

# Cotton Filter Fabrics Functionalization by Chitosan UV-grafting for Removal of Dyes

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Wastewater effluents from textile industry mainly contain dyes used in the dyeing or printing of textiles yarns or fabrics. A lot of technologies can be adopted for dye removal from wastewaters, including biological treatments based on activated sludge, adsorption on activated carbon, or membrane processes. Nevertheless, none of these methods is performing toward all classes of dyes; treatment plants of great dimensions and difficult handling can be required, while costs can be prohibitive.

In a previous work we cationized cotton obtaining a strong improvement of dyes adsorption. In the present work, a cotton fabric was more eco-friendly functionalized by chitosan UV grafting and used as dyes adsorbent. The process parameters for the fabric treatment were optimized in terms of chitosan add-on, impregnation time, temperature, pH, radiation time and curing intensity. The cotton grafted by chitosan was characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared analysis in Attenuated Total Reflection (FTIR-ATR) and X-ray Photoelectron Spectroscopy (XPS).

The material was then tested towards different dye classes: acid, reactive and direct dyes. Batch, kinetic as well as continuous flow assessment tests were carried out, evaluating the adsorption capacity by spectrophotometric measurements. Moreover the influence of pH as well as temperature on the adsorbent capacity of the functionalized cotton were investigated. The material showed good adsorption capacity and very high adsorption rate toward all the investigated dyes. Moreover, by assembling the functionalized cotton in a filter form, good adsorption capacity is ensured even at 25 °C, with good behaviour in terms of filter exhaustion and pressure drop while a positive influence on adsorption capacity was displayed in acid conditions. Finally, regeneration tests by NaOH solution were carried out, with a good release of the adsorbed dye. In conclusion, obtained results show good perspectives for chitosan treated cotton use in wastewater filtration.

## 1. Introduction

Wastewater treatment is becoming ever more critical due to diminishing water resources, increasing wastewater disposal costs, and stricter discharge regulations that have lowered permissible contaminant levels in waste streams. The effluents from the dyeing industries, in particular, containing high amount of inorganic salts, like sodium sulphate or chloride, dyeing auxiliaries and dyes of different classes, are difficult to purify. A lot of wastewater treatments were developed for dyeing industries, among others biological digestion based on activated sludge, adsorption on activated carbon or membrane filtering, as reported by Ranganathan et al. (2007). Moreover some research on bio-based purification processes (Caselatto et al. 2011; Tisma et al. 2012) or oxidative processes (Rosa et al. 2012) are reported. Nevertheless, each of these processes shows limitations: none is performing towards all dyes types, treatment plants of great dimensions can be required, the cost of raw adsorbing materials or producing technologies can be high.

For these reasons, our previous works focused on dye adsorption, choosing as absorbents low cost fibrous materials, mainly cellulose based, submitted to a cationization process using a quaternary ammonium compound (Ferrero and Periolatto 2011; Ferrero and Periolatto 2012a).

In the present work, the idea was to make the process even more eco-friendly, replacing the quaternary ammonium salt with the natural biopolymer chitosan, grafted on cotton by ultraviolet radiation.

The good performance of chitosan as dye adsorbent was widely reported by Crini and Badot (2008) and, in continuous assessment, by Zambrano et al. (2010) while deep studies were carried out by us on the functionalization of textiles by chitosan UV-grafting to confer antimicrobial activity (Ferrero and Periolatto 2012b; Periolatto et al. 2012).

## 2. Materials and Method

### 2.1 Adsorbent preparation

In a previous study about functionalized fibrous materials for the removal of dyes (Ferrero and Periolatto 2011; Ferrero and Periolatto 2012a) a screening test involving different fibrous materials was carried out; best results in terms of performances, even in continuous assessment, were found with a pure cotton gauze fabric, with hexagonal holes 2 mm opening, 49 g/m<sup>2</sup>, so the same was here chosen as substrate.

Low viscosity chitosan, 75 – 85% deacetylation degree (Fluka) was used for gauze functionalization. It was dissolved in aqueous solution of 2 % v/v glacial acetic acid by ripening for 24 h followed by magnetic stirring at ambient temperature for 24 h. A chitosan concentration of 5% wt was used while 2 % on chitosan weight of 2-hydroxy-2-methylphenylpropane-1-one (Darocur 1173, Ciba Specialty Chemicals) was added as photoinitiator. Further steps were spreading of the mixture on the fabrics followed by 12 h impregnation time, drying for about 20 min at 80 – 100 °C and finally UV-curing.

The surface coated fabrics were exposed to UV radiation using a medium pressure mercury lamp with a light intensity on the fabric of about 60 mW/cm<sup>2</sup>, in a small box equipped with a quartz window under nitrogen atmosphere (oxygen content under 20 ppm).

The required radiation dose was obtained adjusting the distance of textiles from the lamp at about 20 cm and the exposition time at 60 s. To assure the complete curing on the fabrics, they were radiated on both the sides.

The weight gain of fabrics, that is the add-on of polymer, was calculated as:

$$\text{Weight gain (\%)} = (w - w_0) \times 100 / w_0 \quad (1)$$

where  $w$  is the weight of grafted fabric and  $w_0$  the weight of the original fabric.

Treated samples were prepared with chitosan add-ons of about 10 %, 25 %, 40 % wt: it is an high percentage, affecting the hand properties of the fabric, nevertheless a soft hand is not required for the final application proposed.

### 2.2 Adsorbent characterization

The surface of cotton grafted with chitosan was characterized by FTIR-ATR analysis, using a Nicolet FTIR 5700 spectrophotometer equipped with a Smart Orbit ATR single bounce accessory mounting a diamond crystal. Each spectrum was collected both on treated and untreated cotton samples by cumulating 128 scans, with 4 cm<sup>-1</sup> resolution and gain 8, in the wavelength range of 4,000–600 cm<sup>-1</sup>.

The surface morphology of chitosan treated fabrics was examined by SEM with a Leica (Cambridge, UK) Electron Optics 435 VP scanning electron microscope with an acceleration voltage of 15 kV, a current probe of 400 pA, and a working distance of 20 mm. The samples were mounted on aluminum specimen stubs with double-sided adhesive tape and sputter-coated with gold in rarefied argon using an Emitech K550 Sputter Coater with a current of 20 mA for 180 s.

XPS analyses were performed with a PHI 5000 Versa Probe system (Physical Electronics, MN) using monochromatic Al radiation at 1,486.6 eV, 25.6 W power, with an X-ray beam diameter of 100 μm. The energy resolution was about 0.5 eV. XPS measurements were performed at a pressure of 1·10<sup>-6</sup> Pa. The pass energy of the hemisphere analyzer was maintained at 187.85 eV for survey scan while the takeoff angle was fixed at 45°. Since the samples are insulators, an additional electron gun and an Ar<sup>+</sup> ion gun for surface neutralization were used during the measurements.

### 2.3 Dye adsorption tests

Three dyes were investigated without further purification: Telon Blue (C.I. Acid Blue 62, by Dystar), with maximum absorbance at 628 nm; Reactive Blue 4 (Sigma Aldrich), with maximum absorbance at 595 nm; and Direct Red 81 (Sigma Aldrich), with absorbance peak at 508 nm.

Three test types were carried out on the different materials: batch exhaustion, kinetic tests and continuous flow assessment.

For the first one, carried out both on untreated and treated substrate, 0.5 g of fabric was put in sealed tubes to make contact with 1000 or 2000 mg/L dye solution with a material-to-liquor ratio 1:100 for 24 h, in

a thermally controlled agitated bath. The influence of both temperature and pH on final bath exhaustion was investigated, namely 25°C and 50°C at pH 2, 4 or 8. The bath exhaustion and consequently the maximum dye adsorption were evaluated by spectrophotometric analysis of the liquors, carried out on a Unicam UV2 (ATI Unicam, Cambridge, UK) spectrophotometer, and by processing the data using Vision 32 software. Adsorption capacity was calculated by the exhaustion test at the highest concentration.

For kinetic tests, four tubes were prepared in the same manner, but samples were drawn from the dye solution at different times to evaluate the bath exhaustion course.

Finally, on chitosan treated fabric, flow tests were performed assembling a filter across a dye solution continuously pumped. The adsorbing material was placed inside a glass tube, between inert fillers, to form a filtering bed about 10 cm high corresponding to 25 g of gauze. According to the best performance obtained in batch, Direct Red solutions, 1000 or 250 mg/L, were pumped onto the filter keeping a constant flow rate of about 2 or 5 mL/min.

Exhausted chitosan treated cotton fabrics were then regenerated by NaOH 0.1M solution to evaluate the dye release.

### 3. Results and Discussion

#### 3.1 Adsorbent characterization

Comparing FTIR-ATR spectra of treated and untreated cotton fabrics (Figure 1), the presence of chitosan is revealed by its typical peak shown only by treated samples at  $1560\text{ cm}^{-1}$  and assigned to NH bending in amide group, in agreement with spectra reported by Sionkowska et al. (2006) related to UV-irradiated chitosan film. The other peaks due to chitosan at  $3,360\text{ cm}^{-1}$  (OH group),  $3,290\text{ cm}^{-1}$  (NH stretching) and  $1,648\text{ cm}^{-1}$  (C=O amide bond) are overlapped to cellulose peaks.

Comparing SEM images related to untreated and treated cotton samples, the presence of chitosan is visible on cotton fibers as a coating, in particular at lower magnifications. Nevertheless, the opening of holes are maintained quite similar to the untreated gauze, showing just a light shrinkage. Moreover, excepted 40% add-on, chitosan covers the net structure maintaining the inter-fibers holes well open; in this way, if the substrate is crossed by a water flux, the pressure drop is limited. Chitosan is spread on the fabric in an homogeneous way, without agglomerated chitosan on the fiber surface, denoting the good quality of chitosan solution and the effectiveness of the impregnation. It is clear till magnification of 1000X, without substantial differences between the structure of treated and untreated samples. At higher magnification it is instead difficult, on treated samples, to distinguish the single fibers, entrapped in the chitosan coating (Figure 2). Moreover no damage, ascribable to UV radiation, was revealed on fibers of treated cotton; it means that the curing radiation had no bad effects on the fibers structure, so even the mechanical characteristics of the original fabric should not be affected.

Finally, chitosan presence on treated fabric was also revealed by XPS survey scan, showing a certain nitrogen amount on the surface due to the amine groups of chitosan (Table 1).

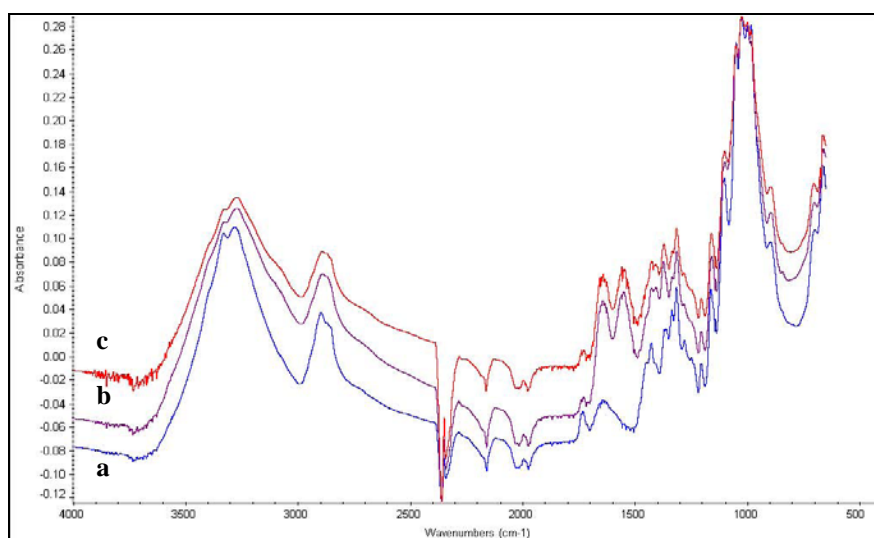


Figure 1: FTIR-ATR spectra. a: untreated cotton, b and c: chitosan treated fabric (10 and 25 % add-on)

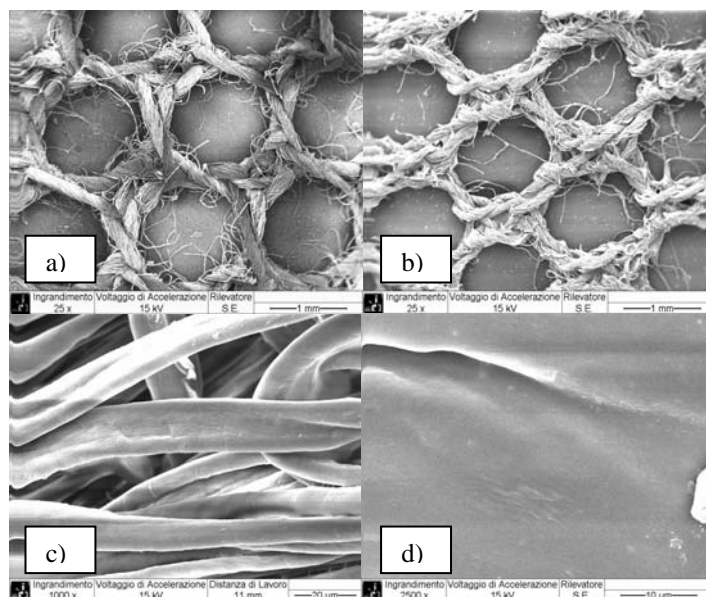


Figure 2: SEM images of a) untreated gauze (25X), b) c) d) chitosan treated samples with 25 % add-on (25X, 1000X and 2500X respectively)

Table 1: XPS survey scan on untreated cotton and 25% chitosan grafted sample

	C [%]	O [%]	N [%]
Untreated	65.1	33.3	-
Treated	58.2	34.9	6.9

### 3.2 Dye adsorption tests

First of all, results of batch adsorption tests show a good performance of treated fabric. In fact, the maximum adsorption values measured are strongly higher than the amount of dye adsorbed by the untreated cotton, lower than 10 mg/g towards all the investigated dyes.

Nevertheless, the increase of chitosan add-on does not correspond to better adsorbent capacity of the gauze. Reactive dye amount adsorbed on the cotton fabric with 25 % chitosan add-on, for example, was double than that adsorbed on fabric with 40 % chitosan add-on (140 mg/g vs 70 mg/g, measured in the same conditions).

Observing the gauze with the highest amount of chitosan grafted, it can be noted, in several points, the formation of a chitosan film covering the whole fabric. In this way, the applied chitosan is, in some extent, not accessible to the dye solution; it means an important reduction of the active surface of the treated fibers and, as consequence, of the accessible chitosan functional groups, responsible of the adsorption phenomena.

At lower add-ons, as it was observed by SEM analysis, chitosan can cover every single fiber, resulting in a surface functionalization of the same, which enables a better treatment efficiency. Moreover, for the good work of the filter in continuous assessment, lower chitosan add-ons can limit the pressure drop, allowing an homogeneous filter exhaustion.

For all these reasons, it was chosen to perform further tests using chitosan treated fabrics with add-ons not higher than 25 %, reducing it at 10 % for the continuous assessment test.

From the results reported in Figure 3, the influence of the adopted pH on the material performance is evident. In acid medium, favourable to the protonation of amine groups of chitosan, the dye adsorption is favoured, with a stronger effect toward acid and direct dyes.

In particular, pH 4 for reactive and direct dyes and 2 for the acid dye can be indicated as optimal values.

All the considered dyes are anionic and it suggests a similar behaviour towards the functionalized gauze; nevertheless, other factors related to the dye molecule can surely influence the affinity of the functional

groups involved in adsorption process: molecular weight, chemical structure,  $pK_a$ , number of functional groups and its position in the dye molecule.

For what concerns chitosan treated cotton, obtained results are in good agreement with Crini and Badot (2008) pointing a pH range 3 - 6 as optimum for the adsorption of dyes on chemically crosslinked chitosan. However dyeing processes of cotton with reactive dyes are commonly carried out in basic media higher than pH 11. In these cases we would expect a low adsorption efficiency unless an adequate pH adjustment is previously performed.

Kinetic curves carried out at pH 4 confirmed the results of exhaustion tests (Figure 4). Reactive and direct dyes showed a very fast adsorption kinetics, reaching more than 90 % bath exhaustion after just 20 minutes. On the contrary the acid dye, after 1 h, reaches only about 40 % exhaustion. The difference can be justified by the lower affinity of the acid dye toward the cellulose substrate and by the fact that the Acid Blue 62 molecule has one anionic group able to interact with cationized amino group of chitosan. Hence longer times are necessary to allow an adequate contact between the substrate and the dye solution, to improve the adsorption process.

Besides pH, the influence of operating temperature was also evaluated, finding a negligible effect. As example, in Figure 5 kinetic curves related to Reactive Blue, at pH 4, both at 25 °C and 50 °C are reported and the curves are practically overwritten. A similar behaviour was found for all investigated dyes, so ambient temperature was chosen as unique temperature in further tests, for a better simulation of the real effluents of dyeing industries.

Operative conditions applied in the continuous assessment tests were quite influential on the performance of the material assembled in filter form. Better adsorption capacity were in fact found decreasing flow rate or dye concentration. A maximum dye adsorption capacity of 37 mg/g was obtained filtering a 1000 mg/L Direct Red solution with a flow rate of about 5 mL/min; this value increased till 50 mg/g decreasing the dye concentration to 250 mg/l and the flow rate to 2 mL/min, even with an incomplete and inhomogeneous exhaustion of the filtering material due to the formation of preferential paths. It confirms the importance of a good contact between dye solution and chitosan treated fabric for a period of time enough to reach an efficient adsorption.

For what concerns the regeneration of the exhausted material, in Figure 6 the course of the dye release in 0.1 M NaOH solution is reported. There was the sudden release of a noteworthy amount of dye, that quickly tended to decrease at negligible concentration. It is related to the decrease of the dye molecules not strongly adsorbed to the gauze and more able to desorption. However, it has to be noted that just 300 mL of NaOH solution can take away 500 mg of adsorbed dye, corresponding to 50 % of filter regeneration.

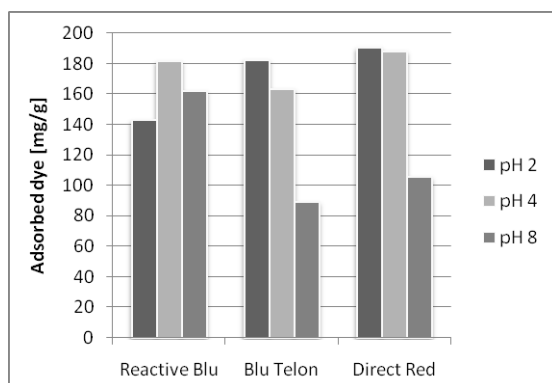


Figure 3: influence of pH in batch adsorption tests on 25 % add-on gauze, at 50°C with 2000 mg/L dye initial concentration, 24 h contact time

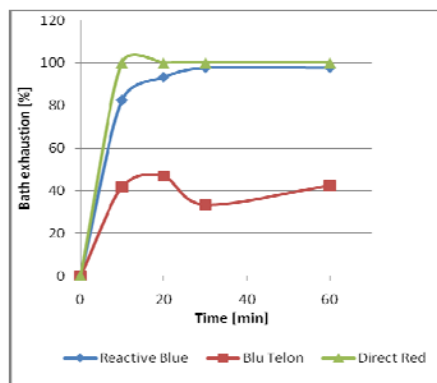


Figure 4: Kinetic curves for batch adsorption on 25 % add-on gauze at 25°C, pH 4 and 1000 mg/L dye initial concentration

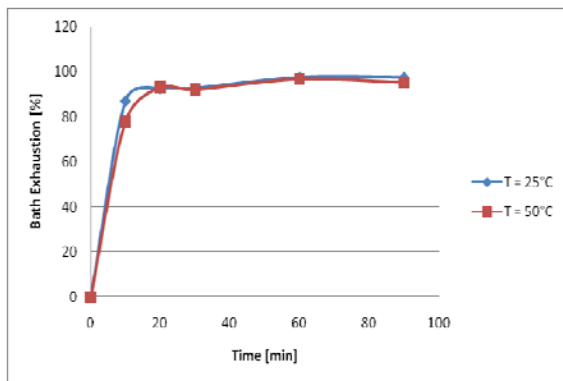


Figure 5: influence of temperature on adsorption kinetics of 2000 mg/L Reactive Blue at pH 4

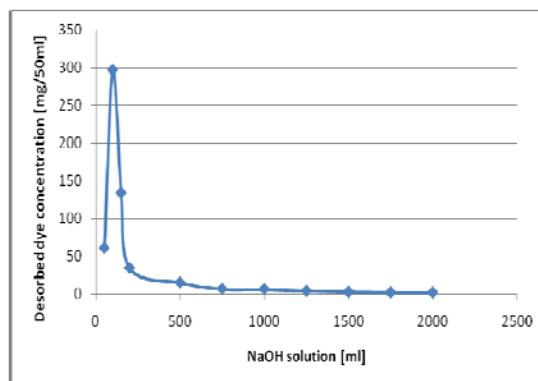


Figure 6: Direct Red release in 0.1 M NaOH

#### 4. Conclusions

The chitosan treated cotton gauze showed good adsorption capacity and very high adsorption rate toward all the investigated dyes. A positive influence on adsorption capacity was displayed in acid conditions while the effect of temperature higher than 25° C was negligible. Moreover, by assembling the functionalized cotton in a filter form, good adsorption capacity is ensured even with 10 % chitosan add-on at 25 °C, with good behavior in terms of filter exhaustion and pressure drop. Nevertheless, the importance of a contact time between dye solution and adsorbent as longer as possible was crucial. It can be improved acting on the physical structure of the gauze. For example, the gauze could be mixed with an inert material or the filter could be assembled in multilayer form, alternating gauze and inert material. Finally, in order to improve the regeneration process, a more concentrated alkali solution could be used, to reduce the solution volume of desorbed dye and to improve the regeneration level of the filter.

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