

Methylene blue dye adsorption using Cellulose Nanocrystals (CNCs) isolated from garlic skin

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Abstract

In this paper, we report the isolation of cellulose nanocrystals (CNCs). During the study, *Allium sativum* skin (garlic skin) was used to evaluate their potential for the synthesis of ZnO NPs. The remaining biomass of garlic skin was further processed to isolate cellulose. The purest form of the cellulose was obtained and further acid hydrolysis was carried out to obtain nanocrystalline cellulose (CNCs). Garlic skin was chosen because it is abundant and so far it has not been extensively investigated as a raw material option to produce CNCs as well as nanoparticles synthesis. Formation of CNCs have been confirmed X-ray diffraction (XRD) for crystal structure, Fourier transform infrared spectroscopy (FTIR) analysis was done for chemical groups and bonding, scanning electron microscope with Energy dispersive X-ray studies (EDX) was carried out to analyze the surface morphology and percentage composition of elements, transmission electron microscope (TEM) for particle size and shape, surface area and pore size of nanomaterials were calculated by Brunauer-Emmet-Teller (BET) analysis. The adsorption study was carried out for the removal of Methylene blue dye. Different concentration of dyes 10 ppm, 25 ppm and 50 ppm was taken during study. **Result:** The scanning electron microscope confirms the formation of the crystalline cellulose having average size 6.41 nm. Energy dispersive X-ray analysis states the formation of high purity of CNCs. BET analysis also confirms the increased surface area of CNCs than untreated cellulose. Different concentration of methylene blue dye was taken during study to check the adsorption efficiency of CNCs. The result showed that, the percent of MB removal increases by increasing adsorbent dosage and decreasing initial dye concentration.

Key words: Nanotechnology, X-Ray Diffraction, Adsorption, Garlic Skin, Cellulose

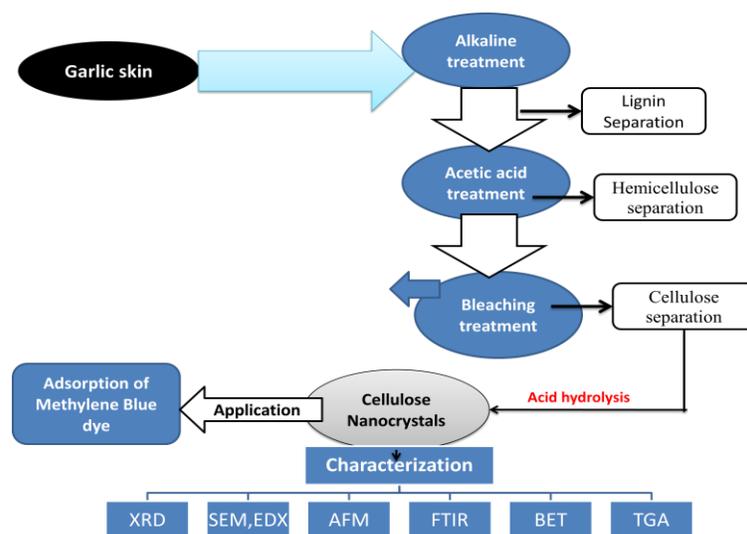


Figure: Graphical representation of Abstract

Introduction

The needs for materials and processes in accordance with the environmental requirements have motivated many scientists to use raw materials from the renewable resources such as lignocellulosic materials (Carlos Augusto de Carvalho Mendes et al., 2015). Social concerns for sustainable green products are encouraging the efficient exploitation of cellulose, the most abundant renewable biopolymer on the earth (Kentaro Abe & Hiroyuki Yano 2009). Production of nano-scale cellulose and its application in composite materials had got increasing attention due to its advanced properties such as high stiffness and strength combined with low weight, flexibility, good dynamic mechanical, electrical, thermal properties, biodegradability and renewability (Franciele Maria Pelissari et al., 2014; Budiman Anwar et al., 2015).

Cellulose is the most abundant material found in nature. Cellulose derivatives are widely used for treatment of wastewater. Native cellulose consists of amorphous and crystalline regions. The amorphous region of cellulose makes it sensitive to acid hydrolysis that disrupts the amorphous region and forms Cellulose nanocrystals (CNCs) (Rasim Batmaz et al., 2014). CNCs are needle-like cellulose particles having at least one dimension equal or less than 100nm with highly crystalline nature. Different types of extraction processes have been used for the production of CNCs but use of sulfuric acid (H_2SO_4) as acid-hydrolysis method is the most well known, efficient, and widely used extraction method (Habibi et al., 2010). Apart from reinforcing material, CNCs can be used in bioenergy, as barrier films, optical films or coatings, in chemical, catalytic and biomedical applications. Addition of CNCs can alter the rheology of various media (liquids, polymer melts, particle mixtures) that are used in many industrial applications such as paints, coatings, adhesive, food, lacquers, cosmetics, cements and drugs (Lima et al., 2004). Recently, CNCs have been used as a substrate to fabricate nano-sized metallic particles. In a suspension of CNCs and metallic salts,

most of the metallic particles can absorb on the surface of CNCs due to electrostatic interactions between oxygen atoms of polar hydroxyl and metallic particles. This effect controls the sizes of metallic NPs by preventing the agglomeration of nanoparticles. (Susan Azizi et al., 2013). The exposed –OH groups on CNC surfaces can be readily modified to achieve different surface properties and have been used to adjust CNC self-assembly and dispersion for a wide range of suspensions and matrix polymers and to control interfacial properties in composites (Samir et al., 2005).

This work aimed to find an alternative to add value to garlic by using their skin as raw material to isolate cellulose crystals in nanometer scale. This study will provide a solution to the problem of discarding the remaining garlic skin.

Experimental

Materials

Sodium chlorite, ethanol, sulfuric acid, acetic acid were procured from Sigma Aldrich. Garlic skin, produced as a byproduct during the processing of garlic, was obtained from vegetable market, sector 21, Gandhinagar, Gujarat.

Separation of cellulose from Garlic skin

For the isolation of CNCs a modified method reported by Jong-Whan Rhim et al., (2015) was used. Garlic skin was washed thoroughly with water to remove dirt and dried in sunlight for 2 days. The dried samples were ground into powder to get garlic skin powder (GSP) and used for further analysis. 100 ml of methanol was added to the GSP sample and incubated for 24 hours. The methanol extract was taken out and garlic skin was separated by centrifugation at 6000 rpm for 10 min. The garlic skin was washed with distilled water and bleached with 0.7 % (w/v) sodium chlorite solution at pH 4, adjusted by 5% acetic acid. The above mixture was boiled for 2 hours with stirring for the removal of lignin from the garlic skin. The residue was subsequently washed with distilled water until it comes to neutral pH. The obtained neutral residue was then boiled with 250 mL of 5% (w/v) sodium sulfite solution for 5 h, followed by washing with distilled water to complete removal of lignin. The resulting component is holocellulose composed of hemi-cellulose and α -Cellulose. The holocellulose solution was treated with 17.5 % sodium hydroxide solution at 20 °C for 1 hour. The solution were filtered and treated with 10% acetic acid to remove sodium hydroxide and washed with distilled water. Finally, the extracted cellulose was dried at 105 °C to get cellulose.

Isolation of cellulose nanocrystals

CNCs were isolated by acid hydrolysis using 65 % sulfuric acid. For the formation of CNCs, 5g of cellulose obtained by above method was hydrolyzed by refluxing with sulfuric acid (cellulose to liquor ratio of 1:20) at 60 °C for 3 h with strong agitation. The hydrolysis was quenched by adding excess amount of distilled water to the reaction mixture. The resulting mixture was cooled to room temperature. thereafter, the suspension was repeatedly centrifuged at 5000 rpm for 15 min and the supernatant was discarded until it became cloudy. The mixture was sonicated for 5 min in an ice bath to avoid overheating. The cloudy suspension was then subjected to dialysis against distilled water until pH reached to neutral. Then, the suspension was freeze-dried to obtain CNCs.

Adsorption experiment

A stock solution of 1g/L was prepared by dissolving the 1 g of MB in a litre of deionized water. The working solutions were prepared by diluting the stock solution with deionized water to give the appropriate concentration of working solutions. The concentration of MB was varied from 10 to 50 ppm.

The UV-Vis Spectrophotometer (DB-20) was used to determine the concentration of MB dye in solution. The concentration of the residual dye was measured using UV-visible spectrophotometer at a ($\lambda_{\max}= 664 \text{ nm}$) by withdrawing samples at fixed time intervals, centrifuged and the supernatant was analyzed for residual MB dye (B. Meroufel et al., 2013). The percentage adsorption was calculated using below formula:

$$\%R = (C_0 - C_t) \times 100 / C_0$$

Where, %R is the percentage removal of dye, C_0 is the initial concentration of Dye, C_t denotes concentration of dye at time t.

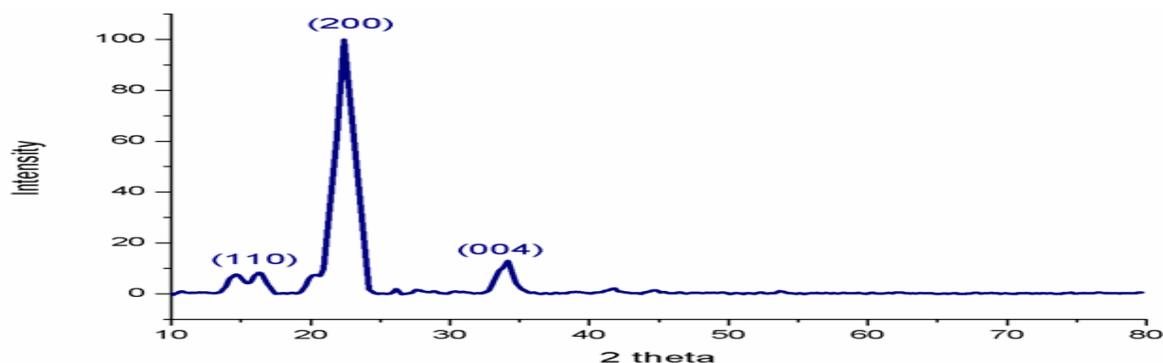
Characterization

The obtained CNCs were characterized using X-ray diffraction spectrum (XRD) recorded by a Rigadu Miniflex diffractometer at room temperature using $\text{CuK}\alpha$ irradiation (154 \AA). Fourier transform infrared spectroscopy (FTIR) was performed using a spectrometer (Perkin-Elmer Spectrum One). The surface morphology was investigated by JEOL JSM scanning electron microscope. Atomic force microscopy was also done to analyze the particle size of CNCs. BET analysis was done to find out surface area to volume ratio of CNCs.

Result and Discussion

XRD pattern

A peak around $2\theta = 16.5^\circ$ and 22.5° and 34.6° which are supposed to represent the typical cellulose-I structure. The cellulose crystals exhibit characteristic assignments of 110, 200, and 004 planes, respectively.



SEM and EDAX analysis

The length and diameter distribution of CNCs were estimated using SEM image. Fig. 2 (a) shows the micro-architecture of CNCs. SEM image shows the CNCs with size of average diameter of 6.41 nm, which was obtained by measuring the 30 individual particles using the ImageJ software. EDX analysis data represented in fig: 2(b) also confirms the purity of CNCs.

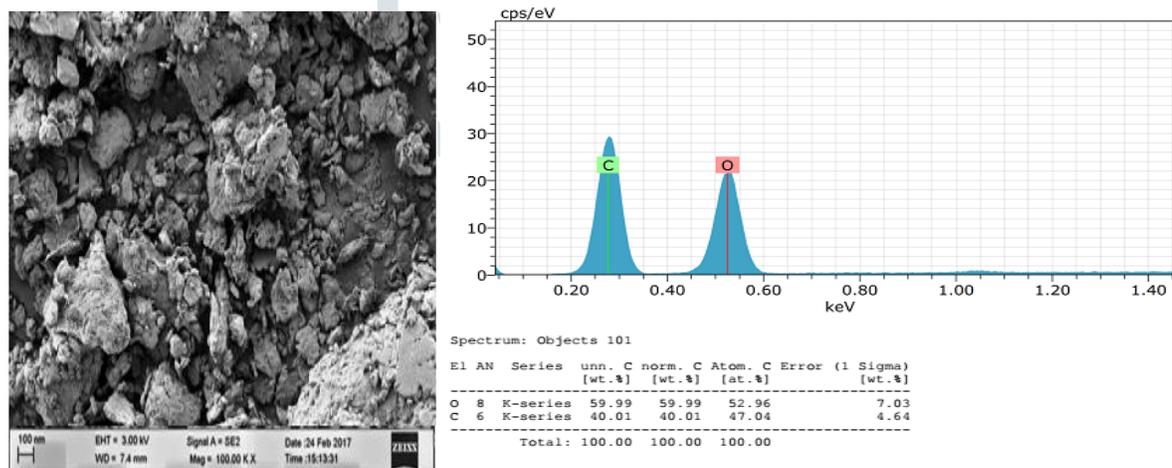


Fig: 2 (a) SEM micrograph (b) EDX analysis of CNCs

FTIR spectra of CNCs are shown in fig.3. The broad band observed at 3443 cm^{-1} corresponds to O-H stretching of the cellulose present in CNCs. This peak also includes inter- and intra- molecular hydrogen bond vibrations found in cellulose (Popescu M C et al., 2011). The band at 2889 cm^{-1} is attributed to CH stretching vibration of all hydrocarbon constituent. The intense peaks at 1651 cm^{-1} related to the absorbed moisture in cellulose (Poletto M et al., 2001). The absorbance bands at

1425, 1366, 1157, 1027 cm^{-1} and 898 cm^{-1} belong to stretching and bending vibrations of $-\text{CH}_2$ and $-\text{CH}_3$ $-\text{OH}$ and $\text{C}-\text{O}$ bonds found in cellulose. The band at 1420-1430 cm^{-1} is related with the amount of the crystalline structure of the cellulose (Viola Hospodarova et al., 2018).

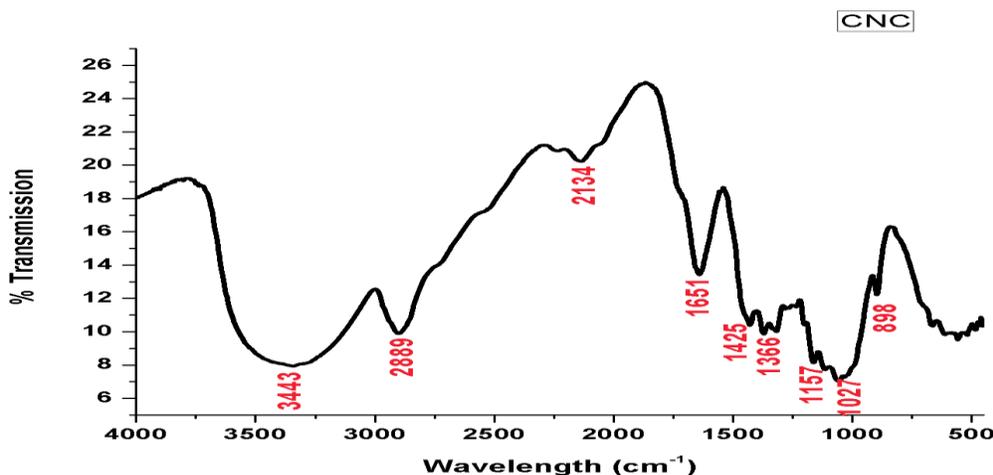
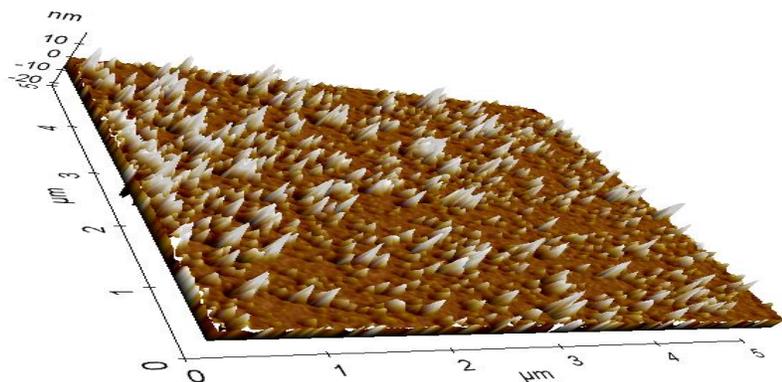


Fig. 3: FTIR spectra of CNCs

AFM analysis

AFM images have been used to estimate the size of CNCs. Figure 4a and b shows both 2D and 3D images obtained using AFM. The sampling areas used were $[5 \times 5 \mu\text{m}]$. AFM micrographs reveal that films are closely packed and granular in nature. Signature of agglomeration of grains is almost absent. Uniform brightness contrast of film exhibits the absence of impurities or clusters (Kalimuthu Hemalatha et al., 2018). The measured roughness parameter was 8.6 nm.



Adsorption study

Comparative adsorption study was done to check the efficiency of cellulose and CNCs to remove dye.

	10 ppm		25 ppm		50 ppm	
	Cellulose	CNCs	Cellulose	CNCs	Cellulose	CNCs
15 min	29.57	33.92	12.54	13.77	5.52	6.94
30 min	45.69	54	16.29	20.32	8.80	11.96
45 min	51.13	64.8	18.46	26.47	10.62	14.21
60 min	54.30	67.06	20.20	29.32	11.72	15.10

Conclusion

During the study, the purest form of cellulose was isolated and CNCs were prepared less than 10 nm in size for the adsorption of MB dye. It was found that due to higher surface to volume ratio of CNCs, they can adsorb higher amount of dye than cellulose. Garlic skin is a waste material and we have used isolation and purification of cellulose nanocrystals, is the novelty of our research work. It has been proved as the best from the waste approach. CNCs have been used as low cost, efficient adsorbent for the removal of MB dye.

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