



Development of Pilot Scale System for Production of Nylon-6 Fibers Grafted with Polydimethylaminoethylmethacrylate (PDMAEMA) for the Application as Ion Exchange



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IN this work an affective and simple technology for pilot scale production of grafted Nylon-6 fibers with Polydimethylaminoethylmethacrylate (PDMAEMA) for ion exchange application is suggested. This technology consists of the creation of antimicrobial substance (AS) in Nylon-6 fibers followed by grafting with dimethylaminoethylmethacrylate (DMAEMA) using Cu^{2+} - $\text{K}_2\text{S}_2\text{O}_8$ redox system. Factors affecting the yield of grafted PDMAEMA were investigated and the optimal conditions for grafting process were evaluated. The availability of modified Nylon-6 fibers grafted with PDMAEMA as polymer sorbent for removal of cations as Cu^{+2} , Pb^{+2} and anions $\text{Cr}_2\text{O}_7^{-2}$, SO_4^{-2} was investigated. The influence of various adsorption parameters on the degree of extraction (R %) and adsorption capacity (SC mg/g) was calculated.

Keywords: Nylon-6, Grafting, Fibers, PDMAEMA, Ion-exchanger.

Introduction

Removal and recovery of heavy metals and anions for wastewater is an important strategy for environmental protection and is of economic concern [1]. The ability of some active polymers to form polymer-metal complexes has been used for removal of metal ions from contaminated water. With chemisorption fibers, a high speed recovery of the metal ions can be achieved because fibers have high surface area. Consequently, the time needs for the diffusion of the metal ions to the chelating groups is much shorter [2-3].

Scientific and technical literature discusses different methods for fabrication of ion-exchange fibers. Among them are the following:

- a. Spinning of fibers from polymers containing ionic groups [4];
- b. Production of fibers from copolymers containing active groups [5];
- c. Creation of active groups in the fibers via reactions in polymer chains [4, 6]; and d. Grafting of fibers with ionic and nonionic monomers with subsequent reactions in the grafted chains [7-9].

The ion-exchange fibers are commonly prepared either by polymer analogous conversion of the reactive groups in the macromolecules of the fibers, or by grafting of various vinyl monomers, containing different function groups, on to the fiber surface [10-11].

Generally, most of the methods used for grafting vinyl monomers onto Nylon-6 fibers have limited usefulness on industrial scale because: (1) formation of homopolymer which need solvents to extract, (2) grafting reaction proceeds with many steps which prevent its technological application, (3) low rate of grafting reaction. It is well known that the ion exchange capacity is one of the basic parameters for selecting the ion exchangers. Thus, the using preparation method for grafting should insure that the grafting reaction will proceed with high rate and without homopolymer formation.

These requirements could be fulfill when Nylon-6 fibers contain quaternary ammonium groups (QAG) capable of forming a complex with the initiator (peroxides) [12]. Further decomposition of the obtained complex leads to the formation of free radicals on the Nylon-6

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fibers thus facilitating their direct grafting with different vinyl monomers with high rate and without homopolymer formation [13-26].

Ion-exchange fibers which contain tertiary amino groups and strongly basic groups such as DMAEMA are characterized with high dynamic activity with respect to acid gases. For this reason, they are recommended for fabrication of filtering elements in universal devices for individual protection of the respiratory organs [3].

The present work aims to prepare ion-exchangers based on grafted Nylon-6 fibers with PDMAEMA. Optimal conditions for the preparation of such fibers on laboratory scale are available. Adjustment and adaptation of these conditions to suit the production of these fibers on pilot scale is the main target of the present work. Here, we report the results of grafting Nylon-6 fibers containing antimicrobial substance (AS) and grafted with DMAEMA using Cu^{2+} - $\text{K}_2\text{S}_2\text{O}_8$ redox system. The ability of modified Nylon-6 nonwoven fabric to form polymer-metal complexes has been used for removal of metal ions and anions from contaminated water.

Experimental Work

Materials

- Nylon-6 used in this study was in the form of fibers (denier = 14). They were kindly supplied by Misr spinning and weaving Company, Elmeahha, Egypt. The fibers were scoured at 80°C for 45 minutes with solution containing 2g/l nonionic detergent, washed with water, squeezed and finally air dried.
- Dimethylaminoethylmethacrylate (DMAEMA), potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$), and copper sulphate ($\text{CuSO}_4\cdot 5\text{H}_2\text{O}$) were all of pure grade chemicals.
- Antimicrobial substance (AS) under trade name "Katamin" (based on quaternary ammonium salt) used in this work was in form of 50 % aqueous solution.
- Non-ionic detergent (Poly sorbate 20, Polyoxy ethylene sorbitan mono laurate)

Methods

Fixation of Antimicrobial Substance (AS) on Nylon-6Fibers

Fixation of AS on Nylon-6 fibers was carried out using a high temperature high pressure laboratory dyeing machine. Required

concentrations of AS solutions (pH=11) were placed in stainless-steel bowls, Nylon-6 samples were immersed in the solutions, and the sealed bowls were rotated in a closed bath containing ethylene glycol at the desired temperature (90°C). The material: liquor ratio (M: L) was 1:50. The bath temperature increased at rate of 2°C/min. After the predetermined durations, the samples were removed from the bath, rinsed repeatedly with distilled water and allowed to dry in the open air.

Grafting of Antimicrobial Nylon-6Fibers with DMAEMA

Nylon-6 fibers samples containing AS were treated with 2% aqueous solution of $\text{K}_2\text{S}_2\text{O}_8$ at ambient temperature. The samples were then removed, washed thoroughly with distilled water, squeezed and dried at room temperature. The samples retained some persulphate which was determined iodometrically. Pretreated samples were introduced into stoppered Erlenmeyer flask containing water, DMAEMA and copper sulphate. The flask was stoppered, kept in water thermostat at prescribed temperature (90°C) and shaken occasionally during the reaction period. After an elapsed time, the reaction mixture was filtered and the residue was washed with water, dried in an oven at 105°C for 2 h. The dried sample was then repeatedly soxhlet extracted with methanol to remove the homopolymer, dried again as previously indicated and weighed. The percentage of grafted polymer was calculated as follows:

$$\% \text{ Graft yield} = \frac{P - P_0}{P_0} \times 100$$

Where: P is the dry weight of grafted sample, and P_0 is the dry weight of parent sample.

Adsorption Procedure

Dried samples 0.1 g of reactive fibers were added into 100 cm³ Erlenmeyer flask containing 30 cm³ of each metal ion solution (80 ppm) and adjusted to the desired pH. The mixture solution was stirred at 25°C. After filtration of the solution, the ion concentration of the filtrates was measured by using atomic absorption.

The degree of extraction (R, %), and sorption capacity (SC, mg/g) were calculated according to the following equations:

$$R = \frac{C_0 - C_i}{C_0} \times 100$$

$$SC = \frac{(C_0 - C_i) V}{m}$$

Where: C_0 is the initial concentration of investigated metal ions in the solution, g/l; C_i is

the concentration of investigated metal ions in the solution at the time of measurement, g/l; V is the volume of solution, ml; m is the mass of the sorbent, g.

Analysis

Potassium persulphate concentration in solution and in the dried Nylon-6 fibers was measured according to the method described by Jenkins [27].

Results and Discussion

Effect of Different Reaction Conditions on the Graft Yield

Effect of Cupric ion concentrations

The effect of the presence of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the reaction medium for grafting Nylon-6 fibers containing AS with DMAEMA on the extent and rate of reaction was studied. The concentration of metal salt was varied from 0.5×10^{-5} to 2.0×10^{-4} mole/l. It was found (Table 1) that, grafting practically did not proceed in the absence of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the reaction medium. The extent of grafting is gradually increased with the increase of the Cu^{2+} concentration up to 1.0×10^{-4} mole/l. Thereafter, the graft yield decreases as the metal salt concentration increases. It was found that, at this Cu^{2+} ion concentration the maximum graft yield (20.2 %) was obtained.

The effect of the grafting reaction time under different Cu^{2+} ion concentrations in the reaction medium on the extent and rate of grafting (R_p) is given in Table 2. It is clear that, the extent of grafting increased with the increase of reaction time. At a lower Cu^{2+} ion concentration a longer duration is needed to result in a higher add-on. It was found that, the proper conditions for maximum graft yield are: 1.0×10^{-4} mole/l of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in the reaction medium and 90°C , and time of 60 min.

Kinetic investigation (Fig. 1) of the dependence of the rate of grafting (R_p) of DMAEMA on Nylon-6 fibers containing AS revealed that, R_p is proportional to 0.39 power of Cu^{2+} .

Effect of DMAEMA Concentration

Tables 3-4 show the effect of different concentrations of DMAEMA on the extent and rate of grafting (R_p). The monomer concentration was in the range from 0.13 mole/l to 1.27 mole/l. It is seen from the data listed in these tables that, the graft yield of PDMAEMA on Nylon-6 fibers increases with an increase in DMAEMA

concentration. Moreover, at a concentration of the monomer equals 0.76 mole/l in the reaction medium, there is a significant increase in the graft yield percent (20.1%). However, the graft yield decreases as DMAEMA concentration increases.

Kinetic investigation (Table 6 and Fig. 2) of the dependence of the rate of grafting (R_p) of DMAEMA on Nylon-6 fibers containing AS revealed that, (R_p) is proportional to 1.1 power of DMAEMA.

Effect of Reaction Temperature

The effect of reaction temperature at different reaction time on the grafting of DMAEMA on Nylon-6 fibers was investigated. It is seen from the obtained data (Table 5) that, the extent and rate of grafting were increased as the temperature increased from $75 \sim 90^\circ\text{C}$. Moreover, at a lower temperature a longer reaction time is needed to obtain a higher add-on on the fibers.

Based on the data listed in Fig. 3 the apparent activation energy of grafting DMAEMA onto Nylon-6 fibers containing AS was calculated and was found to be $68.9 \text{ k J mol}^{-1}$.

Effect of $\text{K}_2\text{S}_2\text{O}_8$ concentration

The effect of $\text{K}_2\text{S}_2\text{O}_8$ concentration under different reaction time on the extent and rate of grafting (R_p) DMAEMA onto Nylon-6 fibers containing AS was studied. The concentration of $\text{K}_2\text{S}_2\text{O}_8$ was varied from 1.02×10^{-4} mole/l to 2.20×10^{-4} mole/l (Table 6). It can be seen that, the extent and rate of grafting (R_p) increase with increasing reaction time for all the studied concentrations. Moreover, these two parameters also increase as the $\text{K}_2\text{S}_2\text{O}_8$ concentration increases.

Kinetic investigation of the effect of $\text{K}_2\text{S}_2\text{O}_8$ concentration on the R_p (Fig. 4) revealed that, the latter is proportional to 0.75 power of $\text{K}_2\text{S}_2\text{O}_8$ concentration. Similar results were reported when GMA [26] and DMAEMA [19] were grafted on Nylon-6 fibers containing Polydiallyl dimethylammonium chloride (PDADMAC).

Based on the above mentioned kinetic investigations of the effect of different factors on the grafting of DMAEMA, one can conclude that the overall equation for the rate of grafting is as follow:

$$R_p \propto [\text{Cu}^{2+}]^{0.39} [\text{DMAEMA}]^{1.1} [\text{K}_2\text{S}_2\text{O}_8]^{0.75}$$

Pilot scale production of Nylon-6 fibers grafted

TABLE 1. Effect of Cupric ions concentration on the graft yield % of DMAEMA onto Nylon-6 fibers.

[CuSO ₄ ·5H ₂ O], mol/l	Graft Yield %
0.0	1.50
0.5 × 10 ⁻⁵	3.60
1.0 × 10 ⁻⁵	5.80
1.5 × 10 ⁻⁵	7.40
4.0 × 10 ⁻⁵	11.0
7.5 × 10 ⁻⁵	16.2
1.0 × 10 ⁻⁴	20.1
1.25 × 10 ⁻⁴	17.4
1.5 × 10 ⁻⁴	13.5
2.0 × 10 ⁻⁴	11.0

Reaction Conditions:

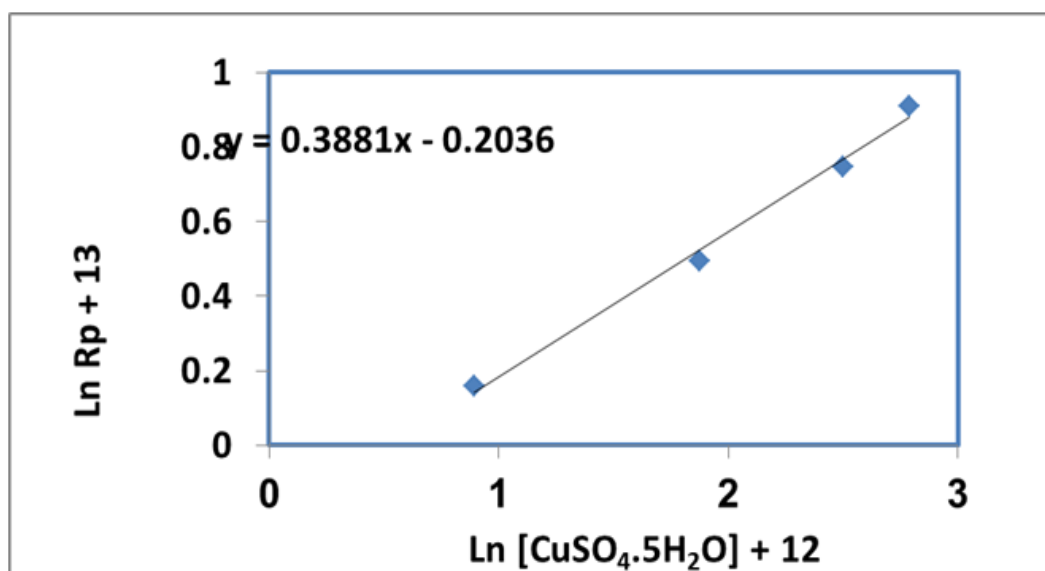
[DMAEMA], 0.76 mol/l; [K₂S₂O₈], 2.20 × 10⁻⁴ mol/l; [AS], 1.63 mgr/gr fibers; Reaction Temperature, 90°C; Reaction Time, 60 min.; M:L, 1:50.

TABLE 2. Effect of Cupric ions concentration on the rate of grafting (Rp) of PDMAEMA onto Nylon-6 fibers.

[CuSO ₄ ·5H ₂ O], mol/l	Reaction Time (min.)					Graft Yield %
	10	20	30	45	60	
1.5 × 10 ⁻⁵	2.5	3.6	4.7	6.5	7.4	
4.0 × 10 ⁻⁵	3.1	4.5	8.7	10.6	11.0	
7.5 × 10 ⁻⁵	4.2	8.3	11.2	14.4	16.2	
1.0 × 10 ⁻⁴	5.3	10.2	15.0	18.5	20.2	

Reaction Conditions:

[DMAEMA], 0.76 mol/l; [K₂S₂O₈], 2.20 × 10⁻⁴ mol/l; [AS], 1.63 mgr/gr fibers; Reaction Temperature, 90°C; M:L, 1:50.

**Fig. 1.** Logarithmic correlation between the rate of grafting (Rp) of DMAEMA onto Nylon-6 fibers on the Cu²⁺ concentration

Reaction Conditions:

[DMAEMA], 5.8 × 10⁻¹ mol/l; [K₂S₂O₈], 2.20 × 10⁻⁴ mol/l; [AS], 1.63 mgr/gr fibers; Reaction Temperature, 90°C; Reaction Time, 10 min.; M: L, 1:50.

TABLE 3. Effect of DMAEMA concentration on the graft yield % onto Nylon-6 Fibers.

[DMAEMA], mol/l	Graft Yield %
0.13	2.20
0.25	5.30
0.38	10.3
0.51	12.5
0.64	16.2
0.76	20.1
0.89	15.5
1.02	12.3
1.14	12.7
1.27	12.5

Reaction Conditions:

[CuSO₄·5H₂O], 1.0×10⁻⁴ mol/l; [K₂S₂O₈], 2.20×10⁻⁴ mol/l; [AS], 1.63 mgr/gr fibers; Reaction Temperature, 90°C; Reaction Time, 60 min.; M:L, 1:50**TABLE 4. Effect of DMAEMA concentration on the rate of grafting (Rp) of DMAEMA onto Nylon-6fibers.**

[DMAEMA], mol/l	Reaction Time (min.)					Graft Yield %
	10	20	30	45	60	
0.38	2.4	3.5	6.7	9.6	10.3	
0.51	3.8	5.5	8.2	12.0	12.5	
0.64	4.1	8.4	11.3	16.3	16.2	
0.76	5.3	10.2	15.0	18.5	20.2	

Reaction Conditions:

[CuSO₄·5H₂O], 1.0×10⁻⁴ mol/l; [K₂S₂O₈], 2.2×10⁻⁴ mol/l; [AS], 1.63 mgr/gr fibers; Reaction Temperature, 90°C; M:L, 1:50.**TABLE 5. Effect of Reaction temperature on the rate of grafting (Rp) of DMAEMA onto Nylon-6fibers.**

Reaction Temperature (°C)	Reaction Time (min.)					Graft Yield %
	10	20	30	45	60	
75	2.0	3.5	5.8	6.7	8.6	
80	3.1	5.3	8.4	10.8	12.2	
85	4.4	8.4	10.5	13.5	15.3	
90	5.3	10.2	15.0	18.5	20.1	

Reaction Conditions:

[DMAEMA], 0.76 mol/l; [K₂S₂O₈], 2.20×10⁻⁴ mol/l; [CuSO₄·5H₂O], 1.0×10⁻⁴ mol/l; [AS], 1.63 mgr/gr fibers; M:L, 1:50.**TABLE 6. Effect of K₂S₂O₈ concentration on the rate of grafting (Rp) of DMAEMA onto Nylon-6fibers**

[K ₂ S ₂ O ₈] x 10 ⁻⁴ mol/l	Reaction Time (min.)					Graft Yield %
	10	20	30	45	60	
1.02	3.3	5.0	7.4	9.8	11.0	
1.58	4.5	6.6	10.5	13.5	14.9	
1.85	5.0	8.1	11.3	15.0	16.3	
2.20	5.3	10.2	15.0	18.5	20.1	

Reaction Conditions:

[DMAEMA], 0.76 mol/l; [CuSO₄·5H₂O], 1.0×10⁻⁴ mol/l; [AS], 1.63 mgr/gr. fibers; Reaction Temperature, 90°C; M:L, 1:50.

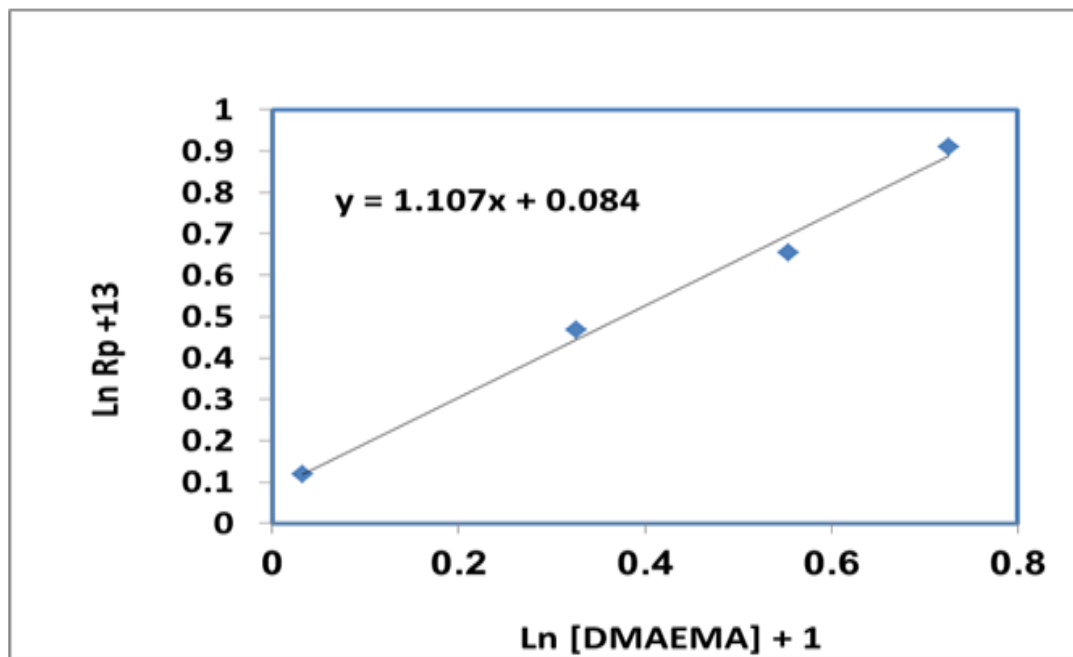


Fig. 2. Logarithmic correlation between the rate of grafting (R_p) of DMAEMA onto Nylon-6 fibers on the monomer concentration.

Reaction Conditions

[CuSO₄·5H₂O], 1.0×10⁻⁴ mol/l; [K₂S₂O₈], 2.20×10⁻⁴ mol/l; [AS], 1.63 mgr/gr fibers; Reaction Temperature, 90°C; Reaction Time, 10 min.; M:L, 1:50.

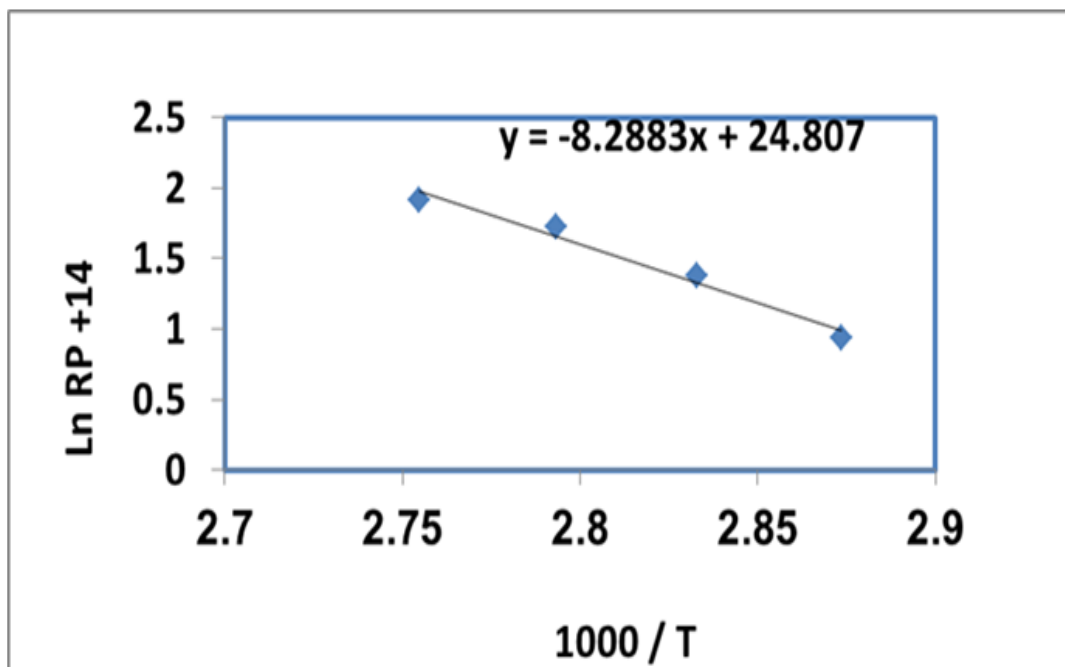


Fig. 3. Arrhenius plots for the graft copolymerization of DMAEMA onto Nylon-6 fibers.

Reaction Conditions

[DMAEMA], 0.76 mol/l; [K₂S₂O₈], 2.20×10⁻⁴ mol/l; [CuSO₄·5H₂O], 1.0×10⁻⁴ mol/l; [AS], 1.63 mgr/gr fibers; Reaction Time, 10 min.; M:L, 1:50.

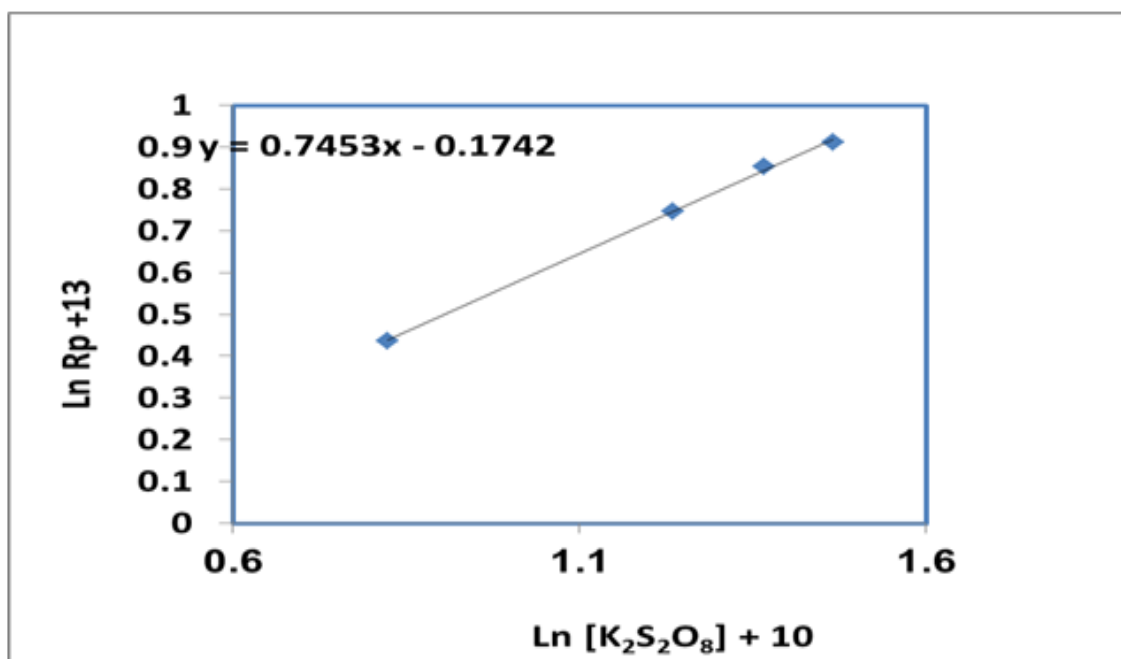


Fig. 4. Logarithmic correlation between the rate of grafting (R_p) of DMAEMA onto Nylon-6 fibers on the $K_2S_2O_8$ concentration.

Reaction Conditions

[DMAEMA], 0.76 mol/l; [CuSO₄·5H₂O], 1.0×10⁻⁴mol/l; [AS], 1.63 mgr/gr fibers; Reaction Temperature, 90°C; Reaction Time, 10 min.; M: L, 1:50.

with PDMAEMA

The production of grafted Nylon-6 fibers with PDMAEMA on pilot scale consists of scouring, treatment with AS, treatment with $K_2S_2O_8$ aqueous solution, and finally grafting with DMAEMA. Scouring, treatment with AS, and treatment with $K_2S_2O_8$ aqueous solution on pilot scale were carried out in Misr El Beida Company in Kafr El Dawar, Egypt. English tops machine Shell-Y42 working under pressure at maximum temperature 100°C, volume 1000 liters and load 100 kg was used for carrying out the above mentioned technological processes under its optimal conditions.

Grafting the scoured, treated with AS and $K_2S_2O_8$ aqueous solutions Nylon-6 fibers was carried out in the pilot plant of Textile Research Division in National Research Centre in Dokki, Giza. Pilot reactor working under pressure at maximum temperature 100°C, volume 50 liters and load 5 kg was used for carrying out grafting reaction under its optimal conditions.

Technological Parameters for the Production of Grafted Nylon-6 Fibers on Pilot Scale

- Nylon-6 fibers were scoured for 30 min at 100°C in a bath containing 1g/l nonionic

detergent.

- The scoured and washed Nylon-6 fibers were treated with AS under the following conditions: [AS], 1-2% (owf); pH, 11; Treatment Temperature, 80-90°C; Treatment Time, 60 minutes; and M:L Ratio, 1:7.
- At the end of treatment with AS Nylon-6 fibers were washed as follows: with cold water; in a bath containing nonionic detergent (1g/l) for 30 min. at 100°C; and with cold water for removing the traces of nonionic detergent.
- The scoured, washed, treated with AS, and washed Nylon-6 fibers were treated with $K_2S_2O_8$ water solution under the following conditions: [$K_2S_2O_8$], 2%; Treatment Temperature, 25°C; Treatment Time, 30 minutes; and M:L ratio, 1:7.
- At the end of treatment with $K_2S_2O_8$ water solution Nylon-6 fibers were washed for two – three times with cold water. The treated with $K_2S_2O_8$ aqueous solution and washed Nylon-6 fibers were squeezed using centrifuge.
- At the end of the squeezing operation Nylon-6 fibers were air dried.

Grafting with DMAEMA

The air dried fibers treated with $K_2S_2O_8$ solution were used for grafting with DMAEMA using pilot scale reactor as follows:

- Weight of Nylon-6 fibers 5kg
- Weight of Cu SO₄.5 H₂O 3.0g
- Reaction Time 60 min
- Weight of DMAEMA 1.0 kg
- Reaction Temperature 90°C
- M:L Ratio 1:6

The pilot scale reactor was used for production of 40 kg of Nylon-6 fibers grafted with 18% PDMAEMA.

Sorption Properties of Antimicrobial Nylon-6 Fibers Grafted with PDMAEMA

The factors affecting the sorption properties [degree of extraction (R %) and sorption capacity (SC mg/g)] of antimicrobial Nylon-6 fibers grafted with PDMAEMA have been investigated. The validity of modified Nylon-6 as ion-exchanger was examined by using Cu^{+2} , Pb^{+2} cations and $Cr_2O_7^{-2}$, SO_4^{-2} anions. These investigations were carried out by using the same method described by Shalaby et al [25]. The effect of adsorption conditions on both (R %) and SC (mg/g) was calculated (Tables 7-8).

Effect of adsorption time

Data listed in Tables 7 and 8 represent the effect of duration on the degree of extraction (R %) and sorption capacity (SC) of PDMAEMA grafted Nylon-6 fibers. It was found that, at short time, nearly 10 minutes, there was a significant increase in R % and SC. This effect was noticed with both cations and anions under investigations. The gradual increase of adsorption time up to 20 minutes is accompanied by an increase in the degree of extraction and sorption capacity. Further increase in the adsorption time have no effect on both R% and SC. It was found that, the adsorption equilibrium was reached within 20-30 minutes from the beginning of adsorption process and that, the order of sorption capacity of the metal ions used is in the following order:



Effect of initial ion concentration

The effect of initial metal ions and anions

concentrations used in the present study on R% and SC was investigated. It was found that, the increase in the heavy metals concentrations is accompanied by decrease in the values of both R% and SC (Table 7). But the opposite holds true in case of anions used. Data listed in Table 8 revealed that, the increase in the initial concentrations of each of SO_4^{2-} and $Cr_2O_7^{2-}$ causes a significant increase in the sorption properties of both anions. The adsorption equilibrium was attained at concentrations of anions ranged from 80 to 100 ppm in the reaction medium.

Effect of the pH

Data listed in Tables 7 and 8 clarify the effect of pH on the adsorption of metal ions and anions. Acidic medium showed lower adsorption values for R % and SC. This may be attributed to increase in the hydrogen ions at the interface which repel the positively charged metal ions and consequently decrease the adsorption percent [26]. The increase of the pH values in the adsorption medium increases the adsorption of metal ions and consequently enhances the R % and SC values. The opposite findings were observed in case of anions.

Effect of Temperature

The effect of temperature on the adsorption properties of metal ions and anions onto grafted Nylon-6 fibers was studied within the range 30-80°C. The results are shown in Tables 7 and 8. It was noticed that, increasing the adsorption temperature from 30-80°C increases the adsorption amount of metal ions and anions. This may be a result of increasing the swelling degree of modified fibers. The percentage of swelling increases as the temperature increases due to the increase in the flexibility of the grafted polymer chains. The data listed in Table 7 showed increase in the degree of extraction (R %) and the sorption capacity SC (mg/g) of both cupric and lead ions, but there is a little effect on the adsorption properties of chromium ion.

According to the abovementioned we can conclude that, when grafted with PDMAEMA Nylon-6 fibers are in contact with the selected, in the present work, heavy metals and anions the adsorption occurred with high efficiency in the following order:



TABLE 7. Effect of Adsorption Time (min.), Initial Concentration (ppm) and Adsorption Temperature (°C) on the Degree of Extraction (R) and the Adsorption Capacity (SC, mg/g) of Metal Ions with Nylon-6 Nonwoven Fabrics Treated with AS and Grafted with PDMAEMA.

Metal Ions	Degree of Extraction (R %)					Adsorption Capacity (SC, mg/g)				
	Adsorption Time, (minutes) ^a									
	10	20	30	60	120	10	20	30	60	120
Cu ²⁺	25.9	27.1	26.4	27.1	27.1	6.2	6.3	6.5	6.5	6.5
Pb ²⁺	22.5	26.6	26.6	26.6	26.6	5.4	6.4	6.4	6.4	6.4
Metal Ions	Initial concentration, (ppm) ^b									
	60	80	100	200	60	80	100	200		
Cu ²⁺	31.9	27.1	24.0	23.8	12.0	6.5	6.3	4.3		
Pb ²⁺	27.0	26.6	21.9	5.0	10.2	10.0	8.7	6.4		
Metal Ions	Adsorption Temperature, (°C) ^c									
	30	40	60	80	30	40	60	80		
Cu ²⁺	27.1	34.4	41.6	66.9	6.5	8.2	10.0	16.0		
Pb ²⁺	26.6	30.8	45.0	62.4	6.4	7.4	10.8	15.0		
Metal Ions	pH									
	4.0	6.0	6.5	4.0	6.0	6.5				
Cu ²⁺	6.1	16.9	15.5	1.5	4.1	3.7				
Pb ²⁺	3.3	18.8	25.0	0.8	4.5	6.0				

Adsorption Conditions:

^a Initial concentration of Metal Ions, 80 ppm; Adsorption Temperature, 30°C.

^b Adsorption Time, 1 hr; Adsorption Temperature, 30°C.

^c Initial concentration of Metal Ions, 80 ppm; Adsorption Time, 1 hr;

^{abc} Adsorption pH, 6.0; [AS], 1.63 mg/gm; Graft Yield % 18.0.

TABLE 8. Effect of Adsorption Time (min.), pH, Temperature (°C) and Initial Concentration (ppm) on the Degree of Extraction (R) and the Adsorption Capacity (SC, mg/g) as Anions with Nylon-6 Nonwoven Fabrics Treated with AS and Grafted with PDMAEMA.

Type of Anions	Degree of Extraction (R %)				Adsorption Capacity (SC, mg/g)			
	Adsorption Time (min.) ^a							
	10	20	30	60	10	20	30	60
SO ₄ ²⁻	52.1	59.9	67.0	68.0	12.5	14.0	16.1	16.3
Cr ₂ O ₇ ²⁻	13.0	22.0	22.8	22.9	3.5	4.1	4.1	4.1
Type of Anions	Adsorption pH ^b							
	4	5	6	6.5	4	5	6	6.5
SO ₄ ²⁻	68.0	57.6	53.1	49.0	16.3	13.8	12.8	11.8
Cr ₂ O ₇ ²⁻	22.9	22.5	22.2	15.1	6.2	5.9	6.0	4.1
Type of Anions	Adsorption Temperature (°C) ^c							
	30	40	60	80	30	40	60	80
SO ₄ ²⁻	68.0	68.8	69.2	70.1	16.3	16.5	16.6	16.8
Cr ₂ O ₇ ²⁻	22.9	23.6	26.4	30.9	4.1	5.2	6.3	7.4
Type of Anions	Initial Concentration (ppm) ^d							
	60	80	100	200	60	80	100	200
SO ₄ ²⁻	37.5	68.0	71.8	72.4	12.8	16.3	15.5	13.4
Cr ₂ O ₇ ²⁻	9.8	22.9	23.0	23.3	3.8	4.1	4.1	4.1

Adsorption Conditions:

^a Initial concentration of Anions, 80 ppm; Adsorption Temperature, 30°C, pH, 4.0.

^b Initial Concentration, 80 ppm; Adsorption Temperature 30°C, Adsorption Time, 1hr.

^c Initial concentration of Anions, 80 ppm; Adsorption Time, 1 hr; pH, 4.0.

^d Adsorption pH, 4.0; Adsorption Temperature, 30°C, Adsorption Time, 1hr. [AS], 1.63 mg/gm; Graft Yield % 18.0.

Conclusion

Development of laboratory conditions for establishment of know-how for the production of ion exchanger Nylon-6 fibers was carried out. Adjustment and adaptation of these conditions to suit the production of that fibers on pilot scale was achieved. The preparation of Nylon-6 fibers as ion-exchange material based on grafting of antimicrobial Nylon-6 fibers with DMAEMA using Cu^{2+} - $\text{K}_2\text{S}_2\text{O}_8$ redox system was carried out. Assessment the application of the produced fibers as ion-exchanger was evaluated for adsorption of Cu^{2+} , Pb^{2+} cations and SO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ anions from aqueous solutions. The effect of adsorption parameters such as pH, duration, initial ion concentration and the adsorption temperature on the degree of extraction (R %) and adsorption capacity SC (mg/g) was calculated. It was found that, the grafted fibers showed high efficiency for adsorption of Cu^{2+} , Pb^{2+} as cations and SO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ as anions.

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References

- Hegazy E. S. A., El-Rehim H. A. A., Shawky H. A. Investigations and Characterization of radiation grafted copolymers for possible practical use in waste water treatment. *Radiat Phys Chem*, **57**, 85-95 (2000).
- Druzhinina T. V., Nazarina L. A. Chemisorption fibers based on graft copolymers: Fabrication and properties. *Khim Volokna*, **31** (4), 252 (1999).
- Druzhinina T. V., Struganova M. A. Fabrication of Polycapraamide sorption fibers with hydrazine group. *Fiber Chemistry*, **33** (1), 5 (2001).
- Kato K., Uchida E. T., Kang Y., Ikada Y. Polymer surface with graft chains, *Progress in Polymer Science*. **28**, 209-259 (2003).
- Hayakawa K., Yamakita H. Preparation of mercaptoethylated graft fibers for adsorption of heavy metal ions. *J Appl Polym Sci*, **21** (3), 665-675 (1977).
- Lavnikova I. V., Zheltobryukhov V. F. Radical Graft Polymerization of Glycidyl Methacrylate and Polycapraamide Fiber. *Russian Journal of Applied Chemistry*, **74** (4), 678-3680 (2001).
- Mascia L., Hashim K., Carboxylic acid functionalization of nylon-6 by radiation grafting and conversion to zinc salts: effects on physical properties. *Colloid and Polym Sci*, **275** (7), 689 - 697(1997).
- Solovey O. M., Shunkevich A. A., Okrovskaya P. A. I., Elinson I. S., Johann J., Iraushek H. Chemically active textile materials as efficient means for water purification. *Desalination* **124**, 182-192 (1999).
- Lin W. P., Lu Y., Zeng H. M. Preparation of the amidoxime group containing chelating fiber and adsorption property of gold. I. Preparation of chelating fiber by amidoximation of polyacrylonitrile fiber. *Reactive Polymers*, **17**, 155-161 (1992).
- Druzhinina T. V., Kilyushik Yu. A., Surina I. V. Production of carboxyl containing derivatives of PMMA and polycabroamide graft copolymer. *Fiber Chem*, **40**, 5, (2008).
- Abaldueva E. V., Druzhinina T. V. Sorption of heavy metals by polyamide chemisorption. *Fiber Chemistry*, **36** (1), 33 (2004).
- Shalaby S. E, Al- Balakocy N. G. A Simple efficient and generally applicable method for grafting of vinyl monomers onto Nylon-6 fabrics, Egypt. Pat. No. 23507 (2006).
- Shalaby S. E, Abdalla N. H., Rabie A. M. Chemical modification of polyamide-6 fibres containing chemically bonded quaternary ammonium groups with 2-dimethylaminoethylmethacrylate. *1st International Conference, Textile Research Division NRC, Cairo, Egypt, 2- 4 Mar. (2004)*.
- Gabrielyan G. A, Shalaby S. E, Druzhinina T. V., Rogovin Z. A., Afanaceva I. S. Modification of polycapraamide fibers, *U.S.S.R. SU 907*, 111(CI. D06 M13/46), 23 Feb. (1982).
- Gabrielyan G. A., Shalaby S. E., Druzhinina T.V., Rogovin Z. A. Modification of polycapraamide fibers, *U.S.S.R. SU 891*, 821 (CI. D06M13/46), 23 Dec.(1981).
- Gabrielyan G. A., Shalaby S. E., Druzhinina T. V., Rogovin Z. A. Graft copolymers, *U.S.S.R. SU 914*, 677 (CI. D01F11/04), 23 March (1982).
- Shalaby S. E., Gabrielyan G. A., Rogovin Z. A. Synthesis of graft copolymers of polycaprolactam with poly (Dimethylamino ethyl methacrylate)

- using the potassium persulphate-copper (2+) ion initiating system, *Vysokomol. Soedin., Ser. B*, **24** (4), 288 (1982). Chem. Abstr. 97, No. 6, 39490n (1982).
18. Shalaby S. E., Afamaceva I. S., Gabrielyan G. A., Druzhinina T. V. Sorption and electrostatic properties of polycaprolactam fibres modified by polyacrylonitrile grafting. *Khim. Volokna*, **2**, 30 (1982).
 19. Shalaby S. E., Piankova A. B., Gabrielyan G. A., Druzhinina T. V., Rogovin Z. A. Synthesis of graft polycaprolactam copolymers using binary mixtures of monomers. *Khim. Volokna*, **3** (10), (1982). Chem. Abstr. 97, No. 10, 73780s (1982).
 20. Shalaby S. E., Gabrielyan G. A., Druzhinina T. V., Rogovin Z. A., Chernukhina A. I. Method for the preparation of multi-graft copolymers of polyamide-6 fibers. *U.S.S.R. SU* **103**, 1971(cl. D01F11/04), 1 April. (1983).
 21. Shalaby S. E., Al-Balakocy N. G., Abo El-Ola S. M. Graft copolymerization of glycidylmethacrylate onto modified nylon-6 fibers. *J. Appl Polymer Sci*, **99**, 613- 618 (2006).
 22. Shalaby S. E., Al-Balakocy N. G., Abo El-Ola S. M. Surface modification of nylon-6 fibers for medical application, *J. Appl Polym Sci*, **104**, 3788-3796 (2007).
 23. Shalaby S. E., Al-Balakocy N. G., Abdel-Fatah O. M., Elshafei A. M. Antimicrobial finishing of regular and modified nylon-6 fabrics. *J. Appl Polym Sci*, **110** (2), 738 (2008).
 24. Shalaby S. E., Al-Balakocy N. G., Beliakova M. K. A simple efficient and generally applicable method for imparting polyester and polyester/cotton fabrics antimicrobial activity. Egypt. Pat. No. 24672. (2010).
 25. Shalaby S. E., Al-Balakocy N. G., Abo El-Ola S. M., Beliakova M. K., Chemical fixation of antimicrobial substance within polyester and polyamide-6 Fibers. *International Journal of Engineering Research and Technology*, **11**, 6853-865 (2018).
 26. Shalaby S. E., Al-Balakocy N. G., Beliakova M. K. Simple method for grafting of glycidyl methacrylate onto nylon-6 nonwoven fabrics for ion exchange applications. *International Journal of Science and Research*, **4**, 689 (2015).
 27. Jenkins A. D., *Polymer Science-Analytical Science Hand Book*, Vols. I and II, North-Holland,

طريقة مطورة لإنتاج ألياف النايلون-6 المطعمة ببولي ثنائي ميثيل أمينو إيثيل ميثاكريلات على مستوى نصف صناعي وتطبيقها كمبادل أيوني

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يقدم هذا البحث طريقه تكنولوجيه سهله وفعاله يمكن استخدامها علي مستوي نصف صناعي لإنتاج ألياف النايلون-6 المطعمة ببولي ثنائي ميثيل أمينو إيثيل ميثاكريلات يمكن استخدامها كمبادلات أيونيه (كاتيونات وأنيونات). وتكمن هذه التكنولوجيا في تثبيت ماده قاتله للميكروبات في الألياف النايلون-6 ثم تطعيمها بمونيمر ثنائي ميثيل أمينو إيثيل ميثاكريلات باستخدام منظومة فوق كبريتات البوتاسيوم ($K_2S_2O_8$) - كبريتات النحاسيك ($CuSO_4 \cdot 5H_2O$) كبادئ للتفاعل. وقد تم دراسة الظروف والعوامل المؤثرة على عملية التطعيم لتحديد الظروف المثلى لعملية التطعيم. واعقب ذلك تحديد قابليه الألياف المحوره بتلك الطريقة للاستخدام كمبادل أيوني لامتناس الكاتيونات (أيونات النحاس والرصاص) والأنيونات (الكرومات والكبريتات). وعلاوة على ذلك تم تحديد العوامل المؤثرة علي عملية التبادل الأيوني وحساب كل من درجة الاستخلاص (R%) وسعة الأمتصاص (SC mg/g).