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Development of 'Environmental Friendly Aminated Nanocrystalline Cellulose' for Decontamination of Arsenic Species from Water Bodies: Bioremediation

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Abstract

Environmental contamination due to anthropogenic and natural sources is increasing day by day because of increase in population, industrialization and urbanization. Arsenic species released into the environment tend to persist indefinitely, circulating and eventually accumulating throughout the food chain, thus becoming a serious threat to the environment. The present study explores the preparation of nanocrystalline cellulose (NCC) from microcrystalline cellulose (MCC) in removing arsenic ions. An investigation was undertaken regarding the adsorption of arsenic ions from aqueous solutions using functionalization onto NCC; Aminated NCC. Novel NCC was characterized on the basis of XRD, SEM and AFM. Aminated NCC was characterized on the basis of FTIR and TGA techniques and found to have enough potential for sorption of arsenic. Batch studies were carried out to characterize As (III) and As (V) removal capability of NCC and Aminated NCC. The different factors affecting arsenic ions adsorption on this substrate such as arsenic ion concentration, pH of the medium, treatment time and as well as biosorbent doses were studied. It was found from the obtained results that; the adsorption % increased with (a) increasing the arsenic ions concentration up to 25 μg/mL then levels off, (b) increasing the pH value within the studied range (2-10), (c) increasing the treatment time up to 40 min then levels off and (d) increasing the extent of biosorbent within the range studied (0.25-2.0 g). The findings showed that aminated NCC can easily be envisaged as a new, vibrant, environmental friendly, low-cost biosorbent for arsenic clean-up operations.

Keywords: Aminated nanocrystalline cellulose; arsenic bioremediation; environmental friendly technique.

1. Introduction

Arsenic is one of the most important pollutants and is naturally found in environment. The source of arsenic is from the discharge of various industries (Gonzaga et al. 2006). Toxicity of arsenic is well known (Kundu and Gupta 2006; Choonga et al. 2007). Arsenic toxicity causes skin lesions, damage mucous membranes, nervous system, gastrointestinal, cardiovascular, genotoxic, mutagenic and carcinogenic effects (Rivas and Aguirre 2010; Bose et al. 2011). WHO has revised the guidelines for arsenic in drinking water from 50 to 10 µg/mL (Mohan et al. 2007). Arsenic about 100 times more than permissible limit, is found in many parts of world (Mandal and Suzuki 2002; Pereira et al. 2007). More toxic As (III) is more difficult to remove compared with As (V) (Burriel et al. 2006). Conventional methods developed for arsenic removal (Nemade et al. 2007) are associated with several disadvantages like unpredictable removal efficiency, high material costs and the generation of toxic sludge; the disposal of which is a burden on the techno-economic feasibility of treatment procedures.

The search for environmental friendly technologies involving the removal of arsenic has directed attention to biosorption. Bioremediation involves processes that reduce overall treatment cost which are particularly attractive (Raj et al. 2010; Kardam et al. 2010). Biological materials have been recognized as environmental friendly sorbents (Anirudhan and Unnithan 2007; Malik et al. 2009; Yeneneh et al. 2011). Current research is oriented towards the enhancement in the sorption and reusability of the biosorbent. The increasing interest in the organic bio nanomaterials and their unique properties has led to intensive research of nanocellulose materials. In view of this, NCC has been explored in order to enhance sorption efficiency by functionalization using Amination.

2. Materials and Methods

2.1 Biosorbent preparation and Functionalization of NCC

MCC (50 g) was mixed with water in a 500 ml beaker. Sulphuric acid (16 ml: 62 wt. %) was slowly added and kept under stirring at temperature 50-60 °C for 3 h. Cellulose sediments were separated from liquid phase by centrifugation at the acceleration 3200 rpm for 10 min; washed with water, sodium bicarbonate (12 ml: 5%) and finally with distilled water to pH about 6.0 ± 0.1. The washed cellulose sediments were diluted with distilled water and subjected to ultra sonication (20 KHz) for 30 min. Dispersion of NCC was evaporated in vacuum , washed with absolute ethanol, acetone and hexane, separating from the solvents at the each washing.

NCC (10 g) was reacted with epichlorohydrin (80 ml) in 100 ml of DMF at 100 ^{0}C and stirred for 1 h. Pyridine (30 ml) was added to the solution. The product was washed repeatedly with ethanol. Dimethylamine (40 ml) was added to it at 70 ^{0}C. The reaction product was washed using distilled water. The above product was loaded with 200 ml of 0.2 M HCl for 4 h at room temperature, washed well to remove excess chloride ions and dried at 60 ^{0}C.

2.2 Biosorption studies

Sorption studies were carried out in batch experiments as a function of biosorbent dosage (2.0–6.0 g), contact time (10–60 min), arsenic concentration (0.05–50 µg/mL), volume of the solution (100-300 mL) and pH (2–10). The arsenic ion filtrates were estimated using Hydride Generation Atomic Absorption Spectroscopy (Perkin Elmer 2380). The percent metal sorption by the sorbent was computed using the following equation:

$$\% \, Sorption = [\frac{(C_0 - C_e)}{C_0} \times 100] \tag{1}$$

where C_o and C_e are the initial and final concentration of arsenic ion, respectively.

2.3 Evidences in support of the confirmation of preparation of NCC and aminated NCC

The crystallinity and size of NCC were recorded by Bruker AXS D8 Advance, (XRD) with Cu Kα radiation at 40 kV and 30 mA in the range $2\theta = 5\text{-}40^o$, at a speed of 2 ^{o}/min. Samples were placed in sample holder. Nanosurf easyscan; V 1.8 atomic force microscope (AFM) was used to record morphological changes and surface roughness with commercial Si nanoprobe tips at scan rate of 0.5-0.8 Hz and oscillating amplitude 0.5 V. The morphology of NCC was evaluated using α- Tech Table Top, SNE 3200, SEM at working voltage of 20 kV with 3.0 K magnification. To access the role of functional groups of the aminated NCC that might be involved in arsenic sorption, FTIR analysis was performed using a Shimadzu 8400 spectroscopy. Thermogravimetric analysis (TGA) was performed using thermo gravimetric analyzer (DTG-60, Shimadzu) to observe the thermal stability of the aminated NCC.

2.4 Reusability of the modified LLSP

Desorption studies were conducted to regenerate the biosorbent as a function of concentration of different desorption reagents: [0.05 M HNO_3] and [0.5 M Citric acid].

2.5 Statistical analysis

Batch experiments were conducted in triplicates (N = 3). For the determination of intergroup mean value differences, each parameter was subjected to the student t test for significance level ($p>0.05$).

3. Results and Discussions

A series of experiments on sorption led to the standardization of the optimum conditions for arsenite (80.22 %) and arsenate (91.56 %) removal at arsenic concentration (25 µg/mL), contact time (40 min), volume (200 mL) and pH 7.5 for As (III) and 2.5 for As (V). Biomaterial dosage varied from 0.05 to 2.0 g. Sorption increased with the increase of dosage. However, no significant increment was observed on further increasing the dosage from 1.0 g onwards. The effect of contact time was studied for 10-60 min. The percent sorption gradually increased to 40 min. Sorption of arsenic ion has been carried out in the range of arsenic concentration (0.5–50 µg/mL) and found an optimal level at 25 µg/mL. The sorption potential has been studied in the pH range of 1–10. The biosorption of As (III) shows gradually increasing trend, attaining maximum sorption at pH 7.5 and biosorption of As (V) is maximum at pH 2.5, while remaining constant in the pH range of 2.5–10.

3.1 Enhancement in sorption efficiency of aminated NCC

X-ray diffraction pattern of NCC shows three strongest peaks at 2θ = 14.84, 2θ =22.76 and 2θ =34.98; respectively which are the characteristic of NCC and belong to cellulose I**.** The crystallinity index was calculated using equation:

$$CI = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \tag{2}$$

and found to be 92.56 %. The grain size was calculated utilizing the Sherrer's equation:

$$t = \frac{k\lambda}{\boldsymbol{B\, Cos\, \theta}} \tag{3}$$

and found to be 4-5 nm. AFM micrograph of NCC indicated that the NCC are triangular more than spherical and with a diameter of some nano meters, uniform growth and mono disperse particle distribution without any pinhole. The average roughness of the particles is 19.251 nm. SEM image of the NCC exhibits trigonal and tetrad structure.

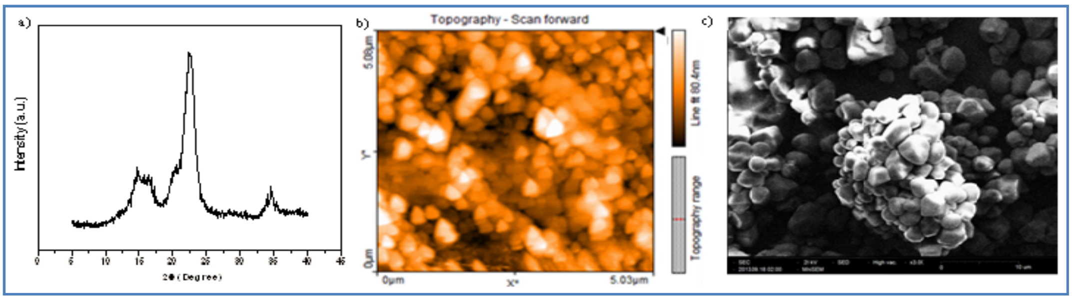

Figure 1: Microscopic characterization of NCC; a) XRD; b) AFM and c) SEM.

The FTIR spectrum of NCC shows broad and strong bands in the range of 3,200 to 3,600 cm^{-1} due to OH stretching bands. The absence of the OH band in the aminated NCC indicates the participation of –OH groups for epoxide formation with epichlorohydrin. Additional peaks at 1456 and 1145 cm^{-1} in aminated NCC indicating the presence of aliphatic CN vibration and $–CH_2–{}^{+}NH(R)_2$ type of nitrogen. Thermograms of NCC, and aminated NCC showed significant differences in the final decomposition temperature.

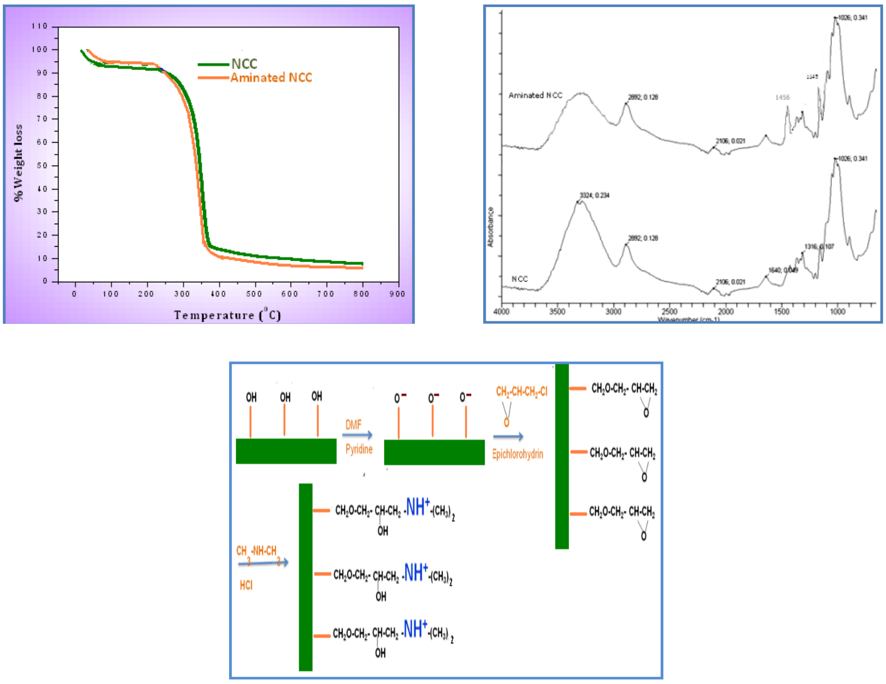

Figure 2: Characterization of NCC and aminated NCC; a) TGA; b) FTIR; c) Schematic diagram of amination reaction.

4. Conclusion

The findings open up new avenues in the abatement of arsenic species. The incorporation of positively charged amine groups in NCC enhanced the binding capacity for negatively charged arsenic species. The percentage sorption of As (III) increases from 22.04 (NCC) to 80.22 % (aminated NCC), while percentage sorption of As (V) increases from 23.26 (NCC) to 91.56 % (aminated NCC). The enhancement of sorption of As (V) compared with As (III) may be due to the fact that As (III) has less affinity with amine groups compared with As (V). The reusability cycles of aminated NCC was found to be increased up to 5 cycles, compared with 3 cycles of NCC. It introduces a less expensive and environment-friendly pre treatment green method prior to high-tech chemical treatments.

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