



Synthesis and Characterization of Silane-Nanocrystalline Cellulose Composites For Arsenic Abatement

KEYWORDS

Arsenic; Nanocrystalline cellulose; Silane; Biosorption.

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ABSTRACT Reduction in arsenic MCL from 50 to 10 ppb has resulted in technical and operational effects on water treatment technologies that have required up-gradation to meet this new standard. This work presents the development of a technique using nanocrystalline cellulose composites reinforced with silane coupling agent, 3-Mercaptopropyltrimethoxy silane (MPTMS) filled in non-woven polypropylene filter bags for efficient arsenic abatement from water bodies providing an economic and simple biosorption technique with high adsorption capacity, MPTMS: 9.48 and 8.57 mg/g for As (III) and As (V), respectively.

1. Introduction

The drastic reduction in minimum contamination limit (MCL) of arsenic from 50 to 10 ppb has led many demands for several operational changes to up-grade arsenic removal for this new lower limit (WHO, 1993). Research towards identifying new technologies/ reinforcement/ modifications to existing technologies has been conducted (Mohan et al. 2007). Intensive research on adsorption of arsenic has established solid base of knowledge, principles and highlighted enormous potential for commercialization particularly at low level decontamination (Raj et al. 2010, Singh et al. 2014).

Polymer nano-composites have been a subject of increasing interest because of their significant enhanced mechanical and thermal stability (Habibi et al. 2010). Highly ordered configuration, low weight and biodegradability are some of special features of nano-scale cellulose polymers which make them promising candidates for the removal of cationic metal species (Ning et al. 2011). However, information on its application towards their suitability for the sorption of anionic species like arsenic is scanty.

Silanes usually improve the degree of cross-linking and are very reactive to -OH groups, followed by hydrolysis-condensation steps of methoxy-silane groups to produce an oligomeric network of polysilsesquioxane (Xie et al. 2010). Therefore, the hydrocarbon chains provided by the application of silane are supposed to restrain the swelling of the fiber. Additionally, this surface functionalization is supposed to incorporate cationic -thiol groups responsible for the sorption of anionic arsenic species. The present piece of work addresses the use of MPTMS-NCC composites for arsenic sorption.

2. Experimental

2.1. Reagents and chemicals

All chemicals were of analytical grade. Stock solutions of arsenic containing 1,000 mg/L As(III) and As(V) were prepared by dissolving NaAsO_2 and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in double distilled water and stored in darkness at 4 °C.

2.2. Preparation of Nanocrystalline cellulose

NCC was prepared by sulfuric acid hydrolysis of microcrystalline cellulose (MCC) (Ioelovich, 2012). MCC (50.0 g oven dried weight) was mixed with H_2SO_4 solution (62 %, w/v) with continuous stirring at 45° C for 45 min. The hydrolysis reaction was stopped by successive centrifugation

at 12,000 rpm for 10 min. until the supernatant became turbid. The sediment was collected and washed against distilled water until the pH of the solution became neutral. After washing, the content was sonicated for 30 min. The cloudy supernatant, containing NCC, was collected.

2.3 Preparation of NCC-Silane composite

3-Mercaptopropyltrimethoxy silane (MPTMS) was pre-hydrolyzed for 2 h under stirring in ethanol-distilled water solution (100 ml; 80/20 v/v). The treatment of NCC (10.0 g) with MPTMS (100 ml) was performed and the resulting suspension was maintained for 2 h under stirring and then removed from the solutions and dried at room temperature (RT) for 24 h. The dried sample was heat treated at 110 °C for 2 h to promote actual coupling (Xie et al. 2009).

2.4. Characterization of NCC and MPTMS-NCC composite

The average crystallite size and crystallinity pattern of MPTMS-NCC composite were recorded using glancing angle X-ray diffractometer (Bruker AXS D8 Advance, Germany) with $\text{Cu K}\alpha$ radiation at 40 kV and 30 mA. FTIR analysis in solid phase in KBr was performed using a Shimadzu 8400 Fourier Transform Infrared spectroscope. Absorption mode FT-IR spectra were recorded in 600-4,000 cm^{-1} range and scanned for 64 times.

2.5. Biosorption studies

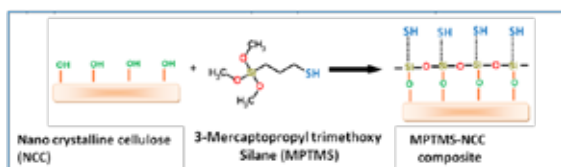
Batch experiments were performed as functions of contact time (10-50 min), volume of test solution (100-300 ml), pH (1-10) and arsenic ion concentration (0.005-50 mg/L) at room temperature. After proper pH adjustments, a filter bag containing biosorbent of known quantity was dipped into arsenic suspension and kept under stirring until equilibrium conditions were reached. Arsenic treated filter bag was taken out and filtrate was subjected for arsenic estimation using ICP OES Perkin Elmer Optima™ 8x00. Percent arsenic sorption was computed using the equation: % Sorption = $\left(\frac{C_0 - C_e}{C_0}\right) \times 100$, where, C_0 and C_e are the initial and final concentrations of arsenic ions.

3. Results and discussion

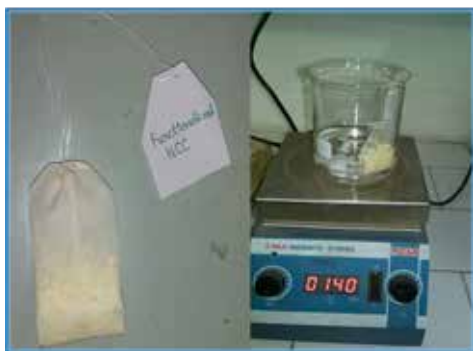
3.1. Structural confirmation of preparation of NCC and NCC-Silane composite

NCC was obtained in 60-70 % yield and was silylated to obtain MPTMS-NCC composite in 82% yield. The degree

of substitution (DS) is in the range of 1.4-3.2. The expected reaction between NCC chains and MPTMS is illustrated in Fig. 1a. Non-woven polypropylene filter bags were prepared containing different amount of biosorbent dose (0.1 - 1.0 g).



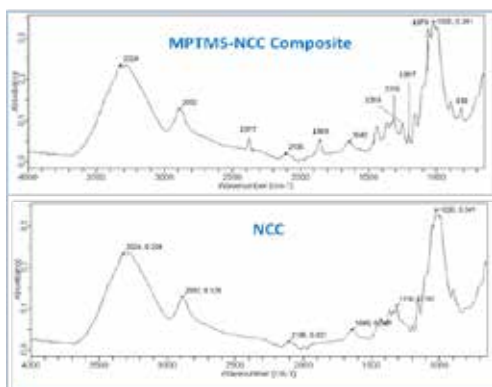
a)



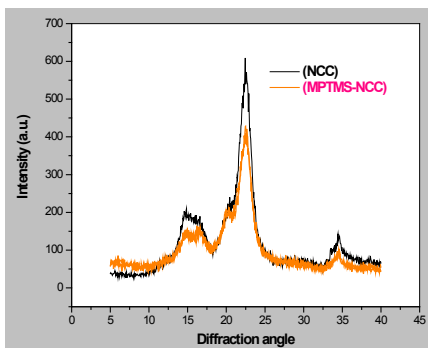
b)

Fig.1 – a). Schematic representation of preparation of MPTMS-NCC composites; b). Non-woven polypropylene filter bags filled with prepared biosorbent for batch experiments.

FTIR spectrum of NCC shows all the characteristic absorption bands of cellulose.



a)



b)

Fig. 2 – a). FT-IR spectrum of i) NCC and MPTMS-NCC composite; b). XRD spectrum of NCC and MPTMS-NCC composite

A broad band at around 3324 cm^{-1} which is attributed to the presence of free and hydrogen bonded $-\text{OH}$ stretching vibrations. The peaks at 2891 cm^{-1} and 1429 cm^{-1} corresponds to the $-\text{CH}$ stretching and $-\text{CH}_2$ bending vibrations. The peak at 1152 cm^{-1} relates to $\text{C}-\text{O}-\text{C}$ anti symmetric stretching vibration. The adsorption band at 1001 cm^{-1} is attributed to $-\text{CO}$ stretching vibration. An absorption band at 896 cm^{-1} arises from the $-\text{glycosidic}$ linkages.

MPTMS modified NCC shows an increase in the relative intensity of the band at $1,076\text{ cm}^{-1}$, which may be related to the $\text{Si}-\text{O}-\text{Si}$ group stretching, which in turn may indicate the formation of the polysilsesquioxane network. On the other hand, the absorption band in the 960 cm^{-1} region, attributed to $\text{Si}-\text{O}-\text{C}$ symmetric stretching, was reduced in the FTIR spectrum of the modified NCC, suggesting condensation of the silanol groups. The existence of siloxane is again confirmed due to the peak 838 cm^{-1} attributed to $\text{Si}-\text{CH}_2$ group. The strong characteristic peak at 1207 cm^{-1} region could be related $\text{Si}-\text{O}-\text{Si}$ bonds. Moreover, a $\text{Si}-\text{CH}_3$ bond peak at 1265 cm^{-1} also appeared clearly due to the formation of polysiloxane network (Abdelmouleh et al. 2004). A peak at 2548 cm^{-1} confirms the presence of S-H group (Rangel-Vázquez et al. 2010).

XRD analysis shows that the acid treatment results into narrowing and higher crystallinity level of hydrolyzed cellulose. Presence of three strong peaks at $2\theta = 14.84, 22.76$ and 34.98 are the characteristics of cellulose I (Klemm et al. 2005). Crystallinity index of NCC and MPTMS-NCC composite were calculated using equation: $\text{CI} = \frac{I_{110} - I_{\text{am}}}{I_{110}} \times 100$, and found to be 92.56 and 68.72 respectively. The crystallite size was estimated from the full width at half-maximum intensity (FWHM) using Debye-Scherrer equation: $D_{hkl} = \frac{K\lambda}{\cos\theta \Delta 2\theta_{hkl}}$, where β is the breadth of the peak of a specific phase ($2\theta = 22.56$), K ; constant that varies with the method of taking the breadth ($K = 0.94$), λ ; the wavelength of incident X-rays ($\lambda = 0.15418\text{ nm}$), θ ; the center angle of the peak, and L ; the crystallite length. The average crystallite size was found to be 6 and 122 nm for NCC and MPTMS-NCC composite respectively.

3.2 Sorption Experiments

A series of batch experiments on sorption led to the standardization of the optimum conditions for As (III - 94.40 %) and As (V - 85.70 %) removal at arsenic concentration (25 mg/L), contact time (40 min), volume (200 mL) and pH 7.5 for As (III) and 2.5 for As (V). The trivalent arsenic species exists in a non-ionic form (H_3AsO_3) in the pH range 2-7 and in the anionic ($\text{H}_2\text{AsO}_3^{-1}$, HAsO_3^{-2}) form (Ghimire et al. 2002) in the pH range 7-10. Optimum sorption of arsenite species in the pH range 7-10 can be assigned to the availability of the negatively charged As (III) species interacting with the positively charge ends of mercapto group present in the MPTMS-NCC composite, which have isoelectric points in the pH range 4.0-8.0 (Samuel 2002). The pentavalent arsenic species exists in the monovalent ($\text{H}_2\text{AsO}_4^{-1}$) and divalent anions (HAsO_4^{-2}) in the pH range 2-9. Maximum sorption of As (V) on cationic adsorbent observed at pH 2.5 can be easily ascribed to its interaction with the anionic ($\text{H}_2\text{AsO}_4^{-1}$ and HAsO_4^{-2}) species, occurring predominantly in this pH range. At pH below 2.5, neutral species of arsenic starts forming and becomes the reason of relative decrease of As (V) sorption on cationic biosorbent.

The reason behind the more adsorption of As (III) then As (V) is explained on the basis of the fact that As (III) shows

high affinity for -thiol groups, then As (V) (Kumaresan et al. 2001).

4. Conclusions

This study demonstrated that silane coupling agents are promising candidates for efficient removal of arsenic from water bodies due to their high compatibility with NCC. The incorporation of positively charged -thiol groups in NCC significantly enhanced binding capacity of negatively charged arsenic species. The work highlighted the application of nanotech and chemical functionalization approach on largely abundant, economic, biopolymer (cellulose) resulting into smart nano-biosorbent with enhanced sorption efficiency and environmental stability.

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