Adsorption of Selected Heavy Metals on Modified Nano Cellulose

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Authors' contributions

This work was carried out in collaboration between all authors. Author ESM designed the study and wrote the protocol. Authors PGK and ANG preformed the statistical analysis, managed the literature search and wrote the first draft of the manuscript with assistance from author SM. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Cellulose is an inexpensive, renewable, bio-based and an abundant raw material suitable for the development of filter membranes for water purification. This is because it has numerous functional groups that afford ease of modification to create active surfaces upon chemical modification. In this study, cellulose was isolated from two abundant biomasses, namely, *Eichhornia crassipes* and *Cyperus papyrus* using the soda process followed by bleaching with peracetic acid. The percent yield of cellulose nanofibrils (CNF) obtained from *E. crassipes* and *C. papyrus* was found to be 31.64 ± 1.46% and 29.55 ± 0.64% respectively. The degree of crystallinity and crystal sizes were calculated to be 71.42% and 0.059 nm for *E. crassipes* and 46.15% and 0.068 nm for *C. papyrus* respectively. The FT-IR absorption of the carbonyl functional group of an ester indicated that effective esterification of cellulose using citric acid was obtained when cellulose nanofibrils to citric

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acid ratio was 1:1. From batch adsorption studies, the capacity for citric acid modified cellulose to remove heavy metals was determined to be 8.36 mg/g Zn^{2+}, 18.06 mg/g Cu^{2+}, 42.69 mg/g Cd^{2+} and 21.64 mg/g Pb^{2+}. In comparison to the % adsorption using unmodified cellulose of less than 5%, the heavy metals adsorption using modified nanocellulose materials were 86.47% Pb^{2+}, 85.20% Cd^{2+}, 77.40% Cu^{2+}, and 70.04% Zn^{2+}. From these results, it was concluded that modified cellulose could be used as a low cost adsorbent for removal of heavy metals and that development of household water filtration units using modified cellulose could be exploited.

1. INTRODUCTION

Even though Kenya is located along the equator, it faces extreme climate variations due to its various landforms, particularly in the Rift Valley. Kenya's current per capita water availability of 792 mm^3 falls below the scarcity threshold of 1,700 cubic metres per person, and the projected population growth will further aggravate the pressures on this limited supply [1]. Ground water exploitation faces several challenges which include rundown of existing boreholes, lack of rehabilitation or replacement of existing ones, low yielding aquifers and heavy metal pollution from mining wastes, landfill leaches, municipal wastewater, urban runoff and industrial wastewaters [2,3].

A wide range of chemical and physical processes that have been used for the uptake of heavy metals and organics from aqueous media include electro-chemical precipitation, ultra-filtration, ion exchange and reverse osmosis. However these methods are expensive for heavy metal uptake, and as such there has been a shift to the use of low cost agricultural products as adsorbents [3]. The ability to remove toxic compounds from the environments rapidly, efficiently and within reasonable costs is the ultimate goal [4]. Biopolymers from renewable sources have the capability to remove heavy metal-ions concentration to low parts per billion residual levels. Among the many other low cost sorbents identified, modified cellulose from agricultural waste has high adsorption capacity for several metal ions [5]. The unique properties of nanocellulose (Cellulose nanofibrils and Cellulose nanocrystals) such as biodegradability, low density, high strength, and high aspect ratio have been discussed in several literatures. The abundance of OH groups on the surface of cellulose favours functionalization of cellulose to be achieved with great ease [6].

In this study nanocellulose was isolated from two abundant biomass, *E. crassipes* and *C. papyrus*, and modified using citric acid. The effectiveness of bonding citric acid onto nano cellulose was estimated by comparing the FT-IR spectra of modified and unmodified nanocellulose and the recovered weights of the treated samples and control [7]. Adsorption of selected heavy metals was analysed according to a method described [8].

2. MATERIALS AND METHODS

2.1 Sample Collection and Preparation

E. crassipes and *C. papyrus* were collected from Juja, Kiambu County. After drying the collected samples were milled using a milling machine (locally assembled, no model number) at the mechanical department, J.K.U.A.T, washed several times and dried in an oven at 105°C to constant mass. Nano cellulose was isolated and chemically modified with citric acid [9]. Dried and ground biomass was mixed with 10% aqueous NaOH solution in a ratio of 1:10. The mixture was stirred for 3 hours at 100°C, followed by filtration of the pre-treated biomass and then washed with 10% ethanol. Hemi cellulose free biomass was then mixed with per acetic acid and the mixture was stirred for 2 hour at 80°C repeatedly, the residue filtered and washed with distilled water repeatedly and oven dried at 100°C to constant weight [9].

2.2 Characterization of Modified and Unmodified Cellulose

The properties of the reaction products were characterized by FT-IR using a shimadzu Fourier Transform Infrared spectrophotometer, (FTS-8400 model). Functional groups present in modified and unmodified cellulose nanofibrils were determined using Shimadzu 8400 FT-IR. The spectral resolution was set at 4 cm^{-1} and the scanning range from 400 to 4000 cm^{-1}. Morphological analysis of nanocellulose and citric acid modified nanocellulose was performed using Scanning electron microscope operated at accelerating voltage of 20 kV at an aperture size of 30 μm.
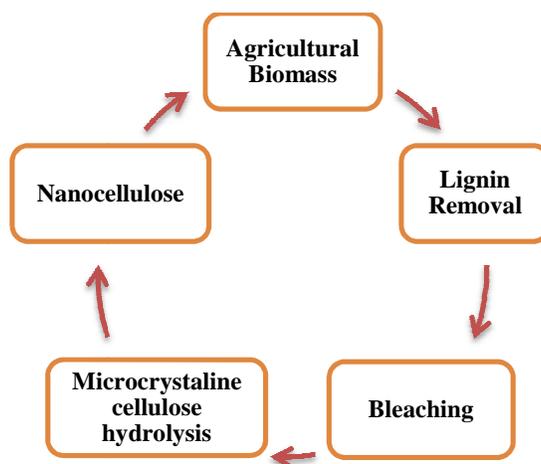
Fig. 1. Schematic representation of extraction of Nano cellulose

2.3 Determination of Degree of Crystallinity and Crystal Size

To determine the degree of crystallinity, wide angle XRD measurements were carried out with a Rigaku miniflex II desktop diffractometer. The degree of crystallinity and crystal size were determined using Rigaku miniflex II defractometer. The X-ray generator was equipped with a copper tube operating at 30 kV and 15 mA and irradiating the sample with a monochromatic Cu Kα radiation with a wavelength of 0.1545 nm. The XRD spectra were acquired at room temperature over the 2θ range of 3°– 60° at 0.05° intervals with a measurement time of 100 minute.

The XRD crystallinity index (CI_{XRD}) for native cellulose was calculated using the peak height method from the following height ratio:

$$CI(\%) = \left[\frac{I_{002} - I_{am}}{I_{002}}\right] \times 100$$

Where I_{002} is the intensity of the 002 crystalline peak at 22° and I_{am} the height of the minimum (I_{am}) between the 002 and the 001 peaks, as shown in Fig. 1. The crystalline size D_{002} was determined using the diffraction pattern obtained from the 002 lattice planes of cellulose:

$$D_{002} = \frac{K\lambda}{B_{002}Cos\theta}$$

Where k is the Scherrer constant (0.94), λ is the X-ray wavelength (0.1545 nm), B in radians is the full-width at half of the peak of 002 reflection and θ the corresponding Bragg's angle [10].

2.4 Batch Adsorption Studies

Adsorption of selected heavy metals on citric acid modified cellulose were investigated according to a method described elsewhere [8]. In this study the effect of pH, initial metal ion concentration, adsorbent dose and the contact time on the amount of metal ion adsorbed were investigated.

3. RESULTS AND DISCUSSION

3.1 Isolation of Cellulose and Percent Recovery

From the results obtained (Table 1), percent recovery of nano cellulose from *E. crassipes* was calculated to be 31.64 ± 1.46% while that from *C. papyrus* was calculated to be 29.55 ± 0.65 percent. The yield obtained was attributed to the fact that biomass is also composed of lignin, hemicelluloses and other extractives which are removed during chemical treatment of the biomass [11]. The swelling capacity of both modified and unmodified cellulose were also determined and are depicted in Table 1. From the results obtained, the swelling ratio of modified cellulose was lower as compared to unmodified cellulose hence an indication that citric acid modified cellulose was more hydrophobic as compared to unmodified cellulose.

3.2 FT-IR Characterization of Modified and Unmodified Nanocellulose

In order to function as an adsorbent, nano cellulose has to be functionalized so as to introduce active sites onto its structure. FT-IR spectra (Fig. 2) obtained in this study revealed the presence of functional groups that are characteristic of cellulose [9]. Spectral bands at 1420-1430 cm^{-1} and 893-897 cm^{-1} can be used to elucidate the crystal structure of cellulosic material and its (1420/893 cm^{-1}) spectral ratio and (1375/2900 cm^{-1}) spectral ratio show index of crystallinity or lateral order index (LOI) and total crystallinity index (TCI), respectively. In cellulosic samples, the spectral ratio (1430/897 cm^{-1}) gives the evidence of cellulose I fraction [12]. Higher value of the given index (LOI, TCI) reveals that the given material contains a highly crystalline and an ordered structure. For these index values, the (1427.2/900.7 cm^{-1}) spectral ratio of *E. crassipes* was found to be 1.58 while that for *C. papyrus* was found to be 1.43 [13].

The esterification mechanism could be confirmed by the FTIR spectra of citric acid modified cellulose (Fig. 2) in which there was a strong, intense band at around 1735 cm^{-1} typical of ester carbonyl groups. The peaks around 1059 cm^{-1} are characteristics of a C=O group of the primary hydroxyl stretching that may be attributed to cellulose structure. The broad absorption peaks around 3355 cm^{-1} also confirms the existence of carboxylic O–H groups (2500–3500 cm^{-1}) after

citric acid modification [14]. The intensity of the absorption band of carbonyl group at 1735 cm^{-1} varies with the ratio of citric acid and cellulose used as a ratio of 1:1 gave the highest intensity compared to the ratios 1:2 - 1:5.

3.3 Degree of Crystallinity and Crystal Size

From WXRD diffractogram of nano cellulose obtained from *E. crassipes* and *C. papyrus*, the diffraction pattern was similar to that of cellulose, which was characterized by two main peaks and a broad amorphous background band. The lower angle peak was the result of merging the diffraction peaks at 2θ = 15° and 16.5° into a broader one, as also reported in other literature [15], where it was assigned to the [001] crystalline plane. The peak observed at 2θ = 22.4° was assigned to the [002] crystalline plane and was used for the calculation of the crystallinity index CI_{XRD} [16]. Compared to all X-ray diffraction approaches, the peak height method gives the highest X-ray crystallinity values [10]. From the WXRD diffractogram obtained Fig. 3, the inter-planar distance (d) for [002] indices was found to be 3.896 and 3.892 for nano cellulose derived from *E. crassipes* and *C. papyrus* respectively. The degree of crystallinity and crystal size of CNF synthesized from *E. crassipes* were found to be 71.42% and 0.068 nm, while CNF from *C. papyrus* was found to have a degree of crystallinity and crystal size of 46.15% and 0.059 nm respectively.
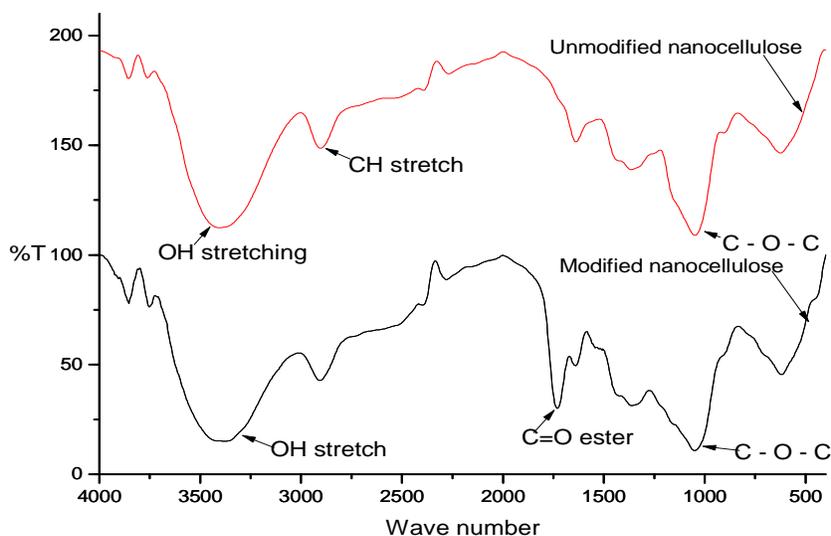

Fig. 2. FT-IR spectra of unmodified and citric acid modified cellulose Ratio 1:1

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3.4 Surface Characterization

Figs. 4 and 5 shows the SEM images of unmodified and citric acid modified nanocellulose. Nano fibrils are dependent on their origin [6,17,18] thus it was observed that the surface morphology of the isolated cellulose nano fibrils of *C. papyrus* and *E. crassipes* differ considerably in all magnifications (Fig. 4). The effectiveness of the pre-treatment process was very high, as particles and fibres whose diameters ranged between 300 nm – 1 µm were observed for the case of *E. crassipes* and 200 nm – 3 µm in *C. papyrus.* Therefore, pre-treatment of *C. papyrus* and *E. crassipes* biomass materials resulted in synthesis of cellulosic nano whiskers of different sizes and composition.

Table 1. Physical parameters of modified and unmodified cellulose

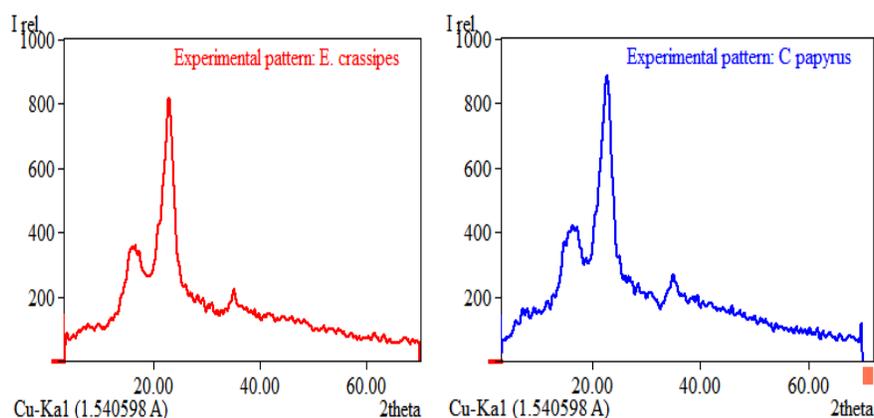| Physical parameter	CNF *E. crassipes*	CNF *C. papyrus*	Modified CNF
Percent yield	31.67 ± 1.46	29.55 ± 0.65	5.25 ± 1.94
Tapped density (g/cm^3)	0.37 ± 0.01	0.28 ± 0.05	0.58 ± 0.03
Bulk density (g/cm^3)	0.28 ± 0.05	0.12 ± 0.02	0.48 ± 0.02
Swelling ratio (%)	141.60 ± 1.34	156.6 ± 1.95	73.6 ± 1.52

Fig. 3. WXRD diffractogram of nano cellulose derived from *E. crassipes* and *C. papyrus*
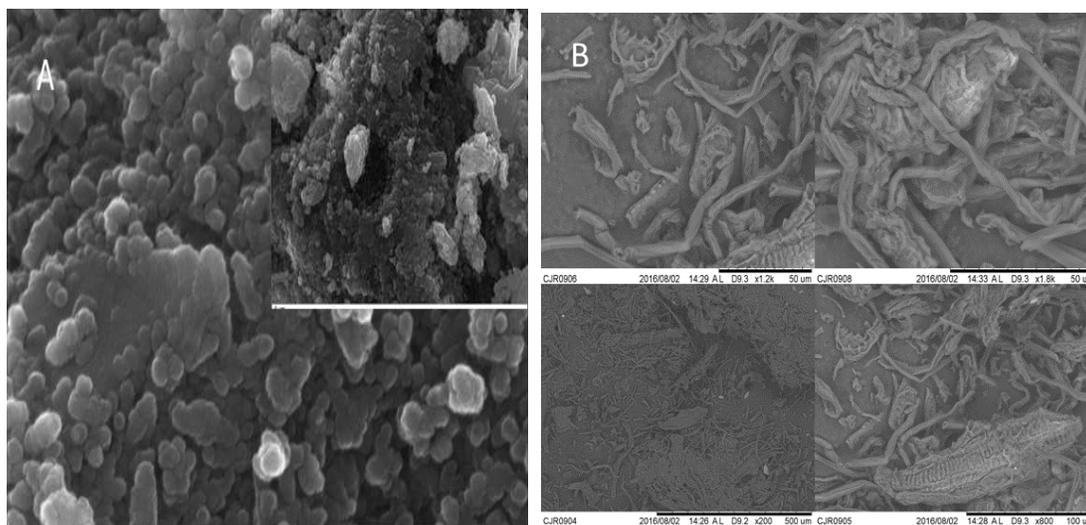

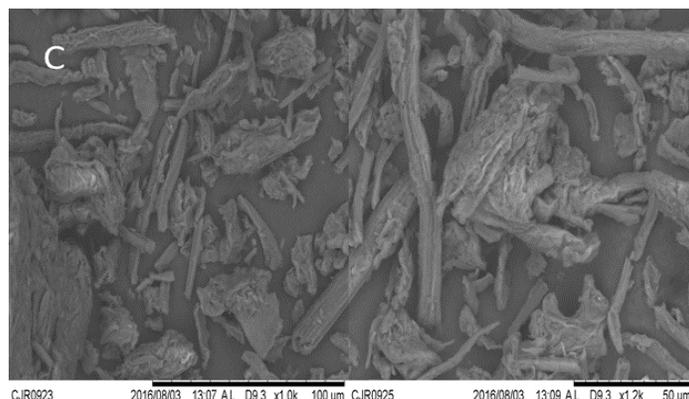**Fig. 4. SEM images of nano cellulose synthesized from *E. crassipes* (A) and *C. papyrus* (B)**

Fig. 5. Citric acid modified cellulose nano fibrils (CNF)

3.5 Determination of Carboxylic Acid Content and Degree of Crosslinking

The effectiveness of bonding citric acid to cellulose was estimated by comparing the recovered weights of the treated samples and control. The cellulose samples were left in pre-weighed filter papers after the post-treatment water rinse and the two together were oven dried to minimize handling losses. The percentage change in weight was calculated to be $5.2 \pm 1.9\%$.

3.6 Adsorption of Selected Heavy Metals with Modified Nano Cellulose

Adsorption of selected heavy metals on citric acid modified cellulose was studied under different condition and the results were reported below.

3.7 The Effect of Varying Contact Time against Metal Ion Adsorbed

The effect of varying contact time against the amount of Pb^{2+}, Cd^{2+}, Cu^{2+} and Zn^{2+} adsorbed were determined at constant pH, revolution and adsorbent dose (0.1 g). From the results obtained (Fig. 6) the amount adsorbed increased and levels offs after 30 minutes respectively. This was because with increased contact time the ratio of surface active sites to the total metal ions in the solution was low and hence all active site had interacted with metal ions in solution and had been occupied [7]. The amount of metal ion adsorbed decreased in the order $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+}$.
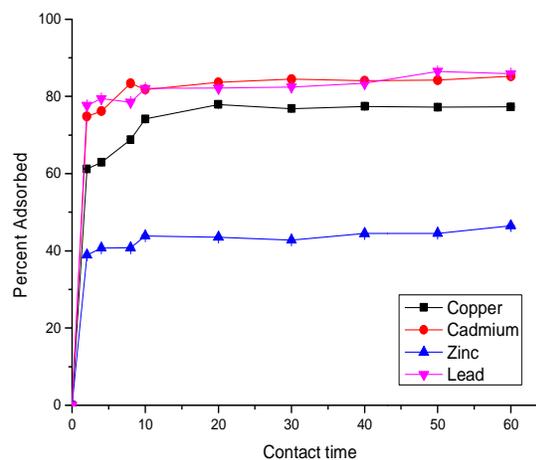

Fig. 6. A graph of % metal ions adsorbed on citric acid modified nano cellulose against contact time

3.8 Effect of Varying Concentration of Metal Ion on Adsorption

The effect of varying the initial concentration of metal ions against amount adsorbed was studied by holding the amount of adsorbent (0.1 g), pH and the revolution (150 rpm) constant (Fig. 7). From the results obtained the amount of metal ions adsorbed decreased with increase in concentration of the initial metal ion solution used. At low ion concentrations, the ratio of surface active sites to the total metal ions in the solution was high and hence all metal ions interacted with the adsorbent and are removed from the solution [7]. However, at high concentrations, the driving force, i.e. concentration gradient was stronger, and the amount of metal ion adsorbed per unit weight of adsorbent, qe, was low.
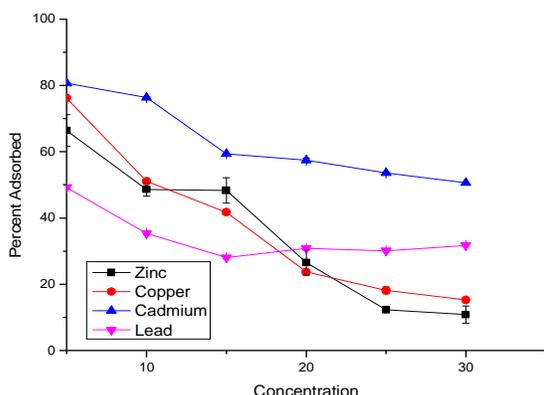
Fig. 7. A graph of % metal ion adsorbed on citric acid modified nano cellulose against concentration (ppm)

3.9 The Effect of Varying Adsorbent Dose on Metal Ion Adsorbed

The effect of adsorbent dose on the adsorption of the heavy metals onto citric acid modified cellulose was investigated (Fig. 8). The concentration of selected heavy metals in spiked water samples were reduced by 86.47% Pb^{2+}, 85.20% Cd^{2+}, 77.40% Cu^{2+}, and 70.04% Zn^{2+} after treatment. It is important to note that the concentration of the metal ions and pH were fixed while the adsorbent dosage was increased. Metals adsorption efficiency was increased with increase in adsorbent dose. This revealed that the adsorption sites remained unsaturated during the adsorption reaction, whereas the number of sites available for adsorption site increased by increasing the adsorbent dose [19]. However, as the adsorbent dose increased the percent removal of metal ion increased and reached a saturated value at the dosage of 0.5 g. Therefore, as the dosage increased, the ratio between the numbers of adsorption sites to the number of heavy metal ions would increase and there would be plenty of un-adsorbed adsorption sites. Another possible reason could be due to the particle aggregation, which would lead to a decrease in total surface area of the adsorbent [8,20].

3.10 Effect of Varying pH on Metal Ion Adsorbed

One of the most important variables in an adsorption process is the pH of the metal solution since pH affects both the chemical speciation and the ionization state of the functional groups present in adsorbent. The adsorption experiments were carried out between pH 3 – 11. The results of the effect of pH on metal adsorption are depicted in Fig. 9. In general, the adsorption capacities increased with increasing pH values. The lowest amount of metal ions adsorbed occurred at pH 3 (8.29 mg/g Zn^{2+}, 17.79 mg/g Cu^{2+}, 18.96 mg/g Pb^{2+} and 22.23 mg/g Cd^{2+}) and the highest at pH 6 (11.29 mg/g Zn^{2+}, 21.85 mg/g Cu^{2+}, 21.704 mg/g Pb^{2+}, and 23.47 mg/g Cd^{2+}). In addition, low pH environment reduces metal sorption due to increased competition of protons for these sites [21].
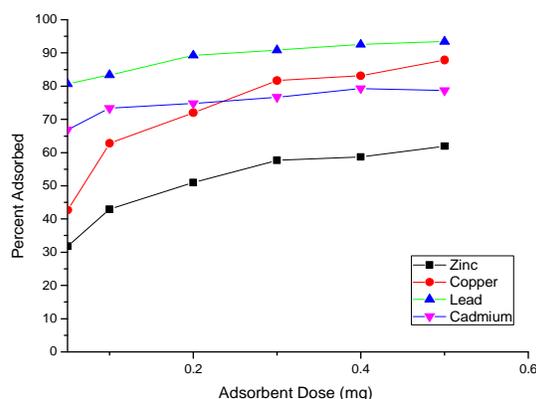

Fig. 8. A Graph of %metal ions adsorbed on citric acid modified nanocellulose against adsorbent dose
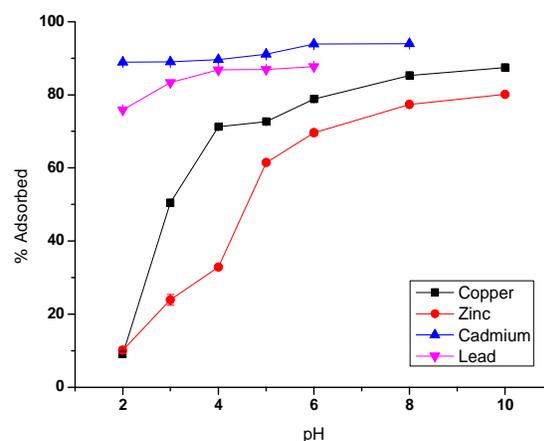

Fig. 9. A graph of % metal ion adsorbed on citric acid modified cellulose against pH

When the pH of the solution was greater than 4, carboxylic groups were deprotonated and the adsorbent surface was negatively charged resulting in higher adsorption capacity. Typically, cation adsorption increased with increasing pH

from near zero to nearly 100% over a certain pH range [21]. This region where there was a sharp increase in adsorption capacity from low to high pH was termed as pH adsorption edge. It's characteristic of a particular adsorbate and, to a lesser extent, to the particular adsorbent as well as the concentrations of surface binding sites [21].

4. CONCLUSION

It can be concluded that physical parameters such as bulk density, tapped density, swelling capacity, degree of crystallinity, crystal size and surface morphology of cellulose nanofibrils were dependent on the biomass used. Modification of nano cellulose with citric acid was dependent on the amount citric acid used. Citric acid modified cellulose can be used as an adsorbent for removal of heavy metals from water. Hence, modified nano cellulose can be used to make suitable filters for removal of metal ions from contaminated water.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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