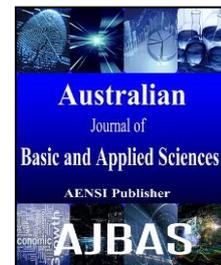




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Nano Crystal Cellulose Incorporated Poly Vinyl Alcohol (PVA) Hydrogel for Industrial Waste Water Treatment

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ABSTRACT

In this work, nanocrystalline cellulose (NCC) was extracted from raw oil palm empty fruit bunch (EFB) fiber using ultrasound assisted hydrolysis. The freeze-thawing cyclic process was applied to fabricate NCC incorporated polyvinyl alcohol (PVA) hydrogel. The aim of this work is to improve the removal capacity of methylene blue (MB) dye from industrial wastewater using NCC incorporated PVA hydrogel. The NCC microstructure was evaluated by X-ray diffraction (XRD) analysis. Scanning electron microscope (SEM) reveals the comparative surface morphology of REFB and NCC. The prepared PVA/NCC hydrogel was then used to adsorb methyl blue (MB) solutions. The gel fraction NCC-PVA hydrogel is lower as compared to neat PVA hydrogel. Due to the presence of NCC, PVA/NCC hydrogel showed much enhanced adsorbing performance as compared to neat PVA hydrogel. The prepared PVA/NCC hydrogel can be one of the potential adsorbent for dyes removal application in the future.

INTRODUCTION

Recently, the released of toxic dyes in wastewaters by industries of textile, rubber, paper, leather, plastics, cosmetic and printing industries has lead to the one of the major environmental problem. The toxic dyes in wastewater give the pollutions that generate several problems for ecosystem (VenkatrajanGopalakannan, NatrayasamyViswanathan, 2016). These dye pollutants need to be removed for healthier ecosystem and environmental. Different techniques are used to remove the pollutant dyes, for instance, biosorption, photo degradation, coagulation, electrochemical oxidation, ozonation, reverse osmosis, adsorption and others (S. Vasudevan *et al.*, 2010). Based on these methods, the adsorption process is a promising technique to remove the dye molecules. The adsorbents which are carbon materials, clay material, biomaterials, nanoparticles, nanocomposites, leaves and fly ash have been used for the removal of dyes (Agarwal *et al.*, 2016).

Nowadays there are increasing research growths in a development of hydrogels. Hydrogels, generally meanings of 'hydro' as water and 'gel' which is substances are defined as a three dimension network structure of hydrophilic polymer containing large amount of water and have capability of moisture adsorption. Hydrogels can be produced by either using natural polymer (eg: starch, gelatine, chitosan, gum acacia), synthetic polymers (eg: PVA, PVP) or blending both of them. Among these sources, PVA have been gaining interest in the development of hydrogels. Poly(vinyl alcohol) (PVA) hydrogels are biocompatible, non-toxic and can absorb a huge amount of exudates (Gonzalez *et al.*, 2014). PVA hydrogels can be produce by a few method such as electron beam irradiation, bulk mixing with crosslinking agents such as glutaraldehyde and freeze thawing cyclic process. Although PVA hydrogel is the promising materials to removed dyes, however PVA like other synthetic

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hydrogels, have a limitation which containing over 50% water, are tend to brittle and have poor microstructural and lack in mechanical stabilities (Elbadawy *et al.*, 2015).

In order to overcome this problem, the additional of nanofiller are used in order to improve thermal and mechanical stability as well water adsorption of hydrogel. Recently, nanocrystalline cellulose (NCC), have gained considerable interest as a promising biomaterial due to their outstanding properties such as high surface area, high mechanical property, hydrophilicity, biocompatibility, and biodegradability (Xuezhuet *al.*, 2013). The NCC also has good stability in water which compatible for mixing of water base polymer solution or emulsions with NCC. Furthermore, due to unique characteristics, NCC has been incorporated as fillers in several polymeric matrices. The aim of this work is to improve removal capacity of methylene blue (MB) dye from industrial waste water using NCC incorporated PVA hydrogel.

MATERIALS AND METHODS

Materials:

EFB Fiber (EFB) was received from MPOB Bandar Lama Bangi. Sodium hydroxide (NaOH), Dimethyl Sulfoxide (DMSO), Sulphuric acid (H₂SO₄), (95-98 wt%) were purchased from Sigma Aldrich and the dialysis bags (MW cut off 12,000-14,000, 25mm) was purchased from SH Kekal Enterprise.

Preparation of Nanocrystalline cellulose (NCC):

The slurry of EFB Pulp was hydrolysed with 64% (w/v) H₂SO₄ solution. The hydrolysis was carried out at 45°C for 1.5 hour in an ultrasound bath, Elma 37kHz (made in German), having device power capacity of 320 W. At the end of hydrolysis process, the suspension of nanocrystalline cellulose (NCC) was centrifuged to remove the acid solution and washed with ultra-pure water until the P^H became neutral. The washed NCC was dialyzed by using dialysis membrane (MW cut off 12,000-14,000, 25mm) against ultra-pure water for several days until the pH of ultra-pure water is constant. Finally, the dialyzed NCC was again exposed in ultrasound bath for 30 min to disentangle them and oven dried at 60°C.

Preparation of PVA/NCC hydrogel:

Neat PVA hydrogel was prepared by dissolving 10 wt% PVA in ultrapure water, the solution PVA dissolving carried out in an autoclave at 120°C. The concentration of NCC was maintained with respect to the PVA weight, 1 wt% NCC was dispersed in the PVA solution using mechanical stirring followed by sonication for 30 min. PVA/NCC suspension was kept in a calm place for 30min to remove unwanted bubbles.

The neat PVA solution and PVA/NCC suspension was poured in the mould and the thickness was maintained around 3mm. The hydrogel formation was carried out by freeze-thawing technique. At firsts these moulds were frozen in a freezer at -85°C for 1 hour, and then exposed in room temperature (25°C) for another 1 hour. Similar cycle was conducted for three times in order to form physical crosslink hydrogel.

Characterization:

X-ray diffraction (XRD):

X-ray diffraction (XRD) data was collected by using a Rigaku Mini Flex II, Japan, operated at 30 kV, at 15mA and equipped with computer software to analyze the data. The REF and NCC specimens were step-wise scanned over the operational range of scattering angle (2θ) between 3 to 50°, with a step of 0.02°, using CuK_α radiation of wavelength λ=1.541Å. The data were recorded in terms of the diffracted X-ray intensities (I) versus 2θ.

Field Emission Scanning Electron Microscope:

The morphology of REF and NCC were observed by using a field emission scanning electron microscope (FESEM) (JOEL, JSM-7800F, Japan). Samples were mounted on aluminium stubs with a carbon tape followed by a sputter coating with platinum to make them conductive prior to the field-emission scanning electron microscopy (FESEM).

Gel fraction:

The weight ratio of the dried hydrogels in rinsed and unrinsed conditions can be assumed as an index of degree of crosslinking or gel fraction. Therefore the gel fraction of samples can be calculated by the following equation:

$$GF (\%) = \frac{M_f - M_c}{M_i - M_c} \times 100$$

Where M_f and M_i are the weights of the dried hydrogel after and before rinsing and extraction, respectively and M_c is the weight of NCC incorporated into the sample.

To perform gel fraction measurement, pre-weighed slice of each sample was dried under vacuum at room temperature until observing no change in its mass. Nearly identical weight of another slice of the same sample was immersed into excess of Ultra pure water (UPW) for 4 days to rinse away unreacted species. Subsequently, the immersed sample was removed from UPW and dried at room temperature under vacuum until the dried mass showed constant weight.

Evaluation of Dye absorption:

The stock solution (1000 ppm) of methylene Blue (MB) dye was prepared by dissolving accurately weighed quantity of dye in 1 L of deionized water. The 10 ppm solution was prepared by diluting the stock solution. The concentration of MB dye was measured by UV-Vis spectrophotometer at the wavelength of $\lambda_{\max} = 664$ nm. A fresh dilution has been maintained during experimental process. The pH of the solution was maintained and kept at constant by adding 0.1 M HCl or 0.1 M NaOH.

RESULTS AND DISCUSSION

Structural Analysis of EFB fiber and NCC:

Fig 1 demonstrates the X-Ray diffraction patterns of raw EFB fiber and NCC. The profile of raw EFB represents the scattering angle at 15.52° , 22.73° and 34.93° exhibiting crystal planes (101), (002) and (040) respectively. The NCC also shows the scattering angles at 14.91° , 22.60° and 34.10° Oudiani *et al* (2011). The observed peaks of 22° and 14.91° representing the 110 and 200 cellulose crystallographic planes which is found in EFB and NCC are associated with the crystalline structure in cellulose I (J.C. C.S. *et al.*, 2016). Additionally, the full width at half maximum (FWHM) values illustrates that scattering peaks of NCC are narrower as compared to the raw EFB fiber. The FWHM (δ), average crystal size (D) in the direction normal to the reflecting plane, the lattice spacing d , and crystallinity index (C_i) are summarized in Table 1. The crystal size was determined by the Scherrer's equation (1) (Wen Ling Zhang *et al.*, 2011).

$$D = \frac{0.9\lambda}{\delta \cos \theta} \quad (1)$$

The crystallographic spacing (d) was calculated by following Bragg's equation (2). The degree of crystallinity (C_i) was calculated using the equation (3) (A.K. M. MoshuiAlam *et al.*, 2016);

$$\lambda = 2d \sin \theta \quad (2)$$

$$C_i (\%) = \frac{I_c}{I_c + I_A} \times 100 \quad (3)$$

where, I_c and I_A are the integrated intensities of crystal and amorphous parts of the samples, respectively.

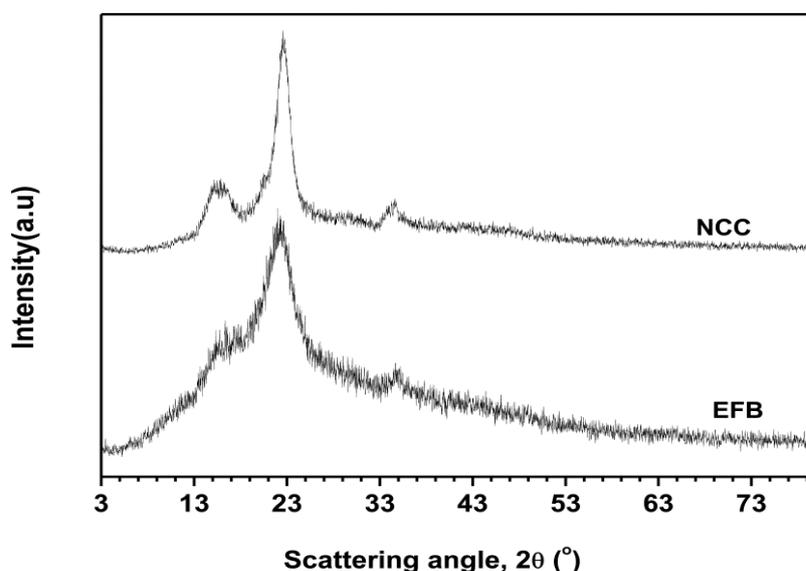


Fig. 1: XRD profiles of EFB fiber and NCC

Table 1: XRD parameters of raw EFB and NCC

Sample	2θ ($^{\circ}$)	FWHM($\Delta 2\theta$) ($^{\circ}$)	D(\AA)	d(\AA)	C_i (%)
EFB	15.52	4.56	17.59	5.71	52
	22.73	1.89	42.90	3.91	
	34.93	3.4	24.51	2.60	
	14.91	2.53	31.68	5.94	
NCC	22.60	1.79	45.30	3.93	83
	34.10	1.70	48.41	2.96	

The crystals size and the lattice spacing of NCC for every plane are increased as compared to raw EFB fiber. Moreover, the crystallinity of NCC was increased by 59.6% as compared to raw EFB fiber. As shown, the crystallinity of NCC is higher than the REFB shows that the increasing in rigidity of crystalline structure and as a result give the higher tensile strength(M.K.Haafiz *et al.*, 2013). The highest crystallinity obtained from NCC is due to the removal of hemicellulose during acid hydrolysis process(Wei Liet *al.*,2011). Another, reason may due to the removal of amorphous region from cellulose thus leaving crystalline regions(M.K. Haafiz *et al.*, 2013). These observations suggested that impurities have been removed from the EFB fiber and nano-cellulose was isolated with high crystallinity.

Morphology of raw EFB and NCC:

Fig 2 illustrates the morphology of raw EFB fiber and NCC. It is obvious that the crack on the surface of raw EFB is visible; additionally the surface is rough and existing some impurities. Whereas a huge number of rod-like nano celluloses are visible in the micrograph of NCC (B). The width of NCC was measured at around 33 to 41nm. Finally, this observation confers that NCC has been extracted from the EFB fiber.

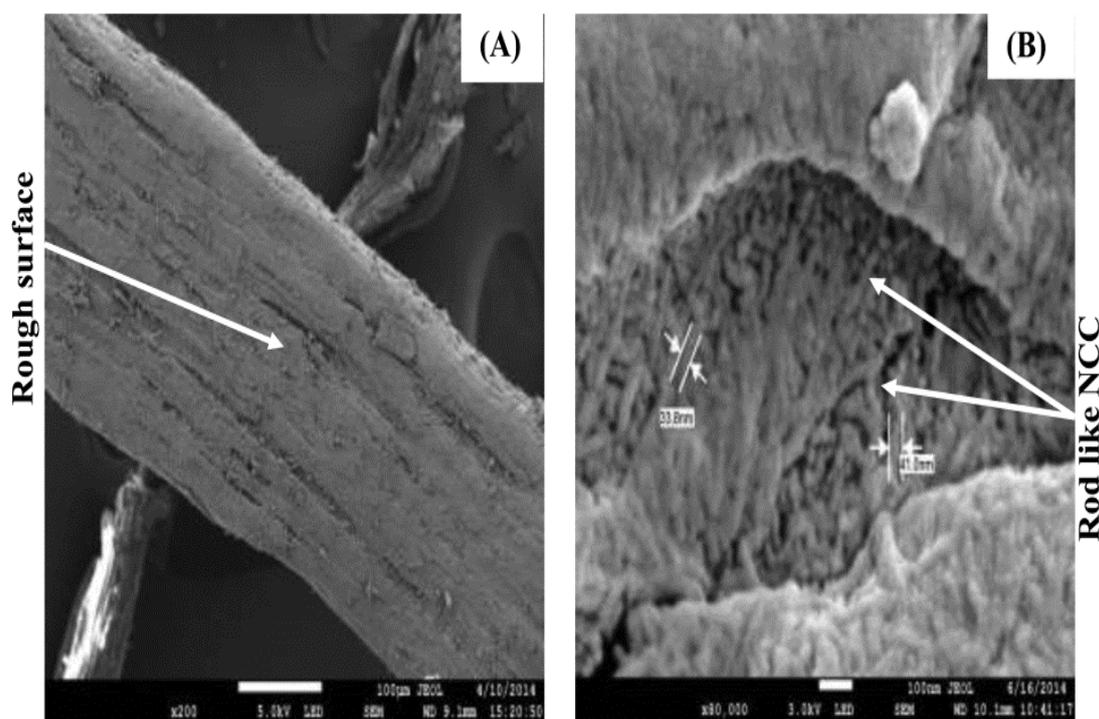


Fig. 2: FESEM Micrographs of raw EFB (A) and NCC (B)

Gel Fraction of Neat PVA and NCC-PVA hydrogel:

Fig 3 represents the gel fraction of neat PVA and NCC-PVA hydrogel. The freeze-thawing technique was led to formation of cross-linking in neat PVA and NCC-PVA aqueous solutions. The gel fraction demonstrates the degree of cross-linking in the hydrogel. The neat PVA shows 78% gel fraction% which suggests that the PVA was approximately crystallized in the highest degree and consequently cross-linked. However, the GF of NCC-PVA hydrogel was reduced by 6.41 due to the presence of physical hydrogen bonding interaction between water and NCC which may reduce the crosslinking reaction and keeps these molecules at a distance leading to lower gel content. Therefore, NCC reduced the crosslinking reaction as well as gelation process of PVA molecules Jong Oh Kim *et al* (2008).

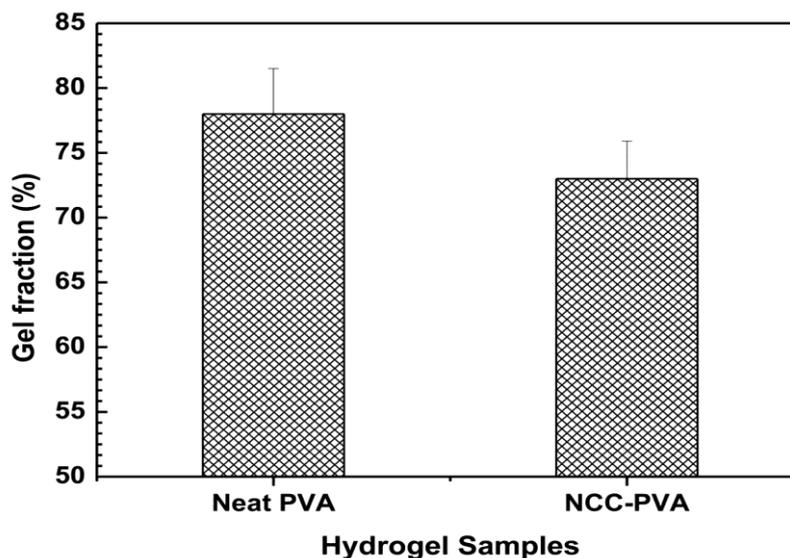


Fig. 3: Gel fraction of Neat PVA and NCC-PVA hydrogel

Dye absorption behavior of neat PVA and NCC-PVA hydrogel:

Fig 4 demonstrates the MB dye absorption behavior of neat PVA and NCC-PVA hydrogel as a function of time. It is obvious that both hydrogel absorbed the dye and the concentration remaining in solution was declined steadily with respect to increasing the retention time Shilpi Agarwal *et al* (2016). Additionally, the dye removal capacity of NCC-PVA hydrogel was higher as compared to the neat PVA hydrogel. Therefore, it is suggested that active side in NCC-PVA hydrogel was enhanced due to the incorporation of NCC filler. This reason attributed to the large number of pendent -OH groups (2 secondary and 1 primary per anhydrous glucose unit) occupied by NCC as a hydrophilic polymer which provide more hydrophilic environment in cross-linked network of PVA hydrogel and thus holding large of amount water molecules. Therefore the incorporated of NCC content into PVA hydrogel will increase the water absorption of the hydrogels. Moreover, NCC has reduced the gel fraction of NCC-PVA hydrogel system as a result increased the overall swelling of dye solution which enhanced the absorption performance as well.

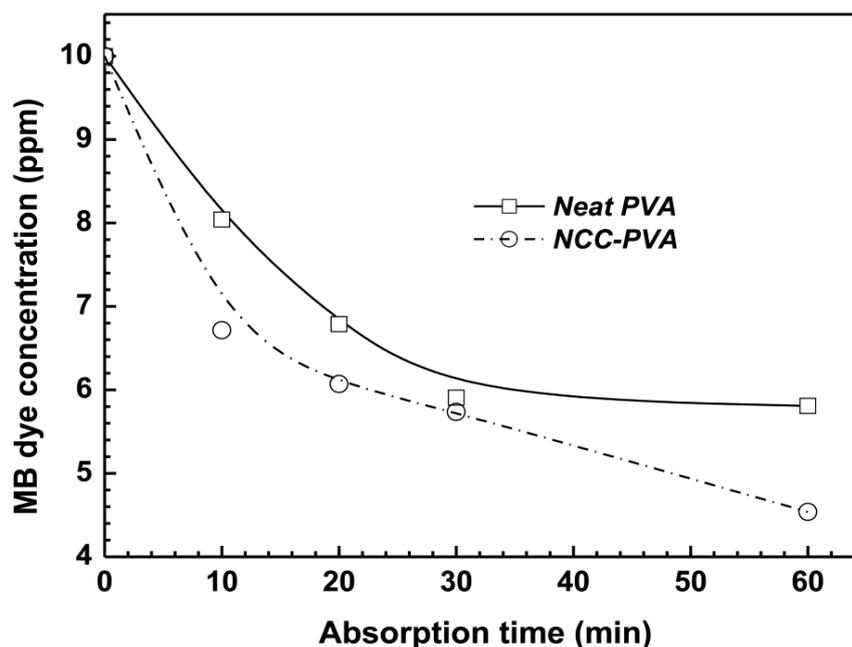


Fig. 4: Dye absorption behavior of neat PVA and NCC-PVA hydrogel at different time

Conclusion:

The NCC was isolated from raw EFB fiber and the microstructure properties of NCC were noticeably improved as compared to raw EFB fiber. Morphology reveals that most of the NCC are as like as rod shape. NCC incorporated hydrogel was fabricated by using freeze-thawing cyclic process. The NCC hindered the cross linking process of PVA in NCC-PVA hydrogel, as a result gel fraction was reduced. The dye removal capacity of NCC-PVA hydrogel was higher as compare to neat PVA hydrogel as a function of time. It is showed that the PVA/NCC hydrogel can be used as a potential adsorbent material for removal of cationic dyes in wastewater industry.

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