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Article · August 2019

DOI: 10.11113/amst.v23n2.154

4 authors:

Haziqatulhanis Ibrahim
Universiti Malaysia Pahang

Norazlianie Sazali
Universiti Malaysia Pahang

Ihsan Naiman
Universiti Malaysia Pahang

Mohd Syafiq Sharip
Universiti Malaysia Pahang

J. Applied Membrane Science & Technology, Vol. 23, No. 2, August 2019, 45–56

Nano-structured Cellulose as Green Adsorbents for Water Purification: A Mini Review

H. Ibrahim[a], N. Sazali[a,b]*, I. N. Ibrahim[a] & M. S. Sharip[a]

[a]Faculty of Mechanical Engineering, Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia
[b]Centre of Excellence for Advanced Research in Fluid Flow (CARIFF), Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

Submitted: 9/3/2019. Revised edition: 9/4/2019. Accepted: 10/4/2019. Available online: 15/7/2019

ABSTRACT

Celluloses are natural polysaccharides that have garnered attentions in recent years due to their sustainability, availability and notable applications in various fields. Whilst demand of clean water sources keep increasing, modified nano-structured cellulose derived from agricultural waste showed a good prospect in adsorbing pollutants from water. To date, large number of studies have reported the performance of nanocellulose in removing wide range of pollutants from effluents. The purpose of this mini review is to present an overview of existing literatures on the utilization of nanocellulose-based materials as adsorbent for water remediation and make aware of possible development of integrating adsorption and nanotechnology for water separation and purification.

Keywords: Nanomaterials, heavy metal removals, adsorption, cellulose, and wastewater

1.0 INTRODUCTION

Various materials have been investigated in the past decades in effort to attain cleaner water sources. Recently, researchers are focusing more in developing a low-cost adsorbent with high sorption capacity, that able to treat waste effluent containing metal ions and other pollutants. Adsorption is a process when adsorbate such as heavy metals or dyes adsorbed onto the surface of liquid or solid adsorbent [1, 2]. Potential of cellulose as natural adsorbent was discovered and reported in several literatures [3–5]. Cellulose can be found abundantly on the Earth with an approximate total production of hundred billion to trillion tons per year [6–8]. Nanocellulose, having properties of high surface area are more promising than natural-sized cellulose. Generally, nanocellulose have been used in various applications and not limited to only water purification. For instance, food industry in 1983 had introduced the usage of nanocellulose as food additive whilst in medical field, nanocellulose membrane are known to be an aspirant for wound dressing [9, 10]. Current studies are investigating the efficiency of nanocellulose as adsorbent in enhancing purity of water.

Natural waters contain low amount of metal ions but due to different contaminations, it is not safe to consume as it exceeds international standards limit (in Table 1) for drinkable water. Few sources of contaminations which is mainly from human activities include wastewater from various factories in industrial area,

* Corresponding to: N. Sazali (email: azlianie@ump.edu.my)
DOI: https://doi.org/10.11113/amst.v23n2.154

agriculture activities and municipal wastewater [2].

Table 1 Drinkable water standards

Toxic contaminant	Permissible limits (ppm)	Reference
Chlorine	5	[11]
Cadmium	0.003	[12]
Chromium	0.05	[13]
Lead	0.01	[14]
Zinc	3	[15]
Nitrate	50	[16]

Presence of toxic pollutants in water source does not only threaten human being but also to all living organisms and the environment, especially aquatic life. Numerous techniques for pollutant removal have been developed in past literatures but still not efficient enough in lowering contaminants concentration to a safe level [2, 17]. Some existing methods to treat the wastewater are reverse osmosis, ion exchange, precipitation and electrochemical treatments [18]. The methods were revealed to have drawbacks in terms of cost, energy and production of sewage sludge [2]. Therefore, the aim of this work is to highlight recent works from various researchers on nanocellulose applications as a green adsorbent for removal of pollutants in waste water.

2.0 NANOCELLULOSE EXTRACTION

Cellulose is made up of several linear β-(1,4)-d-glucose chains, which gathered and formed cellulose microfibrils structures [5, 19]. Representation of its chemical structure is illustrated in Figure 1. Cellulose can be derived from plants, bacteria, algae and tunicates. Following the source and extraction method of the cellulosic material, characteristics as well as quantity of the cellulose will differs [19]. According to Das *et al.* [20], plants are the main source for production of cellulose compared to other sources due to their abundancy in nature. Common plant-based cellulose sources are from agricultural by-products include rice husk, pineapple leaf, corncob, tomato leaves and sweet potato residue [21–25].

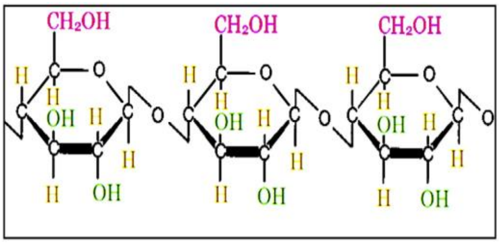

Figure 1 Cellulose chemical structures [19]

There are two treatments for nanocellulose isolation, namely chemical treatment and mechanical treatment in which affects the type of nanocellulose formed after. To obtain nanofibrils form, CNF, cellulosic material undergone mechanical treatment such as micro-fluidization, homogenization, grinding process and sonication [26–28]. Whilst to acquire nanocrystalline-structured cellulose, CNC, further chemical treatment need to be done such as acid hydrolysis, oxidation and cationization [29]. This chemical treatment helps to remove amorphous region (as illustrated in Figure 2) from the nanofibrils, leaving only crystalline region.

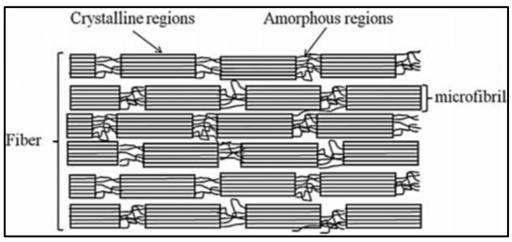

Figure 2 Schematic structure of semi crystalline cellulose fibre [28]

Even though the morphology is different, both CNF and CNC are having same nanoscale diameter size. While the length of nanocrystal is in nanometre, nanofibril have a bigger length size, measured in micrometre. Figure 3 shows the morphology for different nanocellulose family extracted from same biomass source, except for bacterial cellulose.

As aforementioned, different raw materials produced different quantity and composition of cellulose. Extraction of nanocrystal cellulose from pineapple peel by Madureira *et al.* [30] found that lignin is the main component consist in the peel compositions. Besides, hemicellulose and ash were also present in the peel composition with percentage of 16% and 4% respectively before undergoing further chemical treatment. Another researcher attempted an extraction of cellulose from passionfruit peels, where the composition agreed with Madureira *et al.*, having lignin (36.18%) as the major components, followed by cellulose (28.58%) and hemicellulose with 23.01% [31]. On the contrary, a study done by Lu *et al.* found that main component in sweet potato residue was cellulose with 85.47%, followed by 12.81% hemicellulose and lignin 2.27% [25]. Overview for untreated cellulose compositions derived from various sources is shown in Table 2.

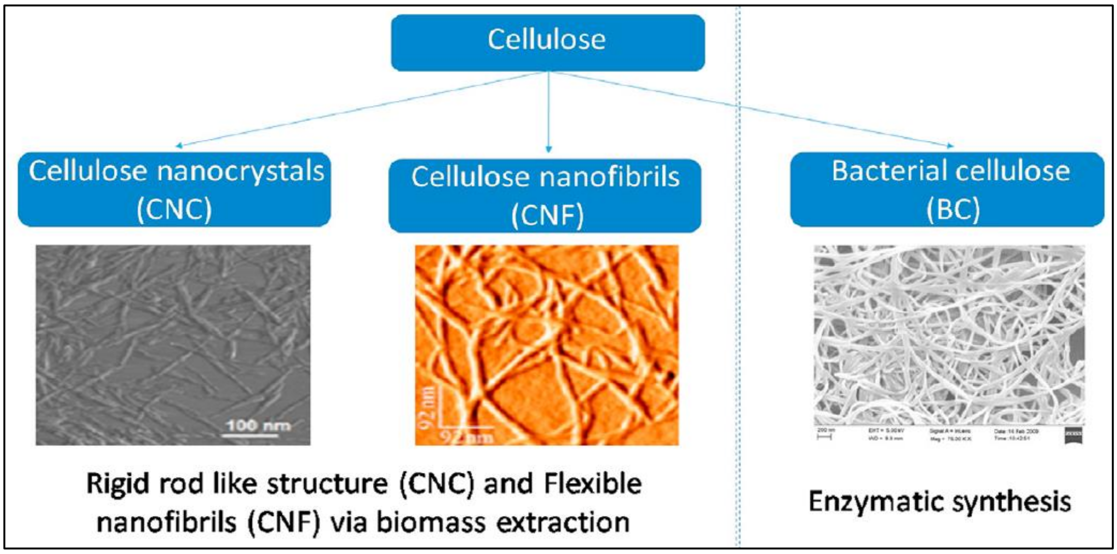

Figure 3 Structure of cellulose nanocrystals, cellulose nanofibers and bacterial cellulose [32]

Table 2 Composition of cellulose and other components from different sources

Source	Percentage of compositions (%)				Ref.
	Cellulose	Hemicellulose	Lignin	Other	
Pineapple leaf	36.3	22.9	27.53	2.85 (Ash)	[22]
Corncob	31.2	43.1	16.5	2.00 (Ash)	[23]
Sweet potato residue	85.47	12.81	2.27	-	[25]
Pineapple peel	16.9	15.8	28.9	3.92 (Ash)	[30]
Passionfruit peel	28.58	23.01	36.18	5.71 (Ash)	[31]
Lime residue	11.46	10.18	7.29	32.15	[33]
Pandan leaves	43	54	44	0.69	[34]

3.0 ADSORPTION BY NANOCELLULOSE

Over the years, utilization of nanocellulose in remediation of water bodies has shown promising performance and classification of nanocellulose as one of the non-toxic nanomaterials led to increasing usage of nanocellulose in adsorption studies [32]. Few advantages of nanocellulose include high surface area, high surface tension, high aspect ratio, good mechanical strength and rigidity, high chemical resistance and ease of surface functionalization [32]. With high surface area, it will provide more active sites for the binding of adsorbate to the adsorbent. Referring to Figure 1, cellulose contains several hydroxyl groups in its structure that are accessible for surface modifications [10].

Kardam *et al.* [35] studied the adsorption capacity of cellulose nanofibrils extracted from rice straw in removal of three synthetic wastewater containing single metal ions; Cd (II) ion, Pb (II) ion and Ni (II) ion. Effect of contact time, metal concentrations and pH were explained in their study. It was found that nanocellulose demonstrated a good adsorption capacity for cationic heavy metals. Sorption percentage of Pb (II), Cd (II) and Ni (II) is 92.78%, 89.51% and 83.68% respectively at optimum conditions of 25mg/l metal concentrations and contact time of 40 minutes. Optimum pH for the study was approximately at pH 6.0. Next, the findings were then compared to fibre from rice straw and natural-sized cellulose from the same source, as illustrated in Figure 4 which proves that nano-sized cellulose has potential in replacing the current adsorbent. Among the three materials, efficiency of nanocellulose fibre in adsorption tests was the highest while rice straw fibres that have the largest structure size displayed the lowest adsorption efficiency.

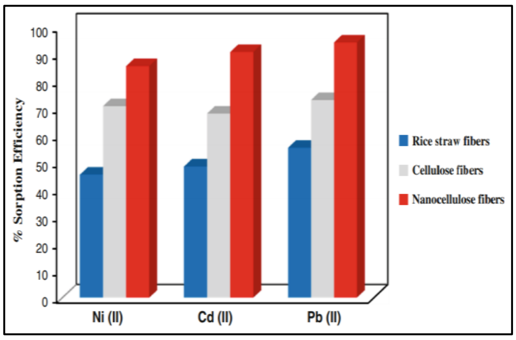

Figure 4 Sorption efficiency comparison for rice straw fibre, cellulose fibre and nanocellulose fibre [35]

Next, Liu *et al.* [36] explored the practicality of two nanostructured cellulose, nanocrystal and nanofibers in eliminating silver ion from water. Their findings are in conform with results from Kardam *et al.* [35] as both types of nanocellulose able to adsorb a satisfactory amount of silver cations contained in synthetic wastewater at pH range from 5.0 to 7.0. From zeta potential test conducted, CNC which was prepared by acid hydrolysis carried 230 µmol/g negative charges from sulphate and carboxylate groups bound to the CNC surface while CNF has only 100 µmol/g surface negative charges [37]. Therefore, more silver ions were adsorbed by CNC compared to CNF with capacity of 34.35 mg/g for CNC and 15.45 mg/g for CNF. Only carboxylate groups were found on the surface of CNF, which justified the lower value of negative charges compared to CNC. The authors concluded that surface functionality, zeta potential and extent of aggregation are important parameters that affect the adsorption performance [36].

Since natural derived cellulose are known to be a great adsorbent for water purification, different modifications were made to the nanocellulose surface by researchers to investigate its adsorption performance. Most of the literatures reported a high adsorption capacity when chemically-modified nanocellulose were used in purification of wastewater [38–41]. Modification to the cellulose surface can be categorized into two which are direct modification and monomer grafting [42]. Example for direct modification to the nanocellulose-based adsorbent are esterification, oxidation and etherification [39, 43–45]. Alkaline treatment during the extraction process of nanocellulose also considered as one of the examples for direct modification [42].

Polyethyleneimine, PEI has been grafted onto nanocellulose. Hong *et al.* [38] recently performed adsorption studies using nanocellulose-based materials to recover platinum ions from waste effluents that consist several metal ions. In their study, CNC was extracted from hard wood pulp whilst CNF were isolated from two different sources; hard wood pulp and tunicates, to compare the efficiency of nanocellulose from different sources. All three types of nanocellulose were grafted with PEI, which results in higher adsorption capacity compared to unmodified nanocellulose. From overall studies, CNF from tunicates species adsorbed the highest amount of platinum ions, followed by CNC from hard wood pulp and lastly CNF from hard wood pulp. Images from Scanning Electron Microscope, SEM, for the samples in Figure 5 explains morphologies of nanocellulose before and after crosslinking with PEI. CNF from tunicates have large surface area, denoted by its open porous structure that allows more metal ions uptake. Maximum adsorption capacity for PEI modified CNF from tunicates, derived from Langmuir isotherm was 625 mg/g.

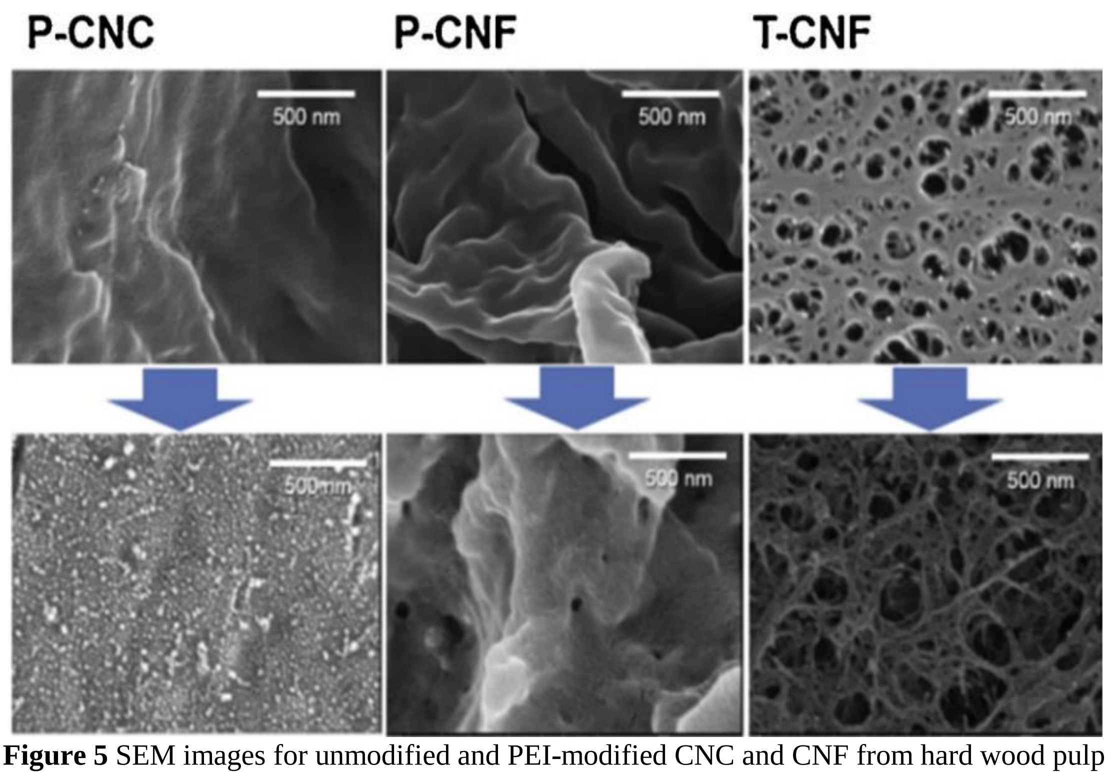

Figure 5 SEM images for unmodified and PEI-modified CNC and CNF from hard wood pulp and CNF from tunicates [38]

Similarly, adsorption performance of TEMPO-mediated oxidized cellulose nanofibrils, TOCNF, functionalized with PEI was described by Zhang *et al.* [39]. Grafting of PEI onto TOCNF via glutaraldehyde crosslinking method had successfully introduced a novel CNF structure consist of carboxyl and amino groups. This helps to increase the efficiency of adsorption due to chelating effect of amino with metal ions from waste water. On the other hand, CNF from bamboo grafted with another type of polymer, (poly)acrylic acid, PAA for removal of Cu(II) ions was reported by Zhang *et al.* [40]. When pH increases, the electrostatic interaction between carboxyl group and cationic heavy metals increases as carboxyl group partially ionized into $-COO^{-}$. The maximum adsorption of Cu^{2+} using CNF-PAA was found to be 0.727 mmol/g compared with only 0.286 mmol/g when unmodified CNF from bamboo was used as adsorbent.

2,3,6 Tricarboxy cellulose nanofiber, TPC-CNF adsorbent synthesised via TEMPO oxidation of cellulose pulp (selective at C-6) followed by periodate-chlorite oxidation (selective at C-2 and C-3) was prepared by Abou-Zeid *et al.*[46]. They evaluated the efficiency of TPC-CNF in adsorbing three metal ions; Cu(II), Ca(II) and Pb(II) ions from water. Also, polyamide-amine-epichlorohydrin, PAE, was crosslinked with TPC-CNF but it produced low efficiency of heavy metals uptake compared to TPC-CNF adsorbent.

Qiao *et al.* [41] in their work attempted the removal of organic pollutants using carboxylated CNC obtained from esterification reaction between maleic anhydride and hydroxyl groups present on cellulose surface. Carboxyl groups from maleic anhydride favours the attraction to cationic dyes through electrostatic interaction. Adsorption test proved a high uptake of crystal violet with maximum adsorption of 243.9 mg/g. It was noted that CNC without further functionalization have lower adsorption capacity (185.2 mg/g) than carboxylated CNC but still exhibits good potential as future adsorbent. From desorption and regeneration studies, carboxylated CNC showed a promising cycling behaviour, having approximately 80% desorption rate after four consecutive cycles as depicted in Figure 6. In the same work, adsorption studies were also done for removal of methylene blue, malachite green and basic fuchsin.

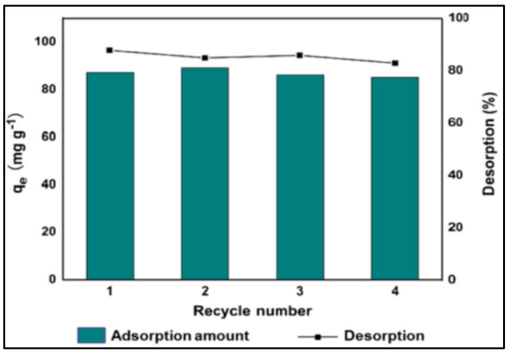

Figure 6 Adsorption-desorption cycle of carboxylated CNC in uptake of crystal violet dyes [41]

Sirviö *et al.* [47] synthesised bisphosphonate nanocellulose in their effort to remove vanadium (V) ions from water. Unlike most of the findings, adsorption performance was favoured at low pH of solution due to complexity of reaction between cationic vanadium with bisphosphonate groups. Maximum adsorption capacity by bisphosphonate nanocellulose calculated using Langmuir isotherm was found to be 1.98 mmol/g at pH 2.0 to pH 3.0. They also reported that nanocellulose structure obtained depends on the reaction time and it will be either in nanofibrils form or nanocrystals form. Table 3 shows an overview for recent literatures for nanocellulose-based adsorbent performances.

Table 3 Nanocellulose-based adsorbent evaluated by previous researchers

Adsorbent	Adsorbate	Isotherm model	Maximum Adsorption	Information	Reference
CNF	Pb (II)	Freundlich, Langmuir	7.06 mg/g, 10.20 mg/g		
	Cd (II)	Freundlich, Langmuir	5.75 mg/g, 11.23 mg/g	Initial metal ions concentrations: 25 mg/l pH 6.0 Contact time: 40 minutes	[35]
	Ni (II)	Freundlich, Langmuir	3.91 mg/g, 11.23 mg/g		
CNC	Ag (I)	-	34.35 mg/g	pH 6.39	[36]
CNF	Ag (I)	-	15.45 mg/g	pH 5.45	
CNC-PEI	Pt	Langmuir	123.5 mg/g	Initial metal ions concentrations: 500 mg/l Temperature: 25°C	
CNF-PEI	Pt	Langmuir	47.5 mg/g	Initial metal ions concentrations: 500 mg/l	[38]
CNF-PEI	Pt	Langmuir	625 mg/g		
TOCNF-PEI	Cu (II)	Langmuir	52.32 mg/g	Initial metal ions concentrations: 50 mg/l Temperature: 30°C pH: 5.0	[39]
CNF-PAA	Cu (II)	Freundlich	0.727 mmol/g	Adsorbent dosage: 40mg/20mL	[40]

Adsorbent	Adsorbate	Isotherm model	Maximum Adsorption	Information	Reference
				pH: 4.5	
CNC	Crystal violet	Langmuir	185.2 mg/g	Initial dyes concentrations: 400 mg/l pH: 6.0	
	Methylene blue	-	177.45 mg/g		
	Malachite green	-	90.09 mg/g	Initial dyes concentrations: 400 mg/l	
	Basic fuchsin	-	256.62 mg/g		
Carboxylated CNC	Crystal violet	Langmuir	243.9 mg/g	Initial dyes concentrations: 400 mg/l pH: 6.0	[41]
	Methylene blue	-	232.05 mg/g		
	Malachite green	-	147.42 mg/g	Initial dyes concentrations: 400 mg/l	
	Basic fuchsin	-	313.95 mg/g		
TPC-CNF	Cu (II)	-	97.9 mg/g	Initial metal ions concentrations: 250 ppm Contact time: 2 hours	[46]
	Ca (II)	-	105.79 mg/g		
	Pb (II)	-	102.64 mg/g		

5.0 CONCLUSION

Nanocellulose-based adsorbent derived from different sources and method were discussed for wastewater remediation. Surface modification improved the material functionality for removal of various adsorbate in most of the reported literatures. Results from adsorption studies showed that adsorption mechanism were controlled by several parameters and need further assessment before applying in actual wastewater due to its complex nature. As a conclusion, functionalized nanocellulose produced better adsorption performance compared to non-functionalized nanocellulose.

ACKNOWLEDGEMENTS

The authors would also gratefully acknowledge the financial support from the Ministry of Higher Education and Universiti Malaysia Pahang under Fundamental Research Grant Scheme (Project Number: Rdu170125).

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