

TEMPO-Oxidized Cellulose Cross-Linked with Branched Polyethyleneimine: Nanostructured Adsorbent Sponges for Water Remediation

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Introduction

Water pollution is a growing worldwide problem caused by the huge increase in anthropic activities. Most of the contaminants, including pesticides, dyes, drugs, surfactants, and heavy metals, are toxic and non-biodegradable, representing a concrete threat to human health and the environment. For this reason, the development of effective systems and processes to decrease water pollution is crucial, especially in those developing countries where rapid industrial growth is often not supported by an adequate system of environmental regulations and controls.^[1–4]

Several approaches have been developed to address this issue, including electrochemical precipitation, membrane separation, electrochemical treatment,^[5] and photodegradation.^[6,7] However, adsorption is still the most effective and efficient solution.^[8] Active carbon (AC) is commonly used as a sorbent ma-

terial for water decontamination, but it is expensive both in terms of production and regeneration.^[9] Moreover, the increasing restrictions on concentration limits of contaminants requires the development of advanced materials capable of combining high adsorption efficiency with low economic and environmental impact. For this reason, in the last years the research for alternative and “greener” adsorbent solutions has attracted increasing attention.^[10–15] In this context, cellulose represents a valuable starting point for next-generation materials to be used for the wastewater treatment. This naturally abundant and renewable biopolymer shows good mechanical properties and can be chemically functionalized in order to modify its physical and chemical behavior according to the required applications.^[16,17]

The preparation of nanostructured materials using cellulose nanocrystals, cellulose nanowhiskers, micro-/nanofibrillated cellulose, and cellulose nanofibers (CNFs) is an innovative and emerging field.^[18–20] CNFs can be advantageously used as templates for the chemical synthesis of inorganic^[21–24] and hybrid materials^[25] and for the preparation of biocompatible organic substrates to be used either as drug delivery vehicles^[26,27] or as scaffolds for tissue engineering.^[28]

CNFs have interesting perspectives for application in wastewater treatment. In particular, CNFs obtained from 2,2,6,6-tetramethylpiperidinyloxy (TEMPO)-mediated oxidation (TOCNFs) showed a good heavy-metal adsorption capacity due to the presence of carboxylic groups on the cellulose backbone.^[29–31] However, the direct use of TOCNFs presents a main limitation, due to the fact they are quite dispersible in water, in particular at basic pH. As a consequence, the corresponding aerogels and hydrogels lack sufficient mechanical stability in the aqueous medium. Therefore, their recovery/removal after the water-

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treatment procedure is neither easy nor economically feasible. For these reasons, the fabrication of CNF-based materials that display high efficiency in removing pollutants along with good mechanical and chemical stability in water, and are thus expected to be easy to handle and recover, is of high interest.

The introduction of amino groups on the cellulose polymer chains represents a valuable approach to increase their adsorption capability towards both organic pollutants and heavy metals. For example, betaine-modified cationic cellulose has been prepared through the reaction of cellulose with betaine hydrochloride for the treatment of water-containing different Reactive Red dyes.^[32] In the context of the removal of heavy metals, microfibrillated cellulose modified with aminopropyl-triethoxysilane has been proposed for the treatment of aqueous solutions containing Ni^{II}, Cu^{II}, and Cd^{II} ions.^[33] Moreover, sorbents made of amphoteric cellulose containing both amine and carboxylic groups were shown to be effective in eliminating Cu^{II} and Cr^{VI} ions from wastewater.^[34]

A convenient substrate containing amino groups suitable for the synthesis of highly efficient adsorbent materials is represented by branched polyethyleneimine (bPEI). bPEI is a commercially available macromolecule, bearing primary, secondary, and tertiary amines, which is widely used in the biomedical field as a gene carrier system.^[35] Very recently its use has been extended to the fabrication of sorbent systems for wastewater treatment. Indeed, porous spherical adsorbents have been prepared by cross-linking pristine cotton cellulose with bPEI and using epichlorohydrin as the reticulating agent. The resulting materials were able to remove Cr^{III} and Fe^{III} cations from water due to the strong chelating action of bPEI amino groups.^[36] Following a more elementary synthetic approach, membranes were obtained by the simple coating of bacterial cellulose with bPEI and successfully used as Cu^{II} and Pb^{II} adsorbents and as catalysts for the reduction of Methylene Blue.^[37]

On the basis of these considerations, we envisaged that water-stable and efficient sorbents could be prepared by the

direct amidation of the TOCNF carboxylic groups with bPEI, without using a supplementary cross-linker. Herein we describe a simple, cheap, and scalable method to prepare efficient adsorbent materials with a sponge-like structure by cross-linking TOCNF with bPEI. The obtained materials, completely characterized by FTIR and ¹³C CP-MAS solid-state NMR spectroscopy, SEM microscopy, and elemental analysis, were successfully tested as water-decontamination systems for different model organic pollutants, including *p*-nitrophenol (pNPh), 2,4,5-trichlorophenol (tCPh), and the antibiotic amoxicillin (AM), and for heavy-metal ions like Cu^{II}, Ni^{II}, Cd^{II}, and Co^{II}.

Results and Discussion

The bPEI-TOCNF adsorbent sponges were prepared according to the synthesis in Figure 1. Cotton cellulose was first oxidized using the TEMPO/NaClO system as described in the Experimental Section. In this way the C6 hydroxy groups of the cellulose chains were partially converted into the corresponding carboxylic groups. The obtained TOCNF showed a content of carboxylic acid units of 1.1 mmol g⁻¹ (value obtained by titration). Following this protocol, defibrillation of TOCNF was possible by increasing the pH, in order to favor the deprotonation of carboxylic groups, and consequently to promote the electrostatic repulsion of negatively charged single fibrils. bPEI was characterized before use by ¹³C NMR spectroscopy (see Experimental Section) in order to quantify the content of primary, secondary, and tertiary amines. The following values, based on 1 g of bPEI, were obtained: RNH₂ (7.43 mmol), R₂NH (9.42 mmol), R₃N (6.36 mmol). A variable amount of bPEI was then added to an aqueous suspension of TOCNF; the final volume was adjusted with water to reach a concentration of dry TOCNF of about 3.5% w/v. In fact, we verified that suspensions with a higher content of TOCNF (higher than 4% w/v) were too viscous to be handled. Suspensions with a lower TOCNF content provided samples with unsatisfactory mechanical stability. In order to

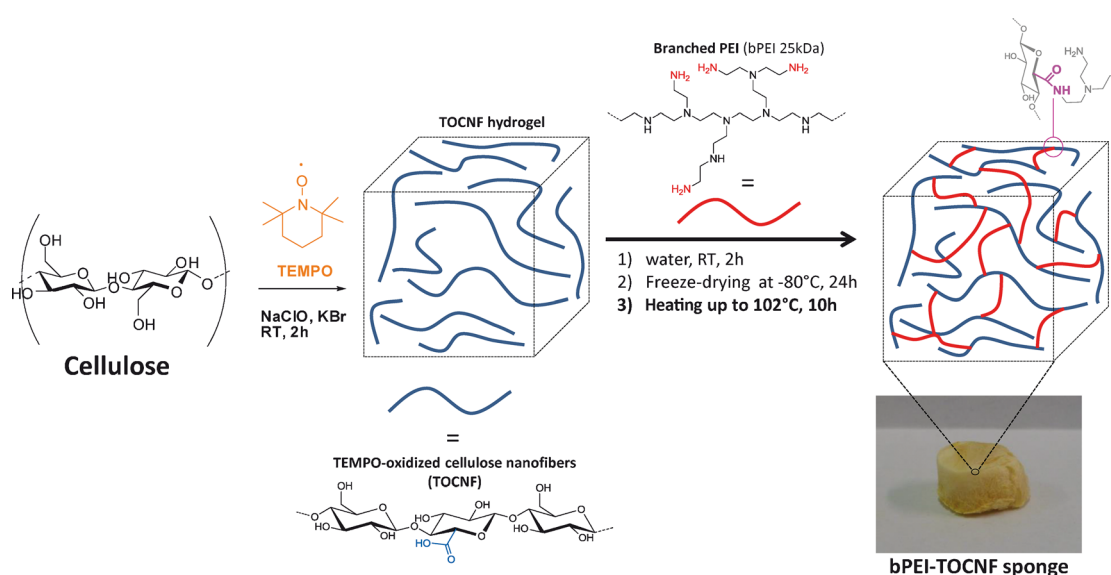


Figure 1. Preparation of bPEI-TOCNF sponges.

see how the amount of bPEI affected the properties of the materials, three set of samples were prepared by changing the ratio between the amount (g) of bPEI and dry TOCNF (0.2:1, 0.5:1, 2:1). Subsequently all the samples were labeled in terms of the bPEI–TOCNF preparative mass ratio, that is, bPEI–TOCNF(0.2:1), bPEI–TOCNF(0.5:1), and bPEI–TOCNF(2:1).

The materials prepared with different bPEI/TOCNF ratios were quite different in terms of morphology and mechanical strength. Figure 2 gives a qualitative impression of the ob-

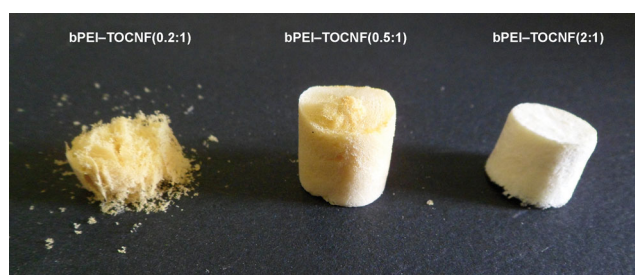


Figure 2. Photograph of bPEI–TOCNF sponges with different bPEI content.

tained samples. In particular, the dry specimen of bPEI–TOCNF(0.2:1) showed very poor mechanical stability, and often appeared as a brittle solid. Increasing amounts of bPEI were beneficial in order to improve the mechanical performance. The dry specimen of bPEI–TOCNF(0.5:1) assumed the form of a soft sponge while the bPEI–TOCNF(2:1) sample was significantly tougher. In water, bPEI–TOCNF(2:1) showed good mechanical stability (Video1, Supporting Information), almost unaffected by the pH conditions (Video2, Supporting Information). Moreover, the bPEI–TOCNF(2:1) sponges showed an interesting shape-recovery capability, in both the wet and dry state (Video3, Supporting Information). These characteristics enhance the potential of the proposed materials as substrates for water treatment. Indeed, the ability of a sorbent material to withstand the mechanical force associated with water flow plays an important role in both the design and operation of the adsorbent unit.^[11,40] The SEM image of bPEI–TOCNF(2:1) in Figure 3 supports its porous structure. In particular, the pore walls show a two-dimensional sheetlike morphology, often described in literature for cellulose-based aerogels obtained from the freeze-drying of aqueous suspensions with a content of dry cellulose higher than 0.5% w/v.^[41]

The mechanical stability and the shape-recovery capability of bPEI–TOCNF(2:1) in aqueous medium can be associated with the covalent cross-linking between the bPEI primary amino groups and the carboxylic groups of the TOCNF after thermal treatment. Indeed, the sponge-like structure of the precursor of bPEI–TOCNF(2:1), as obtained at the end of the freeze-drying procedure but before the thermal treatment, was rapidly destroyed when the specimen was put in contact with water.

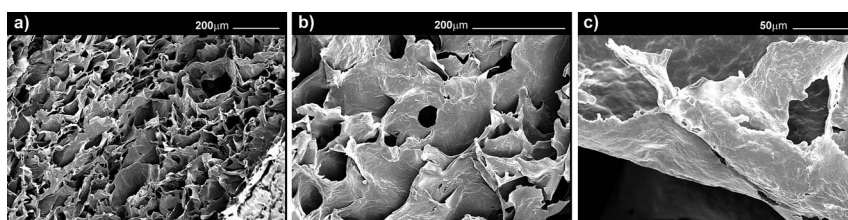


Figure 3. SEM images of bPEI–TOCNF(2:1) sponges at different magnifications.

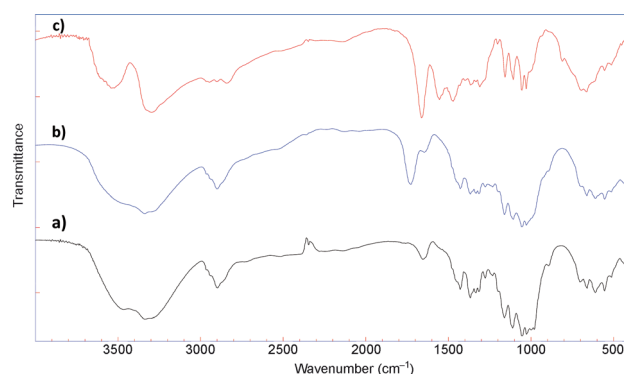


Figure 4. FTIR spectra of a) cotton, b) TOCNF, c) bPEI–TOCNF(2:1).

The formation of peptide bonds was confirmed by both FTIR and ¹³C CP-MAS solid state NMR spectroscopy. Figure 4 shows the FTIR spectra of the pristine cotton (a), TOCNF (b), and the bPEI–TOCNF(2:1) sponge (c). In particular, TOCNF clearly exhibits an intense peak at 1731 cm⁻¹ associated with the C=O stretch of the carboxylic acid moieties. In the bPEI–TOCNF spectrum, the C=O peak is shifted to 1666 cm⁻¹ due to the formation of amide moieties. Moreover, the N–H stretching peak can be clearly seen at 3300 cm⁻¹. It partially overlaps and covers the broad O–H stretching band in the wavenumber range between 3000 cm⁻¹ and 3700 cm⁻¹.

The ¹³C CP-MAS spectra are reported in Figure 5. The top spectrum was obtained for pristine cotton. The assignments of the peaks associated with the carbons of the anhydroglucose units were obtained on the basis of the reported literature.^[16] The middle spectrum was obtained for TOCNF and clearly shows a signal at 171 ppm associated with the carboxylic carbons. The bottom spectrum obtained for bPEI–TOCNF(2:1) shows the presence of the amidic carbons at 165 ppm. The small peak at 175 ppm is attributed to residual carboxylic groups (as COO⁻). Finally, the broad signal at 35–60 ppm is ascribed to the CH₂ carbons of the grafted bPEI. Even if the amount of bPEI used for the preparation of the bPEI–TOCNF(2:1) should provide a large excess of primary amines with respect to the content of carboxylic groups of TOCNF (ca. 1.1 mmol g⁻¹), it is reasonable to expect that a certain fraction of secondary and tertiary amines could be involved in the formation of the corresponding salts with the COOH groups during the preparation of the liquid suspension, limiting the complete conversion of the acidic moieties. In fact, only the carboxylic groups interacting with the primary amines can be

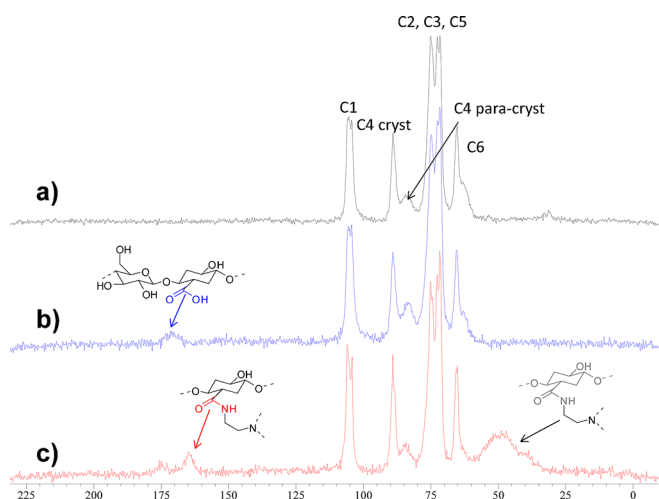


Figure 5. ^{13}C CP-MAS solid state NMR spectra of a) cotton, b) TOCNF, and c) bPEI-TOCNF(2:1).

converted into the corresponding stable amide groups after the thermal treatment, while the other groups remain in the COO^- form (see bottom spectrum in Figure 5).

The elemental analysis of the three specimens provided further useful information. In particular, it was possible to estimate the content of total nitrogen per gram of material, also distinguishing the contents of the amino and amidic nitrogen (see Table 2). Details on the calculations and further data are reported in the Supporting Information. As expected, the total nitrogen content increases from bPEI-TOCNF(0.2:1) to bPEI-TOCNF(2:1). Moreover, the content of amino nitrogen is always greater than the content of amidic nitrogen, especially in the case of bPEI-TOCNF(2:1), which is the most suitable of the three materials for the envisaged environmental applications. The amino nitrogen content refers to all amino groups, as all of them can contribute to the adsorbent capacity of the sponges.

In order to investigate the action of the bPEI-TOCNF sponges in the decontamination of wastewater, we initially chose *p*-nitrophenol (pNPh) as pollutant model. This molecule is an important industrial precursor in the synthesis of different drugs, fungicides, and dyes. The adsorbent capacity of the bPEI-TOCNF samples, prepared with different amounts of bPEI, is reported in Figure 6. The effective N/C ratio, obtained from the elemental analysis of the three kinds of sponges, can be used as a more convenient descriptor to quantify the bPEI content instead of the preparative bPEI/TOCNF ratio. The correlation between these two ratios is reported in the inset in Figure 6. As expected, the efficiency of the materials, in terms of amount of adsorbed pNPh, increases with the N/C ratio, due to the increasing concentration of amino groups on the adsorbent. In fact, the adsorption capacity of the proposed materials may be ascribed to an acid-base interaction between the amino groups of bPEI and the slightly acidic substrate. This assumption is confirmed by the fact that the modification of the pH alters the adsorption efficacy (Table 3). When bPEI-TOCNF(2:1) sponge (about 100 mg) was placed in 10 mL of

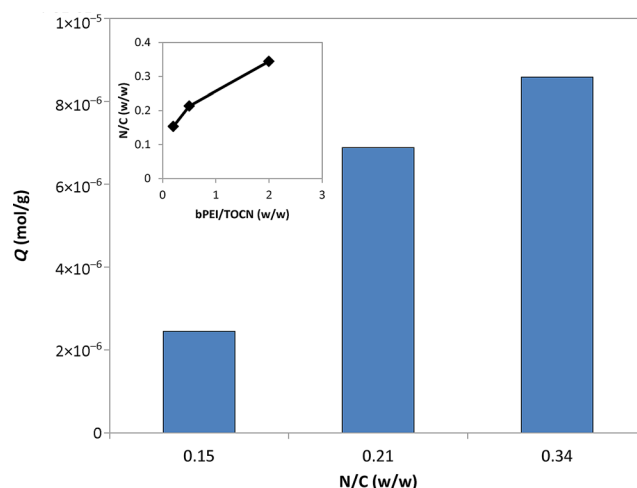


Figure 6. Adsorption of pNPh ($C_0 = 1.8 \times 10^{-4} \text{ M}$) at 25°C for 2 h onto bPEI-TOCNF sponges having different N/C ratios (from elemental analysis). The inset shows the relationship between the N/C ratio and the bPEI/TOCNF ratio based on the preparation of the materials.

pNPh aqueous solution ($C_0 = 1.8 \times 10^{-4} \text{ M}$) at 25°C for 2 h, the amount of adsorbed pNPh was about $8.58 \times 10^{-6} \text{ mol g}^{-1}$, corresponding to a removal efficiency of 69% from the liquid phase (entry 1). The final pH value of the solution was 7.6. When the pH was modified by adding HCl or NaOH, a drastic reduction of the adsorption capability was observed (entries 2 and 3). This property could be possibly used for the regeneration of the sorbent sponges by treating them with acidic water. In this way, the adsorbed molecules could be removed from the solid phase. Although the regeneration of the sorbent substrates is often highlighted by investigators as a valuable property of their materials, the feasibility of a regeneration process has to be always evaluated in a more general context, in particular considering the cost. Aside from the previous considerations, aspects related to the post-adsorption treatment of the bPEI-TOCNF sponges are beyond the scope of the present paper and will not be considered.

The investigation of the adsorbent properties of the bPEI-TOCNF materials was also extended to other model organic pollutants. In particular, we also considered 2,4,5-trichlorophenol (tCPH) and amoxicillin (AM). tCPH is used as a fungicide in paper and pulp mills, as an herbicide, and as an intermediate in the manufacture of other pesticides.^[42] AM was selected because nowadays antibiotics are considered as emerging contaminants in the aquatic environment.^[43] The adsorption kinetics of the three pollutants onto bPEI-TOCNF(2:1) are reported in Figure 7. Different initial concentrations were selected considering the different molar extinction coefficients of the three pollutants (see Table 1). In all cases, the adsorption process is initially quite fast while equilibrium is reached after about ten hours. For example, considering pNPh, after 2 h about 72% of the equilibrium value ($1.09 \times 10^{-5} \text{ mol g}^{-1}$ after 24 h) is reached. Similar observations were made with tCPH (73%, $6.38 \times 10^{-5} \text{ mol g}^{-1}$ after 24 h) and AM (66%, $1.02 \times 10^{-4} \text{ mol g}^{-1}$ after 24 h).

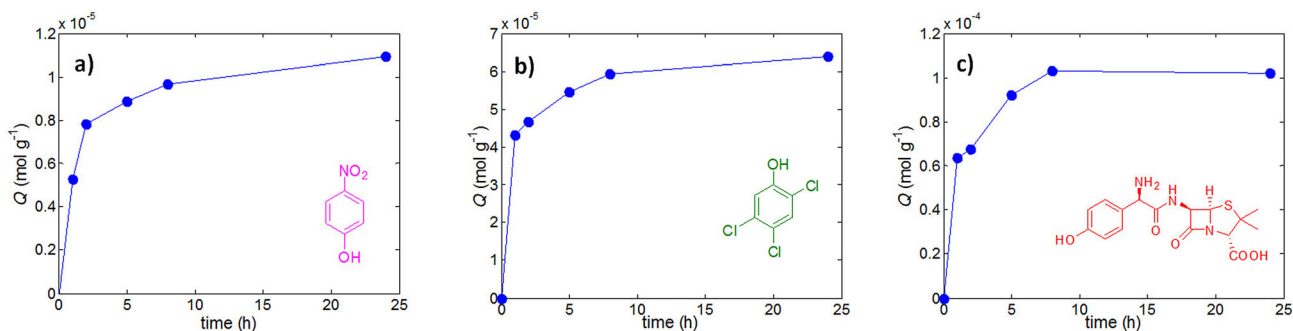
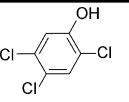
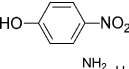
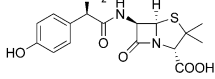


Figure 7. Adsorption kinetics of a) pNPh ($C_0 = 1.8 \times 10^{-4}$ M), b) tCPh ($C_0 = 8.8 \times 10^{-4}$ M), c) AM ($C_0 = 1.7 \times 10^{-3}$ M) onto bPEI-TOCNF(2:1) at 25 °C; volume of solution: 10 mL; mass of adsorbent sponge: 100 mg.

Table 1. Model organic pollutants.				
Pollutant	M_w [g mol ⁻¹]	ϵ [M ⁻¹ cm ⁻¹]	Sol. ^[a] [g per 100 mL]	Conc. range ^[b]
pNPh 	139.11	9717	1.33	1×10^{-4} M to 5×10^{-2} M
tCPh 	197.45	2400	0.12	4×10^{-4} M to 4×10^{-3} M
AM 	419.45	1088	0.34	3×10^{-4} M to 4×10^{-3} M

[a] Solubility at 20 °C. [b] Concentrations of the solutions before the sorbent was added.

The adsorption isotherms data at 25 °C are reported in Figure 8. The experimental data were nonlinearly interpolated with the Langmuir type model (continuous line, [Eq. (1)]), widely used in the literature for the analysis of the adsorption processes.^[44]

$$Q_{eq} = \frac{Q_m b C_{eq}}{1 + b C_{eq}} \quad (1)$$

Here Q_m (mol g⁻¹) is the maximum amount of pollutant that can be adsorbed by the substrate at the specific temperature of the experiments (25 °C in our case), while b (M⁻¹) is a constant related to the adsorption energy. C_{eq} (M) is the concentration of pollutant in the aqueous phase, while Q (mol g⁻¹) is the corresponding amount of the substrate. The obtained parameters are reported in Table 4.

Table 2. Estimation of the content of amino, amidic, and total nitrogen in bPEI-TOCNF sponges (mmol per gram of bPEI-TOCNF) from the elemental analysis data.			
Sponge	Total nitrogen [mmol g ⁻¹]	Amidic nitrogen [mmol g ⁻¹]	Amino nitrogen [mmol g ⁻¹]
bPEI-TOCNF(0.2:1)	4.50	0.89	3.61
bPEI-TOCNF(0.5:1)	6.34	0.80	5.54
bPEI-TOCNF(2:1)	10.86	0.59	10.27

Table 3. Effect of the pH on the removal of pNPh from aqueous solution with bPEI-TOCNF(2:1).		
Entry	pH	Q [mol g ⁻¹]
1	7.6	8.58×10^{-6} (69%)
2	2.0	negligible
3	12.0	negligible

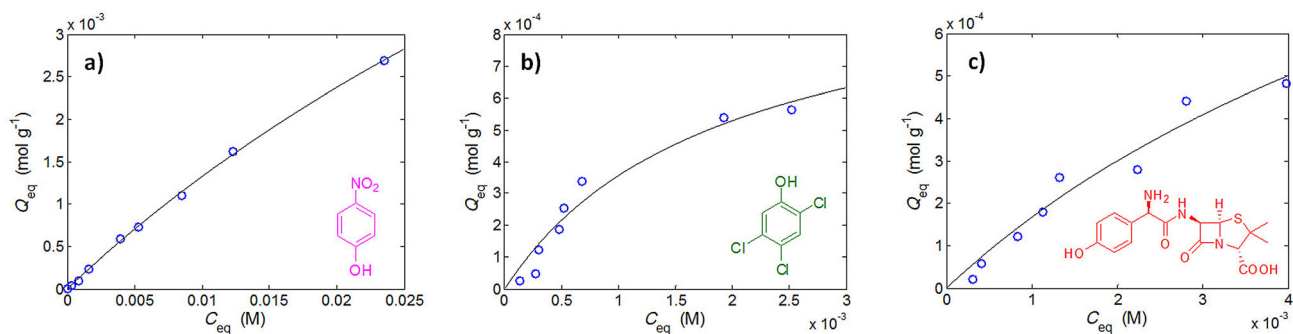


Figure 8. Adsorption isotherms of a) pNPh, b) tCPh, c) AM onto bPEI-TOCNF(2:1) at 25 °C; contact time: 24 h; volume of solution: 10 mL; mass of adsorbent sponge: 100 mg.

Pollutant	$Q_m^{[a]}$	$b [M^{-1}]$
	$[mol\ g^{-1}]$	
pNPh	11.72×10^{-3}	1630 (371.5)
tCPh	1.038×10^{-3}	205 (111.2)
AM	1.521×10^{-3}	556 (176.2)

[a] The numbers in brackets represents the experimental values of Q at the highest C_{eq} as deduced from the graphs of Figure 8.

Adsorbent	Q_m $[mg\ g^{-1}]$	Ref.
microporous activated carbon	184.8	[45]
hypercross-linked magnetic polymer	152.6	[46]
nanographite oxide	268.5	[47]
bPEI–TOCNF(2:1)	1630	present work

The proposed materials have high removal performances, as evidenced by the comparison reported in Table 5 (pNPh as reference) between the bPEI–TOCNF(2:1) and different sorbents recently reported in the literature. Considering the removal of heavy metals from wastewater, bPEI–TOCNF sponges proved to be quite effective due to the presence of chelating amino groups. Figure 9 is photograph of bPEI–TOCNF(2:1) sponges colored by the adsorption of some metal cations (Cu^{2+} , Co^{2+} and Ni^{2+} ; the sponge with adsorbed Cd^{2+} is not shown because Cd^{2+} is colorless).

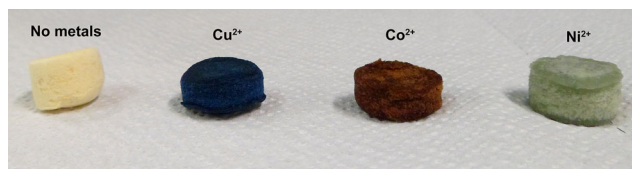


Figure 9. bPEI–TOCNF(2:1) sponges after the adsorption of different metal ions.

More quantitative information can be obtained from Figure 10, which reports the amounts of metals adsorbed onto the sponge. Two sets of data are reported. Red filled bars represent the data obtained from independent adsorptions where a certain amount of bPEI–TOCNF(2:1) sponge (about 300 mg) was put in contact with 10 mL of an aqueous solution of metal salt (0.1 M). Cd and Cu were adsorbed in higher amount than Co and Ni although all the values are on a similar order of magnitude (from $0.97\ mmol\ g^{-1}$ for Co^{2+} to $1.38\ mmol\ g^{-1}$ related to Cd^{2+}). Blue striped bars represent the results from a competitive adsorption with all metals in the same solution (the concentration of each metal being equal to 0.1 M). In this case copper was preferentially removed from the aqueous phase. The amount of Cu adsorbed during the competitive experiment was analogous to the value obtained during the indi-

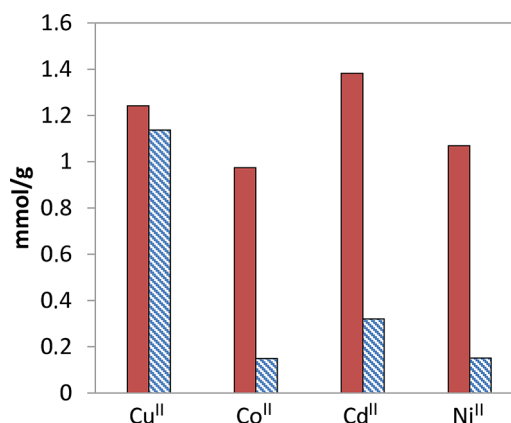


Figure 10. Adsorption of metals onto bPEI–TOCNF(2:1). T : 25 °C; contact time: 12 h; initial concentration: 0.1 M; volume of solutions: 10 mL; mass of adsorbent sponge: 300 mg. Red bars: independent adsorption experiment; blue striped bars: competitive adsorption experiment.

vidual adsorption ($1.4\ mmol\ g^{-1}$ in the individual adsorption and $1.14\ mmol\ g^{-1}$ in the competitive adsorption) but it was significantly higher than the amount of Cd ($0.32\ mmol\ g^{-1}$), Co ($0.15\ mmol\ g^{-1}$), and Ni ($0.15\ mmol\ g^{-1}$). The chelating properties of the commercial bPEI towards different metal ions as well as its selectivity towards copper over other ions have been widely investigated in the literature.^[48,49] These results confirm that bPEI-containing materials have a very high specificity for copper.^[50]

Conclusion

In conclusion, we have shown that cellulose-based adsorbent materials can be easily obtained through a cheap and scalable approach from TEMPO-oxidized cellulose nanofibers (TOCNFs) and branched polyethyleneimine (bPEI). The proposed materials have a sponge-like structure, good mechanical stability in water, and a shape-memory capability. Such properties are guaranteed by the stable amide bonds formed between the carboxylic groups of TOCNF and the primary amines of the bPEI. When the mass ratio between bPEI and TOCNF are increased (from 0.2:1 up to 2:1), the qualitative aspect and the mechanical stability of the materials are positively affected. We have investigated the application of the bPEI–TOCNF sponges for the adsorption of some typical organic pollutants, namely *p*-nitrophenol, 2,4,5-trichlorophenol, and the antibiotic amoxicillin. In all the cases, the materials showed significant adsorption capabilities. Moreover, their application has been successfully extended to the removal of heavy metals, including copper, cobalt, nickel, and cadmium. Our strategy seems to be promising for the development of functional materials derived from natural sources, like cellulose, and prepared using cheap reagents and mild conditions for use in environmental applications.

Experimental Section

General

Branched PEI 25 kDa (bPEI) was purchased from Sigma–Aldrich. The content of primary amino groups was determined from a ^{13}C NMR spectrum of bPEI in D_2O (ca. 100 mg mL $^{-1}$, 10000 scans, probe temperature 30 °C) using inverse gated decoupling sequences to avoid NOE effects, as reported in literature.^[38] A value of 7.43 mmol g $^{-1}$ of primary NH_2 groups was obtained. Details on the calculations are reported in the Supporting Information.

All other chemicals were commercially available and were used without further purification, unless otherwise stated. AM of pharmaceutical grade was in the trihydrate form (M_w : 419.45 g mol $^{-1}$).

Materials preparation

TOCNF was obtained according to the procedure reported in our previous paper.^[23] KBr (1.19 g, 10.0 mmol) and TEMPO (156 mg, 1 mmol) were dissolved in 450 mL of deionized water in a three-necked round-bottom flask. Cotton wool (8.1 g, 50.0 mmol of anhydroglucose) was added to the solution and soaked for 1 h at room temperature, after which 36 mL of a sodium hypochlorite solution 12.5% w/w was added. The pH value was maintained in the range of 10.5–11 by using 0.5 M aqueous sodium hydroxide solution. The obtained suspension was stirred for 6 h. The cellulose fibers were then collected by filtration onto a sintered glass funnel, washed with deionized water (250 mL, 3 times), and re-dispersed in water at pH 11.0 (200 mL). The slurry was sonicated at 0 °C using a Branson Sonifier 250 equipped with a 6.5 mm probe tip working at 20 kHz in continuous mode, with an output power 50% the nominal value (200 W), until an almost transparent liquid was obtained (approximately 1 h of sonication). After acidification (to pH 1–2) with concentrated HCl (37% w/w aqueous solution), the white precipitate was recovered on a sintered glass funnel and washed extensively with deionized water (6 × 200 mL). The final weight of TOCNF paste was measured in order to quantify the cellulose content. The amount of carboxylic groups was determined by conductimetric titration.^[39]

bPEI–TOCNF sponges were prepared from 160 mL of aqueous suspension of TOCNF (3.5% w/v of dry TOCNF) containing a variable amount of bPEI. Three different sets of samples were prepared by changing the preparative ratio bPEI:TOCNF (w/w), namely 0.2:1, 0.5:1, and 2:1. Each mixture was stirred for 1 h and then sonicated for 30 min in an ice bath. The liquid was pipetted into 24-well plates (2 mL in each well) and frozen at –80 °C for 12 h. The freeze-drying at –60 °C for 48 h afforded white cylindrical sponges which were removed from the well-plate and thermally treated in an oven. The temperature was increased stepwise from 60 °C to 102 °C over 8 h. The samples were maintained at 102 °C for 2 additional hours, and subsequently washed with 0.1 M HCl (aq) (5 × 200 mL) in order to remove the unreacted bPEI, 1 M NH_4OH (aq) (2 × 200 mL), and acetone (2 × 100 mL) in sequence. The materials were finally dried in air for 48 h and in an oven (70 °C) for 2 h.

Characterization

The elemental analysis of the bPEI–TOCNF sponges was obtained using a Costech ECS 4010 analyzer. The solid-phase FTIR spectra of the powdered sample with infrared grade KBr were obtained using a Varian 640-IR spectrometer.

The ^{13}C cross-polarization magic-angle-spinning (CPMAS) spectra were recorded with an FT-NMR AvanceTM 500 (Bruker BioSpin S.r.l) with a superconducting ultrashield magnet of 11.7 Tesla operating at 125.76 MHz ^{13}C frequency. The following conditions were applied: repetition time 4 s, ^1H 90 pulse length 4.0 μs , contact time 1.2 ms, and spin rate 8 kHz. The compounds were placed in a zirconium rotor, 4 mm in diameter and 18 mm high. The chemical shifts were recorded relative to glycine standard, previously acquired (C=O signal: 176.03 ppm, relative to tetramethylsilane reference).

Scanning electron microscopy (SEM) was performed using a variable-pressure instrument (SEM Cambridge Stereoscan 360) at 100/120 Pa with a detector VPSE. The operating voltage was 20 kV with an electron beam current intensity of 150 pA. The focal distance was 8 mm. The specimens were used without any treatment.

Adsorption experiments

All the adsorption experiments were performed in batch conditions. Aqueous solutions of the selected organic pollutants were prepared by diluting stock solutions with deionized water. Table 1 reports the range of concentrations considered for each organic pollutant. A 10 mL aliquot of each final solutions was pipetted into a 25 mL conical flask containing about 100 mg of bPEI–TOCNF. All the flasks were shaken at 100 rpm in a thermostatic bath (mod. SW22, Julabo, Allentown, USA) at 25 °C for a variable time. The concentrations after treatment of the solutions containing organic pollutants were determined by UV/Vis measurements using a Hp 8453 UV-spectrophotometer, using specific calibration lines (see Table 1 for molar extinction factors (ϵ) values).

Heavy-metal (Cu^{II} , Ni^{II} , Cd^{II} , Co^{II}) adsorption tests were performed by adding 300 mg of bPEI–TOCNF to 10 mL of a 0.1 M aqueous solution of the metal salt (SO_4^{2-}) and shaking the flask for 12 h at 25 °C. The metal concentrations were measured by ICP atomic emission spectroscopy using a Perkin Elmer Optima 3000 SD spectrometer. Competitive adsorption tests were performed in a similar way, but using an aqueous solution containing all the metals, each at a concentration of 0.1 M.

In all cases, the materials' adsorption capacity was evaluated according to Equation (2)

$$Q = \frac{(C_0 - C) \cdot V}{m} \quad (2)$$

where C_0 and C are the initial and the final pollutant concentration (M), respectively, V is the volume of the solution (L), and m represents the mass of the adsorbent material (g).

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