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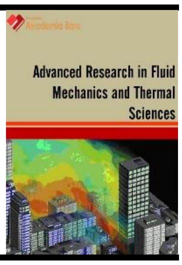

Heat-Treated CNC/PVA Composite from Natural Fibre for Wax Removal of Batik Wastewater Treatment

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ABSTRACT

Cellulose Nanocrystals (CNCs) have significant properties such as low density, high specific resistance, excellent mechanical properties, biodegradability, low-cost, low abrasive nature, and reactive surface for easy modification. Water contamination from various sources has become a serious problem in recent years. Hence, this study will serve the good application of composite nanocellulose in treating the wax from batik wastewater which needs proper treatment before releasing into the environment. This study also was aimed to synthesize CNCs/PVA composite from coconut fibre and used as adsorbent for the removal of wax from batik industry. The adsorption process was optimized based on parameters such as CNCs dosage and contact time. CNCs/PVA composites were prepared by constant mixing of CNCs suspension in PVA solution at 50°C for 1 hour, dried at 60°C overnight and heat treated at 190°C for 1 hour. Design of Experiments (DOE) was used to study the effects of CNCs dosage to PVA polymer (1-6 %v/w), contact time (15 min to 180 min) at a constant temperature and agitation rate of 48°C and 180 rpm respectively. The highest percentage of wax removal recorded was 50.23% at the optimal conditions of 6 %v/w of CNCs dosage at 180 min. By using natural wastes, the cost of pre-treatment process can be reduced, and this method is much simpler than other conventional methods. Besides, the conversion of the waste to a useful adsorbent also indirectly helps in minimizing the solid wastes.

1. Introduction

Batik industry is usually operated at the backyard house, workshops, and small factories without proper waste management systems. Like many other textile industries, this industry also contributes to water pollution since the wastewater contains wax, dyes, heavy metal, fixing agent such as silicate and resins [1]. Most of the treatment including ion-exchange, electrodialysis, biological coagulation,

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skimmers and different types of membrane filtration was reported to be not efficient in removing wax [2]. Membrane-fouling phenomena can occur if the wastewater is not pretreated before it undergoes the membrane filtration. It is a fact that textile industry like batik industry consequently generates hazardous wastewater. Wastewater from printing and dyeing processes are rich in color containing residue of dyes and chemicals [3]. The color of effluent is unacceptable under Malaysian Environmental Regulation. The distinctive feature that makes this industry different from other textile industries is the application of wax as in the design stage. Wax contains toxins and chemical fumes from paraffin waxes could pose serious health hazards such as irritation to eyes, skin and lungs and discomfort to the respiratory system for a long run time. In addition, a high level of toxic discharged into the rivers affect the quality of wastewater effluent, threatening the aquatic life and polluting water resources. This can be proven with the high COD value which is between 700 to 4900 mg/L, higher than the acceptable condition for discharged batik effluent [4]. Table 1 shows some characteristics of batik effluent compared to the standard level allowed by the Environment Quality Act [5, 6]. Batik wastewater has a high pH value which is usually more than pH 10. For proper treatment, wastewater should normally be in the range of 6.0 to 9.0.

Table 1
Characteristics of batik effluent [5-7] *Environmental Quality Act (Industrial Effluent Regulations, 2009)

Parameters	Effluent	Standard B
pH	11.8	5.5-9
COD (mg/L)	4092	200
BOD (mg/L)	341.25	50
TSS (mg/L)	1248	100
Color (ADMI)	1500	-

Note: Standard B is applicable to any other inland waters or Malaysian waters

Wong *et al.,* [8] use kenaf to specifically treat wax in batik wastewater and studied on the several parameters that can affect adsorption capacity which include contact time, weight of kenaf and the different form of kenaf. Based on the result obtained, it is proven that the powder form of kenaf adsorb wax better than the fibrous form because the tiny micropores in powder kenaf has a better trap zones for wax. For both cases, the highest adsorption capacity is when the contact time is 15 minutes and when 1.2g of adsorbent is used. The powder kenaf shown better adsorption since the efficiency of adsorbent depends on the surface area of adsorbent. When the surface area increased, the adsorption efficiency also increased.

On the other hand, Rashidi *et al.,* [2] did study on the removal of from the synthetic batik wastewater using baffle tank pretreatment. The synthetic wastewater used varying in the composition which include wax, resin, sodium silicate and 4 different types of dyes (Remazol Turquoise Blue G133 (Blue 21), Remazol Red 194, Remazol Yellow 14 and Reactive black 5). Rashidi *et al.* found that the wax removal of all different samples has approximately similar result which are more than 89 %. This means that only a slight change when using different types of dyes as in the synthetic wastewater. In addition, COD value decreased around 100mg/L from the initial value after undergoes the pretreatment in the baffle tank.

Rashidi *et al.,* continued the study in 2015 using the same baffle tank but the temperature is increased from the previous study which is from 48˚C to 70˚C. With the flow rate of 570L/h and 1 hour run, the result obtained is more than 92.5% wax removal efficiency was achieved by using this pretreatment method. The operational conditions such as coalescence-melted wax droplet size, type of dye, and amount of air diffused during the treatment cycles can explain the minor changes.

Moreover, there is only a slight difference recorded in wax removal efficiencies when using single or mixed samples.

In another study conducted by Siti Zuraida *et al.,* [9] the performance of Lactobacillus delbrukii shows that 52 % of color removal at the optimum condition at pH 6 and temperature at 37 °C while the microbial growth shows optimum condition at pH 7 and temperature 37 °C. The report concluded that the cell growth increased as the agitation speed increased but color removal decreased as the agitation speed was increased. It is important to find the optimum growth condition of the microbial in order to achieve maximal color removal by Lactobacillus delbruckii.

Considering the fact that CNCs have several advantages including low density, high specific resistance, excellent mechanical properties, biodegradability, low-cost, low abrasive nature, and reactive surface for easy modification, many researchers have extensively studied the extraction of CNCs from the natural plant cellulose fibres [10, 11]. Polyvinyl alcohol (PVA) is commercially used in broad applications as it is water-soluble, biodegradable, non-toxic, and biocompatible polymer [12]. Moreover, the transparency of the neat matrix can be maintained by using CNCs as a filler [13]. Synthetic polymeric materials such as chitosan, polyvinyl alcohol and cellulose is used to develop membranes [14].

Adsorption is one of the common methods used in wastewater treatment. The commercial adsorbent used for removal of waxes is activated charcoal which is efficient in removing contaminants. But, activated charcoal is very expensive because higher production cost and creates environmental issue [15]. In addition, the commercial adsorbents contain organic synthetic products such as polyurethane and propylene; and have difficulty to decompose. In this paper, CNCs were extracted from coconut fibres, reinforced with Polyvinyl alcohol (PVA) for the removal of wax in the batik wastewater.

This study focuses on the preparation of CNCs reinforced PVA polymer composite. The CNCs were extracted from coconut fibres and the CNCs/PVA composites were used to test for the removal of wax from batik wastewater under parameter of adsorbent dosage and contact time.

2. Methodology

2.1 Wastewater Sample Preparation

Batik wastewater sample was collected directly from Institute of Kraftangan Negara located in Rawang, Selangor which is an active learning institute that provides batik printing. The wastewater was stored at 4°C in order to maintain the condition of wastewater sample. Wastewater was analyzed according to standard method for Chemical Oxygen Demand (COD) and pH.

2.2 Preparation of Coconut Fibres

Coconut husks were collected from local market located in Gombak, Selangor. Coconut fibres were extracted manually from coconut husks and washed with distilled water to remove the surface dirt present in the fibres. This step important to remove impurities and waxy substances covering the external surface of fibres' cell walls according to the method described by Rosa *et al.* [16]. Then, the fibres were dried in the oven at 60˚C for 24 hours, grinded until small-sized fibres form. After that, the fibres were stored in air-tight lid containers at room temperature for further use or analysis.

2.3 Extraction of CNCs

Cellulose Nanocrystals (CNCs) were extracted according to the processes of cellulose separation through bleaching and CNCs extraction via acid hydrolysis (section 2.3.2).

2.3.1 Bleaching of fibres

Firstly, the fibres were bleached in the proportion of 1:20 (w/v) with 5% (w/w) H_2O_2 under constant stirring for 90 minutes at 50°C. The bleached fibres were filtered through a Whatman paper filter and rinsed with distilled water. This bleaching process using H_2O_2 was repeated. Finally, the fibres were stirred with 3.8% (w/w) NaOH for 90 minutes at 50°C, filtered through a Whatman paper filter, and washed with distilled water until the pH was neutral to obtain the cellulose bleached pulps. The cellulose bleached pulps were oven-dried at 45°C until a constant weight was obtained and was stored at room temperature for further use.

2.3.2 Acid hydrolysis

The cellulose bleached pulps undergo acid hydrolysis in the proportion of 1:20 (w/v) with high H_2SO_4 concentration (60% w/w), short reaction time (45 minutes), and low temperature (45°C). Next, CNCs extracted were diluted by 10-fold with deionized water and centrifuged three times for 15 minutes at 13 000 rpm (26 400 g) until the supernatant became turbid. Between each centrifugation step, ultrasonic (UNIQUE – Cell Disruptor) was applied at 90% power for 5 minutes to prevent particle agglomeration. Afterwards, the colloidal suspensions were dialyzed with distilled water for 72 hours.

2.4 Preparation of CNCs/PVA Composites

Initially, PVA solution was prepared by dissolving 1 g of PVA powder in distilled water at a concentration of 5 wt % followed by constant stirring at 90◦C 100 ml for 2 hours. CNCs suspension was added to PVA solution. The mixtures were further stirred for 1 hour at 50°C. The final suspensions were then cast in the petri dish evenly to get thin films and dried at 60◦C in order to ensure complete removal of water. After that, the films were subjected to further heat treatment at 190°C for 1 hour. Lastly, the films were kept in desiccator to maintain the moisture content of the films.

The CNCs/PVA was analyzed using Fourier Transform Infrared Spectrophotometer (FTIR) to determine various functional groups present in the composites between the ranges of frequencies 4000–600 cm^{-1}.

2.5 Optimization for Percentage of Wax Removal

Wastewater and composite were introduced into the shake flask. The shake flask was placed in the incubator shaker at 48˚C under agitation speed of 180 rpm. After desired contact time, the composites were filtered from wastewater samples and kept at room temperature overnight until weight became constant. The amount of wax adsorbed, and the percentage of wax removal from batik wastewater were calculated by Eq. (1) and (2) respectively.

$$\text{Wax adsorbed (g)} = (\text{C}) - (\text{A}) - (\text{B}) \quad (1)$$

where
A –Weight of aluminum boat (g);
B –Initial weight of composite (g);

C –Weight of dried composite (g)

$$\text{Percentage of wax removal (\%)} = \frac{W_p}{W_f} \times 100 \qquad (2)$$

where
W_p –Permeate wax (g);
W_f –Feed wax (g)

2.6 Experimental Design

Factorial Central Composite Design (FCCD) was used to optimize the design for percentage of wax removal from batik wastewater with two central points and 13 runs. The interaction of variables on the response and effect of individual parameters was represented by Analysis of variance (ANOVA). Thus, ANOVA was performed to study the significance and fitness of the model.

3. Results

3.1 CNCs/PVA Composite Characterization

Fourier-transform infrared spectroscopy (FTIR) was performed in this study to identify the functional groups present in the CNCs/PVA composite. Figure 1 shows the spectra for 6 %v/w PVA/CNCs composite. The large bands were observed between 3550 and 3100 cm^{-1} which related to O-H stretching due to the intermolecular and intramolecular hydrogen bonds of hydroxyl groups in the PVA matrix [12]. The presence of CNCs produced distinctive changes in the shape and intensity of the main peaks. This was explained by the presence of three additional bands at 1242 cm^{-1}, 1088 cm^{-1} and 1033 cm^{-1} [17].The presence of peak in between 3000 cm^{-1} and 2850 cm^{-1} was the evident for stretching of C-H from alkyl groups. Besides, the vibrational band was observed between 1750 cm^{-1} and 1730 cm^{-1} which assigned to the C=O and C-O stretching from acetate groups in the PVA matrix. This result indicates that the study was success in producing CNCs reinforced PVA matrix composite.

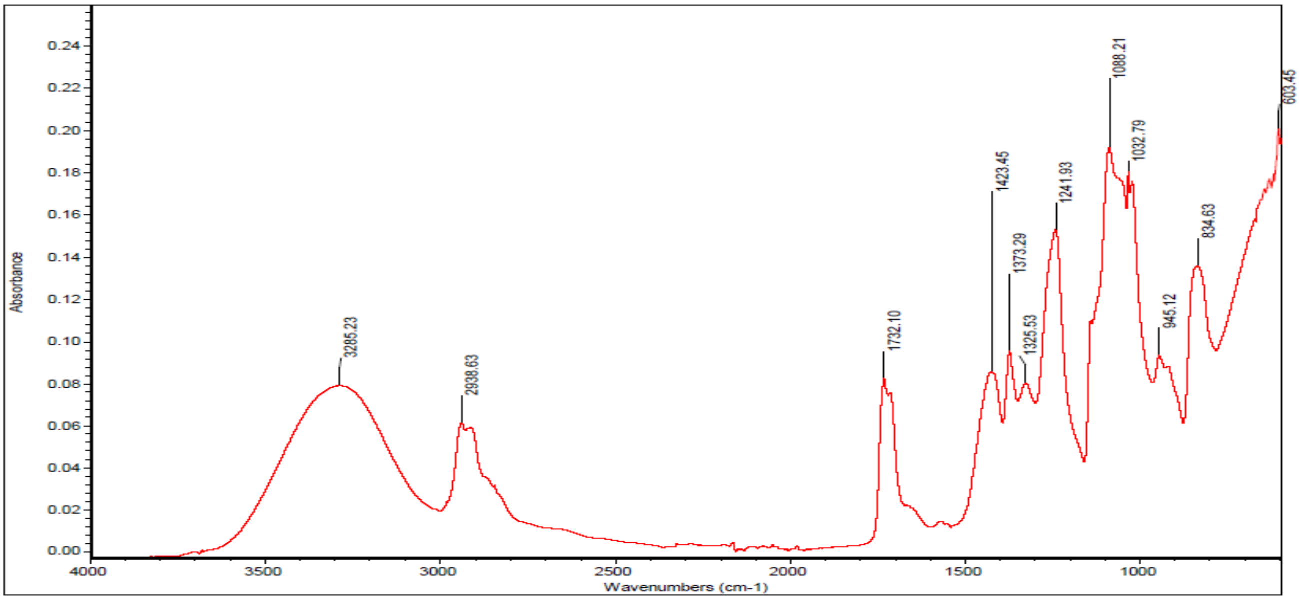


Fig. 1. FTIR spectra corresponding to 6 %w/v of CNCs/PVA composite

3.2 Optimization of Adsorption Process

Figure 2 shows the correlation of the variation in dosage of CNCs and contact time used for the adsorption process. Based on the three-dimensional (3D) plotted in Figure 2, the highest percentage of wax removal was 50.23 % which subjected by the 6 %v/w of CNCs ratio to PVA and the contact time of 180 min. The lowest percentage of wax removal was observed to be 20.47% when using 1 %v/w of CNCs and at 15 min contact time.

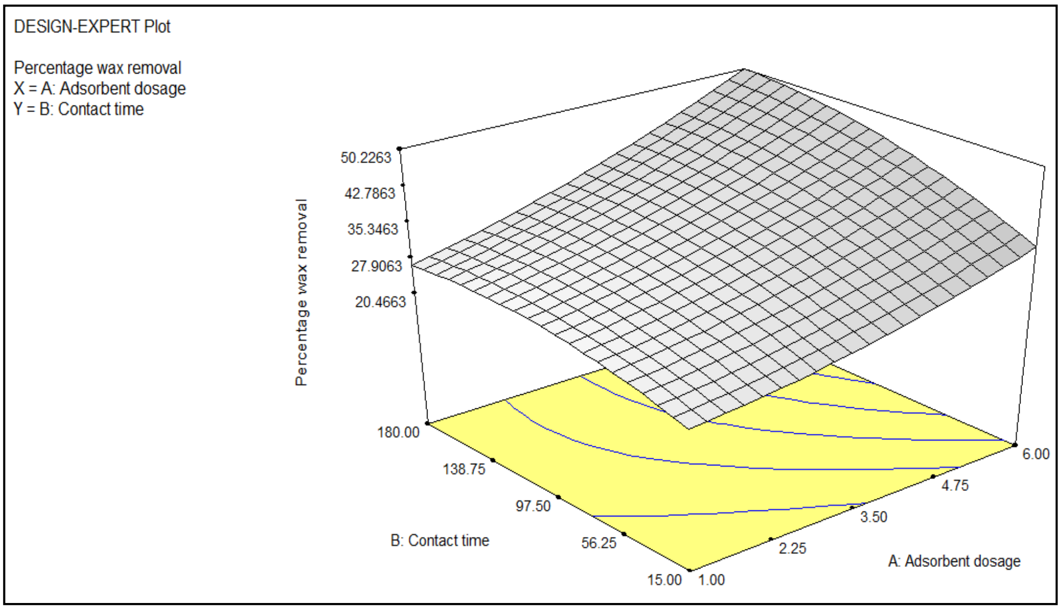


Fig. 2. Effect of CNCs dosage and contact time to the percentage of wax removal

3.3 Characterization of Batik Wastewater

Figure 3 shows that the pH of the samples decreased slightly from the initial value of 10.68 in the range of 0.4 to 1.2 after adsorption process compared to the initial sample of wastewater. This was explained by the removal of a small amount of wax and other unknown impurities which had alkaline properties in the wastewater subjected to the adsorption process which also been reported by Rashidi *et al.,* [2]. In addition, Figure 3 illustrated that the longer the contact time, the greater the amount of pH been reduced. The reduced pH between 9.51-10.27 was in accordance with Rashidi *et al.,* [2] who treated the wax with paraffin.

It had been observed that the batik wastewater was subjected to a difference in color before and after adsorption took placed as shown in Figure 4. This happened due to the conditions during adsorption process which includes agitation, time, temperature and the presence of wax and other compounds which caused the reduction in the reactivity of the dyes [18]. Therefore, the minority groups of the dye components were also removed by the composites along with the wax.

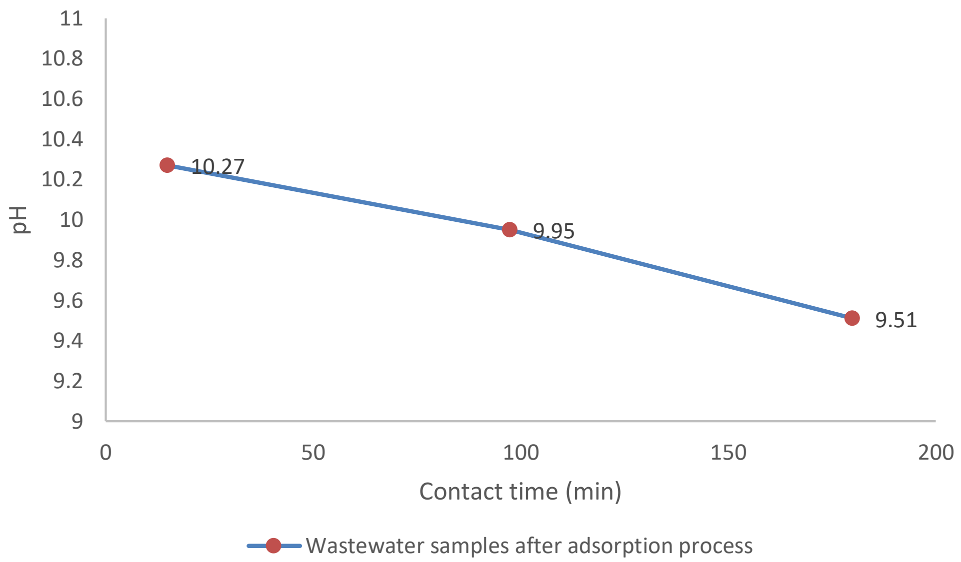
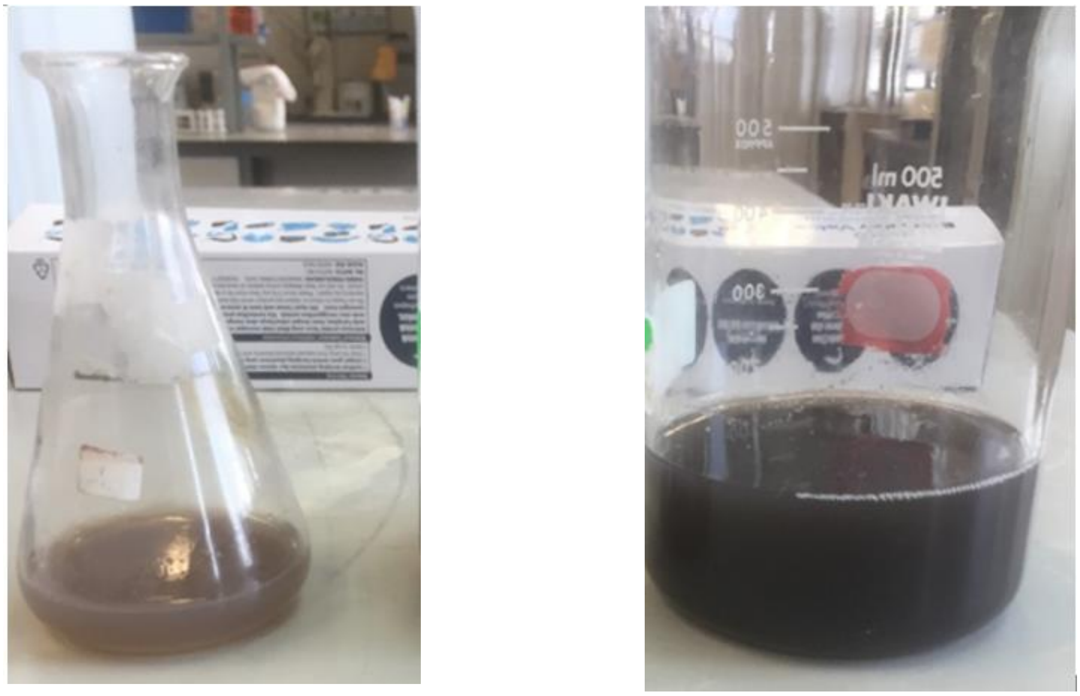


Fig. 3. pH of wastewater samples before and after wax removal



(a) (b)

Fig. 4. **(**a) wastewater after adsorption process at 180 min contact time and (b) wastewater before undergoes any adsorption process

The existence of wax particles in batik wastewater, as well as the other common chemical and physical pollutants such as dyes sodium silicate had a significant impact towards the level of COD. However, based on the study by Rashidi *et al.,* [18], wax particles were the highest contributor for the high level of COD compared to the other pollutant's presence in the batik wastewater. Figure 5 represents the COD value of samples, (with the initial value was 1135 mg/L) with 6 %v/w CNCs dosage at different contact time. It was found that the COD value decreased in the range of 80 mg/L to 270 mg/L after the adsorption process. This phenomenon proved that adsorption process at different contact time did affect the amount of COD of the wastewater samples. In another study, bio equalization tank was used to remove the batik wastewater. A reduction of total suspended solids (72%) was observed due to the separation of settleable components such as alum sulfate, sodium silicate, and floatable wax [19].

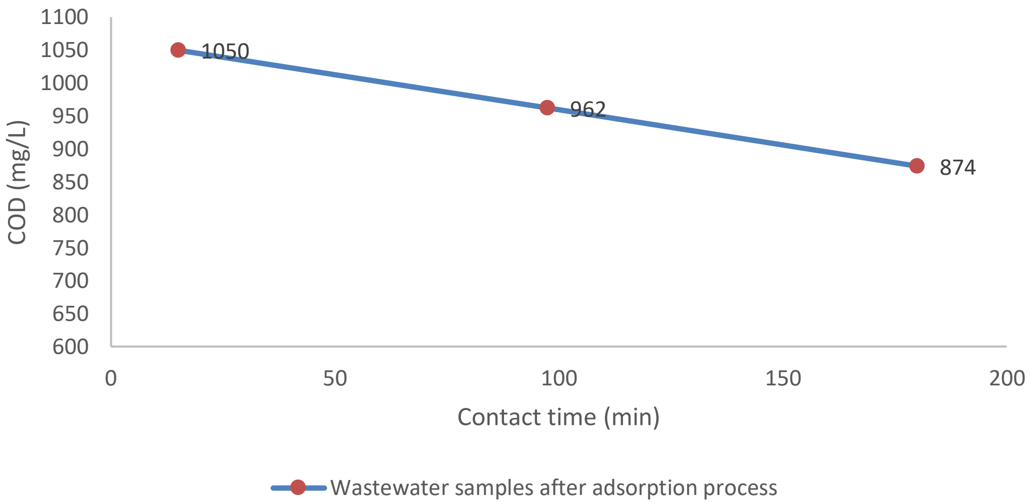


Fig. 5. COD values of wastewater samples

4. Conclusions

In conclusion, the present study had proved that the CNCs extracted from coconut fibres can be alternative source to synthetic adsorbent such as polypropylene. It is a good opportunity to convert coconut husk, an agricultural waste into useful adsorbent. This adsorbent can be an attractive alternative for wastewater treatment as it is inexpensive and readily. The maximum percentage of wax removal, 50.23% was achieved at 6 %v/w CNCs ratio to PVA at 180 min. Looking at the current scenario of environment pollution, there is a great need for research on the treatment of textiles industry effluents by using cheaper materials to protect our environments.

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