

## ACID, ACRYLAMID AND ZEOLITE MODIFICATION OF CELLULOSIC ESPARTO FIBERS FOR DYES DECOLOURISATION

Imed Ben Marzoug,<sup>a</sup> Lamiss Allègue,<sup>b</sup> Faouzi Sakli,<sup>a</sup> and Sadok Roudesli<sup>c</sup>

The decolourisation of reactive and cationic dyes by physical and chemical modified esparto fibers was investigated. Previously the decolourisation of reactive dyes only had been tested and optimized using untreated esparto fibers and those reinforced by zeolite. Non-treated cellulosic esparto fibers can absorb an important amount of dyes. In order to improve absorption properties of esparto fibers, chemical graft copolymerization with acrylic acid (AA), itaconic acid (IA), and a mixture of acrylamide and IA was performed using potassium persulfate as initiator. The effect of physical modification by zeolite was investigated. Reinforced zeolite esparto fibers were obtained from cellulose esparto fibers pre-treated with NaOH, and preformed zeolite powders. The IR spectroscopy, X-ray diffraction, thermal behavior, as well as the surface morphology of the treated fibers were also studied. The results showed that zeolite treated esparto fibers (the first time application of this kind) are more efficient adsorbents than luffa fibers.

*Key words: Esparto fibers; Grafting; Deposition of zeolite; Thermal stability; Characterization methods*

*Contact information: a: Textile Research Unit of High Institute of Technological Studies in Ksar Hellal, Tunisia; b: Mechanical Engineering Laboratory of the Engineering School of Monastir, Tunisia; c: Laboratory of polymers bio-polymers organic materials Scientific University of Monastir, Tunisia; corresponding author: imedmarzoug@yahoo.fr*

### INTRODUCTION

A wide variety of dyestuffs can be found in real effluents, including acid, basic, reactive, and direct dyes, etc. It has been estimated that about 9% of the total amount of dyestuffs produced in the world are discharged in textile wastewater (Allen et al. 2005). Rising concern about environmental issues has prompted the textile industry to investigate appropriate environmentally treatment technology. Effluent aqueous waste containing dye compounds cause serious problems. Removal of dyes from the dye-containing effluents is currently based on a wide variety of physicochemical processes. The search for alternative and innovative wastewater treatment techniques has high importance. Using esparto cellulosic fibers in this field can be very beneficial. In order to improve adsorption and absorption properties of esparto fibers, physical and chemical modification is one alternative. Chemical modification of cellulosic fibers has been used to produce new and unusual properties. Etherification, esterification, grafting, and crosslinking reactions as means of chemical modifications of cellulosic fibers have been studied (Wang et al. 2002). Chemical modification of cellulosic fibers is performed by reaction with the hydroxyl group. Wang (2002) has reported that modification of cotton

fibers with 1-acrylamido-2-hydroxy-3-trimethylammoniumpropane chloride improved their dyeability. Indeed, treated fiber can be dyed with reactive dyes without any other dyebath additions.

Zahran (2006) reported that when cotton fibers were treated with 2-venylpyridine and quaternised with epichlorohydrin or an alkyl bromide, the exhaustion values of dyeing with reactive dyes could be enhanced towards the limiting value (95 to 100 %). Also, ester crosslinking treatment has been found to decrease the fibrillation tendency of lyocell fibers (Fang et al. 2003). The formation of copolymers of cellulose and various synthetic polymers via graft copolymerization has been extensively studied (Naser et al. 1986; Canche-Escamila et al.; Bessadok et al. 2008; Lanthong et al. 2006; Princia et al. 2005). Deposition of zeolite on their surface has also been investigated (Leiva et al. 2005; Ahcène et al. 2004; Aditya et al. 2008). Grafting of vinyl and acrylic monomers onto cellulose using persulfate radicals is common and was studied by different authors (Naser et al. 1986; Canche-Escamila et al. 1999; Bessadok et al. 2008; Lanthong et al. 2006; Princia et al. 2005). Besides, preparing graft copolymers of cellulose with different monomers has been carried out to produce cellulose materials with modified properties, especially for their behavior in dyeing process (Wang et al. 2002). The dicarboxylic acid monomers such as itaconic acid and others have been used as crosslinking agents for cellulose (Sabaa et al. 2002). Modified cellulosic fibers are used in many important applications such as orthopaedic applications (Petrica et al. 2006).

In the present investigation, modification, characterization of treated fibers, and the products' ability to remove reactive and cationic dyes from solution were investigated. The possibility of grafting itaconic acid (IA), acrylic acid, and the mixture of itaconic acid and acrylamide onto esparto fiber and deposition of zeolite on their surface were investigated. The investigation was extended not only for the chemical treatment, but also for the characterization of the treated fibers, including their surface properties, degree of crystallinity, and thermal stability. The treated and untreated fibers were used as a filter for discoloration of water treated with reactive and cationic dyes. These products are able to absorb significant quantities of dyes. Zeolite deposition and grafting of acid substances on the esparto cellulosic fibers can improve ion exchange (Allen et al. 2005) and give new functions to fix and absorb dyes.

## **EXPERIMENTAL**

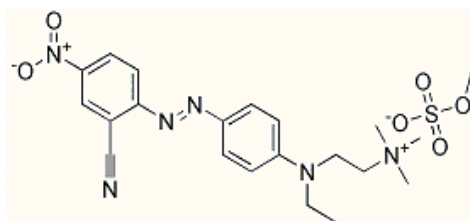
### **Materials**

#### *Fibers*

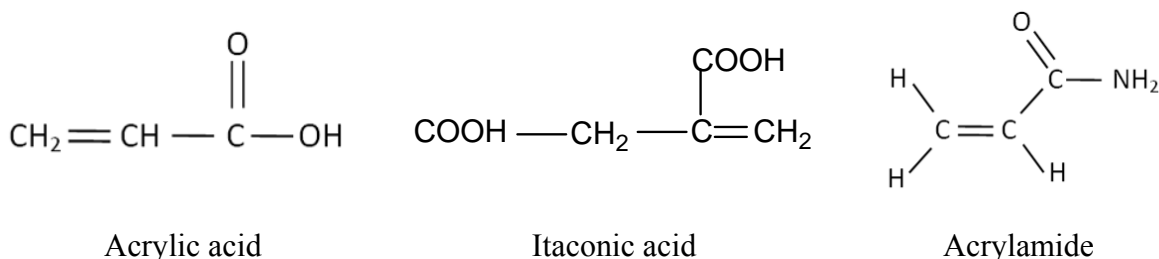
The cellulosic esparto fibers used in this work were extracted using a method containing 30 g/L of sodium hydroxide, 35 mL/L of hydrogen peroxide, 3 g/L of wetting agent (Subitol LSN, BEZEMA), and 25 mL/L of stabilizer of hydrogen peroxide (Contavan GAL). Fibers were treated under pressure (1.5 bars) at a temperature of 90 °C during 90 minutes.

### Chemical reagents

Reactive (Cibacron brilliant red (CBR. 2 B-E), Reactive Red 41, CI 18204) and cationic (Red Astrazon FBL 200 %) dyes were tested. Cibacron brilliant red (CBR. 2 B-E, Reactive,  $\lambda_{\text{max}}$ : 520 nm) was obtained from Ciba. Dye solution was prepared from a solution that was obtained by dissolving weighed quantity (2 g) of brilliant red cibacron (CBR. 2 B-E) in 1 liter of distilled water. Reactive dyes are used frequently and consumed with high quantities. Figure 1 provides chemical formula of red Astrazon.



**Fig. 1.** Chemical formula of red Astrazon FBL 200%  
Cl: Basic Red 24



**Fig. 2.** Chemical formulas of acrylic acid, itaconic acid, and acrylamide

## Methods

### Scanning electron microscopy (SEM) analysis

SEM analysis of untreated and treated fibers was performed using a XL30 ESEM model from SEI.

### FTIR spectrum

The Fourier Transform Infrared (FTIR) spectrum of the fiber of esparto grass in KBr pellets was measured using a Shimadzu Spectrum W 8400 FTIR spectrophotometer.

### X-ray diffraction

X-ray diffractograms are obtained with an analytical X'Pert PRO MPD diffractometer, having an X-ray tube producing monochromatic Cu  $K\alpha$  ( $\lambda = 1.789 \text{ \AA}$ ) radiation.

### Calorimetric analyses

Calorimetric analyses for the various investigated samples were performed using a Perkin-Elmer analyzer. Fibers were weighted then they were placed in perforated melting-pot. Fibers were heated till 300°C temperature at a rate of rate of 10°C.min<sup>-1</sup>. Then they were cooled at a rate of 20°C.min<sup>-1</sup>.

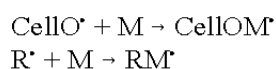
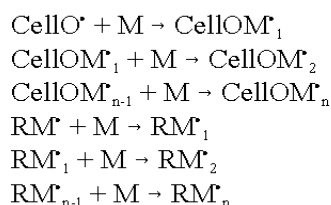
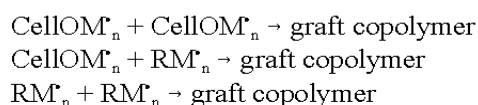
*Experimental conditions*

A suspension of 50 mL of distilled water and 12 g of zeolite was prepared and contacted with 2 g of NaOH-Fiber. This solid–liquid suspension was stirred for 15 min, until macroscopic homogeneity was achieved. After that, the suspension was placed in the oven at 100 °C until a completely dry mass was obtained. The resulting esparto fiber reinforced zeolite was washed with distilled water until obtaining a pH of 6.5 to 7.0, and finally the solid was oven-dried at 100 °C.

The appropriate amount of esparto cellulosic fibers was placed in a water solution under the following conditions: The temperature, polymerization time, initiator and monomer concentrations for AA were 80 °C, 2 h,  $4 \times 10^{-2}$  M, and 1.5 M, and for IA and the mixture of IA and acrylamide the conditions were 80 °C, 1 h,  $4 \cdot 10^{-2}$  M and 1.5 M, 1.5 M, respectively.

*Reactions*

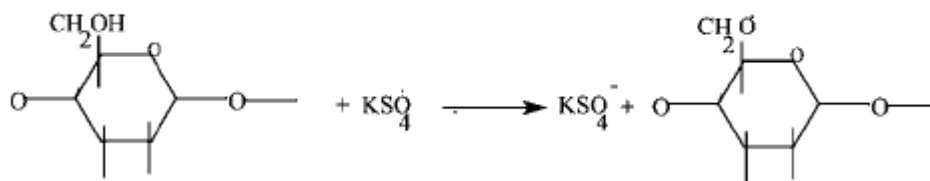
The following steps represent the reaction mechanism as reported by Mosatfa (2005).

**Initiation****Propagation****Termination**

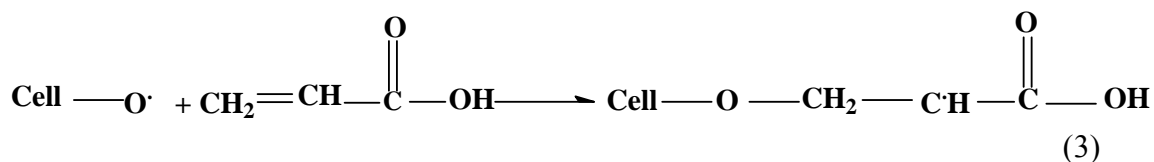
Grafting was initiated by  $\text{K}_2\text{S}_2\text{O}_8$  according to the following reactions:



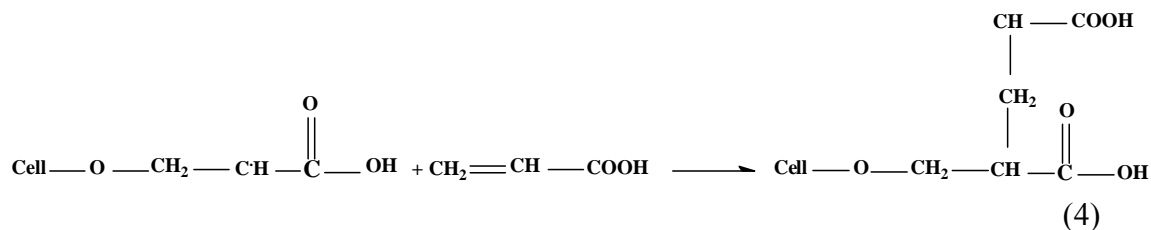
As reported by Naguib (2002), the reaction between potassium persulfate as the oxidizing initiator and cellulose is:



The reaction between esparto cellulosic fibers and acids is given by:



Then,



### Sorption studies

The sorption capacities of fiber (500 mg) were determined by contacting 200 mL solution of known concentration (50 to 500 mg/L) in 250 mL flasks. The solution of dye and the fibers were agitated. Esparto fibers were separated from the solution by filtration. Residual concentration of the dye solutions was determined spectrophotometrically using a Shimadzu UV 2401 PC UV/VIS spectrophotometer.

Decolourisation efficiency was determined spectrophotometrically by monitoring the decrease in absorbance, and calculated according to the following formula,

$$\text{Percentage of decolorisation (\%)} = ((A_A - A_B)/A_A) \times 100 \quad (5)$$

where  $A_A$  is the absorbance at the maximum dye before decolourisation and  $A_B$  is the absorbance at the maximum absorption wavelength of dye after decolourisation. Then absorbed quantity is calculated relative to the initial color quantity dissolved.

## RESULTS AND DISCUSSION

### Image Analyses

Results of SEM analysis revealed aspects of the morphologies of treated fibers. Effects of zeolite deposition, grafting acrylic acid, itaconic acid, and the mixture of itaconic acid and acrylamide with esparto fibers are shown in Figs. 3 through 6.



the chemical structure, a rearrangement in the morphology of the polymeric chain as a result of grafting.

A new band in the diffractogram of a sample treated with itaconic acid appears to show successful modification. A decrease of the peak at  $2\theta = 26.4$  demonstrates the change of structure and the crystallinity of fibers.

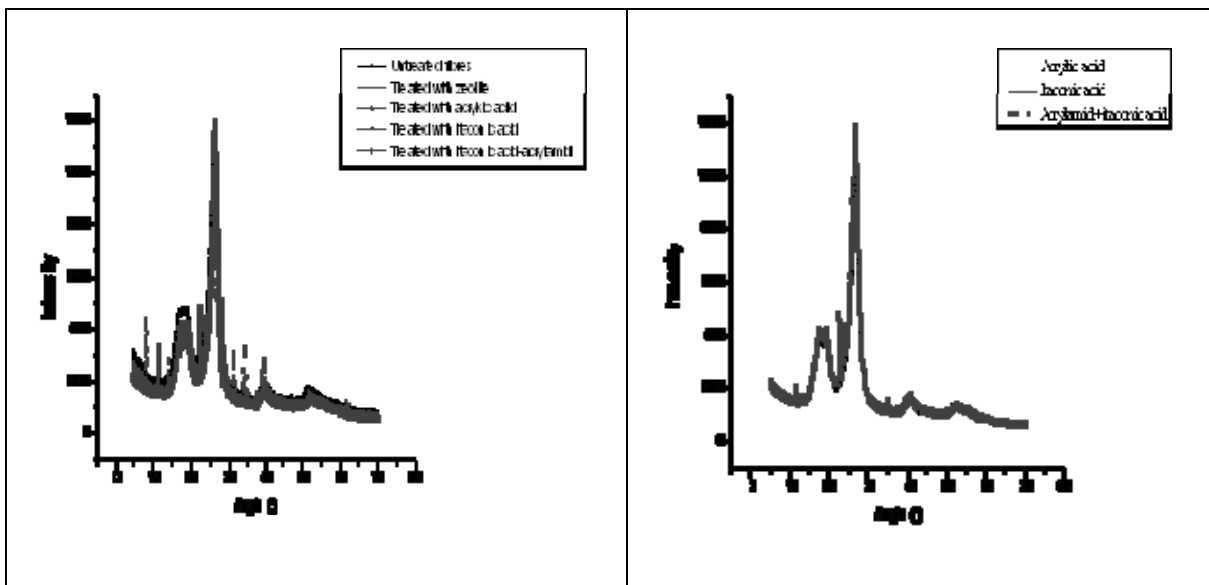


Fig. 7. XRD diffractogram of modified esparto ultimate fibers

### FTIR and Thermal Behavior Results

Results of modification by zeolite, itaconic acid, acrylic acid, and the mixture of itaconic acid and acrylamide are presented in Fig. 8 (a and b).

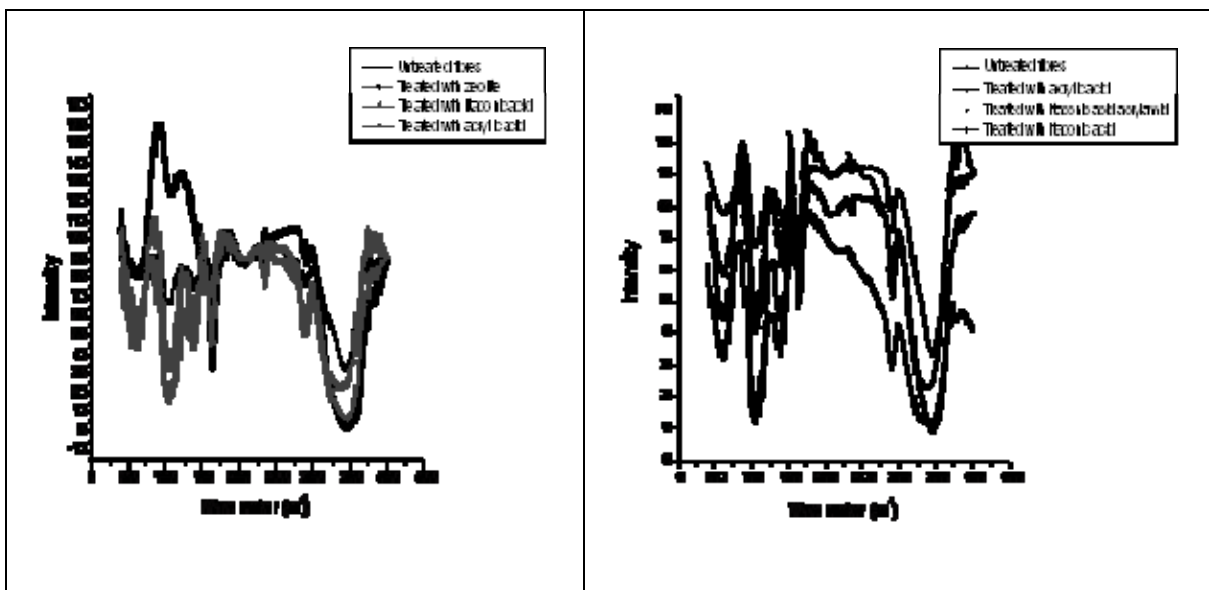
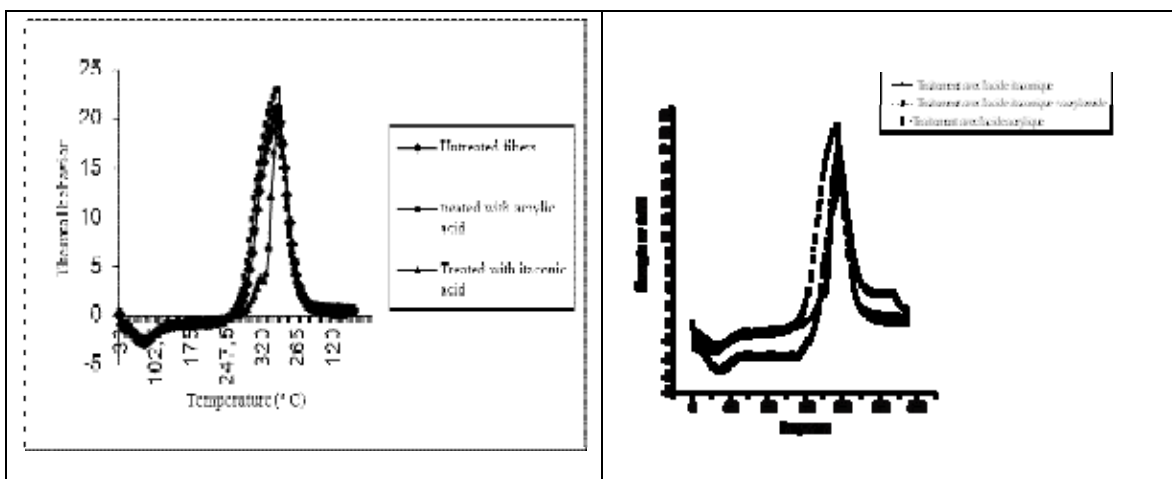


Fig. 8. Infrared spectrum

Figure 9 (a and b) shows the thermal behavior of different treated fibers. The results exhibit differences in chemical composition of treated versus untreated fibers. The results give confirmation of the grafting process. This is illustrated by the appearance of a new band at  $1734\text{ cm}^{-1}$ , characteristic of the carboxylic group of IA or AA. An increase of the intensity of the band at  $2900\text{ cm}^{-1}$  proves the presence of vinylic groups (Mohanty et al. 2000). The sample treated with a mixture of itaconic acid and acrylamide showed the presence of a band at  $2236\text{ cm}^{-1}$ , which indicates  $-\text{CN}$  groups (Mohanty et al. 2000). New bands at 1400 and 1550 are evident, indicating grafting with acidic substances (Pourjavadi et al. 2004).



**Fig. 9.** Thermal behavior

These results show that fibers subjected to different treatments displayed different behavior. The results reveal a decrease in the thermal stability with grafting by itaconic acid. This may be attributed to the low thermal stability of poly itaconic acid (Vu et al. 2002). The increase of stability in the case of reinforced zeolite fibres is linked to the crystallinity of zeolite and his higher stability.

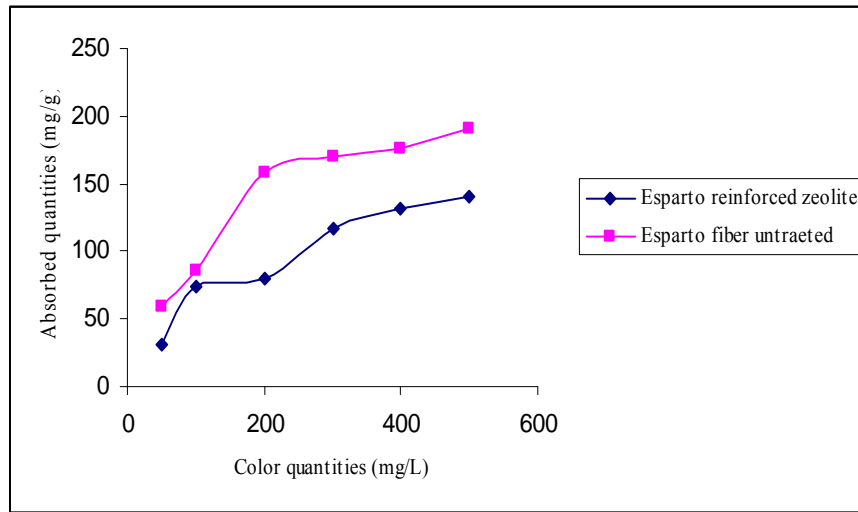
### Dyes Absorbency

Another set of tests was carried out to determine the dye absorbency of zeolite reinforced fibers. Indeed, the fibers treated with zeolite absorbed a maximum quantity of reactive dye equal to  $327\text{ mg/g}$  at 11 pH and  $40\text{ g/L}$  of salt at  $80\text{ °C}$  during 90 minutes.

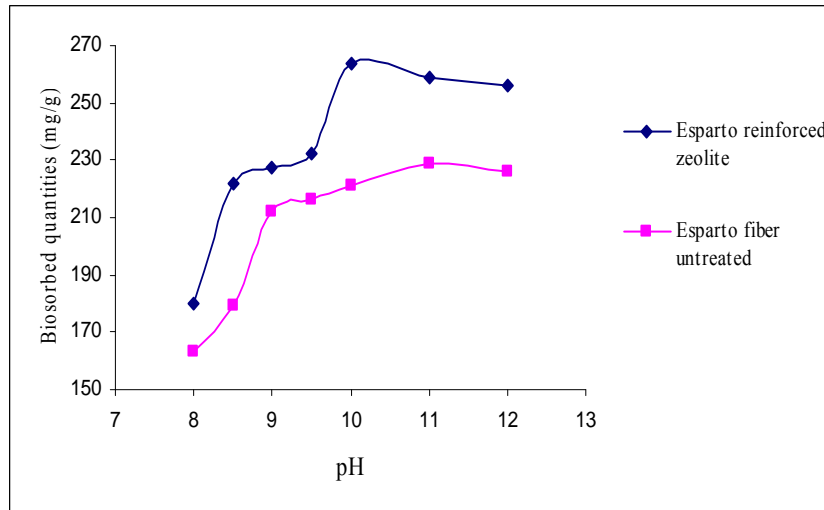
Zeolite and cellulosic esparto fiber are negatively charged under alkaline conditions. But with optimum pH and appropriate quantity of salt, the effect of negative charge is eliminated, and covalent bonds are established (Mazmanici et al. 2005).

Grafting with acrylic acid, itaconic acid, and the mixture of itaconic acid and acrylamid involved formation of covalent chemical bonds. All of these products that are fixed with a strong bond provide fibers with new permanent functions. However, bonds performed between fibers and zeolite are bonds of low energy. So these bonds don't lead to a lasting fixation.

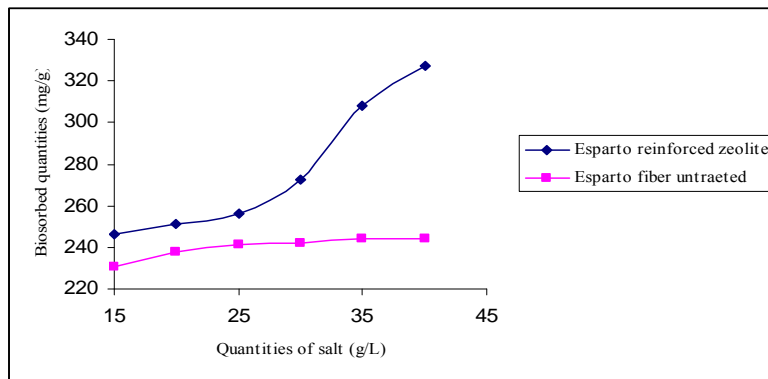




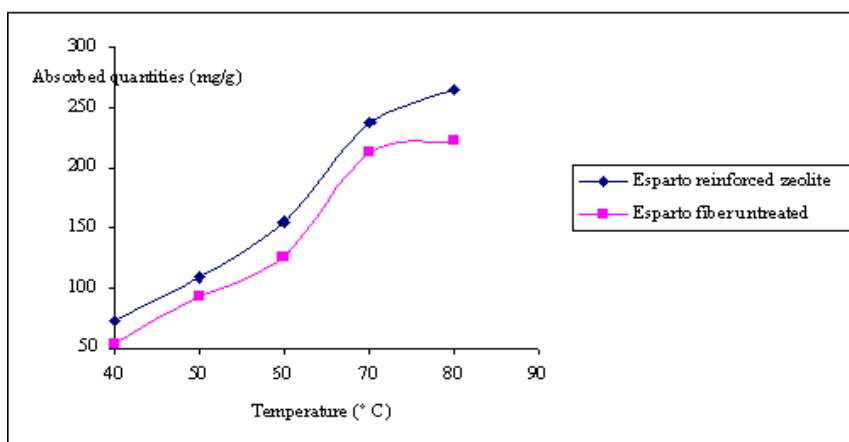
**Fig. 10.** Absorption quantities of esparto fiber and esparto fiber reinforced zeolite



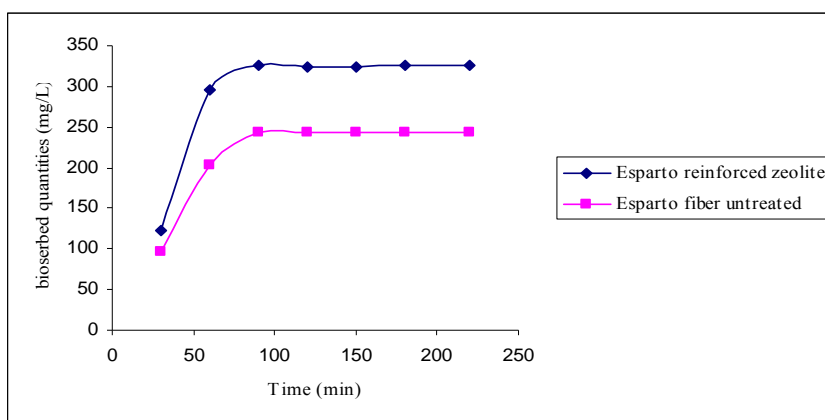
**Fig. 11.** Effect of pH on dye absorption of esparto fibers and reinforced zeolite esparto fibers



**Fig. 12.** Effect of salt quantities on absorption properties of esparto fiber and reinforced zeolite esparto fibers



**Fig. 13.** Effect of temperature on dyes absorption of esparto fibers and reinforced zeolite esparto fibers



**Fig. 14.** Duration effect on dye absorption of esparto fibers and reinforced zeolite esparto fibers

Fibers modified with acrylic acid, itaconic acid, and the mixture of itaconic acid and acrylamide absorbed important amounts of cationic dyes compared to non-modified fibers (231 g/g). The functions fixed on the fibers increased the absorption capacity of the fibers.

Fibers treated with acrylic acid, itaconic acid, and the mixture of itaconic acid and acrylamide can fix cationic dye. Covalent and electrostatic phenomena can be produced (Mazmanci et al. 2005). Treated fibers absorb higher quantities of cationic dyes. Table 1 shows the corresponding absorption values.

**Table 1.** Cationic Dye Absorption

Samples	Acrylic acid	Itaconic acid	Mixture of itaconic acid and acrylamide	zeolite
<b>Absorption g/g</b>	341	348	321	366

## CONCLUSIONS

1. Characterization methods revealed the existence of new chemical groups on esparto cellulose subjected to grafting. Characterization methods demonstrated structural changes and decreased crystallinity. The stability of treated fibers was modified.
2. Added substances can improve the properties of sorbents. Indeed, zeolite increases dyes absorbency. Also, modification of esparto fibers by itaconic acid and acrylic acid can improve their absorbency of cationic and reactive dyes.
3. These materials can be used as filter for discoloration of wastewater (Mazmanci et al. 2005). Indeed, samples treated with zeolite can absorb 366 g/g of cationic dyes. Grafted fibers can absorb until 348 g/g given by treated fiber with itaconic acid. In comparison, luffa fibres can absorb 49 mg/g; thus, treated esparto fibres show a higher capacity.
4. This study reports for the first time, the possibility of treated esparto fibres as a dye biosorbent system for the removal of cationic and reactive dye, from aqueous solution.

## REFERENCES CITED

- Ahcène, S., Berkani, M., and Chater, M. (2004). "Synthèse et caractérisation des zeolites de type ZSM-5, C.R." *Chimie* 7, 713-720.
- Aguir, C., and M'Henni, M. F. (2006). "Experimental study on carboxymethylation of cellulose extracted from *Posidonia Oceanica*," *Journal of Applied Polymer Science* 99, 1808-1816.
- Allen, J., and Coumanova, B. (2005). "Decolourisation of water/waste water using adsorption: Review," *Journal of University of Chemical Technology and Metallurgy* 40, 175-192.
- Bhan, A., Gounder, R., Macht, J., and Iglesia, E. (2008). "Entropy considerations in monomolecular cracking of alkanes on acidic zeolites," *Journal of Catalysis* 253, 221-224.
- Bessadok, A., Marais, S., Roudesli, S., Lixon, C., and Métayer, M. (2008). "Influence of chemical modifications on water-sorption and mechanical properties of *Agave* fibres," *Composites: Part A. Applied Science and Manufacturing* 39(1), 29-45.
- Canche-Escamillaa, G., Cauich-Cupula, J. I., and Herrera-Franco, P. J. (1999). "Mechanical properties of acrylate-grafted henequen cellulose fibers and their application in composites," *Composites: Part A*. 30, 349-359.
- Fang, K., and Hao, L. (2003). "Ester crosslinking treatment for reducing the fibrillation tendency of lyocell fibers," *Textile Res. J.* 73(11), 113-116.
- Lanthong, P., Nuisin, R., and Kiatkamjornwong, S. (2006). "Graft copolymerization, characterization, and degradation of cassava starch-g-acrylamide/itaconic acid superabsorbents," *Carbohydrate Polymers* 66, 229-245.
- Leiva, S., Sabater, M. J., Valencia, S., Sastre, G., Fornés, V., Rey, F., and Corma, A. (2005). "A new synthesis method for the preparation of ITQ-7 zeolites and the characterisation of the resulting materials," *Comptes Rendus Chimie* 8, 369-378.

- Mazmanci, M., and Ünyayar, A. A. (2005). "Decolourisation of Reactive Black 5 by *Funalia trogii* immobilised on *Luffa cylindrica* sponge," *Process Biochemistry* 40, 337-342.
- Mohanty, A. K., Khan, M. A., and Hinrichsen, G., (2000). "Surface modification of jute and its influence on performance of biodegradable jute-fabric/biopol composites," *Composites Science and Technology* 60, 1115-1124.
- Mostafa, Kh. M., (2005). "Preparation and characterization of cotton textile graft copolymer as cation exchanger," *Journal of Applied Sciences* 5(3), 527-531.
- Naguib, H. F., (2002). "Chemically induced graft copolymerization of itaconic acid onto sisal fibers," *Journal of Polymer Research* 9, 207-211.
- Naser Mohamed, A.-S. (1986). "Photo initiated grafting of some vinyl monomers onto cellulose derivatives," El Mansoura University, Faculty of Science, Thesis; 1-47.
- Petrica, S. E., Marra, K. G., and Kumta, P. N. (2006). "Chemical of poly (lactic-co-glycolic acid) hydroxyapatite composites for orthopaedic application," *Acta Biomaterialia* 2, 277-286.
- Princia, E., Vicinia, S., Pedemonte, E., Mulasa, A., Franceschia, E., Lucianoa, G., and Trefiletti, V. (2005). "Thermal analysis and characterisation of cellulose grafted with acrylic monomers," *Thermochimica Acta* 425, 173-179.
- Pourjavadi A., Harzandi, A. M., and Hosseinzadeh, H. (2004). "Modified carrageenan synthesis of novel polysaccharide-based superabsorbent hydrogel via graft copolymerization of acrylic acid onto kappa-carrageenan," *European Polymers Journal* 40, 1363-1370.
- Sabaa, M. W., and Mokhtar, S. M. (2002). "Material characterisation of chemically induced graft copolymerization of itaconic acid onto cellulose fibers," *Polymer Testing* 21, 337-343.
- Vu, D., Marquez, M., and Larsen, G. (2002). "A facile method to deposit zeolites Y and L onto cellulosic fibers," *Composites: Part A* 30, 349-359.
- Wang, H., and Lewis, D. M. (2002). "Chemical modification of cotton to improve fibre dyeability," *Coloration Technology* 118, 159-168.
- Zahran, M. K. (2006). "Grafting of methacrylic acid and other vinyl monomers onto cotton fabric using Ce (IV) ion and cellulose thiocarbonate redox system," *Journal of Polymer Research* 13, 65-71.

Article submitted: November 5, 2011; Resubmitted with formatting changes: February 11, 2011; Peer review completed: March 24, 2011; Revised version received and accepted: April 10, 2011; Published: April 13, 2011.