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Nanocellulose-block copolymer films for the removal of emerging organic contaminants from aqueous solutions

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Abstract: The prevalence of emerging organic contaminants (EOCs) in ground and surface water has sparked the search for more effective methods to remove EOCs from the environment. In pursuit of a solution for this environmental concern, herein we present the development of reusable films based on cellulose nanofibers (CNFs) and the block copolymer, poly(4-vinylpyridine-b-ethylene oxide) (P4VP-PEO) to adsorb sulfamethoxazole (SMX) as an EOC model compound. We hypothesize that the adsorption of SMX was achieved mainly by π-π interactions between the pyridine functionalities of the block copolymer and the electron deficient phenyl group of the SMX. Preceding the preparation of the films, CNFs were modified with the alkoxysilane trimethoxy(2-phenylethyl) silane (TMPES) to increase their stability in aqueous solution. After addition of P4VP-PEO, the process was completed by filtration followed by oven-drying. XPS and FTIR were employed to confirm the addition of TMPES and P4VP-PEO, respectively. Adsorption batch experiments were performed in aqueous solutions of SMX at a neutral pH, obtaining adsorptions of up to 0.014mmol/g in a moderate time of 60 minutes. For the reusability tests, films were immersed in ethanol 95% wt. to elude the adsorbed SMX, rinsed with DI water and dried at room temperature to be reused in a new adsorption cycle. We found that this new composite material could be reused several times with negligible lost in adsorption capacity. The presented films have shown to be highly substantial for water remediation as it finds direct application in the adsorption of electron deficient aromatic compounds and its reusable.

KEYWORDS: Cellulose nanofibers (CNFs), Poly(4-vinylpyridine-b-ethylene oxide) (P4VP-PEO), emerging organic contaminants (EOCs), Sulfamethoxazole (SMX)

1. Introduction

Emerging organic contaminants (EOCs) have been identified to be more frequently present in aquatic ecosystems[1]. EOCs consist of a wide array of different compounds that originate from numerous sources such as: pharmaceuticals, food additives, industrial compounds, personal care products, by-products from water treatment[2], wastewater from hospitals effluents and/or chemical manufacturing plants, as well as, livestock, and agriculture[3]. Wastewater treatment plants typically employ the processes of flocculation-filtration as well as oxidation-chlorination. However, flocculation-filtration methods are not able to completely remove EOC's due to the low concentration of the contaminants and ineffective physical interaction. Moreover, degradation of

EOC using chlorination has been found to produce residual by-products that could be potentially more toxic to the environment[2, 4]. Several promising approaches have contributed to the field of EOCs remediation, especially the use and modification of novel carbon-based materials such as graphene[5] and carbon nanotubes (CNTs)[6]. However, ecotoxicity of such materials could make them undesirable for water remediation[7, 8]. Other carbon-based material that has gained interest for applications in water remediation is nanocellulose (NC). NC includes cellulose nanocrystal (CNC), cellulose nanofibers (CNF), and bacterial cellulose (BC)[9]. These materials have several characteristics such as being environmentally benign, stability, and high surface area-to-volume ratio[9, 10]. NC's are typically used as a supporting composite due to its unique structure that consists of a long chain of glucose, with an outskirt of hydroxyl groups[11]. These hydroxyl groups can be exploited to efficiently modify the surface of NC's with chemical functionalities in order to enhance the adsorption capabilities against EOCs. It is well known that NC is easily dispersed in aqueous solutions due to its hydrophilicity[12], which makes it difficult to remove from the solution after an adsorption process. However, adding hydrophobic moieties to the NC surface can solve this issue while promoting the interaction with hydrophobic contaminants. This process can be completed by the covalent addition of alkoxysilanes that contain one or several hydrophobic groups[13]. Further improvement of the adsorption capabilities can be accomplished by the addition of block copolymers (BCPs), a method that has played a very important role in recent years[14, 15]. Block copolymers are potential candidates for water remediation due to their enhanced functional properties. This is possible because these polymers can be configd into a nearly infinite number of molecular architectures based on the composition and molecular weight of its constituting monomers[16, 17]. This versatility can allow the BCPs to interact with EOCs through physical and chemical interactions.

Here, we present a novel material prepared by the modification of CNFs with the alkoxysilane trimethoxy(2-phenylethyl)silane (TMPES) and the addition of poly(4-vinylpyridine-b-ethylene oxide) (P4VP-PEO). This material was used to fabricate films for the adsorption of sulfamethoxazole (SMX) as a model and current EOC in water. These films are stable in water since the phenyl groups provided by the silane confers hydrophobicity to the CNFs surface. Additionally, the P4VP-PEO present in the structure can interact with SMX by means of electron-donor-acceptor (EDA) interactions to complete the adsorption process. Finally, these films can be reusable by applying a simple method of immersing of the material in ethanol to elude the SMX, rinsing it with water, and drying at room temperature.

Experimental

2.1. Materials and methods

TMPES 98%, glacial acetic acid, and SMX analytical standard were purchased from Sigma-Aldrich. CNFs (3 % wt. aqueous slurry) were acquired from the University of Maine Process Development Center. P4VP-PEO (20 kD – 5 kD) was purchased from the Polymer Source Inc. All reagents were used without further purification.

2.2. Preparation of composite films

2.2.1. Modification of CNFs with TMPES and P4VP-PEO

TMPES was hydrolyzed in a polypropylene container by dissolving TMPES (2:1 respect to the mass of CNFs) under magnetic stirring in ethanol/water 80:20 and by adding a small drop of acetic acid. Hydrolysis was completed after 2h at room temperature. Amidst the hydrolysis of TMPES, the CNFs solution was dispersed in ethanol/water 80:20 with the addition of a small drop of acetic acid in order to match the conditions of the hydrolysis of TMPES. Once the hydrolysis of the alkoxysilane was completed, CNFs solution was added to the TMPES solution under continuous stirring, and the reaction was left to occur for 24h. CNFs solutions containing P4VP-PEO were

prepared following the same procedure stated above. However, P4VP-PEO was added to the mixture of CNFs and hydrolyzed TMPES.

2.2.2. Preparation of TMPES-modified CNFs films and TMPES and P4VP-PEO-modified CNFs films

Once the solution was completely synthesized, ultrasound was employed to obtain a homogeneous dispersed mixture. Using vacuum filtration, it was possible to separate the solid materials and obtain the films. To successfully attain the films without breakage, a nylon filter (0.47μm) was first placed into the vacuum filtration system, and then the solution was added. To avoid shrinkage after filtration, each film was dried with nitrogen gas while inside the vacuum filtration system. After this, the film was peeled off from the nylon filter, placed in an oven at 110 °C for 2h, and then stored in a petri dishes for further use.

2.2.3. Characterization of modified CNFs films

Modified CNFs films were characterized by Fourier-transform infrared (FTIR) using a Bruker Tensor 27 attenuated total reflectance (ATR) spectrometer. The spectral width ranged from 400-4000 cm^{-1} for 32 accumulation scans and 4 cm^{-1} of resolution. X-Ray Photoelectron spectroscopy (XPS) binding energy were obtained using a PHI 5600 spectrometer equipped with an Al Kα mono and polychromatic X-ray source operating at 15 kV, 350 W with a pass energy of 58.70 eV. Films were also analyzed using a JEOL 6480LV scanning electron microscopy (SEM) to assay their surface morphology. Wettability of the films was tested by Contact angle measurements performed with a Krüss drop shape analyzer DSA25S at room temperature. A 1 cm^2 piece of CNFs, TMPES-modified CNFs, or TMPES and P4VP-PEO-modified CNFs films was fixed in the stage of the instrument and a 4.5.0 μL DI water droplet was used for the analysis. Images of the drop were recorded as a function of time and analyses in real-time using Advance software (Version 1.8).

2.3. Adsorption batch experiments of SMX using TMPES-modified CNFs films and TMPES and P4VP-PEO-modified CNFs films

2.3.1. Adsorption as a function of time

Adsorption capacity of the films with or without P4VP-PEO were measured after placing them in contact with a SMX solution for 1 min, 10 min, 30 min, 60 min, and 240 min. 10 mL of 25 ppm SMX solution was used for each sample and shaken at 250 rpm for the stipulated equilibration time. The absorbance of each sample solution was collected before and after the adsorption using a Thermo Scientific Genesys 10S UV-Vis spectrometer. Using the absorbance values, it was possible to calculate the SMX concentrations and then the equilibrium adsorption amount of the films using the following equation,

$$q_e = \frac{(C_0 - C_e)V}{w}$$

where q_e is the equilibrium adsorption amount (mg/g), C_0 is the initial concentration of SMX (mg/L), C_e is the equilibrium concentration of SMX after the adsorption (mg/L), V is the volume of the SMX solution, and w is the mass of the modified CNFs. Experiments were performed in triplicate at 25 ºC.

2.3.2. Adsorption Isotherm experiments

Batch adsorption isotherm tests were carried out in triplicate using TMPES-modified CNFs films with and without P4VP-PEO. The prepared solutions ranged from 1 ppm to 100 ppm, and the contact time was set to 1h. 10.0 mL of each SMX solution was transferred to 50 mL falcon tubes and

a piece of the film was added to the solution. Afterwards, the samples were placed in a shaker at 250 rpm and 25 °C. The absorbance of each sample solution was collected before and after the adsorption and measured using UV-Vis. The equilibrium adsorption amount of the films was calculated using the equation aforementioned in the adsorption as a function of time section.

2.3.3. Reusability testing

In order to assay the reusability of the TMPES and P4VP-PEO-modified CNFs films with, used films were immersed in 95 % wt. ethanol to elude the adsorbed SMX. This process was performed at least 5 times in triplicate for samples used in 1h batch adsorption experiments of 10 mL 25 ppm solution of SMX. The elution time in ethanol was set at 1h in continuous shaking of 250 rpm and 25 ºC. Afterwards, films were rinsed with 200 mL of water to remove the remnant ethanol, dried with compressed air until constant weight and used for another batch adsorption cycle. Equilibrium adsorption amount was calculated and plotted as a function of the cycles.

3. Results/Discussion

3.1. Modification of CNFs with TMPES and P4VP-PEO

Although alkoxysilanes with a wide range of functionalities have been continuously used as coupling agents to promote the adhesion of different polymeric surfaces[13], in this investigation, we aimed to enhance the stability of CNFs in aqueous solution. Previously, we prepared composites of nanocellulose cellulose grafted with a block copolymer intended for the adsorption of EOCs. This composite was easily dispersed in aqueous solution, making their removal after the adsorption difficult and time-consuming[18]. Modifying the surface of CNFs with a hydrophobic functionality limits the solvation of the cellulose making it stable against dispersion. A silane compound, TMPES, was selected (fig 1a) mainly due to its hydrophobic phenyl arm that is separated from the silane by two carbons, which is likely to help in lowering the steric repulsion during the reaction.

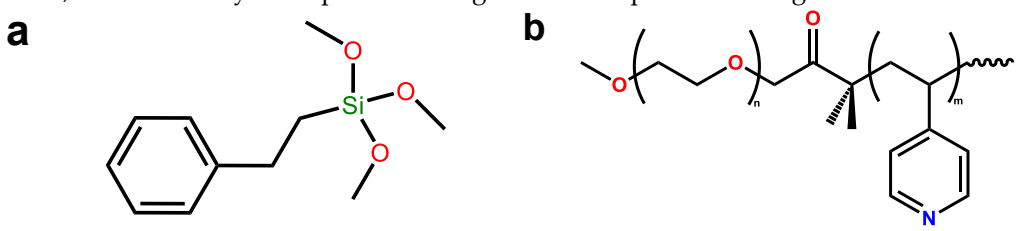

Fig 1. Molecular structure of a) TMPES and b) P4VP-PEO

Due to the lower acidity of cellulosic hydroxyl groups present in CNFs, TMPES would have been unable to form covalent bonds in the CNFs surface[19]. For that reason, it was necessary first to hydrolyze the trimethoxy groups in TMPES to form silanols. This step also promotes the formation of -Si-O-Si- bonds that are resistant to hydrolysis; consequently, they are unable to react with CNFs. Brochier-Salon *et al*, studied the kinetics of hydrolysis of several alkoxysilanes (TMPES included) under acidic conditions using ^{29}Si NMR. This study found that after approximately 3h *ca.* 92% of silanol sites are still available with some formation of -Si-O-Si- groups[20]. Based on those findings, we carried out the hydrolysis for 2h to avoid the presence of -Si-O-Si-. Thus, the resulting silanols would be available to interact with the hydroxyl groups of the CNFs surface via hydrogen bonds. These interactions are reversible, but heat treatment at 110 ºC for 2h is sufficient to form the -Si-O-C- bonds[13].

Once modified, the TMPES-CNFs composite can provide a support for the active adsorbent, P4VP-PEO (Fig 1b). P4VP-PEO is a block copolymer that is responsive to pH due to protonation/deprotonation of the pyridyl group. Also, slight changes in temperature can promote intermolecular interactions of the ethylene oxide chains[21]. Here, we take advantage of the high electron density of the pyridyl groups of the block copolymer to adsorb low electron density EOCs

such as SMX. By means of electron-donor-acceptor (EDA) interactions[22], it is possible to remove the SMX from aqueous solution. Since these types of interactions are reversible, it would enable the reversed adsorption reaction with a simple solvent exchange to allow the reuse of the material (Fig 2c). The addition of solid P4VP-PEO was performed during the reaction of silanols with CNFs. This mixture led to the formation of a matrix where the hydrophilic ethylene oxide chains interact with CNFs and the vynilpiridyl functionalities interact with the phenyl groups of the silane (Fig 2a). Fig 2b shows the actual CNFs films after the modification. It can also be noted that after immersion in water, films can adsorb the liquid despite of the hydrophobic modification. Interestingly, when CNFs films without modification were shaken in water at 250 rpm for 24h, the films dispersed in the solution, while TMPES-modified CNFs films remained undamaged (Fig S1).

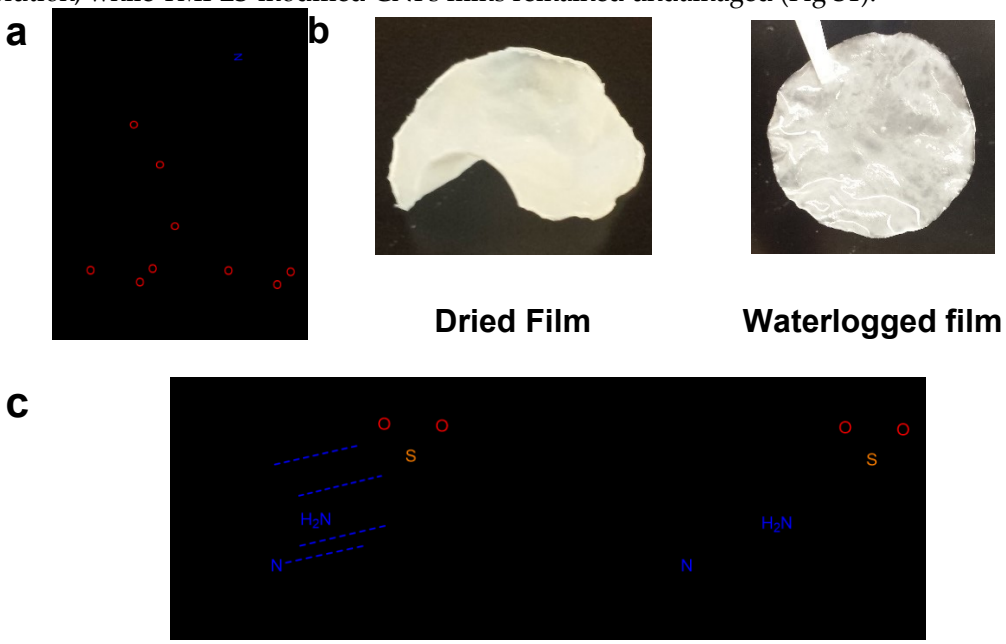

Fig 2. a) Molecular structure of TMPES covalently attached to the surface of CNFs showing the presence of P4VP-PEO. b) photographs illustrating the dried and waterlogged CNFs films. c) schematic of the EDA interaction of pyridyl ring of P4VP-PEO with the substituted phenyl group of SMX and its elution with ethanol.

3.2. Characterization of the modified CNFs films

CNFs and TMPES-modified CNFs were characterized using XPS (Fig 3). The XPS spectrum of the TMPES-modified CNFs clearly shows the peaks corresponding to Si 2s at around 150 eV and Si 2p at 100 eV. These peaks are not present in the XPS spectra of CNFs, confirming the successful addition of TMPES.

Fig 3. XPS spectra of CNFs and TMPES modified CNFs films

Deconvolution of C 1s XPS spectrum of CNFs films shows four peaks that are characteristic of cellulose materials[23](fig 4a). The peak at 284.8 eV corresponds to C-C and C-H bonds. The peak at 286.7 eV is related to carbon atom bond to a single oxygen atom. This peak in general is the most intense due to the large amount of hydroxyl groups in the cellulose structure. The peak at 288.4 eV corresponds to carbon atom bond to two oxygen atoms. The peak at 290.4 eV represents a carbon atom linked to one carbonyl oxygen and one non-carbonyl oxygen. The fitted C 1s XPS spectrum of TMPES-modified CNFs films shows the same peaks as CNFs in addition to one new peak at 287.8 eV (fig 4b). This peak possibly is related to the new bond between Si-O-C obtained after the modification with the alkoxysilane. This type of bond is also found in the deconvolution of Si 2p spectrum of TMPES-modified CNFs films (fig 4c). Here, the peak at 103.2 eV represents one silicon atom bond to one oxygen atom that at the same time is linked to one carbon (Si-O-C)[24]. In addition, the peak at 101.7 eV suggests that there is polymerization of the silane in the surface of CNFs, due to the formation of Si-O-Si bonds[25]. However, this polymerization is small compared to the formation of the covalent bonds with CNFs if we consider the intensity of the Si-O-Si and Si-O-C peaks.

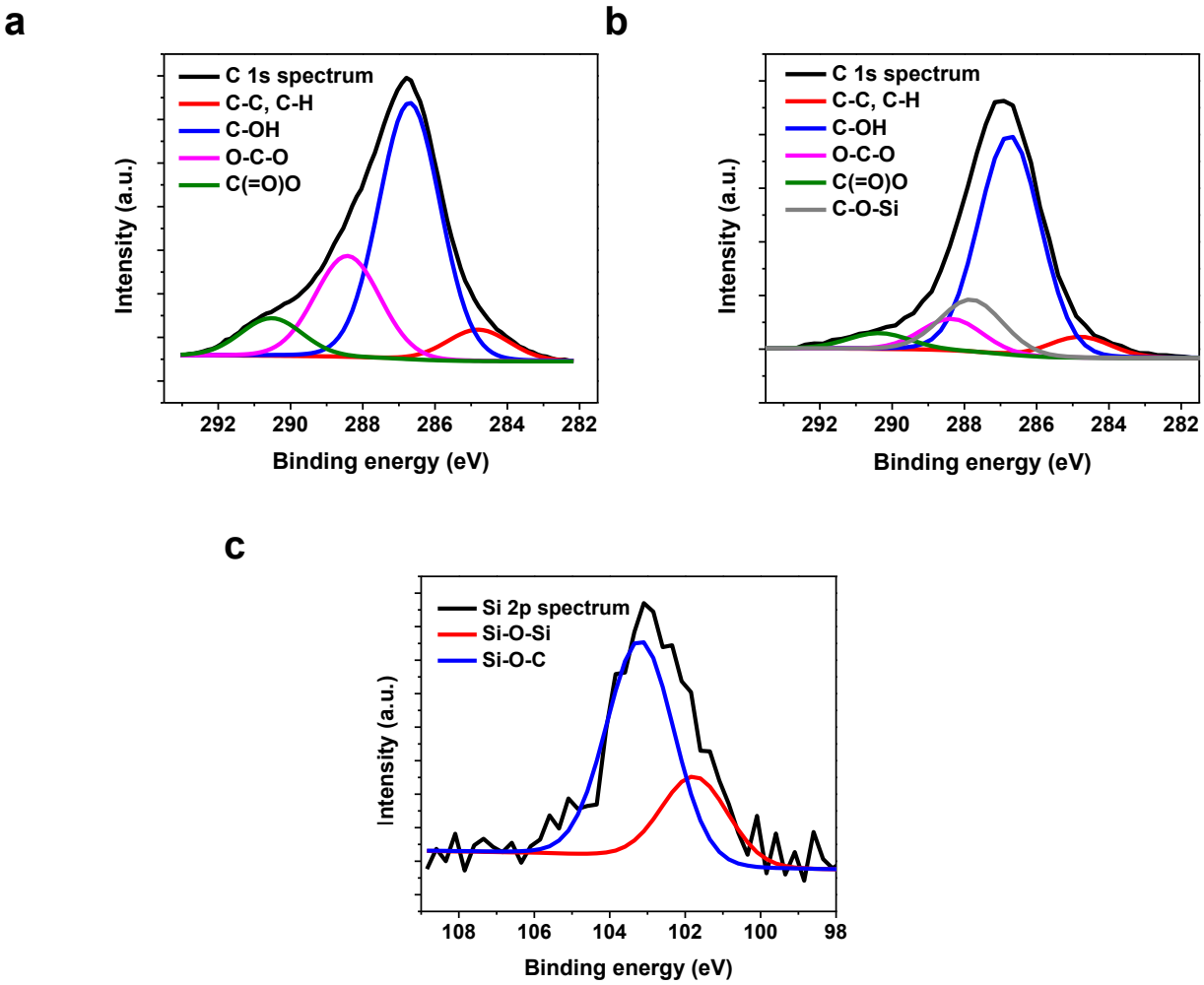

Fig 4. Fitted high resolution C 1s XPS spectra of CNFs (a) and TMPES-modified CNFs films (b). Fitted high resolution Si 2p XPS spectra of TMPES-modified CNFs films (c).

Furthermore, FTIR was used to identify the critical functional group vibrations of the different components of the modified CNFs films. Fig 5 shows the spectra of CNFs highlighting their characteristic functional groups. A signal observed at 3300 cm^{-1} is assigned to the hydroxyl stretching vibration (OH-), the band at 2800 cm^{-1} corresponds to the stretching vibrations of the methylene groups (CH_2-), while a sharp band around 1100 cm^{-1} corresponds to the glycosidic ring stretching. The presence of a small band around 1650 cm^{-1} which is related to adsorbed water is also common. Despite of the modification of CNFs with TMPES, the FTIR spectrum of these films did not show any band related to the phenyl groups of the silane. It is possible that the expected band were overlapped in the region of the CNFs hydrogen bending that ranges from 1300 cm^{-1} to 1600 cm^{-1}. The same effect occurred to the silicon signal expected from 500 cm^{-1} to 1000 cm^{-1} [26]. In the FTIR spectrum of the CNFs films modified with TMPES and P4VP-PEO, it was possible to identify two bands at 1415 cm^{-1} and 1596 cm^{-1} [27]. These bands correspond to the vibrations of the pyridine ring that were also present in the spectrum of P4VP-PEO. This is clear evidence that suggests the successful addition of P4VP-PEO to the CNFs films.

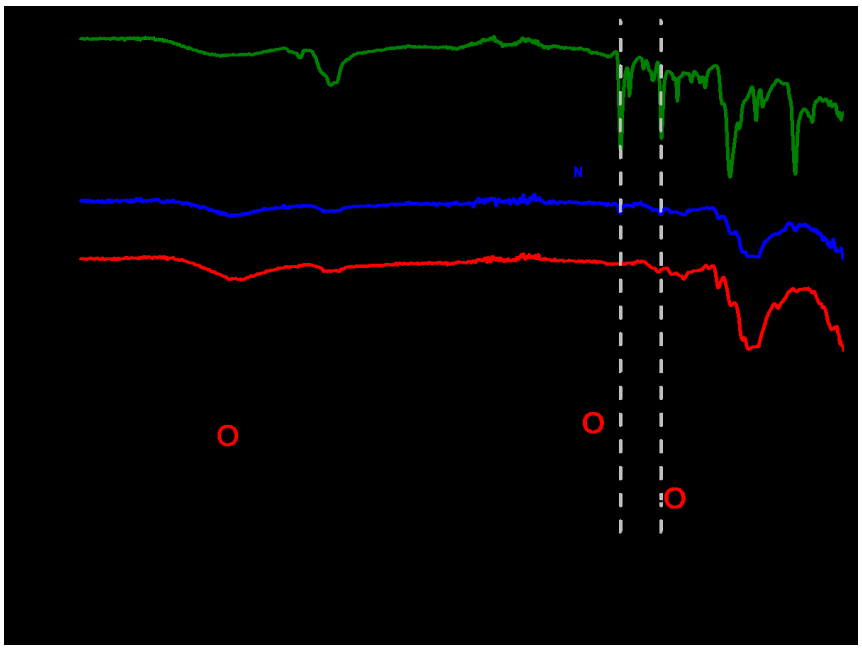

Fig 5. FTIR spectra of CNFs, P4VP-PEO, CNFs + PEMS and CNFs + PEMS + P4VP-PEO

Contact angle (CA) measurements were used to estimate the wettability of CNFs films and CNFs with the respective modifications (fig 6). The phenyl group in TMPES acts as a hydrophobic group that makes the solvation of cellulose fibers difficult. This behavior can be observed in fig 6b, which shows a CA of 85º for TMPES-modified CNFs films at time 0. After 120s, the value decreased to 66º due to water penetration via diffusion through the film. This result is directly related to the ratio of TMPES/CNFs used for the modification that is critical to gradually wet the films and avoid their dispersion in aqueous solution. In contrast, the water droplet penetrated the CNFs film without modification almost immediately after it came in contact with the surface. After 120s, the film started to separate from the surface. This phenomenon is a consequence of the swelling of the material due to high hydrophilicity of cellulose that leads to the penetration of water molecules[28]. TMPES and P4VP-PEO-modified CNFs films had higher wettability compared to CNFs films modified with TMPES. Here, the CA was 56º, which remained steady during the measurement. This increase in the CA is likely an effect of the polyethylene oxide chains in P4VP-PEO that add hydrophilicity to the films[29].

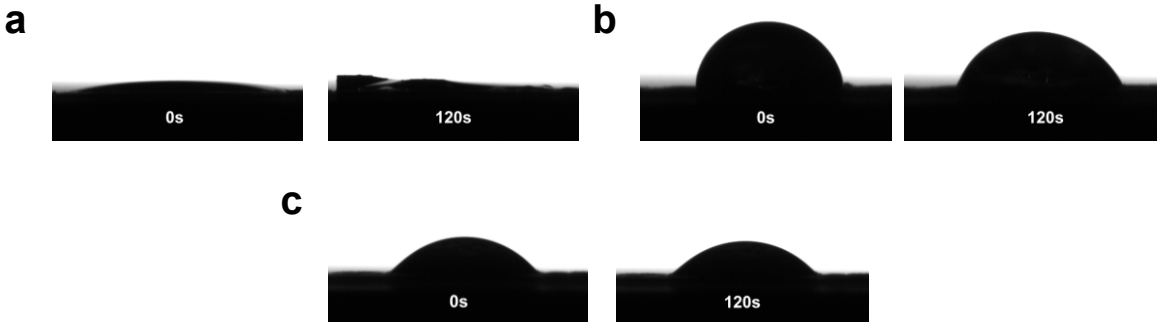

Fig 6. Contact angle measurements of a) CNFs films, b) TMPES-modified CNFs films, and c) TMPES and P4VP-PEO-modified CNFs films.

SEM micrographs of TMPES and P4VP-PEO-modified CNFs films show a rough morphology along the surface (Fig 7). A closer inspection of the images reveals that the surface is composed of tightly agglomerated fibers that are randomly distributed. This is an effect of the method used to prepare the films. Initially, components are suspended in the solution, but once the vacuum filtration begins, modified cellulose fibers accumulate layer-by-layer as shown in the cross-section

image of the films (fig 7c). These micrographs also reveal that the films are quite monolithic with minimal observable porosity, suggesting that only P4VP-PEO found in the surface of the films is readily available to interact with SMX.

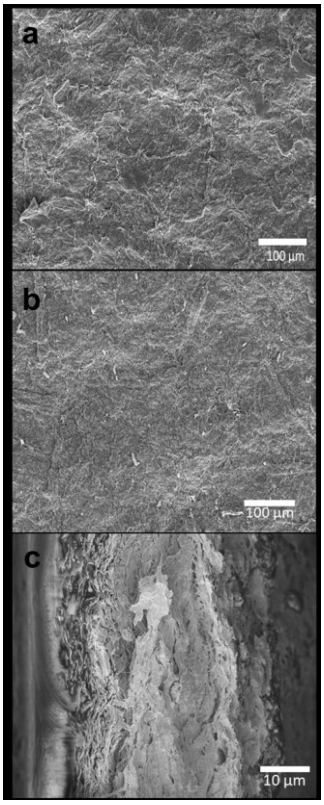

Fig 7. SEM micrographs of (a front side, b) back side, and c) cross-section of TMPES and P4VP-PEO-modified CNFs films.

3.3. Adsorption batch experiments of SMX

Batch experiments were performed in order to assess the adsorption capacity of TMPES and P4VP-PEO-modified CNFs films against SMX as an EOC model compound. Batch experiments using TMPES-modified CNFs resulted in a negligible adsorption, which suggests that only P4VP-PEO is able to adsorb SMX (fig S2). The effect of equilibration time on the adsorption of SMX using TMPES and P4VP-PEO-modified CNFs films is shown in fig 8. This graph displays low q_e when equilibrium adsorption time was set to 1 min. However, taking the measurement error into consideration, the difference between this point and higher equilibration times is minimal; therefore, most of the adsorption could be occurring on the surface of the films. This outcome is supported by the CA measurements data and SEM images that showed a low water penetration and a tightly packed structure, respectively. Fig 8 (right) shows a representation of SMX adsorbed on the surface of the modified CNFs films where P4VP-PEO is readily available. If we follow the trend line of the plot in fig 8, the optimal adsorption equilibrium time is reached at approximately 60 min. After this point, higher equilibrium times did not cause a significant change in q_e. Consequently, 60 min was used as a default adsorption equilibrium time for further batch adsorption experiments.

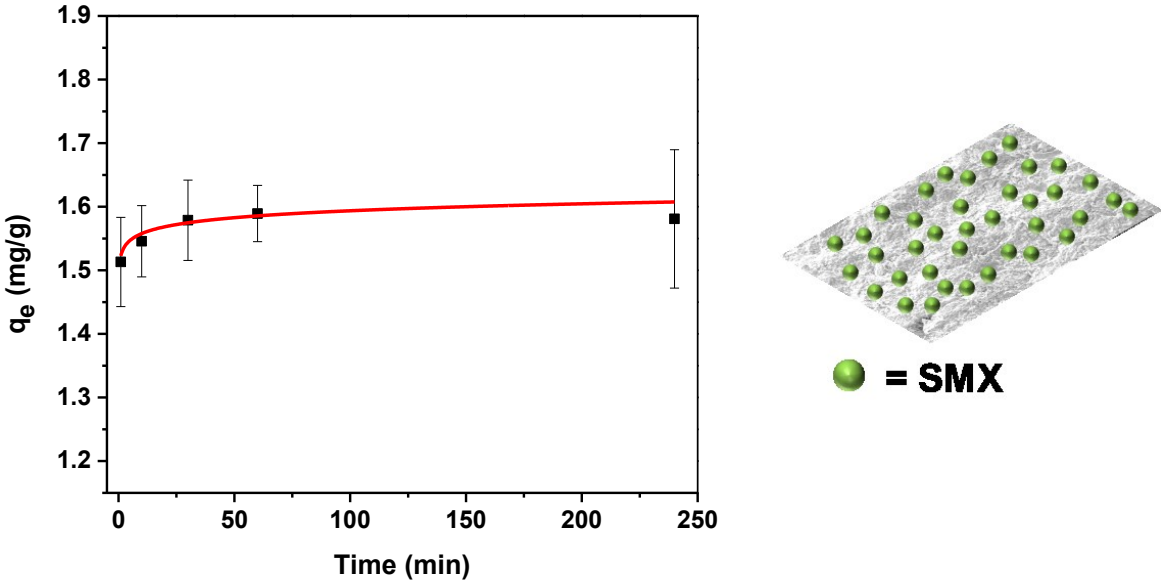

Fig 8. Adsorption capacity of TMPES and P4VP-PEO-modified CNFs films as a function of time (left), with a representation of the superficial adsorption of SMX (right).

The adsorption isotherm of SMX using TMPES and P4VP-PEO-modified CNFs films was obtained at equilibrium time of 1h, neutral pH, and room temperature. After determining the q_e and the SMX equilibrium concentration (C_e), the resulting plot was fitted with the Freundlich mathematical model. The Langmuir model was also utilized, but a poor fitting suggested a distribution of active adsorbent sites rather than formation of a homogeneous monolayer at adsorption equilibrium[30]. The Freundlich isotherm model is an empirical equation introduced to describe the processes of adsorption. In this expression,

$$q_e = K_f C_e^{1/n}$$

q_e represent the equilibrium adsorption amount (mg/g), K_f and n are empirical constants that are related to the adsorption magnitude and effectiveness, and C_e is the concentration in equilibrium (mg/L). Fig 9 (left) shows the non-linear fitting of the q_e as a function of the C_e. This fitting suggested that the modified film had not reached its maximum adsorption capacity. Unfortunately, we were not able to determine the maximum adsorption capacity for two reasons: at higher concentrations of SMX is unstable in aqueous solution (see fig S3) and a reduction of the mass of the films used in the adsorption experiment may result in higher deviations. The linear form of the Freundlich equation

$$lnq_e = lnK_f - \frac{1}{n} lnC_e$$

can be used to determine K_f and n (fig 8, right). In this case, n was determined to be approximately 4.3.In general, values of n > 1 are common and suggest that the adsorption proceeded by physical interactions, and that agrees with our hypothesis of the EDA interactions between SMX and modified CNFs. Moreover, n values between 1-10 can generally be related to satisfactory adsorptions[31].

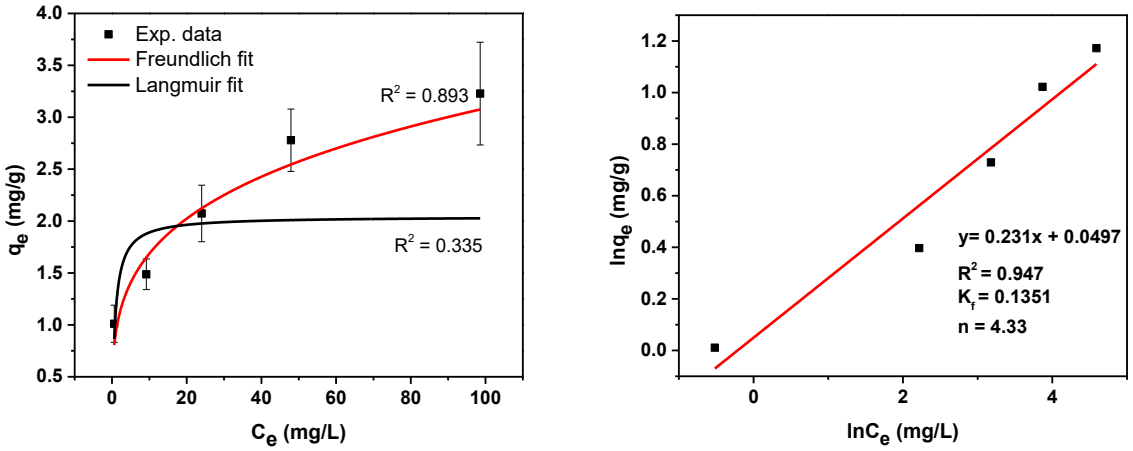

Fig 9. Adsorption isotherm of SMX using TMPES and P4VP-PEO-modified CNFs films fitted with the non-linear forms of Freundlich and Langmuir (left) and linear form of the Freundlich (right).

In terms of the reusability, fig 10 indicates that TMPES and P4VP-PEO-modified CNFs films can be reused with negligible loss in adsorption capacity under the studied conditions. In fact, a small increase in the adsorption capacity can be appreciated after several cycles. This phenomenon can be related to the swelling of the CNFs fibers due to the high concentration of ethanol (95%) used to elude SMX[32]. Presumably, this swelling caused that P4VP-PEO molecules that were initially inaccessible to be exposed; therefore, they became available as new active sites for SMX adsorption.

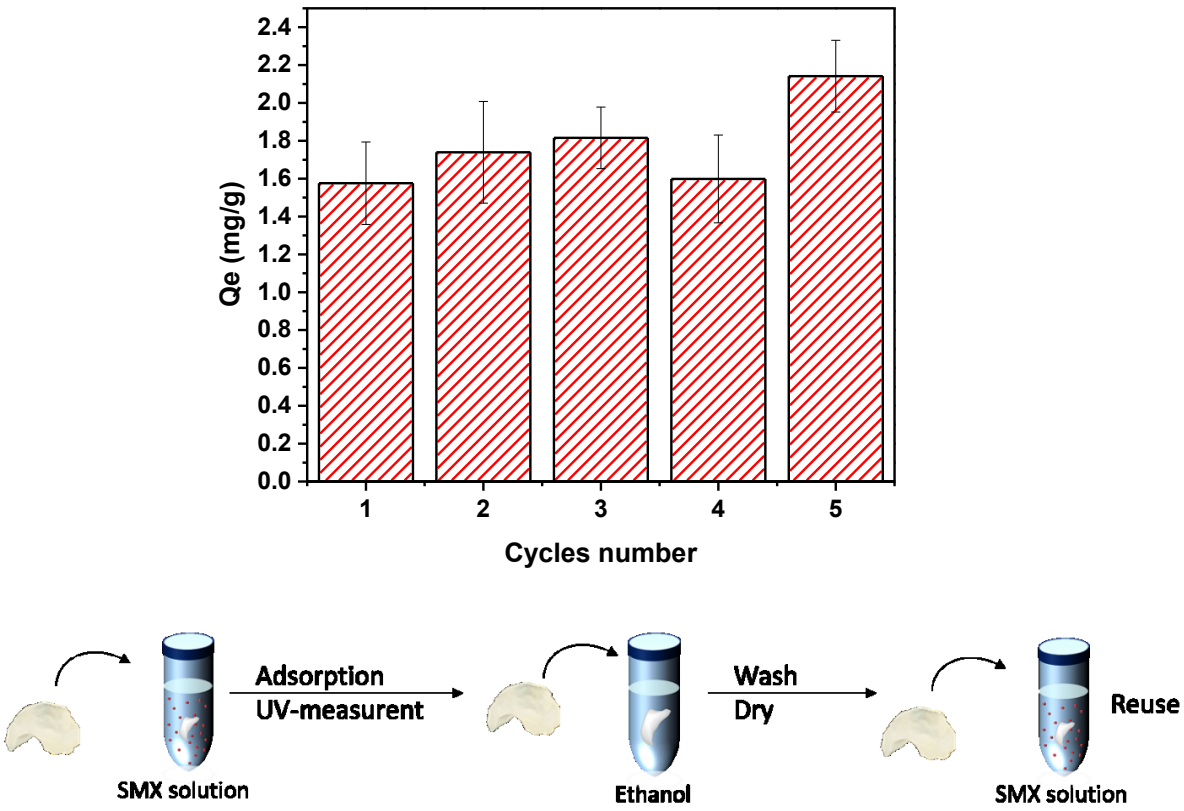

Fig 10. Adsorption capacity of TMPES and P4VP-PEO-modified CNFs films after different adsorption cycles of 25 ppm SMX for 1h equilibrium time (top). Schematic of the reusability process of the modified films (bottom).

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Supporting Information: Supporting information contains other characterizations.

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