evident that the chemisorption capacity of the nano, micro and macro forms of sodium cellulose maleate were 98mg/g, 36 mg/g and 16mg/g respectively at lead concentration of 300 ppm and 4.8 pH, which were the highest values compared to other concentrations. pH= 4.8 was selected based on the uniform pH of the using solution and chemisorb ant. Moreover, in the case of lead ions pH=5.5 is critical. The chemisorptions increases with increase in concentration and then decreases with higher concentration. This was due to the fact that at low concentrations, the ratio of surface active sites to the total metal ions in the solution was high and hence all the metal ions may interact with the adsorbent, which was removed from the solution. This is

only apparent as the number of binding sites remain intact, the concentration of ions decreases but the absolute number of binding sites does not change. As per the Le Chatelier principle, high metal ion concentration in the mobile phase increases, we expect only a marginal increase in concentration of metal ions chemisorbed. The speed of chemisorptions should however increase.

Desorption efficiency of the sodium nano, micro & macro cellulose maleate was studied at 300ppm Pb<sup>2+</sup> solution. The chemisorption – desorption cycle was repeated seven times with same adsorbents and the results are represented. The chemisorption capacity of sodium macro cellulose decreases from 14 to 7mg/g during seven cycles. Similarly, the chemisorption capacity of sodium micro cellulose decreases from 30 to 20mg/g during seven cycles but its capacity was maintained five times constantly with the same chemisorbent. The degradation tendency was high in macro forms than microforms. Remarkably, the chemisorption capacities of Pb<sup>2+</sup> ion on sodium Nano cellulose maleate remained the of same value after seven cycles of regeneration procedure at normal pressure, temperature, 30°C, and pH of 4.6.

### **Effluent studies**

The chemisorption capacities of metals depend on their nature. The chemisorption capacities of various metals at a pH of 3.0 was examined and represented in Fig. 3.14. pH= 3.0 was selected for avoiding the co precipitation property of lead ions with other noted metals. The chemisorption capacity of Cr<sup>+6</sup> is the least when compared to other elements. In this study, the chemisorption follows the order,

Pb<sup>2+</sup>>Cu<sup>2+</sup>>Zn<sup>2+</sup>>Ni<sup>2+</sup>>Co<sup>2+</sup>>Cd<sup>2+</sup>>Cr<sup>+6</sup>.

Different studies on complexation of metal ions with maleic type chelates have shown that octahedral arrangement is preferred by Cr<sup>+6</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup>, tetrahedral by Zn<sup>2+</sup>, square planar by Cu<sup>2+</sup>. Cd (II) tends to bind in both tetrahedral and octahedral arrangements. The maleic acids are located on the primary alcohol group of the glucose units. Obviously, the macromolecular chain poses restrictions on certain configurations, particularly the octahedral one due to severe steric restrictions. This is the reason for the poor adsorption of Cr<sup>+6</sup>, Co<sup>2+</sup> and Cd<sup>2+</sup> ions. The square planar configuration copper and lead offer the least steric restrictions, hence copper and lead coordinate well with the polymeric ligand. Since lead forms stronger coordination compounds with carboxylates, it appears to be more stable than copper though both form similarly coordinated compound with maleic ester of cellulose. The elements like zinc forms tetrahedral coordination whose dimensional stability falls between lead, copper and the other elements.

## **Conclusions**

Removal of heavy metals like Pb<sup>2+</sup> was carried out using the sodium hydrogen maleate of cellulose of different fibrillary consistencies. The maximum chemisorptions capacities of macro, micro and nano forms of cellulose maleate for Pb<sup>2+</sup> were 20, 40 and 115 mg/g respectively at 5.5pH. Surface area of different cellulose matrix was the deciding factor in controlling the chemisorption performance. It was found that the ease of carboxyl functionalization enhanced tremendously as the fibrillary size decreases. The nano-fibres showed much better chemisorption capacity than its micro and macro counterparts. The intra particle model and pseudo second order reaction was well fitted with kinetic data. Isotherm studies confirmed that the experimental results followed the Freundlich model. The effect of temperature, pH, and ion concentration on chemisorption was also studied. It was found that pH of 5.5, lead ion concentration of 300 ppm and the temperature of 400C were the optimum parameters for the chemisorption. The effluent studies showed that the chemisorption property was dependent on the nature of the metal which depended basically on the ease of formation of the geometry of the complex. This work demonstrates that the chemisorption method is an effective platform for a green and sustainable alternative method for heavy metal removal from contaminated water.

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