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Dyes Adsorption on Functionalized Fibrous Materials

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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, among others biological treatments based on active mud, active carbon adsorption or membrane process. Nevertheless none of these methods is performing towards all classes of dyes; treatment plants of great dimensions and difficult handling can be required, while cost of adsorbent materials can be prohibitive.
This research work focuses on dye adsorption, choosing as absorbers low cost fibrous materials, mainly cellulose based, submitted to a cationization process using a quaternary ammonium compound like 3-chloro-2-hydroxypropyltrimethylammonium chloride. This cationic functionalization has been tested toward anionic dyes such as acid, direct, reactive and cationic dyes.
Treated materials were characterized by FTIR-ATR spectroscopy while the treatment efficiency was investigated through exhaustion and kinetic adsorption tests. Comparisons were carried out between treated and untreated samples, showing the cationization effect, and with activated carbon. Best results were obtained with cationized cotton, both in linters or "tulle" fabric form, showing good performance towards all the investigated dyes. These materials were chosen to prepare a prototype of filter that was tested in continuous. Even in this case the good behavior of our material was confirmed, underlined in particular by the comparison with active carbon. In fact, for example, 26 g of treated cotton fabric were able to filter 13 L of 0.25 g/L reactive dye solution before obtaining 5 % of original concentration of the dye in filtered water, with no pressure drop and homogeneous filter exhaustion.
Finally, regeneration tests by bleaching were carried out and it was found that regenerated material maintained good adsorption power.
It can be concluded that cationization is a valid method to produce a competitive dye adsorbent material with great efficiency towards many dye classes and with a good behavior if used in continuous 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. Most industries produce a lot of wet wastes although recent trends in the developed world have been to minimize such production or recycle such waste within the production process.

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Textile industry involves wide range of raw materials, machineries and processes to engineer the required shape and properties of the final product. Waste streams generated in this industry mainly consist on water-based effluents coming from the various activities of wet processing of textiles. In fact huge volumes of water are used in chemical processing involved in preparatory, dyeing, printing and finishing operations.
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, activated carbon filtering or membrane bioreactors, as reported by Ranganathan et al. (2006). Nevertheless, each of these processes shows limitations: none is performing towards all dyes types, depuration plants of great dimensions can be required, the cost of raw adsorbing materials or producing technologies can be high.
For these reasons, this research work focuses on dye adsorption, choosing as absorbers low cost fibrous materials, mainly cellulose based, submitted to a cationization process using a quaternary ammonium compound. Cationization was already used on cotton fabric to improve its affinity towards different dye classes (Frazer, 2002; Subramanian et al., 2006; Montazer et al., 2007) while the application to dye removal was not study in depth (Hashem and El-Shishtawy, 2001; Karnik, 2002; Wang, 2005).

2. Materials and Methods

In this study the adsorption capacity of different cationized substrates was tested towards different dyes classes.
A first screening test involved cationized substrates made of different materials, namely cotton fibers, cellulose sheets, linen blend, polyester (PET) fabric and polyvinyl alcohol (Kuralon K-II) staple fiber. The best results were obtained with cotton. Hence other substrates were consequently neglected while cotton substrate was deeper investigated in form of linters, staple fiber, yarn, plain-weave cotton fabric (144 g/m^2) and tulle fabric (49g/m^2). Among these, cotton linters and tulle fabric were most performant so these materials were tested also working in continuous.
For what concern the cationization process, the substrates were firstly causticized treating them with a solution of 250 g/L of NaOH laboratory grade and 0.03 g/L of Tergitol NP 14 (Union Carbide) non-ionic surfactant. Substrates were dipped in the solution with a material to liquor ratio 1:20 and kept in agitation by magnetic stirring. Since the reaction is hexothermal, temperature rise was monitored and when the system came back to 25 °C, denouncing the complete substrate caustification, 3-chloro-2-hydroxypropyltrimethylammonium chloride (400% on weight fibers) was added as cationization reagent. The obtained solution was maintained in agitation overnight, at ambient temperature, then the cationized material was repeatedly rinsed until reaching pH 7, squeezed and dried in oven at 100 °C.
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 substrates, 0.5 g samples were put in sealed tubes in contact with 1 or 2 g/L dye solution with a material to liquor ratio 1:100 for 24 h at 50 °C, in a thermally

controlled agitated bath. Finally the bath exhaustion and consequently the maximum dye adsorption were evaluated. For kinetic tests four tubes were prepared in the same manner but samples were extracted from dye solution at different times to evaluate the bath exhaustion at each time.

Finally, on cotton cationized linters and tulle fabric, test was performed assembling a filter crossed by a dye solution pumped in continuous. It was to confirm the material performance in operating conditions. The adsorbing material was placed inside a glass tube, between inert fillers, to form a filtering bed 7 cm high corresponding to 20 g of linters and 26 g of tulle. Dye solutions, 0.25 g/L or 0.05 g/L were pumped on the filter keeping a constant flow of about 10 mL/min or 50 mL/min.

Exhausted cationized cotton linters were then repeatedly regenerated by bleaching with sodium hypochlorite to test again its adsorption capacity.

Same tests were carried out with Norit Row 0.8 Supra activated carbon (Norit, Milan, Italy) and with reactive dye solution, in order to make a comparison with a material widely used at industrial level.

The dyes investigated were Telon Blue (C.I. Acid Blue 62) by Dystar, an acid dye with maximum adsorbance at 626 nm; Reactive Blue 4 (Sigma Aldrich), also in hydrolyzed form, with maximum adsorbance at 595 nm; Direct Red 81 (Sigma Aldrich) with absorbance peak at 508 nm and Maxilon Red SL (Basic Red 51) by Ciba, a cationic dye with absorption peak at 525 nm.

Bath exhaustions were evaluated by spectrophotometric analysis of the liquors, carried out by an Unicam UV2 (ATI Unicam, Cambridge, UK) double ray spectrophotometer processing data by Vision 32 software. For each dye a calibration line was built to evaluate data.

Cationized cotton surface was characterized by FTIR-ATR analysis by 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, at 4 cm^{-1} resolution and gain 8, in the wavelength range 4000-600 cm^{-1}.

3. Results and Discussion

Preliminary exhaustion tests revealed the efficiency of cationization treatment to improve the adsorption capacity of the various substrates. It was confirmed for direct, acid and reactive dyes, as can be seen in Figure 1, while for Maxilon cationic dye the improvement of dye adsorption compared to untreated cotton was not relevant due to the repulsive forces between cationic dye and cationized fiber. In fact, untreated cotton showed an adsorption capacity of 68 mg/g, almost unchanged after cationization process.

From Figure 1 it is also evident that adsorption capacity was mostly improved by the cationization of cotton fibers, even if results obtained with other substrates were also of interest. Among cotton fibers, linters showed the best performance in discontinuous test due to its physical structure that assures a great surface area to get in touch with dye molecules.

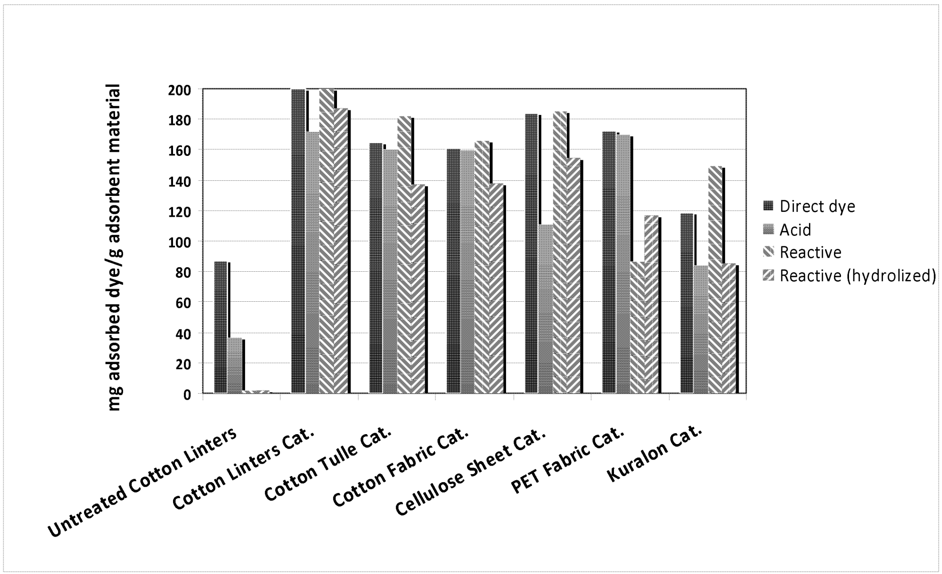

Figure 1: Maximum adsorption capacity of untreated cotton linters and cationized substrates investigated.

On cationized linters the same test were carried out working with a material to liquor ratio 1:1000, with Direct and Acid dye solutions up to 0.25 g/L, at both ambient and 50°C temperature. In this way adsorption isotherms were obtained and it was found that the adsorption capacity was improved by temperature increase. For example, for an initial Direct Red concentration of 0.25 g/L, at equilibrium conditions, the cationized linters showed dye adsorption improvement from 201 mg/g at 25°C to 232 mg/g working at 50°C.

From the kinetic results reported in Figure 2, a very fast adsorption was shown on cationized cotton tulle by Reactive and Direct dyes, with more than 80% dye exhaustion after 10 min of contact time and the total bath exhaustion reached after just 50 min. A bit lower but still of interest was the behaviour of the Acid dye while worst results were obtained with Maxilon dye. Nevertheless, even with this dye, if the contact time is prolonged till to 120 min, a 60 % bath exhaustion can be reached, denouncing a beneficial effect of cationization even with respect to it.

Continuous filtration tests gave good results both for linters and tulle cationized cotton.

Crossing the filter section, dye solution was decoloured while filter acquired an intense coloration showing dye adsorption. Moreover, the filter coloration was progressive along its height with no formation of preferential ways.

The filtered solutions were collected perfectly colourless till reaching an adsorbed dye amount of 107 mg/g for linters substrate tested with 0.25 g/L of Direct Red or 120 mg/g for tulle fabric tested with 0.25 g/L of Reactive Blue.

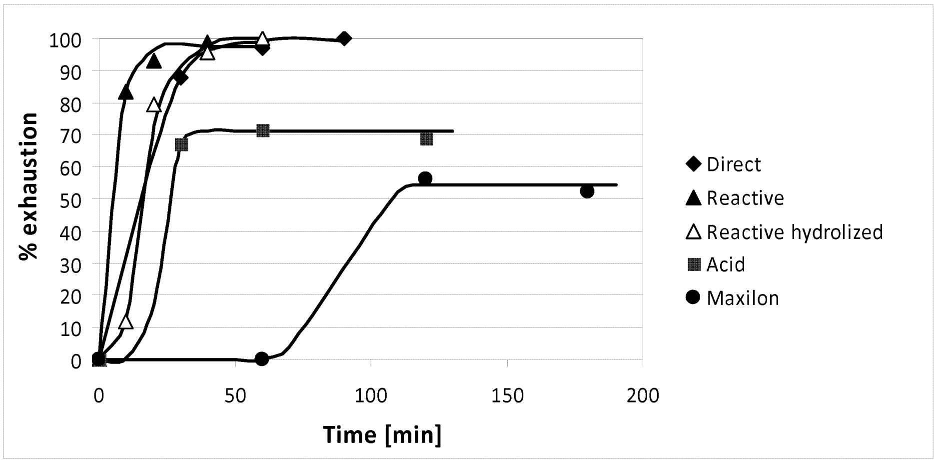

Figure 2: Kinetic curves on cationized tulle cotton (1 g/L initial dye concentration).

The adsorption capacity results are lower than those obtained in batch tests probably due to the liquid flow, causing a consequent lower contact time between the dyed solution and the adsorbent. Lowering dye concentration at 0.05 g/L the performance of cationized linters was enhanced, in fact after filtering 55 L of solution, just about an half of the filter showed a red coloration, with an estimated adsorption capacity of about 300 mg/g or more. But the most important difference between linters and tulle filter was the pressure drop: the compact structure of linters opposes a great resistance to the liquid flow while the open mesh of tulle, even if packed and pressed to form the filter, let the liquid to flow trough it without any resistance. Moreover the exhausted tulle removed by the filter was completely and deeply coloured with homogeneous dye distribution. It makes tulle fabric more suitable than linters for working as filter medium in operating conditions.

On cationized linters some regeneration tests were also carried out. Samples used to adsorb acid and direct dyes were regenerated by bleaching and resubmitted to the adsorption tests twice. Adsorption capacity was maintained with acid dye at 83 % after 1 regeneration cycle, while with direct dye it was maintained at 100 % after 1 cycle and 76 % after 2 cycles, indicating the possibility to reuse the filter more times simply bleaching it. The same test was carried out in continuous, flowing an hypochlorite solution across the filter and then reusing it for dye filtering and comparable results were obtained.

A further comparison was carried out submitting an activated carbon to the same tests performed on cationized cotton: in none of them the carbon performance attained to that of cationized cotton. In batch adsorption tests, the maximum amount of Reactive Blue adsorbed by carbon was 146 mg/g vs 182 mg/g of cationized cotton. Even kinetic curves showed a lowest adsorption rate than our materials, reaching 20% exhaustion after 10 min vs 83%, and 56% after 240 min vs 100% exhaustion reached by cationized cotton after 50 min. But the worst results with activated carbon were found in continuous test: filtering the dye solution in the same flow conditions tested with the cationized tulle cotton the solution was immediately collected with an evident, strong coloration. After filtration of 8.7 L of solution, the dye concentration in the collected liquid reached already a 74% of the initial one.

The treatment effects on cotton were also investigated by FTIR-ATR analysis. Comparing the spectra related to treated and untreated samples, some differences arise. In particular, in the spectra of treated fabrics distinct bands can be observed between 1430 and 1373 cm^{-1} corresponding to aliphatic C–H stretching, bending deformations and rocking vibrations of the methylene groups, according to Kamel et al. (2009).

4. Conclusions

From this study, it can be said that cationized cotton, in particular as tulle fabric, has good perspectives to be used as adsorbent material in dye removal from textile industry wastewaters. It showed in fact good adsorption capacity and very fast adsorption kinetic toward all the investigated dyes with exception to Maxilon cationic dye, but even in this case prolonged contact times can improve results to satisfactory values. Moreover, assembling the cationized cotton in a filter form, good adsorption capacity is maintained, with good behavior in terms of filter exhaustion and pressure drop.

A positive influence on filtration capacity was played lowering dye concentration or enhancing the dye solution temperature. Finally, cationized cotton was largely more effective, in particular operating in continuous, than an activated carbon commonly used in industrial applications for dye removal from wastewaters.

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