

New Nanostructured Cellulose Materials for the Filtration of Pollutants and for the Adsorption of Dyes.

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ABSTRACT

The production of functionalized cotton materials of large use (gauze and sanitary cotton) has been worked up, in order to adsorb polluting substances and dyes from aqueous solutions. Glycidyl methacrylate (GMA) has been used as functionalizing agent. **C1** and **C3** were produced by Fenton reaction, while **C2** and **C4** by electron beam (EB) irradiation (Scheme 1). **C1** and **C2** bear hydrophobic branches, ending with the glycidyl group, on the cellulose surface, while the cellulose surface of **C3** and **C4** is made more hydrophilic by appendages ending with the glycerol group. Aromatic polluting substances like *phenol*, *4-nitrophenol*, *2,4-dinitrophenol*, *2,4,6-trinitrophenol (picric acid)* and *2-naphthol* were all tested with **C1** and **C3** in gauze form. Phenol was not adsorbed at all. The three nitrophenols have shown different adsorption properties towards **C1** and **C3**, in function of the pH. In particular, **C3** shows the best removing performances of nitrophenols in basic water. *2-Naphthol* was efficiently adsorbed by **C1** and, even if in a less efficient way, also by **C3**. On the base of these results, many factors, like the size of the aromatic molecules, their polarity and their acidity, seem to play a role in the efficiency and in the mechanism of the adsorption process. **C1** shows better affinity towards less polar molecules, while **C3** has better performances towards more polar molecules. The murexide dye has been tested with **C2** and **C4**, in gauze and sanitary cotton forms. It has been adsorbed only by **C4**, confirming that the presence of hydrophilic appendages on the cellulose surface is fundamental for the filter efficiency towards polar molecules.

Keywords: cotton filter, glycidyl methacrylate, surface grafting, aromatic pollutants, dyes.

1 INTRODUCTION

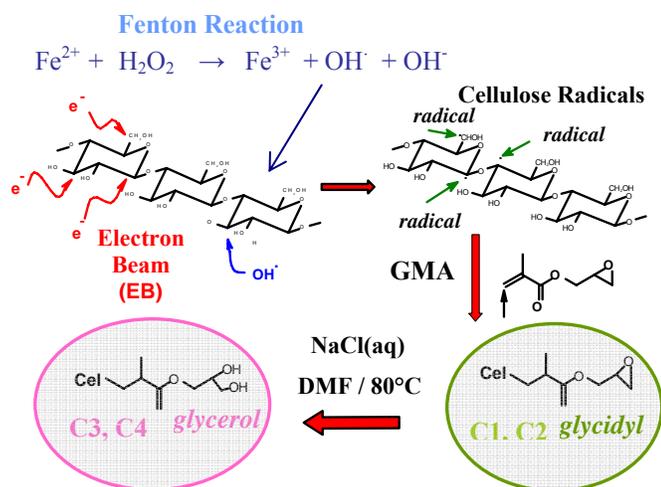
Water pollution by organic compounds has more and more attracted attention all over the world. Among the organic molecules which more often pollute and which have a larger environmental impact surely there are aromatics [1] and dyes [2].

Two different strategies can be pointed out for the removal of aromatic compounds and dyes from wastewater: the first is the chemical degradation of pollutants by some techniques like oxidation, electrolysis and biodegradation. The second is the removal of the pollutants by physical separations like solvent extraction, membrane separation and adsorption. Systems based on the adsorption are effective and operationally simple. One of the most used substrates is activated carbon, which suffers of scarce mechanical properties and has high cost of regeneration [2]. This is the reason why much attention was recently addressed to new adsorbent organic substrates, with improved mechanical properties and high adsorption efficiency, mainly based on synthetic polymers [3] and on natural polymers [4, 5, 6]. Following this approach, cellulose materials have been considered good candidates as substrates for removal of pollutants from water. Cellulose is a well-known natural friendly polymer, with good mechanical properties. As it can be manufactured in many different ways, powders, grains, yarns, fabrics and non woven fabrics, it is suitable to prepare different materials for any kind of application. Cellulose modification by graft polymerization with different monomers has been extensively studied in the last forty years to add new chemical properties. Several strategies have been applied, some of them based on physical techniques [7, 8], other based on chemical processes [9, 10]. One monomer widely used is GMA. We have chosen GMA to prepare cellulose nanostructured materials [1, 3], with the aim of building up cellulose filters for removing pollutants from waters. Such monomer, shown in Scheme 1, has at one end a double bond, that may trap carbon centered radicals, and at the other end an epoxyde group, which can be used for further chemical modifications. The present paper develops GMA-functionalized cotton substrates in the direction of manufacturing new cellulose filters.

2 RESULTS

Scheme 1 summarizes Fenton reaction and electron beam procedures to obtain **C1** and **C2**, respectively, which were further transformed in **C3** and **C4**. Table 1 reports the substitution degree (DS, see below for details), based on

FT-IR spectroscopy (Fig. 1), of different samples **C1**, **C2**, **C3** and **C4**. Adsorption of *phenol* and of *2-naphthol* by **C1** and **C3** has been performed at pH= 7. Adsorption of 4-*nitrophenol*, 2,4-*dinitrophenol*, 2,4,6-*trinitrophenol* (*picric acid*) by **C1** and **C3** were performed both at acid and basic pH. Quantitative data of the adsorption (aromatic substrate mol per g of cotton material) were measured by UV-Vis spectroscopy (molar absorptivity reported in Table 2), see below for details, and reported in function of the DS (Figs. 2 and 5), in function of the contact time (Fig. 3) and also in function of the pH for the nitrophenols (Fig. 4).



Scheme 1: Synthetic pathways to **C1**, **C2**, **C3** and **C4**.

2.1 Fenton Reaction Synthesis of **C1**

In a one-neck round bottom flask (500ml), cotton gauzes (500 mg per gauze range 6-10g), were swelled for half an hour, into a 300 ml of H_2O at 80°C . Then 8 ml of FeSO_4 heptahydrate 0.05M in water were added followed by the one-pot addition of 50 ml of H_2O_2 30% v/v. The mixture was kept, under magnetic stirrer, for 25 min (*activation time*). After the *activation time*, an amount of GMA (range 3-6ml) was added in one portion and accurately stirred to bring in solution the monomer, keeping the reaction vessel at the same temperature of the activation process. After 15 minutes the gauzes were removed and exhaustively washed several time with acetone, squeezing it on blotting paper. The material was then dried in air and further dried in an oven at 80°C (ca. one hour about). Four different **C1** preparations were done, named **C1.A**, **C1.B**, **C1.C** and **C1.D**. The DS reported in Table 1 depends on the mass effects and on the GMA concentration.

2.2 EB Irradiation Synthesis of **C2**

The procedure has been described in a previous work [7]. A variable amount (0,5-20g) of materials (cotton gauze

transformed in sample **C2.A** and sanitary cotton in sample **C2.B**) have been irradiated under N_2 atmosphere with electron beam (400kGy, 300keV, 4mA, 666 sec) to activate their surface generating carbon centered radicals. After the activation, the samples were quenched in a water-methanol solution of GMA (1:1:0.4), using always a higher excess of monomer with regard to the cellulose and a volume of liquid enough to totally cover the materials. The quenching time has been 60min and the temperature of the bath was 80°C . Finally the materials were washed with a sufficient amount of acetone to remove the unreacted monomer.

2.3 Glycidyl Group Conversion in Glycerol. Synthesis of **C3** and **C4**

About 3g of all the samples **C1** and **C2**, reported in Table 1 (**C1.A-D**, **C2.A-B**), were swelled in one-neck round bottom flask (500ml) with 100mL of dimethylformamide (DMF) at 80°C for 2 hours. Then, 100mL of 1M NaCl aqueous solution were added leaving the reaction mixture under stirring at 80°C for 24 hours. At the end, the samples were removed from the solution and exhaustively washed with water and finally with acetone. The materials (**C3.A-D**, **C4.A-B**) were dried in air and further dried in an oven at 80°C (one hour about).

2.4 FT-IR Spectroscopy Analysis

The FT-IR spectra, registered in solid phase mixture of the powdered sample with KBr are diagnostic of the functionalisation, as shown by new signals, absent in cellulose, assigned to the ester group ($\nu = 1734\text{cm}^{-1}$) and to the epoxyde ring ($\nu = 902, 843, 751\text{cm}^{-1}$) of GMA residue (Fig 1).

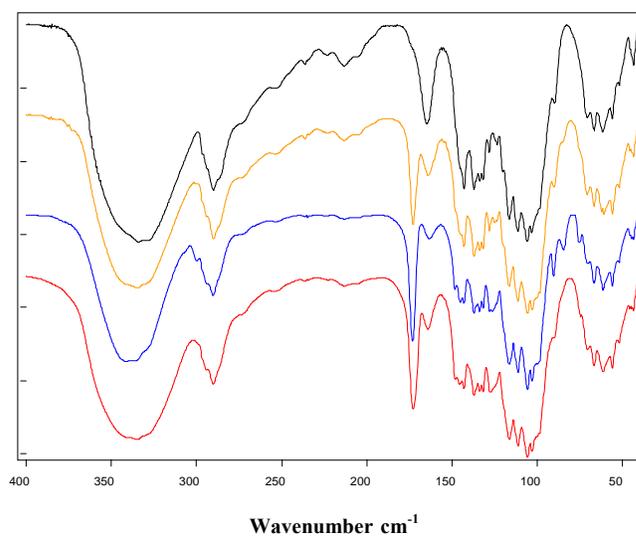


Figure 1: FT-IR spectra: ■ cotton gauze; ■ **C1.D**; ■ **C1.B**; ■ **C3.B**.

The ester characteristic signal was evaluated for every sample to quantify the functionalization (Table 1). Noteworthy, in the spectra of all the samples C3 and C4, as shown by sample **C3.B** derived from **C1.B** in Fig. 1, the epoxy signals disappear, proving the opening reaction occurring. The area of the ester band was normalized referring to another characteristic cellulose band following Eq. 1, resulting equal to the apparent substitution degree DS. It is an average molar ratio between the unit of GMA and the unit of D-glucose and thus can be considered an indicator of the functionalization efficiency.

$$DS_{FT-IR} = \text{area}_{N(\text{ester})} = \frac{\text{area}_{\text{ester}}(\text{manual band integration})}{\text{area}_{\text{cellulose}}(\text{range } 780-465 \text{ cm}^{-1} \text{ integration})} \quad (1)$$

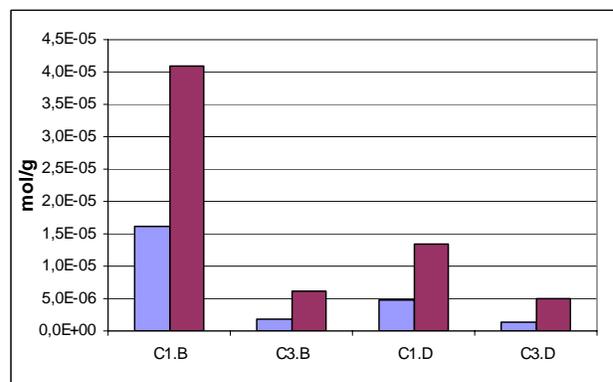


Figure 2: 2-Naphtol: effect of the DS on the adsorption capacity. Initial concentration: ■ 2,0E-4M; ■ 5,0E-4M. $V_{\text{SOL}}=20\text{mL}$; $T=25^{\circ}\text{C}$; $t_{\text{ads}}=24\text{h}$.

Sample	Description	DS	Ester peak band (cm^{-1})	Sample
C1.A	Cotton gauze	0.81	1840-1670	C3.A
C1.B	Cotton gauze	0.52	1875-1680	C3.B
C1.C	Cotton gauze	0.45	1850-1680	C3.C
C1.D	Cotton gauze	0.22	1795-1685	C3.D
C2.A	Cotton gauze	0.7	1850-1670	C4.A
C2.B	Cotton wool	0.65	1850-1670	C4.B

Table 1: Associated samples with DS and FT-IR data.

2.4 Adsorption of Phenol and 2-naphtol

The adsorption properties of the materials were measured by UV-Vis spectrometry. For the evaluation of the adsorption capacity about 100mg of gauze were dipped in 20 mL of aqueous solution of phenol and 2-naphtol ($2.0\text{E}-4\text{M}$ and $5.0\text{E}-4\text{M}$ were tested) and shaken for 24 hours in a thermal bath at 25°C . For the kinetic experiment the amount of gauzes used was about 400mg. Absorbance was measured at $\lambda=270\text{nm}$ for phenol ($\epsilon=1552,3$) and at $\lambda=328\text{nm}$ for 2-naphtol ($\epsilon=1713.8$). Phenol was not adsorbed at all. In turn, Fig. 2 reports the DS effect and the initial concentration effect on the 2-naphtol adsorption capacity of **C1.B**, **C3.B**, **C1.D** and **C3.D**. The presence of the glycidyl group in **C1.B-D** maximizes the 2-naphtol adsorption capacity. The Fig. 3 confirms the data in Fig. 2 and shows that the maximum adsorption value for **C1.A** has been reached in 1 hr.

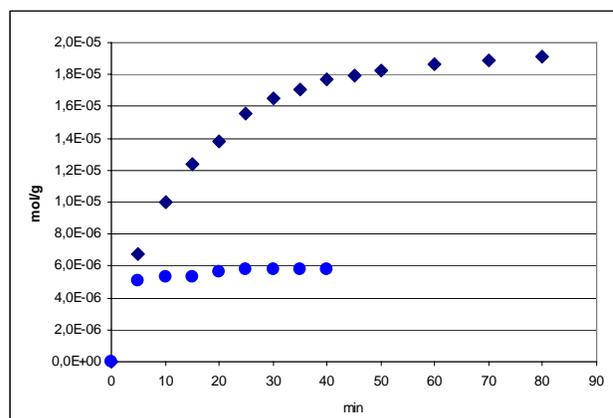


Figure 3: 2-Naphtol: adsorption kinetic. ● **C3.A**; ◆ **C1.A**; Initial concentration: $5,0\text{E}-4\text{M}$; $V_{\text{SOL}}=20\text{mL}$; $T=25^{\circ}\text{C}$; $t_{\text{ads}}=24\text{h}$.

2.5 Adsorption of 4-nitrophenol, 2,4-dinitrophenol and 2,4,6-trinitrophenol

A strong dependence of the adsorption capacity on the pH has been recognized for the three nitrophenols. For this reason two limit conditions have been chosen: $\text{pH} \ll 7$ ($\text{pH} < 3$) and $\text{pH} \gg 7$ ($\text{pH} > 10$). An aqueous solution $2.0\text{E}-4\text{M}$ has been prepared for every aromatic compound. In 50mL of that, were added $100\mu\text{L}$ of $\text{HCl } 0.5\text{M}$ or $100\mu\text{L}$ of $\text{NaOH } 0.5\text{M}$ for shifting the pH to the two limit conditions, $\text{pH} \ll 7$ and $\text{pH} \gg 7$, respectively. In 20mL of the pH modified solutions were dipped about 50mg of gauzes leaving them in the thermal bath for 24 hours at 25°C . The absorbance was measured on the base of the molar absorptivity reported in Tab.2. The Fig. 4 shows that the three nitrophenols behaved in a quite similar manner: **C1.B** slightly adsorbed them in acid, while did not adsorb them in

	$\text{pH} \ll 7$		$\text{pH} \gg 7$	
	$\lambda(\text{nm})$	ϵ	$\lambda(\text{nm})$	ϵ
pNO₂Ph	317	9716.8	400	18376
diNO₂Ph	260	12033	360	14366
Picric Ac	356	14427	356	14650

Table 2: Wavelengths and molar absorptivity used during the experiments.

base. **C3.B** efficiently adsorbed both in acid and in base the dinitrophenol and the trinitrophenol. The less acid 4-nitrophenol was adsorbed only in base. In Fig. 5 the linear DS effect/adsorption was observed in base for the three nitrophenols.

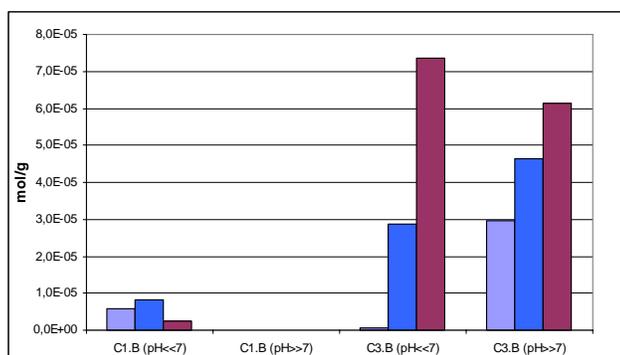
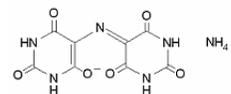


Figure 4: Nitrophenols: effect of the pH on the adsorption capacity. ■ pNO₂Ph, ■ diNO₂Ph, ■ Picr. Ac; Initial []: 2,0E-4M; V_{SOL}=20mL; T=25°C; t_{ads}=24h.

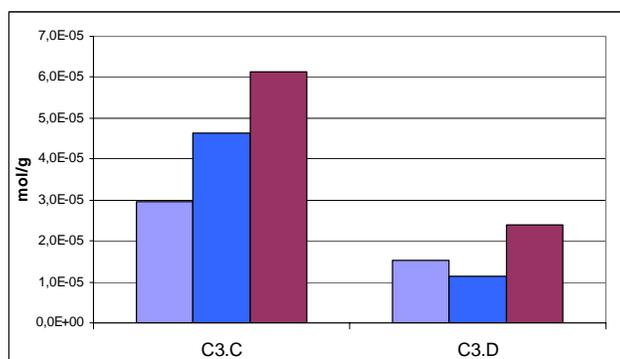


Figure 5: Nitrophenols: effect of the DS on the adsorption capacity. ■ pNO₂Ph, ■ diNO₂Ph, ■ Picr. Ac; In. []: 2,0E-4M; pH=11; V_{SOL}=20mL; T=25°C; t_{ads}=24h.

2.6 Murexide adsorption

Murexide is a salt used as colorimetric reagent for measurement of calcium. About 250mg of derivatized gauze **C2g** and **C4g** and sanitary cotton **C2s** and **C4s** have been dipped in 30mL of murexide aqueous solution (62,6mg in 250mL of water) for 16 hours, and finally exhaustively washed with water. The glycidyl apolar appendage was inefficient in murexide absorption, while the glycerol branch worked very well, as shown in Fig. 6 by **C2g** (DS= 0.35) compared with **C4g** (**C2g** glycerol by epoxyde ring opening) and by sanitary cotton **C2s** (DS= 0.65) compared with **C4s** (**C2s** glycerol by epoxyde ring opening).

Figure 6: Formula and adsorption tests for murexide

3 CONCLUSION

We have worked up a successful approach to prepare on a large scale new nanostructured cellulose materials for the filtration of pollutants and for the adsorption of dyes. We have developed also the analytical methods to test their adsorption properties. Finally we are able to direct the application of suitable materials towards specific organic molecules.

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