THE IMPROVEMENT IN DYEING PROPERTIES OF MODIFIED POLYAMIDE 6.6 MICROFIBERS WITH A CATIONIC DYE

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ABSTRACT

Polyamide 6.6 microfibers were modified to improve its dyeing affinity using a graft copolymerization method. These microfibers were grafted with acrylic acid as monomer. The improvement of the dyeing properties of modified polyamide 6.6 microfibers was investigated using a cationic dye (Red Astrazon 5 BL). It revealed that the dye uptake of the modified microfibers was greater than those unmodified. The kinetic study of the cationic dye used at various grafting rates showed an improvement of the dye build-up rate like its exhaustion. In addition, an increase in the adsorption of the dye quantity fixed on the surface layer of microfibers made up by the grafted molecules was announced. The wash fastness was slightly improved with the grafting rate. The modeling of the adsorption isotherms using Langmuir, Freundlich, and Jossen relations allowed the determination of isotherm constants. The obtained results from this modeling study showed the existence of several models corresponding to various grafting rates.

KEYWORDS

1.INTRODUCTION

Synthetic fibers are becoming more and more important in textile production. At present, many clothes are manufactured from pure synthetic yarns or their blends with natural fibers (Espınosa-Jıme´nez, 2002). Compared to many synthetic polymeric fibers, polyamides are the most used fibers. The growing demand to enhance the fiber properties and to create more sophisticated up-to-date application fields for textile materials leads to the rapid growth of microfibers technology. Microfibers are half the diameter of a fine silk fiber, one-third the diameter of cotton, one-quarter the diameter of fine wool, and one hundred times finer than human hair (Purane, Panigrahi, 2007). In order to be classified as a microfiber, the fiber fineness must be 1 dtex or less (Purane, Panigrahi, 2007). Fabrics produced from microfibers are generally lightweight, resistant-wrinkle, shape retaining, and pilling resistant. They have a luxurious drape and texture. Besides they are also relatively strong, durable in relation to other fabrics of similar weight, more breathable and more comfortable to wear.

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The same dyes are used for microfibers as well as conventional fibers. The dyeing of all synthetic microfibers, especially polyamide 6.6 ones, presents some problems (Burkinshaw, 1995) such as the greater extent of specific surface reflection (greater surface area of microfibers), the increase of the amount of dye to obtain the same visual depth of shade and the wash fastness deficiencies associated with conventional fibers are exacerbated (Keqiang et al., 2002).

The low presence of carboxylic groups leads to microfibers hydrophobic character and a very poor tinctorial affinity for cationic dyes (Makhlouf et al; 2007).

According to the literature, the modifications of the surface of polyamide 6.6 are carried out in order to improve some of their properties (Bhattacharya, Misra, 2004). The chemical grafting is one of the methods of textile fiber surface modifications. The majority of the studies quoted in the literature are focused on the improvement of some textile properties such as hydrophilic, antistatic and antibacterial characteristics (Buchenska, 1998).

The purpose of this study is to investigate the improvement of the dyeing properties of modified polyamide 6.6 microfibers dyed with a cationic dye. The modeling of the adsorption isotherms using Langmuir, Freundlich and Jossen relations will also be discussed.

2. MATERIALS AND METHODS

2.1. Materials

The samples of polyamide 6.6 microfibers generously supplied by the manufacturer Nylstar were used in the experiment in the form of knitted fabrics and their physico-chemical characteristics are presented in **Table 1**. The acrylic acid (AA) monomer, supplied by Fluka, was purified before use by distillation under vacuum and deoxygenated with nitrogen in the presence of metallic copper (Buchenska, 2001). Benzoyl peroxide (BPO) obtained from Acros Chemical Co., and employed as initiator was purified by using chloroform as solvent and precipitated by adding twice its volume of methanol (Buchenska, 2001; Saçak, Oflaz, 1993; Osipenko, Martinovicz, 1990). Red Astrazon 5 BL (CI Basic Red 24) the cationic dye used in this study, was kindly supplied by Dystar. All other chemicals used were laboratory grade reagents.

Table 1: General microfibers characteristics

Characteristic	Value
Diameter (μm)	9.87
Fiber fineness (dtex)	1.00
TiO_2 (%)	1.53
Density (g cm^{-3})	1.14
Crystallinity (%)	40.00
Numbers of NH_2 (μmol g^{-1})	32.00

2.2. Grafting procedure

Polyamide microfibers 1g were introduced into 100 mL of mixture 70/30 (v/v) Water /Hexane. A given amount of initiator (0.03M) was added. Then, the monomer was added to the reaction medium. Copolymerization reaction was carried out for 2 h at 85°C (Makhlouf et al; 2007). As soon as the copolymerization time was reached, the homopolymer was removed with a solution of 6 g/L NaCl and 1 g/L NaOH. After soxhlet extraction with this solution, the grafted fibers were dried in an oven at 60 °C until they reached a constant weight (Sabaa, Mokhtar, 2002).

The grafting rate (%G) was established gravimetrically. Finally, weight gain measurements were calculated from the weight uptake applying the following formula (Somanathan et al; 1995; Hebeish et al; 1981):

$$\%G = 100 \times \frac{(M - M_0)}{M_0} \qquad (1)$$

where, M_0 and M are the weights of the polyamide 6.6 fibers before and after graft polymerization, respectively.

2.3. Hot water setting treatment

In order to ensure a good dimensional stabilization, the polyamide 6.6 microfibers were pre-set by hot water-setting at 130°C during 45 min. For this pre-setting method, a laboratory-scale dyeing machine "Datacolor-Ahiba nuance" was used.

2.4. Dyeing of polyamide 6.6 fabrics

All dyeings of polyamide 6.6 knitted samples were carried out using a laboratory-scale dyeing machine "Datacolor-Ahiba nuance". These samples were dyed at a liquor ratio of 80:1, using stainless steel dyepots, each of 120 cm^3 capacity. **Figure 1** illustrates the dyeing temperature profile for the cationic dye (Makhlouf et al; 2008a).
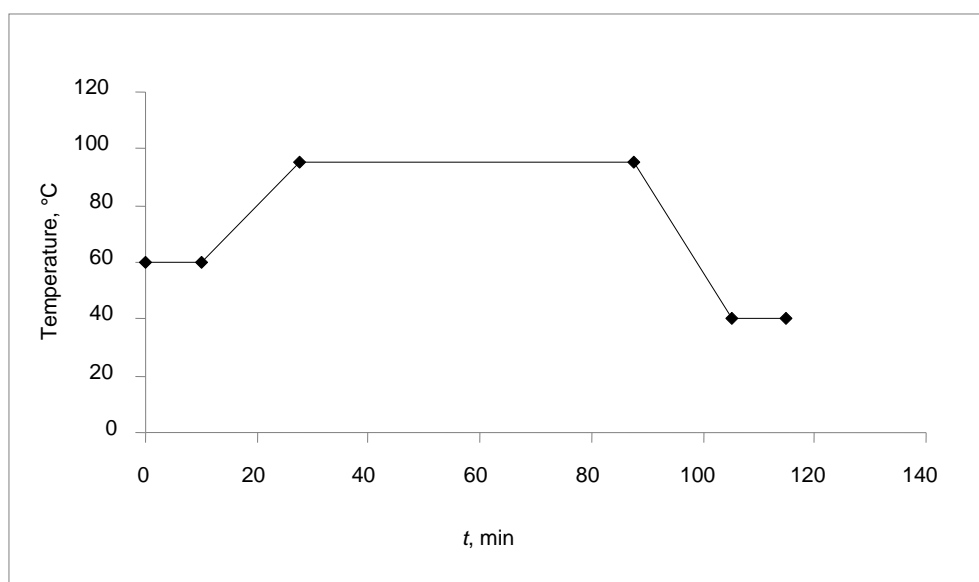

Figure 1: The dyeing temperature profile for the cationic dye

At the end of the dyeing, the dyed fabrics were removed and rinsed in distilled water at 60°C during 15 min, and then dried in an oven at 80°C. The dyeing of polyamide 6.6 by the cationic dye was carried out under the following conditions:
-**Conditions of dyeing**
(MLR): 1:80 (1 gram of matter in 80 mL of bath)
Wight of sample: 1 g
-**Composition of dye bath**
Dye: X% owf (of weight of fabric) with X ∈ { 0.3 ; 1; 2; 3 ; 4 ; 5}
CH_3COOH 80 % : 2 % (4.5 <pH< 5)
CH_3COONa : 1.5 %
Na_2SO_4 : 10 %

2.5. Analysis of dyeing

2.5.1. Determination of dyebath exhaustion

The extent of dyebath exhaustion was determined spectrophotometrically. The absorbance of each dyebath solution before and after dyeing was measured, using a 1cm path length quartz cell housed in a

UV-2401 PC Spectrophotometer Schimadzu, at the maximum wavelength (λ_{max}=513 nm) of cationic dye used in this study.

The percentage dyebath exhaustion (%E) was calculated using Eq.(2):

$$\%E = 100 \times \frac{(A_0 - A_f)}{A_0}$$ (2)

where, A_0 and A_f are the absorbances of the dyebath before and after dyeing, respectively.

2.5.2. Determination of time of half dyeing

Dyeing of polyamide 6.6 microfibers was performed using 2% dye (owf). Samples from the dye bath were removed immediately after the prescribed dyeing time and the amount of dye remaining in the liquor was determined by spectrophotometric techniques at the maximum wavelength (λ_{max}=513nm). For each dyeing time, the graph representing the dye uptake versus dyeing time was drawn. The time of half-dyeing t $_{1/2}$ (min) was determined on the basis of these curves.

2.5.3. Determination of diffusion coefficient

The diffusion coefficient *D* was calculated by using the relation of the following equation (kim et al; 2005):

$$D = \left[\frac{C_t}{C_{eq}} \right]^2 \frac{16\pi r^2}{t} (cm^2 s^{-1})$$ (3)

where, C_{eq} is the dye exhaustion in the equilibrium (mg/g), C_t the dye exhaustion at a time (*t*) (mg/g), *r* is the radius of fiber (cm) and *t* is the time (s).

2.6. Wash fastness properties of dye

The wash fastness properties of the dyed samples were assessed using the standard *ISO 105-A02* wash fastness test protocol (ISO 105-A02, 1990). The change in shade and the degree of cross staining were assessed visually using grey scales.

3.RESULTS AND DISCUSSION

3.1. Dyeing
3.1.1. The effect of the grafting rate on the dyeing kinetic

Using the cationic dye (Red Astrazon 5 BL) **Figure 2**, dyeing investigations were carried out on unmodified and modified polyamide 6.6 microfibers having various grafting rates (3, 6 and 12%). Prior to dyeing and for fibers stabilization, polyamide 6.6 microfibers were maintained in hot water at 130°C during 45 min.
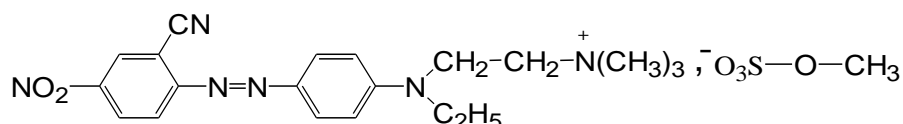

Figure 2: The chemical structure of Red Astrazon 5 BL

During the dyeing, the comparison tests were carried out in relation to time of the build-up in temperature. The follow-up of the dyeing kinetics corresponded to the determination of the microfibers dye concentration through time. A plot of the amount of cationic dye adsorbed per gram polyamide 6.6 Y_e

(mg/g) versus contact time (t) for unmodified and modified microfibers at various grafting rates is shown in **Figure 3**.
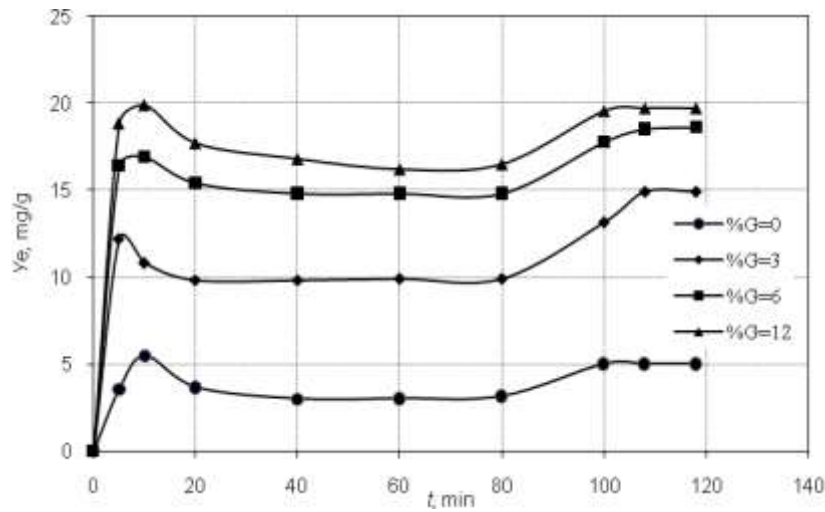

Figure 3: Dyeing kinetics of the dye Red Astrazon 5BL on unmodified and modified polyamide 6.6 microfibers

This figure indicates that the dyeing process followed the same shape for unmodified and modified polyamide 6.6 microfibers and that the unmodified polyamide 6.6 microfibers have a weak affinity for cationic dyes, since 20 % only of the total dye quantity introduced into the initial bath is adsorbed on microfibers. Whereas, for modified polyamide 6.6 microfibers, an increase in the grafting rate leads to an increase in the amount of cationic dye adsorbed onto these microfibers. Thus proving that the grafting had a greater influence on the dyeing properties of polyamide 6.6 microfibers. As a result, increasing the grafting rate, the dyeing equilibrium is achieved more quickly, and the rate of dyebath exhaustion becomes more significant. Indeed, for all the grafting rates studied, the bath exhaustion reaches the higher state.

It is also noticed that a decrease of the amount of cationic dye was adsorbed onto these samples at a time ranging from 20 to 80 min (**Figure 1**). This decrease is due to the increase of temperature from 20 °C. Indeed, this increase of temperature leads to the best solubility of cationic dye in the bath, which decreases the dye build-up. However, as the cooling starts from 80 °C, the amount of cationic dye adsorbed per gram polyamide 6.6 (Y_e) increases reaching 20 mg/g.

The evolution of the amount of dye (Y_e) according to the grafting rate (%G) is shown in **Figure 4**.
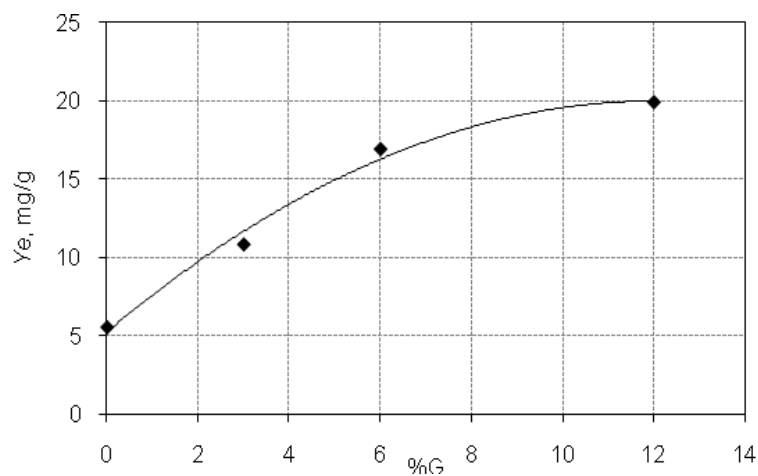

Figure 4: Evolution of the amount of dye (Y_e) according to the grafting rate (%G)

As shown in this figure, the tendency curve for polyamide 6.6 microfibers is not straight but logarithmic branche. It is noted that up to 6% value, the amount of dye (Y_e) is directly proportional to the grafting rate. The linear variation from 0 to 6% shows that the grafting occurs in monolayer. While, above 6% the variation is no longer linear. A little increase of Y_e for %G=12 is noted, which shows that the grafting is achieved in multilayer. Thus indicating that it is not usually important to graft microfibers with the higher rates.

3.1.2. The effect of the grafting rate on the time of half-dyeing

The time of half-dyeing is one of the most significant elements in the evaluation of the dyeing kinetics since it gives an approximate idea on the dye build-up rate on microfibers (Militky, Rais, 1975).
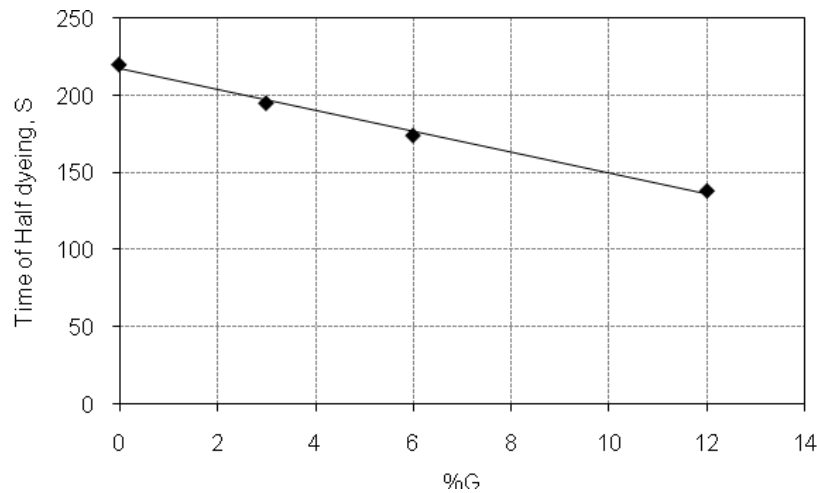

Figure 5: Variation of the time of half-dyeing versus the grafting rate

The variation of the time of half-dyeing versus the grafting rate is shown in **Figure 5**. It is found that the tendency curve is approximately straight. As observed, the time of half-dyeing depends on the grafting rate. Indeed, an increase in this parameter leads to a slight decrease in the time of half dyeing. The grafting improves; on the one hand, the tinctorial affinity by the means of the anionic groups of the grafted molecules. On the other hand, it decreases amorphous zones and increases crystalline ones leading to a decrease of the tinctorial affinity (Makhlouf et al; 2007). Since the time of half-dyeing presents a reduction according to the grafting rate, then it is clear that the increase in tinctorial affinity is more significant.

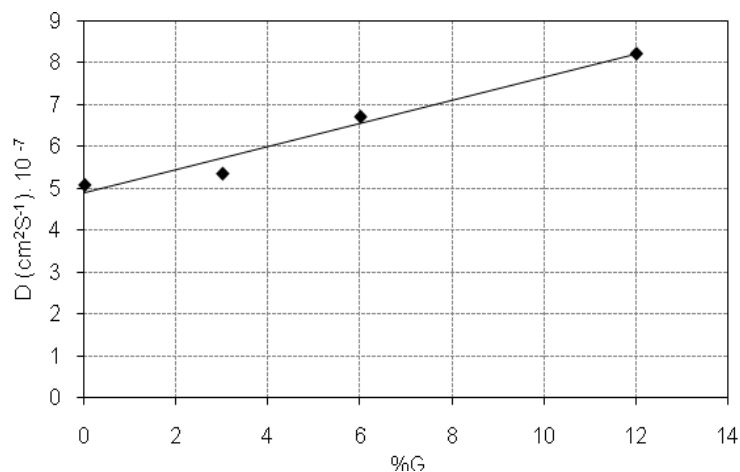### 3.1.3. The effect of the grafting rate on the dye diffusion

Figure 6: Variation of the diffusion coefficient versus the grafting rate

It can be clearly seen from **Figure 6** that the more grafting rate is, the more the diffusion coefficient is. This is due to the existence of an ionic force between the dye and the modified polymer (kim et al; 2005). Indeed, the force of attraction greatly increased with the increasing number of the active sites distributed on the microfibers surface. Therefore, this force facilitated, on the one hand, the migration of the dye towards microfibers and on the other hand the diffusion of the dye inside the microfibers.

3.2. Washing fastness

The washing fastness properties of both unmodified and modified polyamide 6.6 microfibers dyed with cationic dye are measured. The change in shade and the degree of cross staining are assessed using the visual grey scale. The values found during the tests of wash fastness carried out on samples at various grafting rates are gathered in **Table 2**.

Table 2: Evaluation of wash fastness at different grafting rates

Dye concentration	Change in color				Staining cotton				Staining polyamide 6.6			
(%)G	0%	3%	6%	12%	0%	3%	6%	12%	0%	3%	6%	12%
0.3%	3/4	4/5	4	4	3/4	4/5	4/5	4/5	3/4	4/5	4/5	4/5
1%	3/4	4	4	4	3/4	4/5	4/5	4/5	3/4	4/5	4/5	4/5
3%	3/4	4	4	4	3/4	4	4	4	3/4	2/3	4	4
4%	3/4	4	4	4	3/4	4	4	4	2/3	2/3	3/4	4
5%	3/4	4	4	4	4	3/4	4	4	2	2/3	3/4	4

The comparative results of wash fastness show that the unmodified microfibers have an average washing fastness which is inferior to that of modified ones. This result can be attributed to the slight force of attraction between the dye and unmodified samples which is due to the low number of the negatively charged sites on unmodified microfibers. However, for modified microfibers, the washing fastness is slightly improved (from 3/4 to 4) by the increase of the grafting rate. Indeed, this improvement is due to the increase of the number of the anionic sites able to ensure electrostatic interactions to which Van-Der-Waals and hydrogen interactions are added (Zhao et al; 2004). As reported in the literature, the color fastness varies with the changes in the fiber structure and with its properties (Zhao et al; 2004).

3.3. Dye adsorption of cationic dye onto polyamide 6.6 microfibers

In this part, the adsorption isotherms of unmodified and modified polyamide 6.6 microfibers having different grafting rates at 95 °C were studied. Plotting of the amount of dye adsorbed per gram polyamide 6.6 (Y_e) (mg/g polyamide 6.6) versus the concentration of the dye remaining in solution C_e, is shown in **Figure 7**.
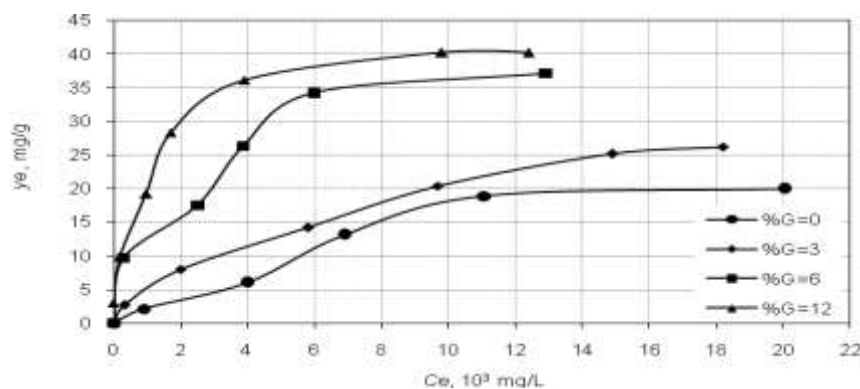

Figure 7: Adsorption isotherms of Red Astrazon 5 BL on unmodified and modified polyamide 6.6 microfibers having various grafting rates

It is found that the unmodified polyamide 6.6 microfibers have a low affinity for the cationic dye. This confirms the results already obtained in the kinetic study. It can also be seen from this figure that the amount of the dye adsorbed per gram of modified polyamide 6.6 microfibers increases the grafting rate. This indicates that the modified polyamide 6.6 microfibers have a higher adsorption capacity of cationic dye compared to the unmodified ones. This is due to the presence of the anionic groups able to interact by an ionic mechanism with the (N$^+$) cations present in the structure of the cationic dye molecule (Red Astrazon 5 BL) as shown in **Figure 8**.
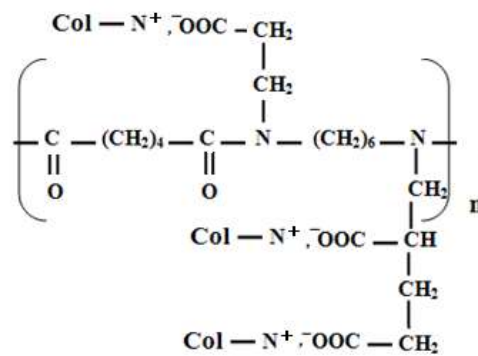

Figure 8: The mechanism of dye fixation

3.4. Adsorption Isotherm models

The equilibrium adsorption isotherm is very important to design the adsorption systems. For solid-liquid systems, several isotherms are available. The polyamide 6.6 adsorption data for the cationic dye (Red Astrazon 5 BL) was treated with the Langmuir, Freundlich and Jossen relations.

3.4.1. The Langmuir isotherm

The Langmuir isotherm takes an assumption that the adsorption occurs at specific homogeneous sites within the adsorbent. This isotherm is represented by the following equation (Chiou, Hy, 2002; Choy Keith et al; 1990):

$$Y_e = \frac{Q.b.C_e}{1 + b.C_e} \qquad (4)$$

A linear form of this expression is:

$$\frac{C_e}{Y_e} = \frac{1}{Q.b} + \frac{C_e}{Q} \qquad (5)$$

Where C_e is the equilibrium dye concentration (mg/g); Y_e is the amount of dye adsorbed at equilibrium (mg/g); Q (mg/g) is the maximum amount of the dye to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e and b is the constant related to the energy of adsorption (L/mg). The linear plot of C_e/Y_e versus C_e is obtained from this model as shown in **Figure 9**.
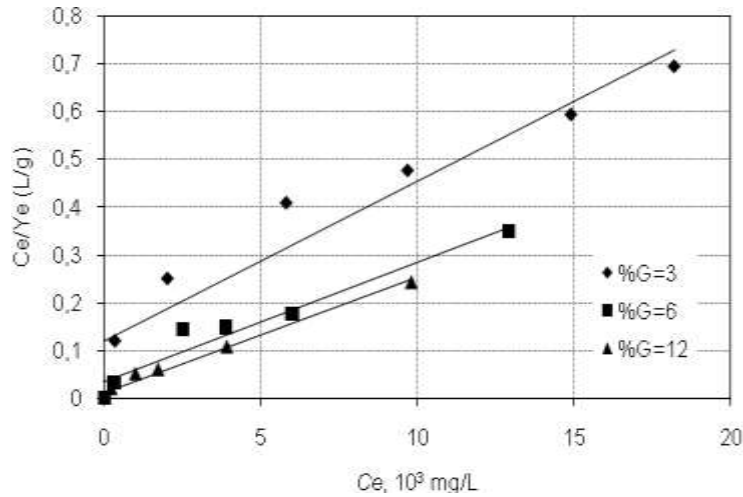
Figure 9: Langmuir isotherms for the cationic dye (Red Astrazon 5BL) on modified polyamide 6.6 microfibers (temperature=95 °C)

The values of Q and b are calculated from the intercepts and slopes of different straight lines representing the different grafting rates. The Langmuir equilibrium constant K_L= Q.b (L/g) is measured at different grafting rates; **Table 3** lists the calculated results.

There is a good agreement between the experimental value Y_{ref} (limit value of Y_e) and the calculated value Q. Therefore, if the Q values rise too the grafting rate is increased, indicating that an important amount of cationic dye has been adsorbed by the modified microfibers surface.

Referring to the literature, the closer the values of b to zero, the more heterogeneous the microfibers surface is (Makhlouf et al; 2008b). The b values indicate that the modified polyamide 6.6 has a maximum affinity for cationic dye at higher rate of grafting (%G=12). This result highlights that the modified microfibers surface becomes more homogeneous.

Table 3: Langmuir isotherm constants for the adsorption of Red Astrazon 5 BL onto modified polyamide 6.6 microfibers at different grafting rates

%G	K_L (L/g)	Q (mg/g)	b (L/mg)	Y_{ref} (mg/g)	R^2
3	5.80	32.25	0.18	26.20	0.983
6	28.33	41.66	0.68	37.10	0.986
12	66.51	43.47	1.53	40.20	0.988

3.4.2. The Freundlich isotherm

The Freundlich isotherm is commonly used to describe adsorption characteristics for heterogeneous surface (Chiou, Hy, 2002; Choy Keith et al; 1990). This isotherm can be expressed as in Equation 6:

$$Y_e = P.C_e^{1/n} \tag{6}$$

where P and 1/*n* are the Freundlich isotherm constants. Equation (6) linearizes in logarithmic form.

$$\log Y_e = \log P + \frac{1}{n} \log C_e \tag{7}$$

For the convenience of data fitting and parameter evaluation, p is used as a relative indicator of adsorption capacity and 1/n of the adsorption intensity (The magnitude of the exponent 1/n gives an indication of the favorability of adsorption). Therefore, plotting *Ye* versus *Ce* yields a non-regression line which permits the determination of 1/n and p. The values are presented in **Table 4** and the Freundlich equation isotherms are shown in **Figure 10**.
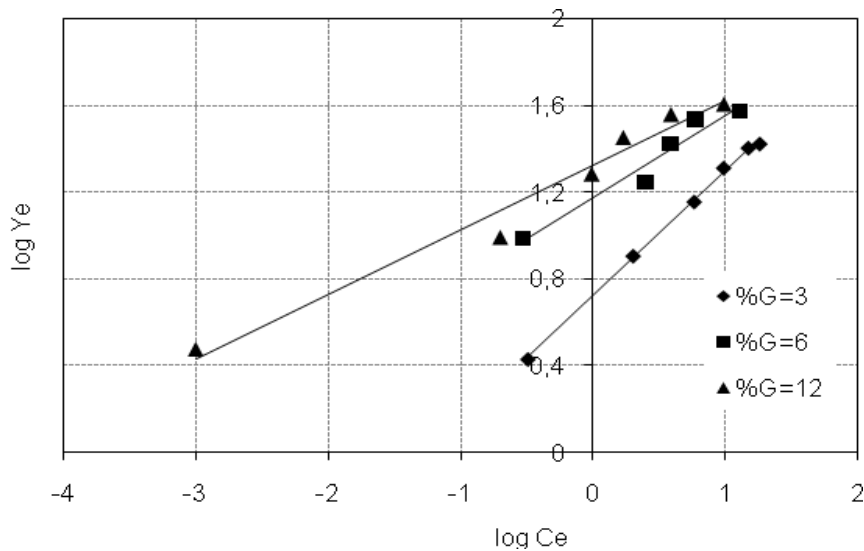

Figure 10: Freundlich adsorption isotherm of cationic dye onto modified polyamide 6.6 microfibers at 95°C

Table 4: Freundlich isotherms constants of adsorption of Red Astrazon 5 BL onto modified polyamide 6.6 microfibers at different grafting rates

%G	P	n	R²
3	5.26	1.80	0.973
6	14.15	2.43	0.984
12	20.84	3.40	0.978

From **Table 4**, the values of n>1 obtained represent favorable adsorption conditions for all experiments (Chiou, Hy, 2002). As the P values rise when grafting rates are increased. Indeed, the variation of p versus the grafting rate is not linear indicating that the grafting is carried out into multi-layer and that the surface is heterogeneous.

3.4.3. The Jossen isotherm

The Jossen isotherm, taking into account both the Langmuir and Freundlich isotherm equations and the mechanism of adsorption is hybrid and does not follow ideal monolayer adsorption (Weber, Mathews, 1976). The equation is as follows:

$$Y_e = \frac{i \cdot C_e}{1 + j \cdot (C_e)^m} \tag{8}$$

This isotherm represents three constants, namely, *i*, *j* and *m*. These constants obtained from adsorption data by an iterative procedure using a computer program, are given in **Table 5**.

Table 5: Jossen isotherms constants of adsorption of Red Astrazon 5 BL onto modified polyamide 6.6 microfibers at different grafting rates

%G	i	j	m	R^2
3	8.36	0.94	0.68	0.990
6	10.73	0.02	1.82	0.882
12	33.91	0.59	1.10	0.982

To assess isotherms and their ability to correlate with the experimental results, the theoretical plots arising from the application of each of the above isotherms to the adsorption data for Red Astrazon 5 BL onto the modified polyamide 6.6 microfibers at 95 °C are compared in **Figures 11, 12** and **13**.
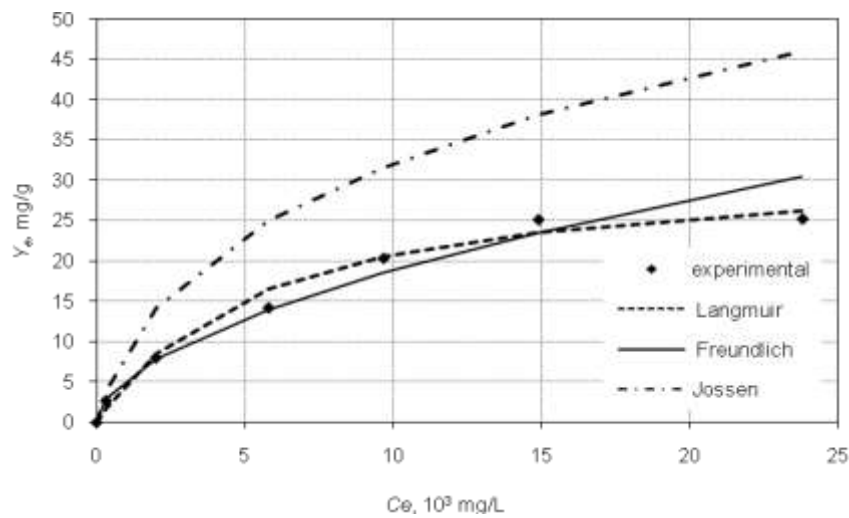

Figure 11: Comparison of theoretical isotherms with experimental data for the adsorption of Red Astrazon 5BL on modified PA 6.6 microfibers %G=3 (temperature=95°C)

Figure 12: Comparison of theoretical isotherms with experimental data for the adsorption of Red Astrazon 5BL on modified PA 6.6 microfibers %G=6 (temperature=95°C)
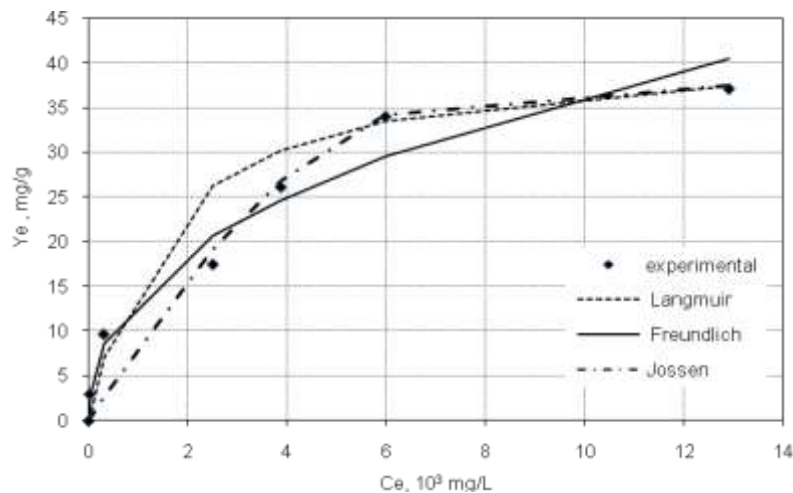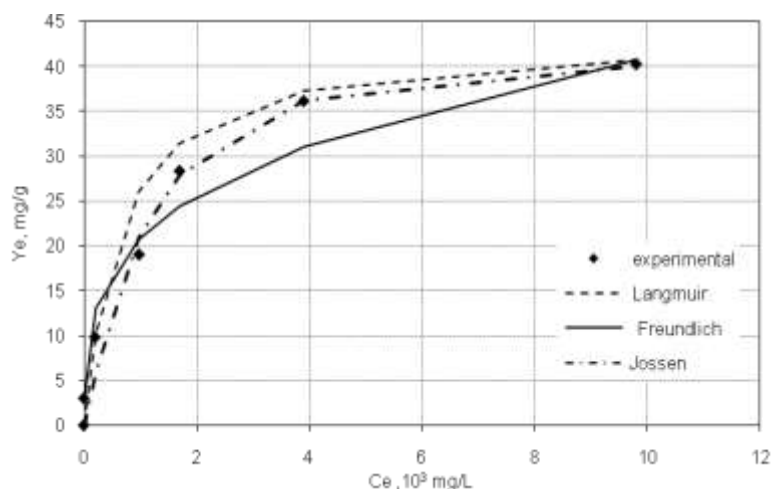
Figure 13: Comparison of theoretical isotherms with experimental data for the adsorption of Red Astrazon 5BL on modified PA 6.6 microfibers %G=12 (temperature=95°C)

The obtained results show that several models exist and correspond to various grafting rates.

Figure 11 shows that for the %G=3 the Langmuir model gives the best fit to the experimental data over the whole studied concentration range.

Figure 12 indicates that for the %G=6 the Freundlich model fits the experimental data in particular for the low-concentration range. The Jossen model is more adequate for the high-concentration range.

Figure 13 shows that for %G=12, Langmuir and Freundlich models are unable to characterize the adsorbent/adsorbate system. However, it can be concluded that among all concentrations range studied Jossen model is the best one to fit the experimental data.

The sample with 3% grafting have, grafted molecules which are sparse enough in a way that enable them to fix the dye molecules as predicted by the Langmuir model. Above 3% grafting, the grafted molecules become denser, which creates mutual repulsions (steric hindrance). Besides, the dye fixation becomes intricate. Hence, this leads to the model that assembles at the same time the Freundlich and Jossen models for %G= 6%. While it leads to the Jossen model for the %G=12.

4. CONCLUSION

This study highlighted the improvement of the dyeing properties of modified polyamide 6.6 microfibers dyed with cationic dye. It obviously revealed an improvement of the dye bath exhaustion of modified microfibers compared to those unmodified. This is due to the increase in the number of carboxylic groups on microfibers which are responsible for the adsorption of the cationic dye (Red Astrazon 5 BL).

The kinetic study showed an improvement in the dye build-up rate. In addition, an increase in the grafting rate rises the dye quantity fixed on the modified microfibers.

According to wash fastness tests, a slight improvement of the cationic dyeings at different grafting rates is noticed (from 3/4 to 4).

Adsorption data were modeled by using the Langmuir, Freundlich and Jossen adsorption isotherms. The results will assist in gaining a better understanding of adsorption mechanism of the dyeing process and the influence of grafting in the dyeing properties of polyamide 6.6 microfibers. It appears that the adsorption capacity depended on the grafting rate and that the models used in this study vary with this rate.

REFERENCES

Bhattacharya, A., Misra B. N. (2004). Grafting: A versatile means to modify polymers - techniques, factors and applications. *Progress Polymer Science,* 29., 767-814.

Buchenska, J. (1998). Modification of polyester fibers by grafting with poly(acrylic acid). *Journal of Applied Polymer Science,* 65., 967-977.

Buchenska, J. (2001). Grafting of poly(acrylic acid) on polyamide yarn. *Journal of Applied Polymer Science,* 80., 1914-1919.

Burkinshaw, S.M. (1995). *Chemical principals of synthetic fiber dyeing*, Blackie Academic & Professional, ISBN: 0 7514 0043 2, Wester Cleddens Road, Bishopbriggs, Glasgow G64 2 NZ, UK.

Chiou, M.S., Hy, L. (2002). Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. *Journal of Hazardous Materials*, 93., 233-248.

Choy Keith, K.H., McKay, G., Porter, J.F. (1990). Sorption of acid dyes from effluents using activated carbon. *Resources Conservation and Recycling*, 27., 57-71.

Espınosa-Jıme´nez, M., Padılla-Weıgand, R., Ontıveros-Ortega, A., Perea-Carpıo, R., Ramos-Tejada, M. M., Chıbowskı, E. (2002). Investigation of the polyamide 6,6 dyeing process with acid blue 45 dye. Part I. Thermodynamics of acid blue 45 adsorption. *Journal of Adhesion Science Technology,* 16., 285-301.

Hebeish, A., Shalaby, S. E., Bayazeed, A. M. (1981). H_2O_2-induced graft polymerization of acrylic acid on poly(ethylene terephthalate) fibers. *Journal of Applied Polymer Science,* 26., 3245-3251.

ISO 105-A02, "*Methods of Test for Colour Fastness of Textiles and Leather*", 5th ed, Society of Dyers and Colourists, Bradford, UK, 1990.

Keqiang, C., Zhongxun, C., Jianwei, X. (2002). Analyzing the dyeing behavior and chromaticity characteristics of polyester microfibers. *Textile Research Journal,* 72., 367-371.

kim, T.K., Son, Y.A., Lim, Y. J. (2005). Thermodynamic parameters of disperse dyeing on several polyester fibers having different molecular structures. *Dyes and pigments*, 67., 229-234.

Makhlouf, C., Marais, S., Roudesli, S. (2007). Graft copolymerization of acrylic acid onto polyamide fibers. *Applied Surface Science,* 253., 5521-5528.

Makhlouf, C., Kacem, C., Roudesli, S., Sakli, F. (2008a). Dyeing behaviour of unmodified and modified polyamide 6.6 fibers of different levels of fineness. *Journal of Applied Sciences,* 8., 77-85.

Makhlouf, C., Baouab, M.H.V., Roudesli, S. (2008b). Use of the [Copper (II)/MAA–nylon] complex for the adsorption of residual acid dyes. *Adsorption Science and Technology,* 26., 433-447.

Militky, J., Rais, J. (1975). The approximate solution for diffusion- controlled dyeing from a finite bath. *Journal of the Society of Dyers and Colourists*, 93., 344 - 348.

Osipenko, I. F., Martinovicz, V. I. (1990). Grafting of the acrylic acid on poly(ethylene terephthalate). *Journal of Applied Polymer Science*, 39., 935-942.

Purane, S. V., Panigrahi, N. R. (2007). Microfibers, microfilaments and their applications. *AUTEX Research Journal*, 7., 3.,148-158, ISSN 1470 9589.

Sabaa, M. W., Mokhtar, S. M. (2002). Chemically induced graft copolymerization of itaconic acid onto cellulose fibers. *Polymer Testing*, 21., 337-343.

Saçak, M., Oflaz, F. (1993). Benzoyl-peroxide-initiated graft copolymerization of poly(ethylene terephthalate) fibers with acrylic acid. *Journal of Applied Polymer Science,* 50 (11)., 1909-1916.

Somanathan, N., Balasubramaniam, B., Subramaniam, V. (1995). Grafting of polyester fibers. *Journal of Macromolecular Science: Pure and Applied Chemistry,* 32., 1025-1030.

Weber, W.J., Mathews, A. P. (1976). Effects of external mass transfer and intraparticle diffusion on adsorption rates in slurry reactors. *AAAIChE Symp. Ser. Water,* 73., 91-98.

Zhao, G., Wu, L. R., Curiskis, J., Deboos, A. (2004). Dyeing properties of blends of wool/modified polyester fibers- effects of temperature. *Textile Research Journal,* 74., 27-33.