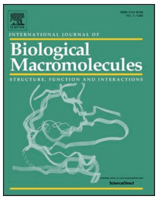
International Journal of Biological Macromolecules 232 (2023) 123342

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac



Review

Comparison between nanocellulose-polyethylenimine composites synthesis methods towards multiple water pollutants removal: A review

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ARTICLE INFO

Keywords:
Bio-based adsorbents
Crosslinking
Covalent bonding
Adsorption
Water remediation

ABSTRACT

Nanocellulose/polyethylenimine composites have attracted growing attention due to their versatility as new materials for application in different fields. Water remediation is one of the traditional applications of these composites and their investigation as adsorbents for single water pollutants is well established. However, most water resources such as rivers, lakes, and even oceans contain complex mixtures of pollutants. Despite several recently published reviews on water purification technology, they only focused on these material as single pollutant removers and hardly mentioned their capacity to simultaneously recover multiple pollutants. Therefore, there is still a gap in the archived literature considering nanocellulose/polyethylenimine composites targeting water remediation with multiple water pollutants. In this review, methods for synthesizing such composites are classified and compared according to the mechanism of reactions, such as chemical crosslinking and physical adsorption, while outlining advantages and limitations. Then, the water pollutants mainly targeted by those composites are discussed in detail to expound the relationship between the synthesis method and the type and adsorption capacity. Finally, the last section presents challenges and opportunities of these nanocellulose/polyethylenimine composites as emerging sorbents for sustainable multiple water pollutants purification technologies. This review aims to lay out the basis for future developments of these composites for multiple water pollutants.

1. Introduction

The combination of cellulose nanomaterials or cellulose nanofiber matrices (CNMs) with polyethylenimine (PEI) has led to the production of a wide range of composites, which have found ample application in different fields, such as paper making [1–4], wastewater treatment [5–8], drug release [9–12], sensing [13–15], heterogeneous catalysis [16], and others [17]. The potential utility of these composites has attracted significant interest from the scientific community. The number of publications in this field has progressively increased in the last 20 years (Fig. 1), with most of them (58.3 %) dedicated to sorbent systems for water remediation [17].

Being active in this research topic, we found that most research focused on using cellulose or nanocellulose/polyethylenimine composites to target singular water pollutants. However, most water resources such as rivers, lakes, and even oceans contain complex mixtures of pollutants, including dyes, spilled oils, organic solvents, and heavy metals [18]. A paradigm shift from single pollutants to multiple pollutants control is crucial to tackle real-world water purification challenges [19,20].

The synthesis method of the nanocellulose/polyethylenimine composites largely determines the type and ability of contaminants that these composites can remove. Therefore, it is essential to review the methods for synthesizing such composites, and how they work towards removing different types of pollutants to lay out the bases for future development of these composites for multiple water pollutants. In this review, the aim was to study the reported adsorption capabilities of the CNM-PEI composites from a single contaminant, finding the most common ones that can be used as comparison in the transformation route to multiple contaminant removal. Likewise, we aim to close the gap in the exploration between the relationship of synthesis methods and the type and capacity of adsorbed pollutants.

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https://doi.org/10.1016/j.ijbiomac.2023.123342
Received 23 November 2022; Received in revised form 3 January 2023; Accepted 15 January 2023
Available online 28 January 2023

2. Current synthetic strategies of CNM-PEI composites

When the different reported cellulose–PEI composites are compared, it can be noted that they were formed mainly by following two formation mechanisms: chemical crosslinking and physical adsorption. These are summarized in the scheme presented in Fig. 2. The first approach, chemical crosslinking, can be subdivided into two types: with or without additional agents. These methods are largely dependent on whether the cellulose or CNMs have been pre-functionalized or not. Starting from cellulose sources without pre-functionalization often requires the use of proper crosslinkers to obtain stable and resistant composites. On the contrary, when operating in the presence of pre-functionalized cellulose, the formation of covalent bonds between the two building blocks by direct crosslinking is possible under proper and controlled reaction conditions [17]. Thus, a strong covalent bond can be obtained by heating [21] or by using condensation agents [22], without requiring additional molecules to act as bridges between the materials [17].

The second alternative is the direct assembly of the polymers by physical crosslinking between them. To achieve this, interacting forces such as hydrogen bonding, electrostatic forces, van der Waals forces, chain entanglements, and ionic & hydrophobic interactions dominate. Thus, this allows for the maintenance of surface functional groups available as active point on the materials. Following, a detailed comparison between each method and the resulting composites was done.

2.1. *Chemical crosslinking*

2.1.1. *Using additional chemical crosslinker*

CNM-PEI composites can be synthesized by several chemical crosslinkers, such as glutaraldehyde (GAL) [23,24], epichlorohydrin (EPI) [25,26], γ-(2,3-epoxypropoxy) propyltrimethoxysilane (GPTMS) [27], Tri-functional trimethylolpropane-tris-(2-methyl-1-aziridine) propionate (TMPTAP) [28], among others. For this formation pathway, a common feature is that the chemical crosslinker combines CNM and PEI together to form a complex through chemical bonds. The crosslinking agent may increase the complexes mechanical properties or help to form a porous structure. Moreover, some of them can introduce functional groups, increasing the trapping of the water pollutants. Meanwhile, when these crosslinkers are introduced into the composites, their toxicity must also be considered. Therefore, the reaction mechanism, functionality of each crosslinker in CNM-PEI composites, and its toxicity will be discussed in detail.

The most frequently used crosslinkers are glutaraldehyde (GAL) and epichlorohydrin (EPI) because their use is operationally simple, and the reaction conditions are mild. For the GAL processing, the reaction can be conducted in one pot by simply stirring the reagents in polar solvents at room temperature [23,24]. The use of GAL involves the crosslinking between PEI and cellulose through the formation of a Schiff base and a hemiacetal (Fig. 3 A).

When using EPI as the crosslinker, heating (60–90 °C) was not necessary but can improve reactions. Alkaline condition was required to open the epoxide ring and promote ether formation to crosslink the cellulose and PEI as shown in Fig. 3 (B) [25,29]. However, the CNM-PEI composites synthesized by these two methods exist in the form of powders, which have poor separability and recyclability [28]. To solve this problem, the latest research synthesized aerogels by a combination of freeze-drying and GAL crosslinking [30]. Besides, it still cannot be ignored that both GAL and EPI have been reported to be highly toxic for humans and animals [17,31–33]. As alternatives, recent research suggested the use of new crosslinkers, such as GPTMS [27] and TMPTAP

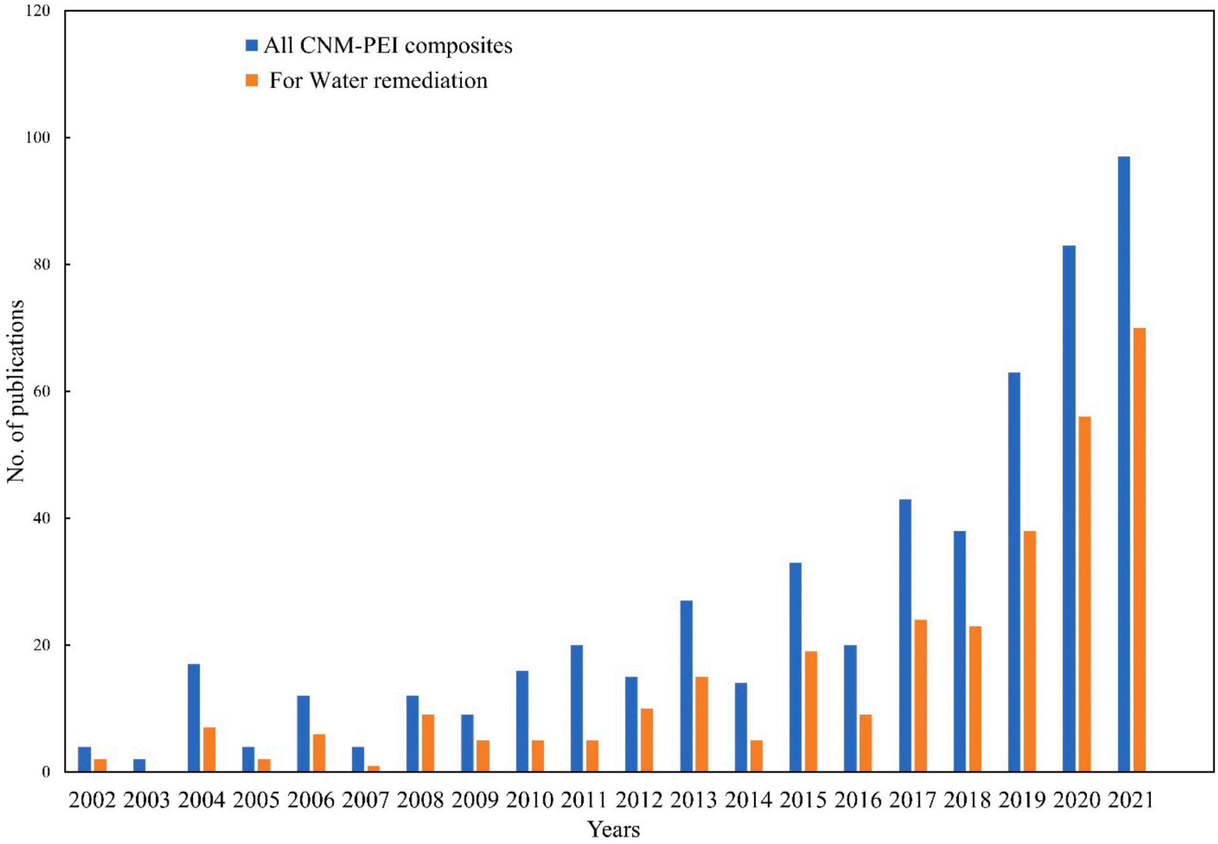

Fig. 1. The number of publications describing CNM-PEI composites and their utility for water remediation during past 20 years. The data is from Web of Science based on the search function: (polyethylenimine OR PEI) AND (cellulose OR nanocellulose OR cellulose nanofiber (CNF) OR cellulose nanocrystal (CNC)) for All CNM-PEI composites; (polyethylenimine OR PEI) AND (cellulose OR nanocellulose OR cellulose nanofiber (CNF) OR cellulose nanocrystal (CNC)) AND (water OR water remediation OR water treatment OR removal).

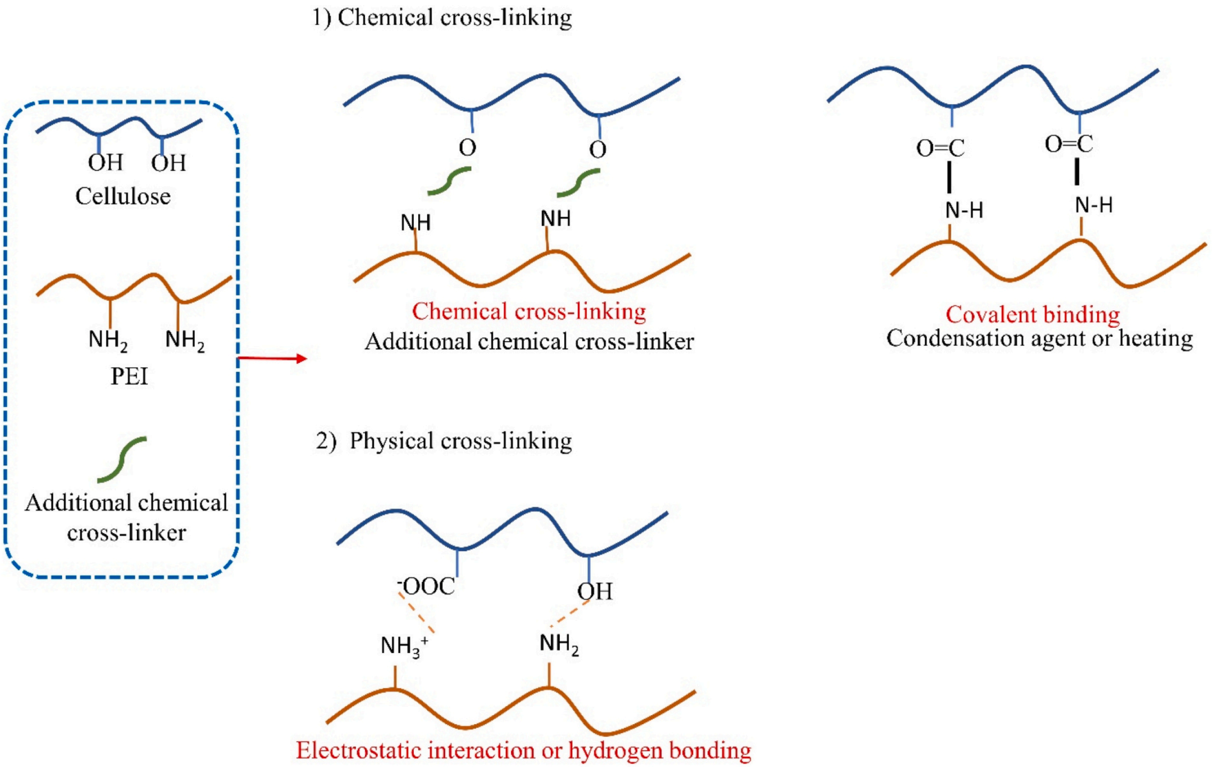

Fig. 2. The synthesis strategies of CNM-PEI composites and reaction mechanism.

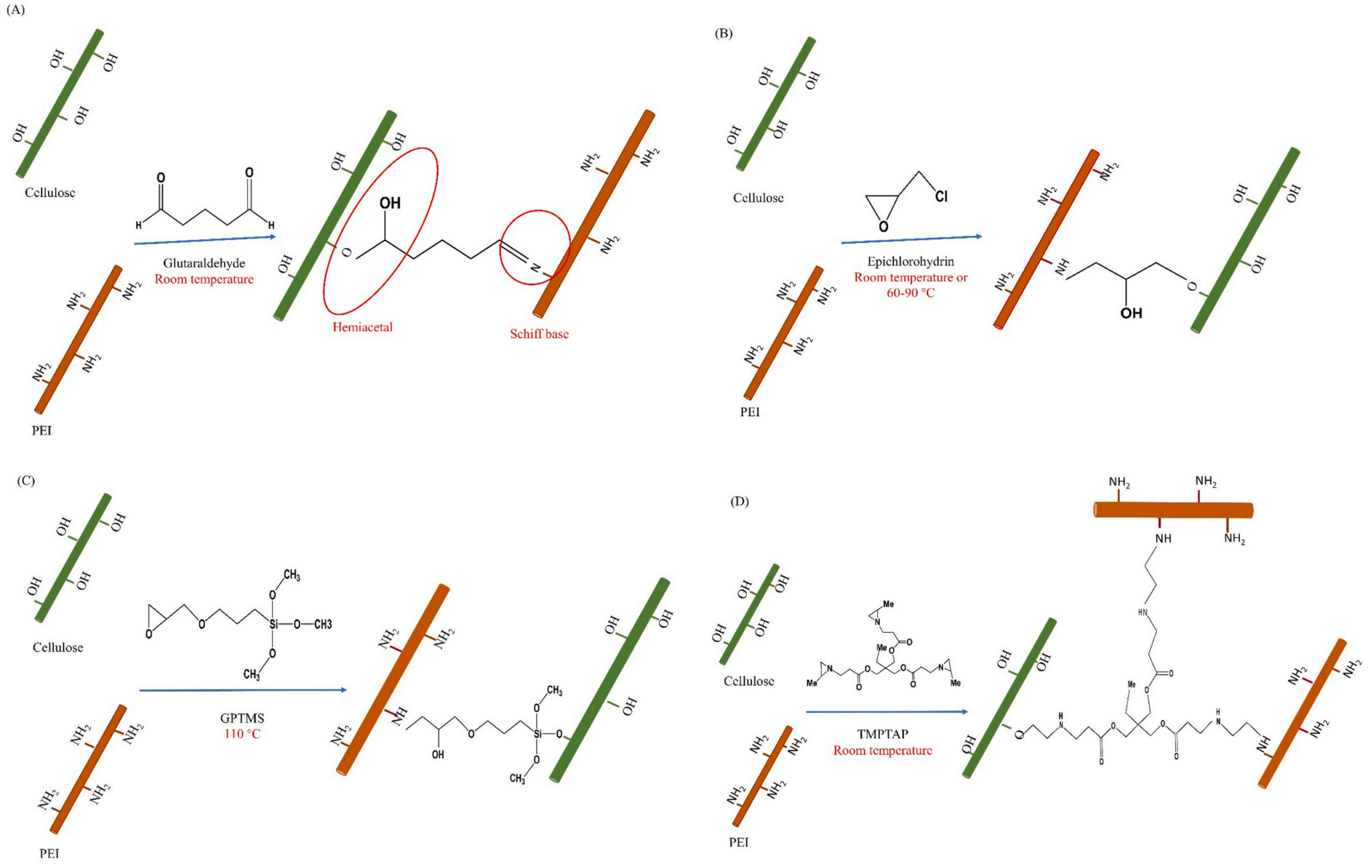

Fig. 3. Reaction mechanism of different chemical crosslinkers.

[28] instead of GAL and EPI to synthesize CNM-PEI aerogels.

For the GPTMS crosslinking process, condensation between the trimethoxy silane and cellulose hydroxyl groups results in covalent linkage (Fig. 3 C). This reaction started by the PEI being added into the mixture of cellulose and the crosslinker, the epoxide group on the end of GPTMS reacted sequentially with the amine groups on PEI, yielding robust networks [27,34,35]. The obtained mixture was introduced to liquid nitrogen via a syringe pump at a controlled rate to form uniform spherical beads. Afterward, these frozen beads were subjected to freeze-drying at −45 °C to produce the aerogel beads [34,35]. No toxicity was observed in cellular studies of the GPTMS-containing paste after 7 days, which showed GPTMS as superior to GAL and EPI [36].

Another crosslinker reported in literature was TMPTAP (Fig. 3 D). This is a relatively safe skeleton tri-functional aziridine reagent, which is also an important intermediate for synthesizing massive nitrogen-containing biologically active compounds [37]. There, COOH-CNF spontaneously reacted with TMPTAP via a ring-opening reaction in an aqueous solution at room temperature and then crosslinked PEI into the composite. One of the advantages of this method is that TMPTAP acted not only as a crosslinker but also introduced many amino and oxygen-containing groups into the composite, thus increasing the adsorption ability for water pollutants [28]. All the synthetic processes involving chemical crosslinkers mentioned above can be operated under mild conditions. However, GPTMS and TMPTAP are relatively safer than GAL and EPI. In addition, TMPTAP was then superior to GAL, EPI, and GPTMS when it comes to introduction of additional functional groups to increase their trapping ability for water pollutants. Thus, TMPTAP seems as the ideal chemical crosslinking agent for the synthesis of CNM-PEI composites.

2.1.2. Direct covalent bonding between COOH-CNF and PEI

As seen in the previous section, a lot of the current methods for synthesizing CNM-PEI composites involved additional chemical crosslinking agents that can react under mild conditions. However, secondary

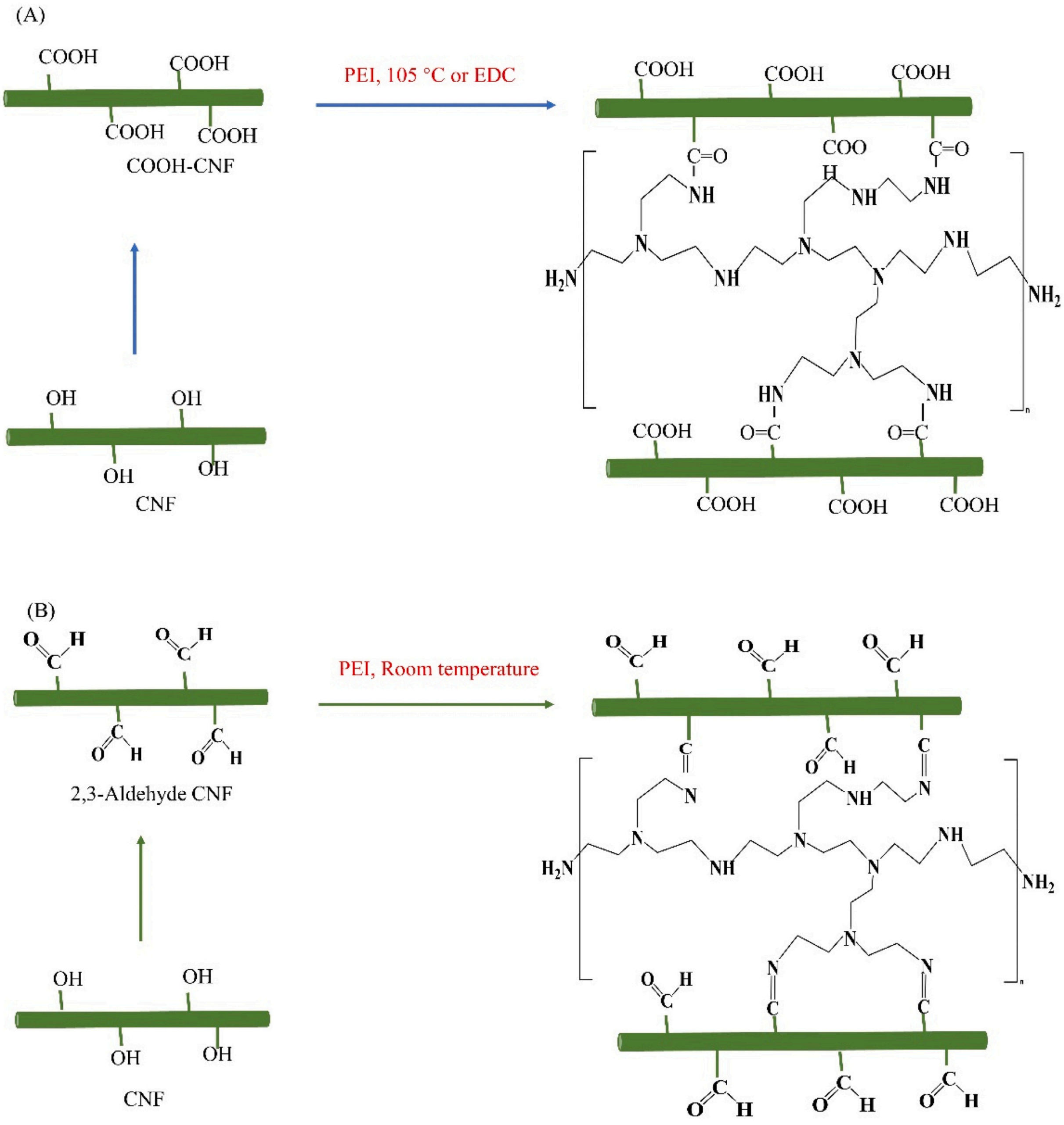

Fig. 4. Reaction mechanism by covalent bonding.

pollution or toxicity caused by chemical crosslinking agents is an issue that could emerge and should be prevented. To avoid these problems, some research focuses on seeking a way to directly promote the crosslinking of covalent bonds between nanocellulose and PEI without adding additional chemical crosslinking agents. However, the reactivity of hydroxyl groups on nanocellulose is not compatible with the amino groups in PEI to form stable, covalent complexes without chemical crosslinkers. Therefore, nanocellulose needs to be pre-functionalized to introduce the functional group that can covalently bond with the amino group [17]. The most popular pre-functionalized methods were TEMPO-mediated or sodium periodate oxidization. These can introduce carboxyl and aldehyde groups into nanocellulose, respectively. Both functional groups can be covalently bound with the PEI amino groups by amide or Schiff base reaction under proper conditions. At present, heating and adding condensation agents to promote the combination of CNMs and PEI have been reported.

2.1.2.1. By heating. The addition of heat into solutions containing anionic cellulose and PEI allows for the materials to break the energetic barrier to promote the condensation of the functional moieties and forming covalent bonds. This mechanism has been used to form COOH-CNF and PEI composites with a sponge-like structure, good mechanical stability, and a shape-memory capability in water [21]. The composite formation was carried out in a multistep process. First freeze-drying was done to form a foam, followed by heating in an oven over a temperature ramp of 60 to 102 °C, over 8 h followed by heating at 102 °C for 2 h, thus forming amide bonds between the two components during the thermal treatment [21] (Fig. 4 A). Interestingly, a later study found that their mechanical properties can be further enhanced by the introduction of a natural crosslinker, citric acid [38]. This approach made it possible to obtain cellulose nano sponges (CNS) due to their inner nanostructure and nano porosity [17,39,40]. However, the problem with this method is that the synthesis of COOH-CNF/PEI nano sponges needs a combination of freeze-drying and heating over 100 °C, both of which are energy-intensive processes [17,39,40].

2.1.2.2. By condensation agents-EDC. CNM/PEI composites could also be formed by using condensation agents, such as EDC (N-ethyl-N′-(3-(dimethylamino) propyl)carbodiimide) (Fig. 4 A), which promotes amide bond formation between the amines of PEI and the carboxyl groups of TEMPO-oxidized cellulose, instead of thermal treatment in the absence of additional chemical crosslinkers [22]. The advantage of this synthetic route relies on the possibility of operating at room temperature [17,22]. The disadvantage is that the EDC needs to be removed by a dialysis process after crosslinking, which is a time tedious process.

2.1.2.3. By Schiff base reaction. Another alternative is the formation of the composite through Schiff base reaction. The CNF were pre-functionalized by sodium periodate oxidation to introduce aldehyde groups. Then a cryogel was prepared by freeze-induced chemical crosslinking between the aldehyde groups and hydroxyl groups on CNF. Finally, the cryogels were added to the PEI solution to functionalize to form the CNF-PEI composites cryogels by a Schiff base reaction (Fig. 4 B). The CNF/PEI hybrid aerogels exhibited good structural stability and shape recovery in water. Moreover, the squeeze-deformed CNF cryogel was recovered to its original shape upon contact with water [41]. The results of this study have made a breakthrough in improving the mechanical properties of CNF-PEI composites without heating, freeze drying and other conditions.

2.2. *Physical adsorption*

The downside of the chemical crosslinking strategies is the problem of using toxic reagents, the chemical residues produced, and the extra cost added with new reactants [42]. Condensations promoted by high temperature are energy intensive processes. An alternative strategy involves physical crosslinking strategies that are governed by non-covalent interactions such as electrostatic interactions, hydrogen bonding, hydrophobic association, or chain winding [43]. In addition, the technology of physical crosslinking is much simpler (Fig. 5). Li and co-workers made a shape memory aerogel from COOH-CNF and PEI via electrostatic combination without additional chemical crosslinking. These aerogels were generated by maintaining the total concentration of COOH-CNF and PEI at 12 mg/mL at pH 10 for 4 h at room temperature followed by freeze-drying for 3 days at −91 °C. The CNF/PEI hybrid aerogels exhibited good structural stability and shape recovery in water [44]. In our research, a COOH-CNF/PEI hydrogel was also formed by a combination of cationic chelating and physical adsorption. The COOH-CNF was chelated by zinc ions to form a preliminary hydrogel which was then put into the PEI solution to functionalize at room temperature, resulting in COOH-CNF/PEI hydrogel composites (unpublished). These studies have confirmed that a physical adsorption method is also a good option for the synthesis of CNF-PEI composites for water remediation.

3. Possible interfacial interactions with CNM-PEI composites

It is very important to comprehensively understand the underlying mechanisms of adsorption to fully exploit the utility of CNM-PEI for water remediation. Due to the abundant amino groups added to the surface with PEI, as well as the presence of residual carboxyl and aldehyde groups, electrostatic interactions are prevalent. Moreover, the high density of hydroxyl groups on the cellulose backbone would allow hydration and the formation of hydrogen bonding between molecules in the media and exposed surfaces, as well as other van der Waals interactions. Likewise, cellulose structures are known to adsorb molecules into the hydrophobic crystalline face as their main entropic strategy to decrease the free energy in water systems [45]. The understanding of adsorption mechanism is helpful to design optimal composites targeting more types and amounts of pollutants. Therefore, this section focuses on the adsorption mechanism of the different types of water pollutants onto CNM-PEI composites.

3.1. *Metal ions*

Taking Cu (II) as a model for divalent ions, previous studies showed that the adsorption capacity of CNM-PEI could be attributed to a large amount of amino functional groups (primary amine, secondary amine, and tertiary amine groups) and oxygen-containing functional groups (hydroxyl and carbonyl groups) available. These moieties provided abundant electrostatically charged sites for the adsorption of cations like Cu (II) [28]. Based on this, if the chemical crosslinker is rich in the amine group and oxygen-containing functional groups, it will increase the adsorption capacity for the ions.

Thus, one can roughly predict the order of metal ion adsorption capacity of CNM-PEI composites obtained by various synthetic methods according to the content of oxygen or amino groups introduced by chemical crosslinkers. The order is: TMPTAP>GPTMS>GA, EPI > covalent bonding by heating and EDC, physical adsorption> covalent bonding by Schiff base reaction if the same moles of chemical crosslinker were added with same moles of CNF and PEI. However, considerations on porosity, surface area, and structure need to be made to confirm this.

3.2. *Toxic dyes or other organic chemicals*

Most of the research focused on the removal of toxic dyes by adsorption onto CNM-PEI composites [4,26]. PEI with abundant amine groups were immobilized on the surface of COOH-CNF/PEI hydrogel. When COOH-CNF/PEI hydrogels were put into aqueous solution whose pKa is lower than the pKa of PEI, amine groups on hydrogels would translate to positively charged ammonium groups [24]. These positively charged ammonium groups could form the cation-π interactions, which

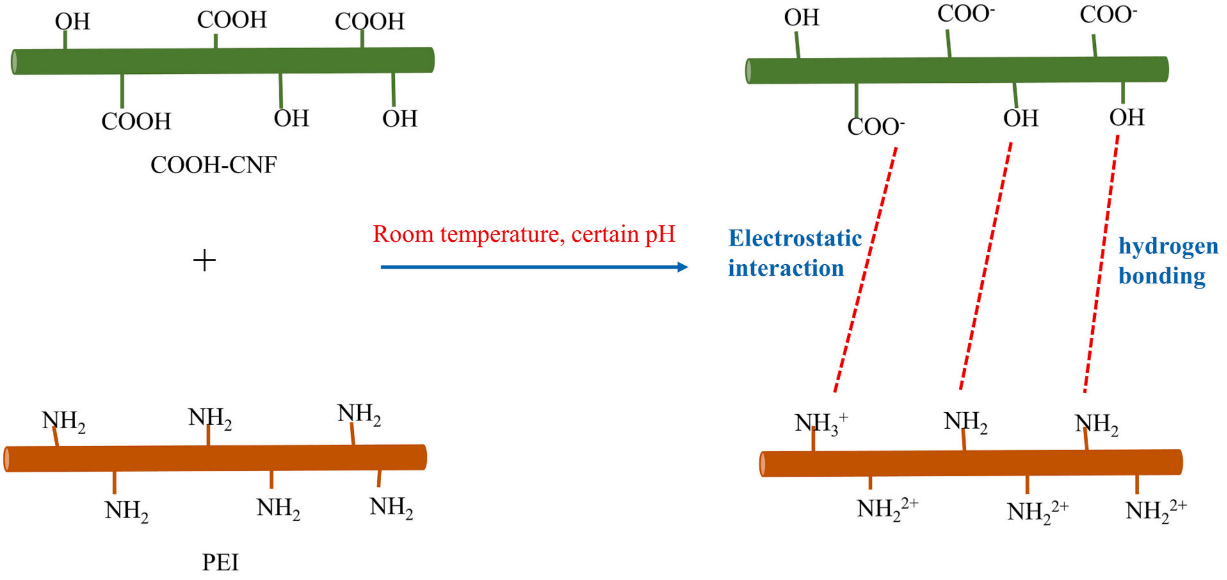

Fig. 5. The synthesis of CNM-PEI composites by physical adsorption.

are electrostatic attraction between positively charged cations and negatively charged electron-rich π systems [46]. Besides, positively charged ammonium group could also produce strong electrostatic attraction towards the negatively charged anionic dye molecules [26]. Furthermore, hydrogen bonding, hydrophobic interaction, and Van der Waals forces all could exist between the hydrogels and methyl blue dyes [46]. Finally, it cannot be ignored that the multilayer adsorption caused by π–π stacking is also a pathway of interaction between dye molecules having rich π systems [47].

In general, cation-π interactions show higher strength than hydrogen bonding, and in some cases, even charge–charge interactions, which are arguably one of the strongest noncovalent interactions in aqueous solutions [47–49]. However, according to other research, the strong electrostatic attraction between PEI and methyl blue dyes is prevalent, being the main reason PEI functionalized cellulose composites adsorbed the methyl blue dyes [24]. More research is needed to determine which role is dominant among those.

For the cationic or non-ionic organic chemicals without π-systems, the adsorption is limited to these pollutants' capacity to form electrostatic attraction, van der Waals interaction or hydrogen bonding with the hydroxyl groups and other polarizable functionalities. Another important consideration is that the conditions of the system will also determine the pollutants adsorption onto cellulosic materials since the system's free energy needs to be decreased. Thus, the presence of salt and the exchange of water molecules for molecules on the surface would also favor the adsorption of the molecules, even when other phenomena are not driving it. For example, coupling hydrophobic molecules onto hydrophobic faces and points in the CNM-PEI composites will liberate water and cosolvents, increasing the entropy of the overall system.

4. Applications of CNM-PEI composites for water remediation

Nowadays, the research of CNM-PEI composites in the field of water remediation focuses mostly on heavy metal ions and organic dyes; with only some studies focusing on removing the emerging contaminants (ECs) that have been recently detected in natural environments. Different aspects of the composite, such as processing, conformation, and experimental conditions, determine the availability and reactivity of the active sites, modulating the removal efficiency [17]. All these aspects are mainly determined by the synthesis method. Therefore, it is necessary to compare the synthesis methods and the types and amounts of pollutants adsorbed. Understanding this will help select the method that can be used to synthesize CNM-PEI composites capable of targeting multiple types and higher amounts of pollutants.

4.1. Removal of metal ions

A general overview of cellulose–PEI composites achieved by different methods for removing heavy metals is provided in Table 1. Regardless of their methods of preparation, cellulose-PEI composite materials are well-suited for the adsorption of metal ions due to the large amount of charged moieties on the surface of the particles, as well as their capacity to chelate metal ions. The most tested metal ions include Cu (II), Pb (II), Cd (II), Ni (II) [50], Cr (VI) [51], As (III), As (V) [52], Fe (III), Cr (III) [53], and Zn (II) [54,55]. Among all the metal ions of interest, Cu (II) has been widely taken as a reference in adsorption studies since it is well adsorbed, and the sorption is easy to detect by a simple UV analysis [17].

While comparing the adsorption capacity of such complexes, differences have been noted depending on the method of synthesis. TMPTAP crosslinked TEMPO-oxidized CNF and PEI aerogels had the highest adsorption capacity with up to 485.44 mg/g (Table 1) [28]. This difference is due to TMPTAP acting not only as a crosslinker but also introducing amino and oxygen-containing groups, which all can chelate Cu (II) ions, thus increasing the adsorption capacity of the material. Based on Table 1, the order of the maximum adsorption capacity of CNM-PEI composites obtained by the various synthetic methods for Cu (II) is TMPTAP> GAL, EPI > covalent bonding by heating > physical adsorption> GPTMS> covalent bonding by Schiff Base reaction. This order is like the order we predicted only according to the content of carboxyl or amino groups introduced by synthetic process in the adsorption mechanism section except for the GPTMS.

It was also found that the composites that presented the highest adsorption capacity for Cu (II) ions, were also more likely to be highly adsorbent to other ions (Table 1). PEI-functionalized A4 paper has the higher adsorption capacity for Cu (II) (435 mg/g) and Cd (II) (370 mg/g) as compared to TEMPO-oxidized cellulose-PEI sponges [54,55]. Likewise, TEMPO-oxidized CNF/PEI aerogel performed better than the PEI-dialdehyde bacterial cellulose composites for the adsorption of Cu (II) and for Pb (II) with 357.44 mg/g and 141 mg/g, respectively [44,57]. Therefore, the adsorption capacity order of this kind of material to other ions can be roughly judged according to the adsorption capacity order of copper ions.

Moreover, in a closer view, the TMPTAP crosslinked TEMPO-

Table 1
Cellulose–PEI composites used for removal of metal ions.[a]

Composites	Synthesis strategies	Metals ions and their maximum adsorption capacity (mg/g)		Reference
TEMPO-CNF/PEI aerogels	Crosslinker	TMPTAP	**Cu (II) 485.44**	[28]
PEI-functionalized A4 paper		GAL	**Cu (II) 435**, Cd (II) 370, Ni (II) 208, Cr (VI) 68	[56]
PEI-carboxymethyl cellulose nanofibrils aerogel			**Cu (II) 380.03**	[58]
PEI-CNF aerogel			**Cu (II) 135.1**	[29]
PEI-TEMPO oxidized cellulose hydrogels			**Cu (II) 109.89**, Pb (II) 279.32	[59]
PEI-nanowood			**Cu (II) 93**	[60]
PEI-modified COOH-CNF powders			**Cu (II) 53**	[23]
PEI-modified microcrystalline cellulose			Cd (II) 217, Pb (II) 357	[61]
PEI-cellulose aerogel beads			Cr (VI) 229	[51]
PEI functionalized coffee cellulose membranes			As (III) 13, As (V) 46	[52]
Cellulose/PEI powder		EPI	**Cu (II) 285.7**	[25]
Porous spherical PEI-cellulose powders			Fe (III) 377.19, Cr (III) 83.98	[53]
Hyperbranched PEI modified cellulose fiber powders			As (III) 54.13, As(V) 99.35	[62]
Cellulose aerogel beads		GPTMS	**Cu (II) 163.40**	[34]
Cellulose nanofiber (CNF)-supported cryogel			**Cu (II) 138**	[63]
PEI modified cellulose-based adsorbent		GMA	**Cu (II) 102**	[64]
PEI coated bacterial cellulose nanofiber membranes		GDE	**Cu (II) 90.01**, Pb (II) 130	[65]
PEI -TEMPO oxidized cellulose sponges	Covalent bonding between carboxyl and amine group	Heating	**Cu (II) 194**, Cr (III) 94, Cd (II) 84, Zn (II) 125	[54]
TEMPO oxidized cellulose-PEI cellulose sponges			**Cu (II) 89.6**	[21]
PEI -TEMPO oxidized cellulose sponges			Zn (II) 100	[55]
PEI-TEMPO oxidized wood aerogel		EDC	**Cu (II) 59.8**	[66]
TEMPO-Oxidized cellulose nanocrystal-PEI powders			Cr (VI) 358.42	[27]
PEI- dialdehyde bacterial cellulose	Covalent bonding between aldehyde and amine group	Schiff base	**Cu (II) 148**, Pb (II) 141 mg/g	[57]
TEMPO-NFC/PEI aerogel	Physical adsorption	/	**Cu (II) 175.44**, Pb (II) 357.44	[44]

[a] The bolded word mark the most common pollutant that can be used for direct comparison

Table 2
Comparison of the adsorption capacities of TEMPO-oxidized CNF/PEI cross-linked by TMPTAP with other types of materials for Cu (II).

Composites	Maximum adsorption capacity for Cu (II) (mg/g)	Reference
TEMPO-CNF/PEI aerogels crosslinked by TMPTAP	485.44	**[28]**
Magnetic tubular carbon nanofibers	375.93	[67]
Electrospun polyacrylonitrile-based lace nanostructures	354	[68]
Chitosan derivative	192.31	[69]
Graphene oxide/polyethylenimine sponge	150.9	[70]
Graphene oxide functionalized chitosan-magnetite nanocomposite	111.11	[71]
Solid carbon nanoonions via catalytic *co*-pyrolysis of lignin and polyethylene	100	[72]

oxidized CNF and PEI aerogels had the highest adsorption capability compared with other materials, as shown in Table 2. Most CNM-PEI composites showed higher adsorption capability than other materials, which indicates that CNM-PEI composites have excellent performance for metal ions.

4.2. Removal organic dyes

Water pollution caused by synthetic dyes has received considerable attention since such dyes are extensively utilized in diverse industries such as textile, food, paper, drugs, leather, among others [73]. Nowadays, over 100,000 dyes are commercially available [17]. Most of these dyes feature toxic, nonbiodegradable, and carcinogenic features which cause adverse effects on human health and ecosystems [73]. During the washing process, a certain fraction of dyestuffs unavoidably ends up in the wastewater discharged into the environment.

Cellulose–PEI composites have also been used to remove these toxic dyes. A general overview of cellulose–PEI composites for the removal of toxic dyes is provided in Table 3. The removal efficacy has been demonstrated for both cationic and anionic dyes but most of the research focuses on the anionic examples. PEI-modified cellulose aerogels crosslinked by GAL showed high adsorption capacity for anionic Rose Bengal, methyl orange, and methyl blue reaching 1290, 1226, and 1200 mg/g, respectively [26]. The strong adsorption performance of cellulose-PEI composites for anionic dyes was mainly ascribed to an electrostatic interaction between the cationic charges of the amino groups of PEI and the negative charges of anionic dyes, with a sorption efficiency depending on the charge present both on the surface of the composite and the contaminant dye [17]. Conversely, the adsorption capacity of cellulose-PEI composites for cationic dyes is lower than that of anionic dyes. It shows enormous difference for different cationic dyes: the adsorption capability up to 970 mg/g for Cationic Basic Yellow, but just has 6 mg/g, for methylene blue. The reason is not very clear. Further research is needed to be able to explain this behavior.

Unlike the research on metal ions, where most studies choose copper ions for reference, making it easier to compare different methods and materials, the use of standard reference dyes is not common. Thus, it is more difficult to compare the adsorption capacity of materials arising from different synthetic tactics. For methyl orange, the adsorption capacity of CNF/PEI aerogel crosslinked by EPI was up to 1226 mg/g [26], which was higher than that achieved with PEI-MFC aerogel (500 mg/g) which was generated by covalent bonding between aldehyde and amine group by Schiff base reaction [41]. In addition, the adsorption capacity of PEI modified cellulose-based bio-adsorbent crosslinked by GAL for the cationic dye bright yellow was 571.43 mg/g [24], which was also higher than that of an Aldehyde-CNF/PEI (160 mg/g) obtained by Schiff base reaction [74]. This difference might be because GAL or EPI not only functioned as a crosslinking agent but also introduced additional

Table 3
Cellulose–PEI composites used for removal of different toxic dyes.

Composites	Synthesis strategies		Metals ions and their maximum adsorption ability (mg/g)	Reference
PEI-modified cellulose aerogels	Crosslinker	GAL	Anionic Rose Bengal, 1290 Anionic Methyl Blue, 1200 Anionic Alizarin Red, 360 Anionic Acid Orange 7, 280 Anionic Ponceau S, 220	[26]
PEI modified cellulose-based bioadsorbent			Anionic Reactive Yellow, 971	[24]
Oxidized cellulose membranes modified with PEI			Anionic Xilenol Orange, 241	[75]
CNF/PEI aerogel		EPI	Anionic Methyl orange,1226	[46]
Aldehyde-CNF/PEI cryogels or powders	Covalent bonding between aldehyde and amine group	Schiff base reaction	Anionic Brilliant Blue, 1000 Anionic Congo Red, 990 Anionic Reactive Red, 950 Anionic Eosin Y, 215	[74]
PEI-MFC aerogel			Anionic Methyl orange, 500	[41]
PEI modified cellulose-based bioadsorbent	Crosslinker	GAL	Cationic bright yellow 571.43	[24]
Oxidized cellulose membranes modified with PEI			Cationic Methylene blue, 144	[75]
PEI-modified cellulose aerogels			Cationic Methylene blue 6.0	[26]
Aldehyde-CNF/PEI powder	Covalent bonding between aldehyde and amine group	Schiff base reaction	Cationic Basic Yellow, 970 Cationic Bright Yellow, 160	[74]

charged oxygen atoms, which can form hydrogen bonding with oxygen and nitrogen atoms in methyl orange.

When compared with other materials (as shown in Table 4), the adsorption capability of CNM-PEI composites for anionic Rose Bengal, methyl orange, and methyl blue and cationic basic yellow was among the highest. Demonstrating that these composites also presented excellent adsorption performance for toxic dyes.

4.3. *Emerging contaminants (ECs)*

ECs are a large and relatively new group of compounds and can potentially cause deleterious effects in aquatic and human life at environmentally relevant concentrations which are becoming a growing concern [91]. At present, there are few studies focusing on using the CNM-PEI composites for removal emerging contaminants [21] [22]. *P*-nitrophenol (*p*NPh) is an important industrial precursor in the synthesis of different drugs, fungicides, and dyes. It has been found that TEMPO-oxidized cellulose-PEI prepared by the direct amination of the COOH-CNF carboxylic groups with PEI by heating, and without using a supplementary crosslinker, can be used to adsorb the *p*NPh, as well as other ECs like 2,4,5-trichlorophenol and amoxicillin. Their adsorption capacity reached 1630, 205 and 556 mg/g, which are higher or like that of other materials (Table 5). Interestingly, Swasy and her collaborators found that PEI-functionalized cellulose nanocrystals can potentially serve as a new and viable remediation technique based on their ability to effectively degrade various pesticides such as malathion, deltamethrin, and permethrin with 100 %, 95 %, and 78 % degradation in water, respectively [22]. Therefore, the CNM-PEI composites also have an immense potential for removing and eliminating emerging contaminants. More attention should be paid to the removal of the emerging contaminants by CNM-PEI composites.

4.4. *Oil spills*

Furthermore, it is possible to apply CNM-PEI composite for the cleaning of oil spills [99]. CNC-PEI aerogel crosslinked by di-epoxide and then coated by graphene were used to selectively absorb organic solvents with a weight ratio ranging from 25 to 58 g/g. Therefore, CNM-PEI based composite also showed satisfactory performance to clean oil spills.

5. Challenges and opportunities of CNM-PEI composites for multiple water pollutants

Although CNM-PEI composite sorbents demonstrated satisfactory sorption capabilities to remove different classes of contaminants, ranging from heavy metals, organic dyes, some emerging contaminants, and oil spills; most of these studies focused on the removal of a single water pollutant under an ideal model system condition. Realizing that this ideal condition may not exist because polluted water systems are often contaminated with a wider array of pollutants, an urgent call for a multipollutant modeling approach aimed to target simultaneous uptake of coexisting water pollutants is needed. In particular, the performance efficiency for simultaneous uptake of coexisting water pollutants from different pollutant classes using CNM-PEI sorbents has rarely been reported in the literature and can be considered as one of the major gaps in adsorption studies. A shift of current conventional single-pollutant modeling towards a multipollutant approach should be undertaken for a more inclusive coverage of water pollutant assessment using emerging CNM-PEI sorbents. It is unclear what would happen in complicated multiple pollutants system, including metal ions, dyes, and oil spills. The big challenge may be how to test the amount change of each single pollutant in a mixed system with multiple pollutants.

6. Conclusions

Different strategies have been used to synthesize the CNM-PEI composites as adsorbents for water remediation due to their superior adsorption performance compared with other materials. In this review, synthesis mechanism, processing, adsorption capability, toxic properties, and recyclability of CNM-PEI composites were compared.

By doing this, we found that TAMPT seems to be an ideal chemical crosslinking agent due to easy processing, high adsorption capability and non-toxic properties. TMPTAP acted not only as a crosslinker but also introduced many amino and oxygen-containing groups into the composite, thus increasing the adsorption ability for water pollutants. Based on this, the incorporation of chemical crosslinker has the capability to introduce more functional groups, appears to confer higher contaminant removal performances. Likewise, the accessibility of a high number of amino groups on PEI, the presence of hydroxyl, carbonyl, and carboxylic groups on cellulose fibers and nanofibers, also opens the possibility of introducing other functional groups. Moreover, CNM-PEI based composites demonstrated to be capable of adsorbing metals, dyes, emerging contaminants, and oils. Therefore, there is enough knowledge developed to transition CNM-PEI composites into a

Table 4
Comparison of the maximum adsorption capacity of CNM-PEI composites for Rose Bengal, methyl orange, and methyl blue dyes with other materials.[a]

Dyes	Absorbents		Shape	Maximum adsorption ability (mg/g)	References
Rose bengal (−)	Other materials	Chitosan/PVA	Powder	44.4	[76]
		Kappa-carrageenan/tamarind kernel powder	Hydrogel	168.1	[77]
		Polyethylenimine-functionalized cellulose beads	Beads	467.9	[78]
		Dextran hydrogel	Hydrogel	1700	[79]
	CNM-PEI composites	**PEI-modified cellulose aerogels**	**Aerogels**	**1310**	**[26]**
Methyl orange (−)	Other materials	Chitosan/polyvinyl Alcohol/zeolite electrospun composite	Membrane	153	[80]
		Chitosan microspheres	Microspheres	207	[81]
		Amino-functionalized three-dimensional graphene	3D-networks	270.3	[82]
		Functionalized carbon nanotube	Powder	310.2	[83]
		3D hierarchical GO-NiFe LDH	Sandwich-like structure	438	[84]
	CNM-PEI composites	**PEI-modified cellulose aerogels**	**Aerogels**	**1226**	**[26]**
Methyl blue (−)	Other materials	Cellulose membrane prepared from corn stalk	Membrane	8.8	[85]
		BaFe12O19 ferrite particles	Powder	223.9	[86]
		Poly (methacrylic acid-*co*-2-(dimethylamino) ethyl methacrylate) and carboxylated cellulose nanofibrils	Aerogel	598.8	[73]
		Diethylenetriamine-functionalized hollow polymer particles	Powder	1341	[87]
		B-Cyclodextrin functionalized SBA-15	Powder	1790.9	[88]
	CNM-PEI composites	**PEI-modified cellulose aerogels**	**Aerogels**	**1333**	**[26]**
Basic yellow (+)	Other materials	Fe@graphite core–shell nanocomposite	Nanocomposite	52.4	[89]
		Graphene oxide-Polyethylenimine-Polyvinyl alcohol	Hydrogel beads	**862.1**	[90]
	CNM-PEI composites	**Aldehyde-CNF/PEI**	**Powder**	**970**	**[74]**

[a] Bold text highlighting the CNM-PEI composites

Table 5
Compare CNM-PEI composites with other materials for emerging contaminants adsorption capability.

Contaminants	Composites	Maximum adsorption capability (mg/g)	Reference
p-Nitrophenol (*p*NPh)	Microporous activated carbon by $FeCl_3$ activation	184.9	[92]
	Hypercrosslinked magnetic polymer	152.6	[93]
	Nanographite oxide	268.5	[94]
	TEMPO-Oxidized Cellulose-PEI	**1630**	[21]
2,4,5-Trichlorophenol (tCPh)	Macroporous polymers foams (MPFs)	167.7	[95]
	Organo-acid-activated bentonite	244.6	[96]
	TEMPO-Oxidized Cellulose-PEI	**205**	[21]
Amoxicillin	CoFe2O4-modified biochar derived from banana pseudostem	99.99	[97]
	Mesoporous Fe3O4/SiO2/CTAB–SiO2	362.7	[98]
	TEMPO-Oxidized Cellulose-PEI	**556**	[21]

multipollutant modeling approach aimed attargeting simultaneous uptake of coexisting water pollutants.

The current problem is that CNM-PEI composites are usually in powder form which has poor separating capacity and recyclability. Freeze-drying can help to transfer powders to aerogels, but increased energy consumption needs to be accounted for. How to generate stable 3-D structure adsorbents under mild conditions is still the goal of future efforts.

The comprehensive understanding presented herein opens the way for the fabrication of more sophisticated and functionalized systems, which would be capable of providing higher contaminant removal performances, even in multipollutant systems. Moreover, the origin of the CNM can be varied, making these biomass-based materials candidates for sustainable solutions for a wider range of uses.

Abbreviations

CNMs	cellulose nanofiber matrices
PEI	polyethylenimine
CNF	cellulose nanofiber
CNC	cellulose nanocrystal
GAL	glutaraldehyde
EPI	epichlorohydrin
GPTMS	γ-(2,3-epoxypropoxy) propyltrimethoxysilane
TMPTAP	tri-functional trimethylolpropane-tris-(2-methyl-1-aziridine) propionate
CNS	cellulose nano sponges
EDC	N-ethyl-N′-(3-(dimethylamino)propyl)carbodiimide
ECs	emerging contaminants
GMA	glycidyl methacrylate
GDE	glycerol diglycidyl ether
PNPh	p-nitrophenol
tCPh	trichlorophenol
AM	amoxicillin

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Funding

This work was supported by the National Science Foundation CAREER award (2119809) through the BMAT program in the Division of Materials Research and the EPSCoR program. Likewise, the USDA National Institute of Food and Agriculture, Hatch program (ALA013-

17003), and McIntire-Stennis program (1022526) are acknowledged for the support of this work. The authors also want to acknowledge the support from Chinese Scholarship Council (201906300036).

CRediT authorship contribution statement

Yufei Nan: Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft. **Diego Gomez-Maldonado:** Conceptualization, Methodology, Formal analysis, Visualization, Writing – review & editing. **Daniel Whitehead:** Methodology, Writing – review & editing. **Ming Yang:** Writing – review & editing. **Maria Soledad Peresin:** Conceptualization, Methodology, Visualization, Supervision, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Data availability

No data was used for the research described in the article.

Acknowledgements

None.

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