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Facile functionalization of cellulose from discarded cigarette butts for the removal of diclofenac pharmaceutical from water

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Graphical abstract

Highlights

- Cellulose nanofibers and crystals were synthesized from discarded cigarette butts.
- Cellulose nanofibers were functionalized with phosphate ions to synthesize HPO-CNFs.
- Effect of pH on diclofenac and adsorption mechanism was elucidated by HPO-CNFs.
- Adsorption capacity of HPO-CNFs for diclofenac was 107.90 mg/g.
Abstract
In this study, cellulose nanocrystals (CNCs), and cellulose nanofibers (CNFs) were extracted from discarded cigarette butts (DCBs), and investigated for their efficiency for diclofenac (Dfc) removal from water. CNFs extraction process involved cleaving of acetyl group by alkali treatment and etched with phosphate ions (HPO) from phosphoric acid to obtain the variably charged HPO-CNFS. To obtain CNCs, sulfuric acid was used to cleave phenol moieties from CNFs under high temperature and agitation. SEM, FT-IR, SEM-EDS, Raman spectroscopy were used to analyze the physico-chemical properties of synthesized cellulose materials. The SEM images revealed the exfoliated fiber strands of CNFs after extraction procedure, and the difference in the crystal structure of CNCs₃₀ and CNCs₆₀. The EDS analyses revealed the presence of higher amount of carbon in DCBs compared to other forms of synthesized celluloses. The FT-IR analyses revealed functional group shifts and bond reductions after various treatment steps, while the HPO attachment on the CNFs surfaces was confirmed by the presence of P-O bonds. Raman analyses revealed clear crystals in the CNCs₆₀ compared to the other celluloses. The adsorption capacity of HPO-CNFS for diclofenac removal was found to be 107.90 mg g⁻¹ and Langmuir model fitted well to the adsorption data.

Keywords: Discarded cigarette butts; Cleaving; Celluloses; Adsorption; Diclofenac.

1. Introduction
Discarded cigarette butts (DCBs) commonly referred to as “cigarette butts” are one of the most littered items globally (Chevalier, et al., 2018, Rebischung, et al., 2018). DCBs are mainly deposited in terrestrial and aquatic habitats, where they pose a serious threat to the
environment due to their inability to easily biodegrade, and the presence of many trapped toxic agents in the filters after usage. The toxicity stems from thousands of trapped carcinogenic agents in the filters after usage, which can leach into the environment, and eventually enter into the food web (Register, 2000). Apart from their toxicity, they cause reduction in the aesthetic value of the environment, notably beaches, streets, public lawns, and also choke drains, which can cause flooding (Novotny, et al., 2009). The predominant material of DCBs has evolved from plastic to cellulose acetate (Capehart, 2006), with a strong lignin networks which shields the cellulose from microbial degradation (Christopher, et al., 2014) making DCBs environmentally persistent. The estimated volume of DCBs produced worldwide, the persistency, as well as the toxic content after usage, suggest that highly efficient disposal or recycling strategies are needed to solve the menace of DCBs litter. Existing disposal strategies, such as landfilling and incineration, have been reported to be unsustainable worldwide due to economic and environmental concerns (Yuan, et al., 2006). In both incineration and landfilling, cases of toxic emissions and leaching of toxic pollutants have been reported (Knox, 2005, Yuan, et al., 2006). To reduce the impact of pollution from DCBs, an environmentally friendly recycling strategy is needed, which will yield new useful products with less or no formation of detrimental end products. Recycling of DCBs into other products have been reported (Lima, et al., 2018, Teixeira, et al., 2017, Xiong, et al., 2019). DCBs also possess a bulk reserve of cellulose based on the parent material and the extracted cellulose has the potential, as cellulosics from other sources, to be transformed into films, membranes, and fibers. Cellulose nanofibers currently have been exploited as reinforcement agents in composites (Kumagai, et al., 2019), and surface-modified to obtain an effective heavy metals adsorbent (Abu-Danso, et al., 2018). The main barrier in the transformation of DCBs into cellulose is finding an efficient procedure to remove the acetate groups and the myriad of pollutants to obtain cellulosics and further
puriﬁcation to achieve the desired cellulosic product without altering the original cellulose structure. A successful conversion of DCBs into useful cellulosic products will solve the problem of pollution by DCBs through recycling and contribute to an effective circular economy.

This work focuses on the conversion of discarded cigarette butts (DCBs) into cellulosics via multiple cleaving, ﬁrstly, using robust alkalization to extract cellulose nanofibers (CNFs) by acetyl group cleaving of DCBs and subsequent application of H_2SO_4 to cleave lignin under high temperature and agitation and acetic buffer conditioning. Secondly, to synthesize phosphate ions etched CNFs (HPO-CNFs) by the interaction of phosphoric acid, dissociated in water as the source of negative phosphate ions with the phenol ring of lignin. This procedure explores the clustered glycoside regions of lignin in DCBs, which presents a broad surface area from the repeating units and enhances binding of chemical entities through ion exchange. The synthesized HPO-CNFs were used for the removal of diclofenac (Dfc), an important pharmaceutical compound, from aqueous medium and the performance of HPO-CNFs as an adsorbent was assessed by studying optimum solution pH, contact time, competing ions and initial adsorbate concentration in batch studies. Different kinetic and isotherm models were applied to study the adsorption mechanisms.

2. Materials and methods

2.1. Materials

Sodium hydroxide, sodium chlorite, and acetic acid were purchased from Sigma-Aldrich Oy, (Finland), and ethanol was purchased from Altia Oyj, (Rajamaki, Finland). Sulfuric acid was purchased from Fisher chemical, (UK). Diclofenac sodium, and phosphoric acid (Hygroscopic) were obtained from Acros organics (Geel, Belgium).

2.2. Conditioning of discarded cigarette butts (DCBs)
Discarded cigarette butts (DCBs) were collected from designated public cigarette smoking points and bars in Kuopio, Finland. The filters were soaked in water to remove covering papers and also wash out ash and left-over tobacco. Burnt tips were cut off and washing was repeated. The conditioned DCBs were then thoroughly dried at ca. 30 °C in an air-circulating oven. Dried DCBs (ca. 10 g) were initially washed in ethanol by stirring vigorously for ca. 4 h to remove all stains and then washed in water for ca. 3 h to remove all traces of ethanol. The filters were then dried thoroughly at ca. 30 °C in an air-circulating oven. For the next procedure, the dried cigarette filter strands were sorted manually for entangled filter strands.

2.3. Synthesis of cellulose nanofibers (CNFs) from DCBs

To initiate acetyl groups cleaving, the conditioned DCBs were thermally treated at ca. 60 °C with 5% (w/v) NaOH solution for 6 h under vigorous stirring. The resultant fibers were thoroughly washed in deionized water to neutralize the pH and dried afterwards. For further conditioning, CNFs fibers were shredded manually and stabilized following the procedure reported in literature (Silvério, et al., 2013) with slight modifications. Approximately, 4 g of the conditioned fibers were dispersed into acetic buffer solution (15 g NaOH, 40 mL glacial 1.7 wt% NaClO₂ in 500 mL deionized water) and stirred vigorously at ca. 60 °C for 6 h. The conditioned CNFs were recovered from the buffer solution by mesh sieving and dried in air circulating oven at ca. 25 °C and milled.

2.3.1 Synthesis of phosphate ions (HPO) etched CNFs (HPO-CNFS)

The previously synthesized CNFs were thoroughly pulverized in a blender, ca. 0.1 g amount was placed in a 50 mL tube containing 30 mL 0.5 M hygroscopic phosphoric acid (H₃PO₄) and tightly sealed. The mixture was agitated on a stirrer at 200 rpm for 4 h to allow enough etching action on the lignin and allow exchangeable ions between the robust phenolic units of lignin and the dissociated negative phosphate ions. The internally generated heat energy from the whirling action in the tube was used to drive the phosphate ions etching, hence the tube
was tightly sealed to prevent heat lose. After the set exchangeable time, the tightly sealed tube was left to cool without opening. The obtained HPO-CNFS were washed by centrifugation to remove the excess phosphoric acid and placed in the oven with mild heat to promote dehydration in the medium. The dried HPO-CNFS were pulverized and stored.

2.4. Synthesis of cellulose nanocrystals (CNCs) from DCBs

Cellulose nanocrystals were obtained via acid hydrolysis of obtained CNFs, as described in the latter section following a modified version (Abu-Danso, et al., 2017). To assess the effect of hydrolysis duration on CNCs synthesis, 30 min (CNCs\textsubscript{30}) and 60 min (CNCs\textsubscript{60}) durations were studied as shown in Fig 1. Two glass beakers labeled (CNCs\textsubscript{30} and CNCs\textsubscript{60}) containing 100 mL sulfuric acid solution (10 M) were placed on a hot magnetic plate (Heidolph MR3001, Germany) and heated to ca. 40 °C. The CNFs (ca. 4 g) were dispersed into each of the beakers under continuous stirring to begin the hydrolysis. The hydrolysis was terminated at each set time by adding over ten folds of water to the mixture and washed repeatedly by centrifugation at 7000 rpm for 5 min without NaOH neutralization. The washing was completed at the point where the supernatant and filtrate could no longer be separated. The mixture was dialyzed against water until the exchanging water molecules reached neutral pH. The cellulose suspension was ultrasonicated (UP400S Hielscher, Germany) and centrifuged to separate the excess water and CNCs and freeze dried.
Fig. 1. Schematic representation for the syntheses of different forms of celluloses (CNFs, CNC$_{30}$, and CNC$_{60}$) from discarded cigarette buts (DCBs).

2.5. Characterization methods and techniques

The pH point of zero charge analysis of the synthesized HPO-CNFs was determined following previously reported procedure (Abu-Danso et al 2018). Briefly, a solution of 0.01 M NaCl was prepared and 25 ml of the solution was placed in different tubes. Initial pH ($pH_o$) of the solutions was adjusted from 2 to 10 using 0.1 M HCl or NaOH as reported in other study (Mosleh, et al., 2016a). An amount (0.004 g) of HPO-CNFs was added to each solution and the mixture was agitated on a shaker for 24 h. Afterwards, the mixture was filtered. The plot of change in initial and final pH ($\Delta pH$) against initial pH was used to determine the pH$_{zpc}$ of the HPO-CNFs. Fourier transform infrared spectroscopy (FT-IR) analysis was conducted to study the changes in functional groups between the precursor (DCBs), synthesized CNFs, CNC$_{30}$, CNC$_{60}$ and HPO-CNFs using Thermo Nicolet iS50 model (Thermo electron, Madison USA). The spectra were recorded in the range of 500–
3800 cm\(^{-1}\) at 40 scans. The surface morphology of the DCBs and all synthesized cellulosics were examined using Zeiss sigma HDVP (Carl Zeiss GmbH, Oberkochen Germany), at different magnifications and voltages. The samples were mounted on a SEM stub smeared with graphite conductive adhesive and gold-coated using agar auto sputter. Samples for EDS analysis were mounted on a SEM stub without coating to reduced interference in the elemental count. The EHT was increased to ca. 15 kV with varying magnifications for optimum resolution. The Raman spectra of the synthesized cellulosics were analyzed with Olympus DXR2xi (Thermo Fisher Scientific, Madison, USA) between 50 to 3300 cm\(^{-1}\) spectral range at 20 scans. The sample was placed on a small metal cup and the measurements were switched between 20× and 50× objective lenses for optimum spectral recording using 785 nm laser operating at 25 mW power. DCBs samples for the analysis of heavy metals, trapped in the DCBs, were washed and placed in digestion cones containing a known volume of concentrated sulfuric acid. The mixture was then digested for 1 h in a Mars 6 Iwave microwave digester (LT scientific, USA). The heavy metals present in the solution, after digestion, were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer Analytik Jena Zeenit 700, Jena, Germany).

2.6. Batch adsorption experiments

Adsorption experiments were conducted in batch mode to study the removal of diclofenac (Dfc) from aqueous medium by HPO-CNFS. Diclofenac sodium (C\(_{14}\)H\(_{10}\)Cl\(_{2}\)NNaO\(_2\)) salt was used to prepare the stock solution and kept in the dark to prevent photodegradation. Working solutions were prepared from the stock solution by dilution with milli Q water and the pH was adjusted by adding 0.1 M HCl or NaOH. A desired amount of synthesized HPO-CNFS was added to the tubes containing 10 mL of 20 mg L\(^{-1}\) Dfc at pH ca. 5.5 and the mixture was agitated at 200 rpm at room temperature until equilibrium was achieved. The mixture of HPO-CNFS and Dfc solution was separated by filtration through cellulose acetate membrane.
filters (pore size 0.45 µm, Sartorius, Gmbh Germany) after the set equilibration time and the residual concentration of Dfc was analyzed using a double beam Shimadzu UV-2401 PC UV-VIS Spectrophotometer (Shimadzu corp. Tokyo, Japan) at a wavelength of $\lambda_{\text{max}} = 287$ nm.

The amount of Dfc adsorbed by the HPO-CNFs was determined using eq. (1):

$$q_e = \frac{(C_i - C_e) \cdot V}{m} \quad (1)$$

where $q_e$ is adsorption capacity of HPO-CNFs (mg g$^{-1}$), $C_i$ is initial concentration of Dfc (mg L$^{-1}$), $C_e$ is final concentration of Dfc (mg L$^{-1}$), $V$ is the volume of Dfc solution (L), and $m$ is weight of HPO-CNFs (g).

Percentage removal (R%) was calculated from eq. (2):

$$\text{(R\% removal)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

3. Results and discussion

3.1. Heavy metals analysis in DCBs

The analysis of heavy metals trapped in DCBs is presented in Fig. 2. The analysis revealed that copper (Cu) ions (ca. 779 ng g$^{-1}$) are present in high amount, followed by nickel (Ni) ions (ca. 493 ng g$^{-1}$). The lowest heavy metal detected was cobalt (Co) (ca. 29 ng g$^{-1}$). From the analysis of ten random samples, chromium metal recorded the highest deviation in the amount trapped in the DCBs as shown from the standard deviation bar (Fig. 2).

This suggests that the amount of heavy metals that are trapped in the DCBs is not uniform although the sizes are similar (15-35 mm). The reasons for the differences in the composition of heavy metals are difficult to explain. However, the tobacco plant is well known to accumulate soil and atmospheric heavy metals, and it is only the cigarette manufacturing process that affects the amount of trapped heavy metals. The differences in the metals composition therefore depend on the manufacturer and the brand as reported in other study (Bernhard, et al., 2005). Nonetheless, heavy metals were liberated from the synthesized...
celluloses due to the metal elution properties of NaOH (Abu-Danso, et al., 2018). The proposed elution phenomenon in this regard is represented in the equation $M(X) + \text{NaOH} \rightarrow M(\text{OH}) + \text{Na(X)}$ where $M$ represent a metal and $X$ represents a metal complex (NO$_3$, SO$_4$, PO$_4$ etc.).

Fig. 2. Heavy metals analysis found in DCBs (error bars represent standard deviation. $N = 10$).

### 3.2. Scanning electron microscope analysis

Scanning electron microscope images of DCBs, synthesized CNFs, CNC$_{30}$ and CNC$_{60}$, taken at different magnifications and voltages, are presented in Fig. 3 (a-d). The DCBs image (Fig. 3 a) revealed a smooth and almost unblemished strands which also depicts the pristine nature of the DCBs after several washes. After acetyl group cleaving, the smooth strands of DCBs disappeared and revealed a rough non-uniform CNFs strands (Fig. 3 b), similar to
CNFs strands from cotton (Abu-Danso, et al., 2017). The rough surfaces also suggest a successful fiber exfoliation and preservation of fibrils after the strong alkali, thermal and acetic buffer treatments. These fibrils present platforms which can serve as a surface for attachment during surface modification strategies. The HPO modified CNFs (HPO-CNFs) revealed surface morphology (Figure S 1) similar to CNFs which suggests that the modification procedure overall had less effect on the structure of the material. The CNFs strands were however, disintegrated into irregular structures after sulfuric acid hydrolysis for 30 mins to yield CNCs, as shown in Fig. 3 (c). The CNCs yield after 30 min did not show distinct crystals which suggests that the amorphous regions had not been significantly reduced from the fibril surface, as also found by (Klemm, et al., 2011) resulting in a paste-like looking image. This was in contrast to the image taken for CNCs after 1 h acid hydrolysis as shown in Fig. 3 (d). The 1 h hydrolysis treatment resulted in the formation of distinct crystals with sharp edges and flat broad surfaces, which suggested the liberation of more crystalline regions out of the semi-crystalline of cellulose fibers. The differences in the images in Fig. 3 (c) and (d) show the importance of hydrolysis time on the production of CNCs. The SEM image of HPO-CNFs after adsorption of Dfc (Dfc-CNFs) (Figure S 1) showed slight fiber exfoliation which suggests the adsorbent is resilient. that the presented in the supplementary material.

3.3. Fourier transform infrared spectroscopy (FT-IR) analysis

The FT-IR analyses of all synthesized celluloses and the precursor (DCBs) are presented in Fig. 3 (e-f). Peaks that were common in all the samples included the peaks at ~2880 cm\(^{-1}\) assigned to methoxy (CH\(_3\)-O-) stretch due to the presence of lignin and uncomplete delignification, and ~1015 cm\(^{-1}\) assigned to saturated C-H functional groups of celluloses. Three intense peaks were recorded in DCBs spectra at ~1736, 1367, and 1212 cm\(^{-1}\). The peak at ~1736 cm\(^{-1}\) is assigned to C=O of acetyl group also reported in other study (Teixeira, et al.,
2017), and the peak intensity suggests a strong presence of these carbonyl moieties with less or no interferences. The sharp and intense peak at ~1367 cm\(^{-1}\) is assigned to lignin’s phenol group and at the neck of the phenol peak is a weak peak at ~1433 cm\(^{-1}\) attributed to OH bend (Coates, 2000). The OH bend at the phenol neck of the spectra suggests the presence of guaiacyl component of lignin found in soft wood which has less hydrogen (H) components indicating that the DCBs was produced from soft wood in agreement with (Christopher, et al., 2014). The peak at ~1212 cm\(^{-1}\) is assigned to a strong presence of etherified phenol of guaiacyl in agreement with other study (Faix, 1991) and it is the strongest evidence that DCBs were made from soft wood. The region from 3600 to 3000 cm\(^{-1}\) of the spectrum where OH functional groups are found (Jafari, et al., 2018), a strong masking of the OH bonds of celluloses occurred in the DCBs. After the alkali and thermal treatments of DCBs, the synthesized celluloses revealed significant changes in the FT-IR spectra including evidence of acetyl group cleaving by the disappearance of C=O peak, and a reduced lignin as a result of the removal of some guaiacyl moieties. The peak assigned to aromatic ring vibrations was not clearly defined in the DCBs, however after the treatments, it emerged at ~667 cm\(^{-1}\) in all the synthesized celluloses, which indicates suppression by, perhaps, the presence of acetyl group. The nature of the aromatic ring peak of CNFs suggests the presence of other substituents on the ring which were subsequently liberated after the acid treatments resulting in sharp peaks recorded with the synthesized CNCs. The attachment of phosphorous (P) functional groups on the surface of CNFs after phosphate ions etching is seen by the appearance of a sharp peak at ~1229 cm\(^{-1}\) on the HPO-CNFS spectra. This peak is attributed to P=O stretch as also reported in other studies (Coleman, et al., 2011, Ghanadpour, et al., 2015, Suflet, et al., 2006). The peak however, reduced in intensity after Dfc adsorption.

3.4. Raman spectroscopy analysis
The predominant molecular orientation in all the synthesized celluloses and their crystal structures were analyzed to further explain the bond networks. Overall, two clear spectral regions were recorded. The region between ~2900 to 2890 cm\(^{-1}\) end of the band and, from ~1600 cm\(^{-1}\) to the lower end of the band where most of the peaks were gained (Fig. 3 g). The Raman peak at ~2900 cm\(^{-1}\), recorded for both CNCs\(_{30}\) and CNCs\(_{60}\), is assigned to a mixture of symmetric and asymmetric C-H stretch bond arrangement as reported in other studies (Blackwell, 1977, Jähn, et al., 2002, Liang and Marchessault, 1959). The symmetric C-H arrangement is due to polymerization and regular intramolecular bonds with well-defined positions and or bond angles. The asymmetric bond arrangement is due to a wider and complex networks of multiple bond angles which an evidence of the presence of other disorganized structures. This phenomenon is in line with the study of (Nishiyama, et al., 2003) who found disorganized intermolecular network of H-bonds in a synchrotron x-ray analysis of highly crystalline cellulose. The slight shifts in these peaks between all the celluloses is attributed to differences in crystalline purity transformation hence, the CNCs\(_{60}\) showed a well-defined and comparatively sharper peak. The weak peak in the range of ~1470-1459 cm\(^{-1}\) is assigned to CH\(_2\)OH of anhydroglucopyranose however, the shifts in the peak suggests different signals of cellulose’s stereo chemistry which suggests that treatments might have resulted in different types of celluloses (cellulose I or II), as also reported in other study (Jähn, et al., 2002). The scope of this study however, did not cover the classes of celluloses. The glycosidic linkages (β 1→4) of the repeated units of the celluloses were confirmed by the peak at ~1099 cm\(^{-1}\) and assigned to (C-O-C)\(_s\) skeletal vibrations. These peaks are well defined in the CNFs peak, but it is characterized by conflicting vibrations at the neck of the peaks of the synthesized CNCs due to other -O- related vibrations. The peak recorded at ~635 cm\(^{-1}\) for all the celluloses, attributed to lignin (Agarwal and Ralph, 1997),
showed a significant difference between the CNFs where the peak is pronounce and CNCs where the peak diminished due to acid cleaving of lignin.

3.5. Point of zero charge analysis

The point of zero charge analysis (pHzpc) analyses of HPO-CNFs is presented in Fig. 3 (h). The pH_zpc was found to be 3.22 which implies that at pH < 3.20, the HPO-CNFs surface was negatively charged, and hence can potentially be used in the sorption of cationic pollutants, and at pH > 3.22, the surface of the synthesized HPO-CNFs is positively charged and can potentially adsorb anionic adsorbates. It is important to note that phosphate ions ampholyte characteristics can influence the charge characteristics of a system by controlling the protonation and deprotonation activity. The effect of this amphoteric behavior is further discussed in section 3.7.

![Fig. 3. SEM images of (a) DCBs (b) CNFs strands (c) CNC30 (d) CNC60, FT-IR spectra of (e) DCBs, CNFs, CNC30 and CNC60 (f) HPO-CNFs, and HPO-CNFs after Dfc adsorption (Dfc-CNFs), (g) Raman spectra of CNFs, CNC30 and CNC60, and (h) pH_zpc analysis of HPO-CNFs.](image)

3.6. Energy dispersive spectroscopy (EDS) analysis
The EDS elemental composition (atomic%) from the precursor to the synthesized celluloses is presented in Table 1. The results revealed that the atomic percentage of carbon was reduced, while oxygen was increased in all the synthesized celluloses, after acetyl group cleaving. This can be attributed to the removal of acetyl functional groups from the lateral glycosidic links on the DCBs structure. During the alkali curing, an overwhelming presence of (OH-) acting as the nucleophile in the system was provided via dissociation of strong alkali in H2O.

This condition enabled a persistent attack on the carbonyl group and eventually cleaved π (pi) bonds in the acetyl (C=O) functional groups. The plausible reaction scheme for the process (Fig. 4) proceeds in two phases to produce free alcohols which can be easily washed away from the cellulose. The first phase of the process is a two-part reaction involving the formation of OH- species by dissociation of NaOH in H2O, the second part proceeded with the destruction of the carbonyl group by nucleophilic attack of the π bonds to shift electrons onto oxygen to form a radicalized oxygen. At the second phase, the vulnerable oxygen is protonated by the free H+ ions lurking in the system to produce alcohols which were removed from the resulting cellulose by vigorous washing.

Overall, the atomic composition (Table 1) showed that the primary goal of acetyl group cleaving was successful, and the subsequent FT-IR analysis of CNFS revealed a significant presence of phenolic functional groups due to lignin. This outcome implies that the effect of alkali induced acetyl group cleaving on lignin structures was minimal. Nonetheless, this minimal alkali oxidation of the complex functional groups of lignin produces C-C and C-O linkages which has been reported to influence the polymerization of celluloses (Christopher, et al., 2014, Isikgor and Becer, 2015). It is probable that the differences in the C and O composition could have been influenced by marginal lignin oxidation. Furthermore, (Agarwal and Ralph, 1997) found slight difference in the functional group composition of milled wood.
lignin, therefore, we expected alterations in the atomic composition, after the chemical
treatments of DCBs. The P element found in the EDS analysis suggests the successful
migration of phosphorus into the structural framework of lignin. In fabricating the HPO-
CNFs, the reaction conditions between the hygroscopic H$_3$PO$_4$ in a polar solvent (H$_2$O) is
crucial since optimum conditions are required to prevent fiber damage. In this strategy,
negative phosphate ions are formed by proton losses at the second dissociation step of H$_3$PO$_4$
to form a weaker HPO$_4^{2-}$ ions. The interaction thereof between CNFs and the formed ions is
an etching action based on the ion exchange rather than acid destruction of CNFs fibers.
These negative phosphate ions, so formed, are expected to enhance adsorption processes.

Table 1. EDS elemental (atomic %) analyses of DCBs, CNFs, HPO-CNFS CNCs$_{30}$ and
CNCs$_{60}$.

<table>
<thead>
<tr>
<th></th>
<th>DCBs</th>
<th>CNFs</th>
<th>HPO-CNFS</th>
<th>CNCs$_{30}$</th>
<th>CNCs$_{60}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>32.8</td>
<td>42.5</td>
<td>41.0</td>
<td>36.3</td>
<td>44.8</td>
</tr>
<tr>
<td>C</td>
<td>66.8</td>
<td>55.8</td>
<td>58.6</td>
<td>63.7</td>
<td>54.9</td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>0.2</td>
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</tbody>
</table>
Fig. 4. Plausible reaction pathway of acetyl group cleaving using NaOH catalyzed by H$_2$O and heat treatment on DCBs.

3.6. pH dependent adsorption mechanism

Understanding the mechanism of pollutant adsorption gives further information on the adsorbent-adsorbate interaction. The solution pH affects the magnitude of protonation-deprotonation of the pollutant, which eventually causes attraction or repulsion actions between the adsorbent and the pollutant. The complex nature of lignin makes the interaction of phosphoric acid and the phenol ring of lignin a complex process. Nonetheless, attaching phosphate ions to the phenol ring on the CNFs to fabricate phosphate ion etched cellulose nanofibers (HPO-CNFs) was successful, as also shown by the results from EDS analysis. The plausible reaction of H$_3$PO$_4$ and lignin to form HPO-CNFs and their subsequent complexation with Dfc molecules is summarized in Fig. 5. In the proposed mechanism, a reductant (HPO$_4^{2-}$) formed from dissociated phosphoric acid reduced the –OCH$_2$ functional group of the phenol-ring, and the OH group of both lignin and cellulose through etching action, since the mild acid was not strong enough to cleave the lignin from the cellulose base. This resulted in HPO doped CNFs surfaces to form HPO-CNFs having weak negative charges (Fig. 3 h) with the potential for complexation with positively charged entities. To
make Dfc a suitable candidate to be adsorbed by the synthesized HPO-CNFs, the pH was adjusted to 5.5 to change the net charge to positive by exchanging the free electrons from the O and π bonds. The mechanism of conversion of Dfc to a net positive molecule involves the attachment of H⁺ ions to N-H, to convert it to NH₂⁺, O to OH and, conversion of π bonds to form OH (Fig. 5). It will, however, be difficult to assess the extent to which all the π bonds are broken, however, low acidity (pH < 3) provides excess H⁺ which is detrimental to the Dfc molecule. The converted OH groups will have an acidic behavior since it can donate H⁺ and hence, positively charged as reported (Smith, 2007). This amphoteric characteristic of Dfc and the variably charged HPO-CNFs surfaces resulted in a variable adsorption driven by electrostatic attraction as also reported with biochar by other researchers (Ye, et al., 2017a). Herein, the protonated part of the Dfc resulted in a favorable adsorption onto the negatively charged sites of the HPO-CNFs, while the amphoteric part of Dfc also resulted in favorable adsorption depending on the suitability of the adsorption site. This behavior of adsorbents and adsorbates in adsorption influenced by pH has been reported in other study (Kim, et al., 2016). Consequently, a sharp reduction in adsorption was noticed as a result of the loss of amphoteric property of Dfc and the inability of the negatively charged sites of the HPO-CNFs to further adsorb positive Dfc molecules. The effect of pH on the adsorption process is further discussed in section 3.8.1.
Fig. 5. Plausible reaction scheme of pH conversion of Dfc to a positively charged molecule, conversion of CNFs to negatively charged HPO-CNFS and plausible adsorption of Dfc.

3.7. Adsorption of Dfc by HPO-CNFS

3.8.1. Effect of pH

The influence of pH on the adsorption of Dfc onto synthesized HPO-CNFS was studied over pH range of 3 to 10 to study the effect of protonation-deprotonation of H⁺ ions on the adsorbent and adsorbate and the results are presented in Fig. 6 (a). The adsorption trend obtained from the results revealed that adsorption capacity increased initially in low pH medium until pH ~5.6, where the highest uptake capacity of 29.6 mg g⁻¹ was recorded. The adsorption capacity decreased consistently thereafter. This phenomenon is explained from the
behavior of Dfc in acidic and basic media. At pKa value of 4.15 (Sangster, 1994), Dfc is deprotonated beyond pH ~5.5, therefore, a charge repulsion between the partially negative HPO-CNFS surfaces and the deprotonated Dfc occurred which resulted in decreasing adsorption capacity. The adsorption trend also suggests that deprotonation is fast therefore, the decline in adsorption capacity is also fast. This trend of pH dependent pollutant remediation has been reported in adsorption studies (Abu-Danso, et al., 2018), and photocatalytic degradation (Mousavinia, et al., 2016, Mosleh, et al., 2016b, Mosleh, et al., 2017, Mosleh, et al., 2018, Lu, et al., 2019). To assess the performance of unmodified cellulosics (CNFs and CNCs) for Dfc removal, adsorption experiments were conducted with all three synthesized cellulosics under similar experimental conditions and the results are summarized in Fig. 6 (b). The results revealed that the HPO-CNFS has the highest potential as a result of surface modification, while CNCs exhibited the lowest removal of Dfc from aqueous medium.

3.8.2. Effect of contact time

In order to understand the sorption mechanism and to know the equilibration time for maximum uptake, the sorption of Dfc on HPO-CNFS was studied as a function of contact time, which is an important parameter to study (Azad, et al., 2015, Azad, et al., 2016a, Ghaedi, et al., 2016, Asfaram, et al., 2018) and the results are presented in Fig. 6 (c) together with kinetic modelling. The results revealed that adsorption was rapid between 0 to 70 min., but stabilized after ca. 70 min., which indicated that equilibrium has been reached. At equilibrium, the adsorption capacity for Dfc removal by HPO-CNFS was found to be 32.37 mg g⁻¹ representing ca. 96% removal efficiency. Three well-known adsorption kinetic models were used to analyze the process. Pseudo-first order model (Lagernren, 1898) is given by eq. (3):

\[ q_t = q_e (1 - e^{-k_1 t}) \]  

(3)
where \( q_e \) is the amount of Dfc adsorbed (mg g\(^{-1}\)) at equilibrium, \( t \) is time (min) and \( k_1 \) is the pseudo-first order (min\(^{-1}\)) rate constant.

Pseudo-second order model is given by eq. (4): (Ho and McKay, 1999)

\[
q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}
\]

where \( k_2 \) is the pseudo-second order rate (g mg\(^{-1}\) min\(^{-1}\)) constant and assumes a chemical rate determining step.

Avrami model (Avrami, 1939) is given by eq. (5):

\[
q_t = q_e \left(1 - e^{-\left(k_{av} t \right)^n}\right)
\]

where \( K_{AV} \) (min\(^{-1}\)) is the Avrami constant.

The correlation coefficient (\( R^2 = 0.999 \)) and the slight deviation between the calculated (\( q_{e \text{cal}} \)) and the experimental (\( q_{e \text{exp}} \)) values (Table 2), suggest that the pseudo-second order kinetic model could best describe the adsorption kinetics. The low root mean square error (RMSE = 0.65) also suggests reduced error in the data analysis for the pseudo-second-order model. The assumption of the pseudo-second order indicates that the adsorption is driven by a chemical process and the plausible mechanism has been explained in the pH dependent adsorption mechanism section.

3.8.3. Adsorption isotherms

In order to evaluate the adsorption potential of HPO-CNFs for Dfc removal, the equilibrium adsorption of Dfc was studied as a function of Dfc concentration as reported in other studies also (Jamshidi, et al., 2015b, Jamshidi, et al., 2016, Azad, et al., 2016b) and the adsorption isotherms are shown in Fig. 6 (d) together with isotherm modelling. The Freundlich model (Freundlich, 1906) which predicts a non-uniform adsorbent surface attachment and assumes a heterogeneous surface and multilayer adsorption is determined from eq. (6):

\[
q_e = K_F C_e^{1/n}
\]

where \( K_F \) and \( n \) are constants in the adsorption system.
The Langmuir model (Langmuir, 1918) which assumes a monolayer adsorption for an adsorbent with specific localized sites by ions of identical energy such that the attached ions have no lateral interaction between adsorbed ions. The Langmuir model is given by eq. (7): 

\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  

(7)

where \( q_e \) is the amount (mg g\(^{-1}\)) of pollutant adsorbed by adsorbent at equilibrium and \( C_e \) is concentration of adsorbate remaining at equilibrium (mg L\(^{-1}\)), \( q_m \) (mg g\(^{-1}\)) represents maximum monolayer adsorption capacity and \( K_L \) is the Langmuir constant. The Sips model (Sips, 1948), combines features of Freundlich and Langmuir models. The Sips model can be written as (8):

\[ q_e = \frac{q_m (K_s C_e)^m}{1 + (K_s C_e)^m} \]  

(8)

where \( K_S \) (L mg\(^{-1}\)) is the Sips affinity constant.

Dfc adsorption isotherms data fitting is presented in Fig. 6 (d). The results revealed that the isotherms data could be best described by the Langmuir model based on the correlation coefficients \( R^2 = 0.999 \) and the low root mean square error (RMSE = 9.65) values, recorded in the data fitting as compared to the other studied models (Table 3). These results suggest that the adsorption of Dfc by the synthesized HPO-CNFs is a monolayer adsorption process. The maximum adsorption capacity was found to be 107.90 mg g\(^{-1}\). The comparison of removal capacity of HPO-CNFs for Dfc with other materials is summarized in Table S 1.
**Fig. 6.** (a) effect of pH on the adsorption of Dfc (20 mg L\(^{-1}\)) by HPO-CNFs (0.4 g L\(^{-1}\)), (b) comparison of adsorption capacity of HPO-CNFs, CNFs, and CNCs for Dfc (concentration: 5-70 mg L\(^{-1}\)) adsorption, (c) adsorption kinetic modelling of Dfc (20 mg L\(^{-1}\)) by HPO-CNFs (0.4 g L\(^{-1}\)), (d) adsorption isotherms modelling of Dfc (concentration: 5-70 mg L\(^{-1}\)) HPO-CNFs (0.4 g L\(^{-1}\)).
Table 2. Adsorption kinetic parameters of Dfc removal by HPO-CNFs (HPO-CNFs dose = 0.4 g L\(^{-1}\), Dfc concentration = 20 mg L\(^{-1}\) (~ 25 \(^{0}\)C)).

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Parameter</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>(q_{e \text{ exp}}) (mg g(^{-1}))</td>
<td>31.82</td>
</tr>
<tr>
<td></td>
<td>(q_{e \text{ cal}}) (mg g(^{-1}))</td>
<td>29.93</td>
</tr>
<tr>
<td></td>
<td>(k_1) (min(^{-1}))</td>
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<tr>
<td></td>
<td>RMSE</td>
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<tr>
<td></td>
<td>(R^2)</td>
<td>0.988</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>(q_{e \text{ exp}}) (mg g(^{-1}))</td>
<td>31.82</td>
</tr>
<tr>
<td></td>
<td>(q_{e \text{ cal}}) (mg g(^{-1}))</td>
<td>32.37</td>
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</tr>
<tr>
<td></td>
<td>RMSE</td>
<td>0.65</td>
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<tr>
<td></td>
<td>(R^2)</td>
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<tr>
<td>Avrami</td>
<td>(q_{e \text{ exp}}) (mg g(^{-1}))</td>
<td>31.82</td>
</tr>
<tr>
<td></td>
<td>(q_{e \text{ cal}}) (mg g(^{-1}))</td>
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<tr>
<td></td>
<td>(k_2) (g mg(^{-1}) min(^{-1}))</td>
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<td></td>
<td>RMSE</td>
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<tr>
<td></td>
<td>(R^2)</td>
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Table 3. Isotherm model parameters and values of Dfc removal by HPO-CNFs (HPO-CNFs dose = 0.4 g L\(^{-1}\), Dfc concentration = 5-75 mg L\(^{-1}\) (~ 25 \(^{0}\)C)).

<table>
<thead>
<tr>
<th>Isotherm model</th>
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<th>Value</th>
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<tr>
<td>Langmuir</td>
<td>(q_{e \text{ exp}}) (mg g(^{-1}))</td>
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<tr>
<td></td>
<td>(q_{e \text{ cal}}) (mg g(^{-1}))</td>
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<tr>
<td></td>
<td>(K_L)</td>
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<td></td>
<td>(R^2)</td>
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</tr>
<tr>
<td></td>
<td>RMSE</td>
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</tr>
<tr>
<td>Freundlich</td>
<td>(K_F)</td>
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</tr>
<tr>
<td></td>
<td>(n)</td>
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</tr>
<tr>
<td></td>
<td>(R^2)</td>
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</tr>
<tr>
<td></td>
<td>RMSE</td>
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<tr>
<td>Sips</td>
<td>(q_{e \text{ exp}}) (mg g(^{-1}))</td>
<td>106.99</td>
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<tr>
<td></td>
<td>(K_s) (L mg(^{-1}))</td>
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<tr>
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<td></td>
<td>RMSE</td>
<td>10.57</td>
</tr>
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</table>
3.8.4. Effect of competing ions

The effect of competing ions on the adsorption of Dfc by synthesized HPO-CNFS was studied in the presence of different concentrations (20, 40, and 80 mg L\(^{-1}\)) of cations (Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), and Zn\(^{2+}\)) and anions (Cl\(^-\), NO\(_3^-\), CO\(_3^{2-}\), and SO\(_4^{2-}\)) in a binary system at pH ~5.5. The aim of the experiment was to assess the effect of presence of competing ions (with similar and also opposite electrostatic charge) on adsorption of Dfc since the presence of competing ions has an effect on pollutant’s remediation (Ye, et al., 2017b, Ye, et al., 2019). The results, as shown in Fig. 7 (a and b), revealed that in the presence of the studied competing ions, the cations hindered the adsorption process. This was expected since the net charge on the Dfc molecule at the studied pH was positive, hence, an electrostatic repulsion occurred between the positively charged Dfc and the cations in the system. Competition for the same adsorption sites between the positively charged Dfc molecules and the competing cations also occurred, therefore, the adsorption of Dfc decreased in the presence of cations. However, the slight ability of the synthesized HPO-CNFS to adsorb Dfc in the presence of equal and even higher concentrations of the cations (Fig. 7 a) suggests that the adsorbent is robust towards targeted adsorbate which fits the goal for modifying the CNFs. On the contrary, it was found that the adsorption remained unaffected in the presence of the different concentrations of the studied anions (Fig. 7 b). It can be explained due to fact that there was no electrostatic attraction between negatively charged anions and the partially negative HPO-CNFS surfaces which resulted in the uptake of the positively charged Dfc molecules.

3.8.5. Regeneration studies

To study the resilience of the synthesized HPO-CNFS as an adsorbent for the removal of Dfc by repeated usage, adsorption-desorption experiments were conducted with 0.1 M NaOH, 0.1 M HNO\(_3\) and H\(_2\)O as eluents and studied over four regeneration cycles. The results as
summarized in Fig. 7 (c and d) revealed that after 4 cycles, the HPO-CNFS were able to exhibit over 80% removal efficiency with 0.1 M HNO$_3$ as eluent. The other studied eluents exhibited less than 10% removal efficiency at all the studied cycles. After adsorption of the Dfc by HPO-CNFS, ca. 80% of Dfc on the surface of HPO-CNFS was desorbed (Fig. 7 d) at the first cycle by 0.1 M HNO$_3$ eluent, after which the percentage desorption reduced to ca. 50%. Although, the percentage desorption after the first cycle reduced to 50%, the HPO-CNFS was able to exhibit 80% removal efficiency in the subsequent adsorption.

Fig. 7. Effect of competing ions (a) cations, and (b) anions on the adsorption of Dfc (20 mg L$^{-1}$) by HPO-CNFS (0.4 g L$^{-1}$), (c) percentage removal efficiency, and (d) percentage desorption from the HPO-CNFS after each regeneration cycle. Error bars represent standard deviation (N = 3).
4. Conclusions

Although the dangers posed by used cigarette filters to the environment has been fairly reported, their recycled potential has however, been less reported. In this study, cellulosics were successfully extracted from DCBs by initial acetyl group cleaving using robust alkalization catalyzed by heat to obtain CNFs. Lignin was further cleaved from the obtained CNFs to synthesize CNCs by acid hydrolysis using different hydrolysis time. Finally, CNFs were etched with negative phosphate ions to obtain a negatively charged adsorbent (HPO-CNFS) for the removal of Dfc from aqueous medium. The SEM analyses revealed the different transformations from the precursor to the obtained cellulosics after different treatments. The EDS analysis revealed differences in atomic percentage composition from the precursor to the synthesized cellulosics due to different syntheses treatments. The synthesized HPO-CNFS showed potential as an efficient Dfc adsorbent with a maximum removal capacity of 107.90 mg g⁻¹. The results from this study suggest that cellulosics, extracted from DCBs, offer a promising potential for the removal of Dfc from water. Analysis of the DCBs revealed the presence of different amounts of trapped heavy metals.

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