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ORIGINAL ARTICLE

Sustainable removal of methylene blue dye from textile effluent by using cellulose nanocrystals extracted from sugarcane bagasse

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Abstract

Adsorption has proven to be a cost-effective option for treating wastewater containing dyes and other pollutants, as it is a simple and low-cost technique. In this work, cellulose nanocrystals (CNCs) were extracted from sugarcane bagasse using the acid hydrolysis technique and used as an effective adsorbent for removing methylene blue dye. The chemistry behind the segregation of cellulose nanocrystals from sugarcane bagasse and its adsorption of methylene blue dye from textile wastewater has been discussed. The obtained nanocrystals were characterized by Fourier transform infrared spectroscopy (FTIR), ultraviolet–visible spectroscopy, X-ray diffraction (XRD), and thermos gravimetric analysis (TGA). The dye solution was subjected to extracted CNC, observed the dye absorption capacity, and found that the absorbance of the dye solution after treatment was decreased compared to the stock solution. With an increase in treatment time from 30 to 90 min, there was a rapid decrease in absorbency values obtained through UV spectroscopy.

Keywords Sugarcane bagasse · Acid hydrolysis · Cellulose nanocrystals · Methylene blue dye · Textile wastewater

1 Introduction

The textile industry is one of the largest industries in the world. Effluents from textile plants are categorized as the most adulterating of all industrial sectors, considering both volumes produced and effluent composition. During the dyeing process, a portion of applied dyes remains unfixed to the fabrics and is washed out in the effluents, which consequently causes pollution, affects aquatic lives, and causes several health hazards in humans. Researchers introduced many methods to improve the dye uptake by the fiber in different ways to minimize the amount of leftover dye [1]. Many methods are available to remove the dye from effluent water, including coagulation, adsorption, precipitation, electrochemical techniques, and enzyme decolorization. Out of all these methods, adsorption was practical and useful in the industry [2, 3]. So many adsorbents were introduced by authors, including the sources from natural and synthetic. Synthetic adsorbents were very effective for color removal from effluent water, for example, activated carbon, but their use was restricted due to its high cost. Adsorbents extracted from natural sources can effectively remove color like waste banana pith, maize cobs, sugarcane bagasse, sawdust, rice, and peanut hull [4–7]. These adsorbents can be used as such, or they can be treated with some chemicals to modify their structure for efficient removal of color at a low price [8, 9], for example, acid treated banana peel, oil palm trunk powder, and zinc chloride-activated palm kernel shell [10–12].

Banana peel among various adsorbents, sugarcane bagasse (SB) is a better sustainable dye adsorbent because of its availability of 3 tons for every 10 tons of sugarcane crushed. SB has been used alone in its native form or ball milled to increase the surface area [13] and chemically modified [11] with phosphoric acid to effectively remove methyl red dye

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from wastewater and compare its performance with activated carbon. The results were interesting and very effective in batch reactors as a low-cost adsorbent [9].

Ethylenediaminetetraacetic dianhydride (EDTAD) was used to modify the SB to remove methyl blue dye chemically. After chemical modification, SB was found to have increased carboxyl groups in its structure, leading to a significant increase in dye removal compared to control SB [6]. Succinic anhydride was used to modify the SB chemically and studied its adsorption behavior on cationic dyes (methyl blue) by varying concentrations of adsorbent, time, and pH. According to the results, it has fitted well with the pseudo-second-order kinetic model [12]. Studies were also conducted on increasing the surface area of SB by simple ball milling and found that increasing the surface area from 0.57 to 1.81 m^2/g resulted in a slight gain in dye removal [6].

Nanocellulose (NC) has distinctive low density, good mechanical properties, and biodegradability. In addition, it can also be easily modified and has a high surface area and typical morphology. Cellulose nanocrystal (CNC) was extracted from Carex meyeriana Kunth (CMK) and used as an adsorbent to remove methylene blue (MB) from an aqueous solution. Results found that the adsorption capacity of 217.4 mg/g higher than the CNC obtained through acid hydrolysis can be more economical and promising [7]. Adsorbent prepared using cellulose nanocrystals treated with pristine and functionalized with polydopamine and melamine–formaldehyde used to effectively remove MB and methyl orange dye mixtures. The results showed the effective removal of dye mixtures at 85.78% and 100% for dye mixture [14]. Carboxylated cellulose nanocrystals were developed by eco-friendly means using Fe^{2+}/H_2O_2 mixture and efficiently used as an adsorbent to remove MB dye from the wastewater. The results reported that 95.6% of dye has been removed from the wastewater [15]. Nanocellulose fibers with high-density carboxylic groups were prepared by using natural wasted pomelo peel with H_2O_2. The resultant adsorbent showed excellent adsorption towards malachite green (MG) and Cu(II), with an adsorption capacity of 530 mg/g to MG and 74.2 mg/g to Cu(II) [16]. Further to extend the use of CNC in adsorption, another sustainable natural resource identified was sawdust. CNC was extracted from sawdust, incorporated with zinc oxide, and used as a novel adsorbent to remove MB from wastewater [8]. CNC was also extracted from jute fibers and used effectively to remove MB dye from water [9].

So far, CNC has been extracted from different sustainable sources, but no work has been reported till now on the extraction of CNC from SB. Since CNC has several advantages in the adsorption of MB dye and considering SB's availability, a design was developed to use this adsorbent. This study mainly focuses on the extraction of CNC from sugarcane bagasse using the acid hydrolysis method and evaluates its efficiency in removing methyl blue dye from the effluent water.

2 Materials and methodology

2.1 Materials

Sugarcane bagasse was collected from nearby local sources, washed with cold water, and dried under sunlight. Reagents used in this study were sodium hydroxide, sodium chlorite, acetic acid, nitric acid, and sulfuric acid of laboratory grade, and methylene blue dye was used in this study.

2.2 Preparation of CNCs from sugarcane bagasse (SCB)

SB was washed with regular water to remove dust and dirt and dried until all moisture content in the bagasse dried. SB was then pretreated to remove lignin and hemicellulose before acid hydrolysis for the separation of CNC from lignocellulosic biomass. In the process of pretreatment, 10 g of washed and dried SB was then treated with 300 ml of 5%(w/v) NaOH at 80 °C for 1 h to remove waxes and ash content in raw SB. Pretreated bagasse was washed and dried to remove residual NaOH and then bleached with 250 ml of 3.3% (w/v) $NaClO_2$ and 30 drops of CH_3COOH at 90 °C for 1 h for the removal of lignin. Sodium chlorite was an excellent bleaching agent that aids in removing lignin and produces holocellulose (cellulose + hemicellulose). The main objective of this process was to break down the lignin structure and disrupt the crystalline structure of cellulose.

After the bleaching process, the samples were washed and dried. Then the samples were treated with 200 ml of 1 M HNO_3 at 80 °C for 1 h to neutralize the chemicals present. This treatment was done to remove lignin and hemicellulose from SB altogether. This purification treatment removes a large amount of resistant hemicellulose strongly associated with cellulose.

Delignified fibers were washed, dried, and then treated with 64% sulfuric acid (H_2SO_4) at 45 °C for 30 min. The ratio of fiber to the acid solution was 1:10 (w/v). Acid hydrolysis will hydrolyze the amorphous region in the fiber and leave only the crystalline region, which was required for CNCs preparation. The typical mechanism is that the hydrogen ions(H^+) from acid can easily invade the loose, amorphous regions of cellulose to break the 1,4 β glucoside bonds, resulting in the hydrolysis of amorphous regions. In contrast, the crystalline region of cellulose could be retained, which is attributed to the inherent compact

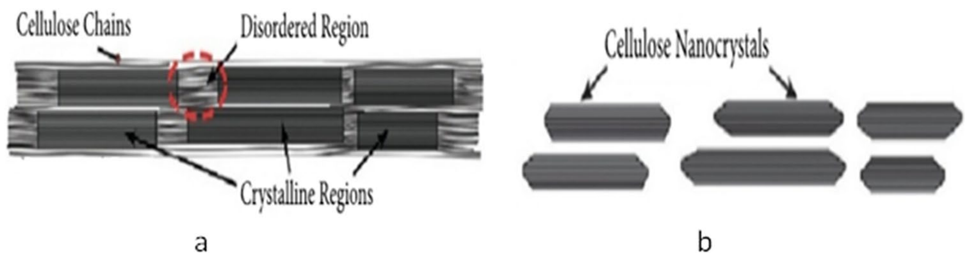

Fig. 1 Acid hydrolysis (**a**) idealized cellulose microfibril suggesting configuration of the amorphous and crystalline region, **b** CNCs after acid hydrolysis dissolved the disordered regions

structure that prevented the permeation of the acid. This is clearly shown in Fig. 1. Therefore, the hydrolysis of mineral acid can obtain the complete crystalline structure of CNCs.

After each washing step, the hydrolyzed cellulose sample was washed several times and submitted to the centrifugation stage (5000 rpm for 30 min) to separate the crystals from the solution. In a centrifuge under the influence of gravitational force, CNCs separate from acid hydrolyzed cellulose suspension solution, which is shown in Fig. 2. The yield percentage of obtained CNC was 36.17% can be found by using Eq. 1.

$$\text{Yield \% of CNC} = \frac{W\text{ final}}{W\text{ initial}} \times 100 \quad (1)$$

where w final — CNC weight, w initial — the weight of hydrolyzed cellulose sample.

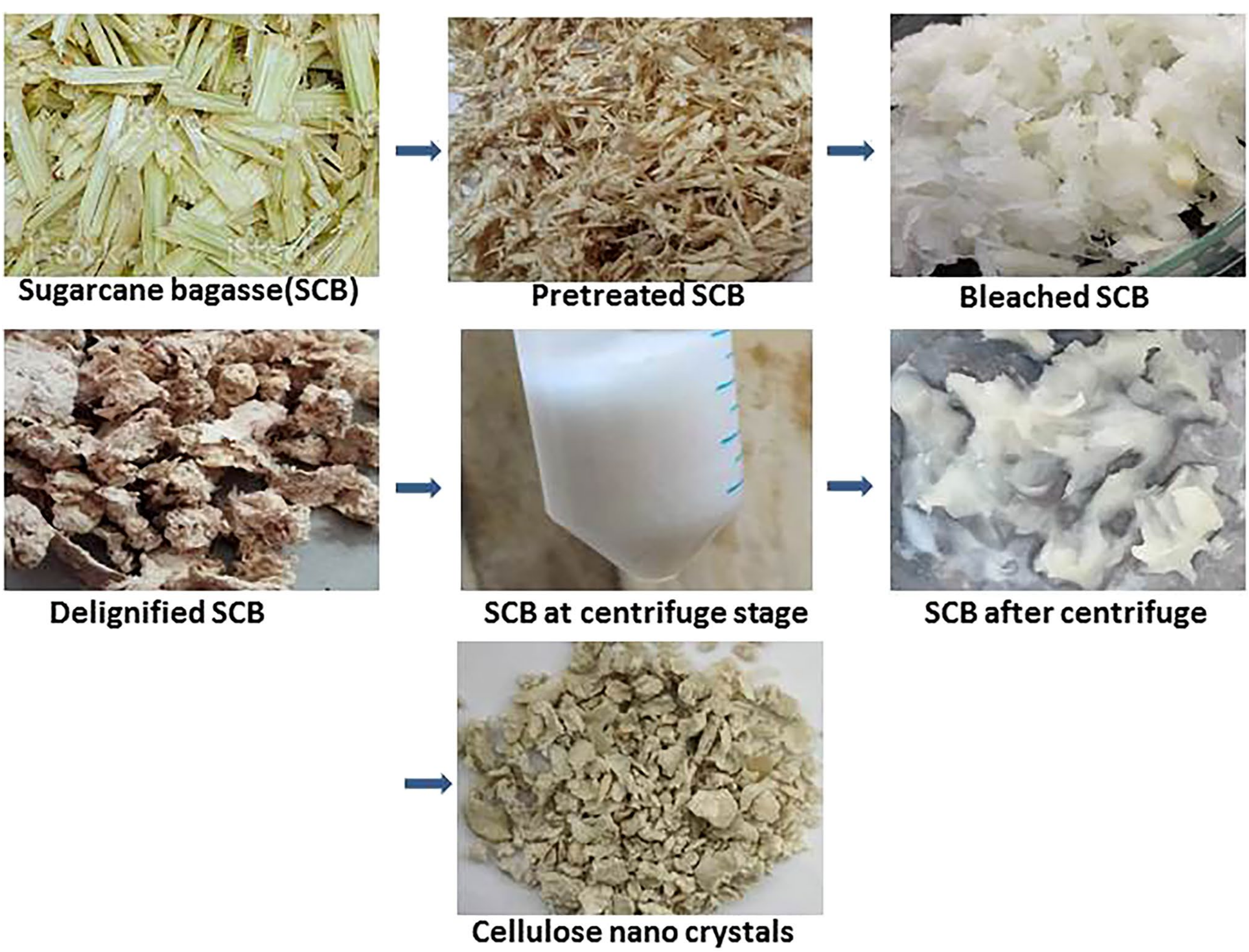

Fig. 2 Production stages of cellulose nanocrystals from sugarcane bagasse

2.3 Cellulose nanocrystals

Sulfuric acid hydrolysis of native cellulose introduces negative charges on the surface of CNCs due to the formation of sulfate ester groups. A negative charge on the surface of CNCs also makes it a possible candidate for the adsorption of positively charged dyes. The cationic MB dye molecules were adsorbed on the anionic CNC in the mixture through electrostatic interactions.

2.4 Adsorption

The stock solution was prepared by dissolving 1 g of the methylene blue dye in 1 L of distilled water. For the analysis, the dye solutions with different concentrations were prepared by diluting the stock solution with distilled water. Figure 3 shows the adsorption studies performed at different dye concentrations and treatment periods. The initial dye concentrations in the experiments were selected in the range of 0.001% and 0.0001%. The dye solution (100 ml) of desired concentration was taken in a steel vessel and agitated with 0.8 g and 0.4 g of CNC adsorbent at room temperature (35 °C) in a shaking water bath for desired periods. At the end of adsorption tests, samples were filtered, and the filtrate was analyzed. The initial dye bath and residual dye concentration were determined using the UV–Vis spectrophotometer. At the end of adsorption tests, samples were filtered, and the filtrate was analyzed. The initial dye bath and residual dye concentration were determined using the UV–Vis spectrophotometer. Dye removal percentage can be assessed by following Eq. 2.

$$\text{Dye removal } \% = \frac{C0 - Cf}{C0} \times 100 \qquad (2)$$

The dye removal efficiency of each test can be obtained by knowing the initial (C_0) and final (C_f) dye concentrations.

2.5 Desorption

MB dye was absorbed from the adsorbent using the chemical regeneration method shown in Fig. 4. The adsorbent coating was dipped in solvents, i.e., HCl of 10 mg/g, at 30–60 °C for 45 min. The solvents used in this study were HCl and ethanol at a ratio of 50:50.

Fig. 3 **a** Methylene blue dye at 0.0001% treated with CNC (trail 1); **b** methylene blue dye at 0.0001% treated with CNC (trail 2); **c** CNC before adsorption and after adsorption

3 Results and discussions

The CNCs adsorbent obtained from sugarcane bagasse was characterized for the presence of chemical groups, its heat stable capacity, X-ray diffraction, and studied for the dye adsorbent capacity.

3.1 Fourier transform infrared spectroscopy

FTIR spectroscopy was done to show the characteristics and composition of CNC and dye solution through analysis of its functional group. FTIR spectra of CNC obtained from SCB before and after adsorption are shown in Fig. 5a and b. CNC

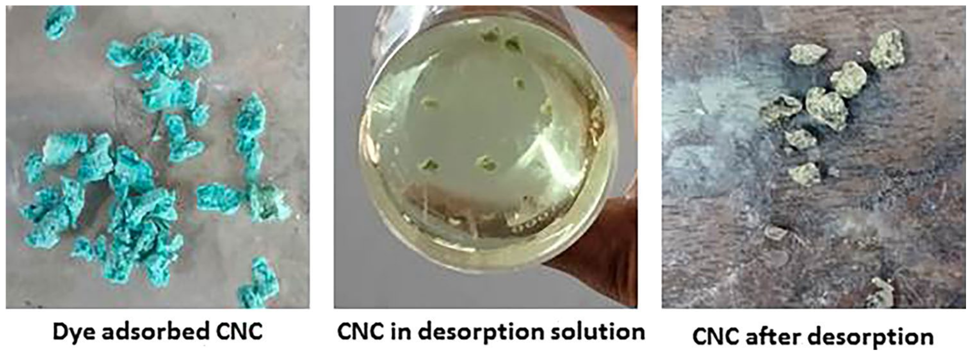

Fig. 4 Desorption of methylene blue dye from cellulose nanocrystals

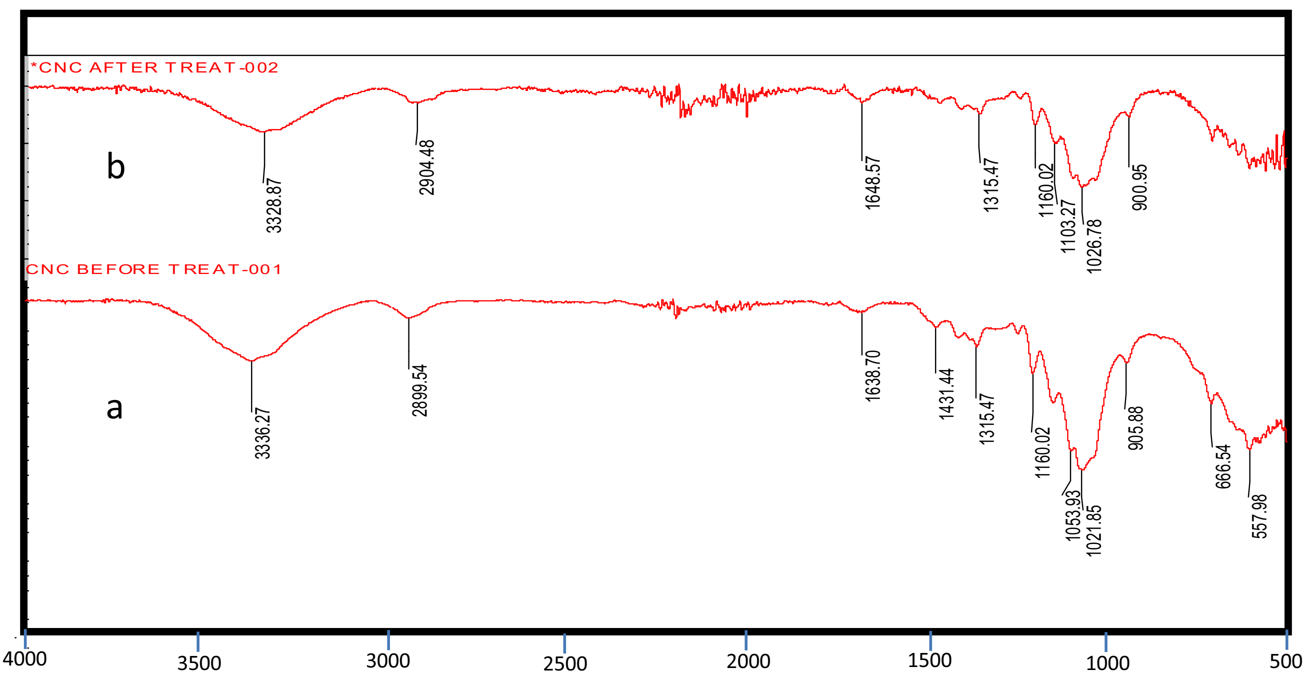

Fig. 5 FTIR of CNC **a** before adsorption and **b** after adsorption

Table 1 CNC characteristic FTIR spectral assignment

S. no	Assignment	Cellulose wavenumber (cm^{-1})	Cellulose nanocrystals wavenumber (cm^{-1})
1	C–O–C polysaccharide vibration	1162–1172	1160.02
2	-OH group stretching vibration	3650–3200	3336.27
3	C-H stretching vibration	2897–2900	2899.54
4	Water absorbed	1632–1645	1638.7
5	CH_2 bending vibration	1425–1468	1431.44

characteristic FTIR spectral assignment is given in Table 1. FTIR spectrum of isolated CNC displayed characteristics adsorption patterns corresponding to the specific functional group of cellulose. The peak at 1160.02 cm^{-1} is due to C–O–C polysaccharide vibration. The sharp transmittance peak at 3336.27 cm^{-1} represents OH group stretching vibration, the peak at 2899.54 cm^{-1} corresponds to CH stretching vibration, and the peak at 1638.7 cm^{-1} may be due to the bending mode of adsorbed water. The peak at 1431.44 cm^{-1} may be due to the bending vibration.

However, the frequency of vibration of the peak at 1431 cm^{-1} becomes smaller in the spectra of CNC after adsorption suggesting the entrapment of MB onto the surface of CNC in acceptance with the findings of Oyewo et al. [8]. FTIR spectrum of CNC after treatment was not different from the spectra of CNC before treatment. It indicates that there were no new bonds formed after the adsorption of dyes. From this, it was clear that dyes adsorbed onto the surface of CNC by just physical adsorption. FTIR spectrum of dye solution before and after treatment was similar. Even after adsorption, the dye solution was not disturbed by other materials, which shows that the integrity of CNC was not disturbed during the adsorption process. This was witnessed in Fig. 6a and b.

3.2 Thermogravimetric analysis

TGA is an analytic technique used to determine the material (CNC) thermal stability and fraction of volatile compounds by monitoring the weight change as a sample is heated at a constant rate. From Fig. 7, it was clear that the weight loss below 150 °C could be attributed to H_2O evaporation. Between 250 and 350 °C, the weight loss was caused by cellulose degradation due to depolymerization, dehydration, or decomposition of glycosyl units, followed by the formation of charred residues [10]. The weight loss at the end of the TGA run could result from the oxidation

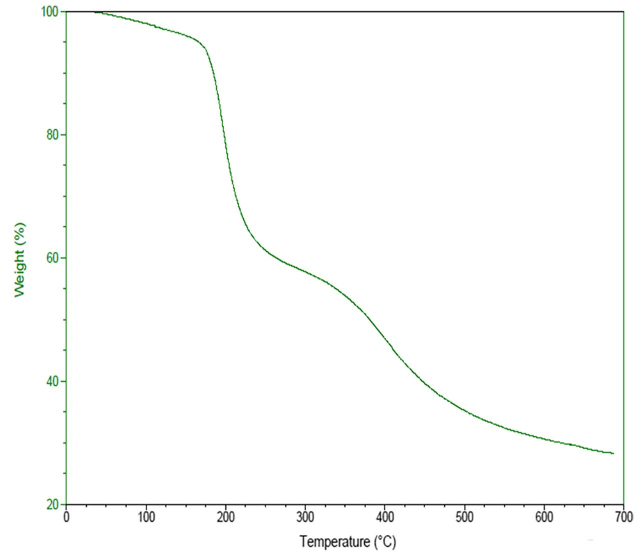

Fig. 7 Thermogravimetric analysis of CNC

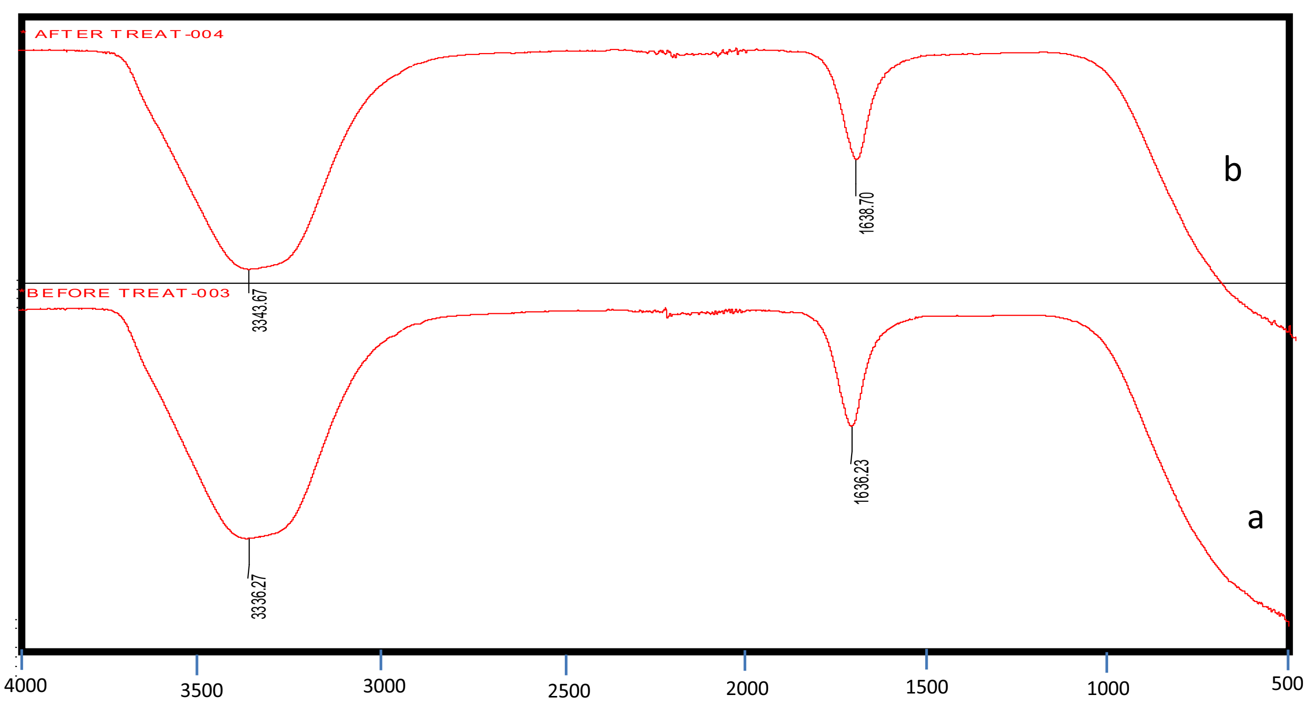

Fig. 6 FTIR of MB dye solution **a** before adsorption and **b** after adsorption

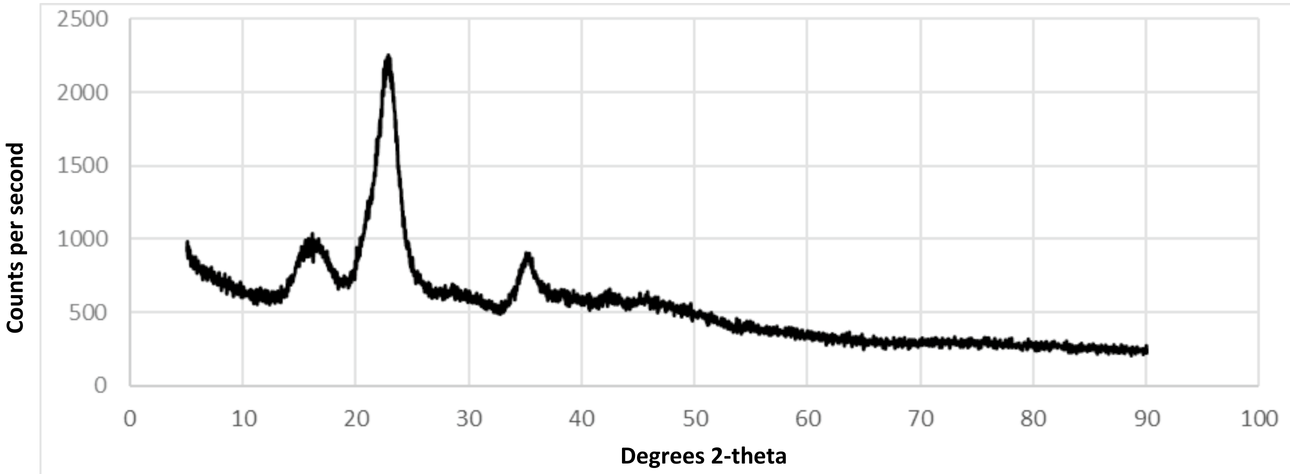

Fig. 8 XRD graph for cellulose nanocrystals

and breakdown of charred residue into a gaseous product with low molecular weight.

3.3 X-ray diffractometer

Powder X-ray diffraction is a technique used to characterize CNC using X-rays. Figure 8 shows the XRD graph obtained for CNC. This graph between wavelength and diffraction theta gives the idea of the crystalline and amorphous region in CNC. The crystallinity index (CI) was determined empirically according to the Segal equation (Eq. 3) of crystallinity index as mentioned and characterized the crystallinity index of CNC to be around 48.85%.

$$CI = \frac{It-Ia}{It} \times 100 \quad (3)$$

The Segal crystallinity index was calculated according to the equation, where It is the total intensity of the peak for CNC, and Ia is the amorphous intensity.

3.4 Visual observation

3.4.1 Adsorption

The dye adsorption experiments resulted in the exhaustion of dye from the dye bath solution into the CNCs adsorbent. The CNC, after adsorption treatment, was found to obtain

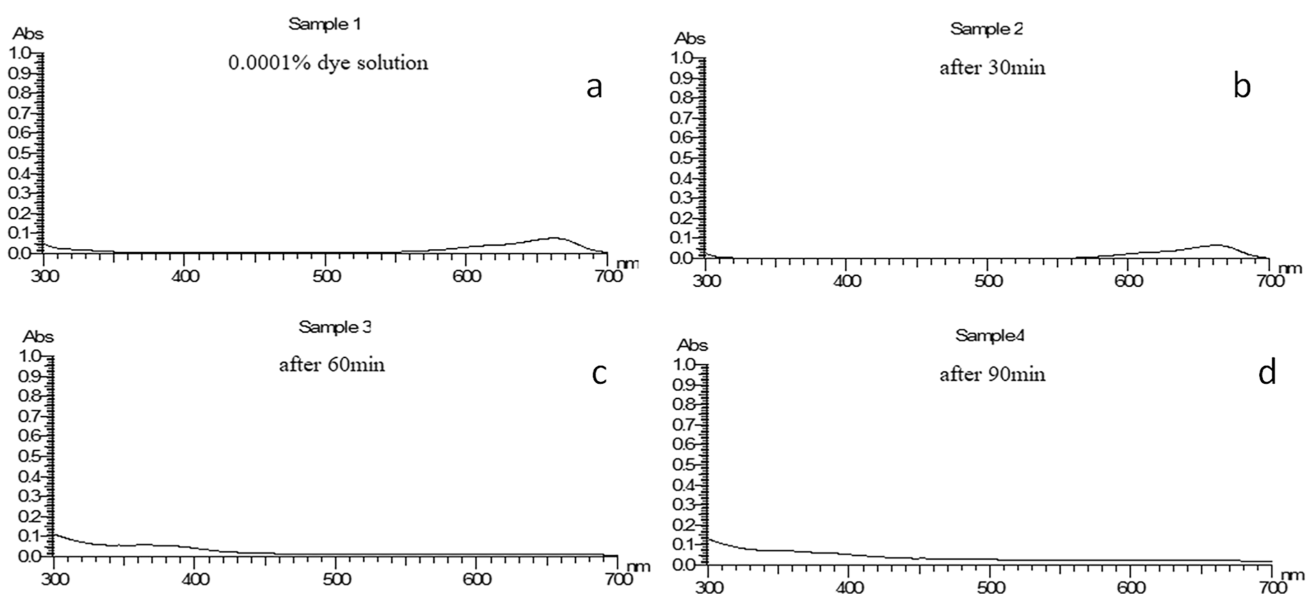

Fig. 9 Absorbency curve of CNC at the different time durations: **a** stock solution, **b** 30 min, **c** 60 min, **d** 90 min

a strong color change from yellowish white to blue. This color change represented the intake of methylene blue dye used [17]. Meanwhile, the effluent solution was found to lose its color, which stands as a proof point for the dye transfer from dye solution to CNC. One such observed trial is given in Figs. 9a and b.

3.4.2 Desorption

The dye desorption experiment resulted in removing methylene blue dye from cellulose nanocrystals adsorbent into the desorption solution. The CNC, after desorption treatment, was found to obtain an intense color change from blue to yellowish white. This color change represented the desorption of methylene blue dye from CNC. This color loss is a proof point for the desorption of methylene blue dye from CNC. One such observation is given in Fig. 9c.

3.4.3 Dye adsorption test

In the stock solution of 0.0001% dye shade, cellulose nanocrystal adsorbents were introduced and agitated in the shaking water bath. Its dye absorption was tested using UV–Visible spectrophotometer at different durations of 30, 60, and 90 min. The absorbance vs. wavelength curve was studied using UV–Vis spectrophotometer given in Fig. 9.

The control (stock solution) showed an absorbance peak at 660 nm, rendering the dye solution's blue shade shown in Fig. 9a. The absorbance of dye solution after treatment decreased compared to the stock solution. The curve keeps falling with an increase in time and becomes almost straight from the lowest treatment time seen in Figs. 9b, c, and d. It was seen that CNC offered a higher dye removal percentage of around 80.26% after 60 min of adsorption, after which adsorption decreases due to desorption. Hence, the optimum treatment time can be 60 min for adsorption of methylene blue dyes from effluent.

4 Conclusion

The prime objective of this work is to produce cellulose nanocrystals adsorbent from sugarcane bagasse by acid hydrolysis method for treating methylene blue dye effluent. The dye removal efficiency has been analyzed. CNC has added advantage over activated carbon production (from energy mapping). CNC made from SB completely adsorbs methylene blue dye solution, and there is no new bond between dye and CNC. It is just physical adsorption. From TGA, it was concluded that for the adsorption to occur without any degradation, the adsorption temperature should be maintained below 150 °C. Desorption of MB dye from CNC in HCl and ethanol solution was successful; however, it affects the CNC itself during adsorption. Therefore, this adsorbent can be effectively utilized as an alternative sustainable source for removing MB dye from the effluent water collected from textile processing industries.

Author contribution VKR initiated the project and designed the experiment. RD co-designed the experiment to remove methylene blue dye from textile effluent using cellulose nanocrystals extracted from sugarcane bagasse. KSK, BV, and CP drafted the manuscript. VKR, RD, KSK, BV, and CP provided key comments for manuscript writing. All authors read and approved the final manuscript.

Data availability Not applicable.

Code availability Not applicable.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication All authors agree to the publishing of the paper.

Conflict of interest The authors declare no competing interests.

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