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Development of grafted cotton fabrics ions exchanger for dye removal applications: methylene blue model

M.S. Mohy Eldin[a,b,*], M.H. Gouda[c], M.A. Abu-Saied[d], Yehia M.S. El-Shazly[c], H.A. Farag[c]

[a]*Faculty of Science, Chemistry Department, University of Jeddah, Osfan, P.O. Box 80203, Jeddah 21589, Saudi Arabia, Tel. +20 3 4593 414; email: m.mohyeldin@mucsat.sci.eg*
[b]*Polymer Materials Research Department, Advanced Technology and New Materials Research Institute, MuCSAT, New Borg El-Arab City 21934, Alexandria, Egypt*
[c]*Faculty of Engineering, Chemical Engineering Department, Alexandria University, Alexandria University Community Development Centre, Alexandria, Egypt, Tel. +20 3 4249062; Fax: +20 3 4250193; emails: marwagouda17@yahoo.com (M.H. Gouda), yehiaelshazly@hotmail.com (Y.M.S. El-Shazly), abualy2125@yahoo.com (H.A. Farag)*
[d]*Polymer Materials Research Department, Advanced Technology and New Materials Research Institute, Scientific Research and Technological Applications City, New Borg Al-Arab City 21943, Alexandria, Egypt, Tel./Fax: +20 34593414; email: mouhamedabdelrehem@yahoo.com*

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ABSTRACT

In this study, grafted cotton fabrics ions exchanger for methylene blue (MB) removal from wastewater was developed. This goal has achieved through two successive steps. The first step was concerned grafting of the fabrics with polyacrylonitrile followed by activation of the nitrile groups using hydroxylamine as the second step to induce ion exchange sites. Factors affecting the two steps were studied, and their impacts on the characters of the modified fabrics were monitored. FT-IR and TGA data provided evidence of the grafting and the amination. Furthermore, the morphological changes were mentioned via SEM investigations. Finally, the aminated grafted cotton fabrics were tested as an adsorbent for removing MB from the aqueous solutions. The adsorption process was carried out in a batch mode and the effects of the contact time, the initial dye ion concentration, the pH, and the temperature on the adsorption were investigated. The experimental results revealed that the prepared adsorbent is capable of removing more than 92% of MB molecules from synthetic solution of concentration up to 300 ppm at pH ranged from 3 to 11 at temperature varied from 25 to 55˚C.

Keywords: Cellulose; Acrylonitrile; Grafting; Adsorption; Basic dye removal

1. Introduction

Worldwide increase demands new fabrics, increasing the consumption of dyes that is estimated in 800,000 t annually. Dyes are released from different industries like textile, paper, plastic, rubber, leather to the wastewater streams. Without proper treatment, this could exert a great impact on the environment. Dyes are considered to be a particularly dangerous organic compound for the environment [1]. Synthetic dyes

*Corresponding author.

have increasingly been used in the textile and dyeing industries. This activity resulted in the discharge of highly colored effluents that affect water transparency and gas solubility in water bodies. Also, many dyes are believed to be toxic and carcinogenic. Most of them are completely resistant to biodegrading process [2]. So biological treatment by activated sludge does not always meet with great success and, in fact, most of these dyes resist aerobic biological oxidation [3].

Hence to protect the environment and to meet the stringent government law, many researchers try to find an effective and economical way of dye-containing wastewater treatment, for example, oxidation techniques: electrochemical oxidation, peroxides, ozone, etc.; physicochemical techniques: adsorption, ion exchange, coagulation, flocculation; membranes: nanofiltration, reverse osmosis, etc.; biologic techniques: enzymatic decolorization processes [1–7]. Sometimes, the combined use of two techniques provides better results. The high cost of the complicated treatment and energy use of the methods mentioned above cause limitation of their applications and some of this method like coagulation produces concentrated waste creating another disposal problem [8]. Hence, there is a constant need to search for an optimal technology while considering its cost, materials employed, and its efficiency [9]. Among these mentioned processes, adsorption is a very effective separation technique, and now it is considered as an economical and efficient method for the removal of dye from water effluent [10]. Hence, it is imperative to find alternate low-cost sorbent as agricultural, industrial, natural waste materials have tested for their dye and heavy metal sorption potential [9–13]. Of these materials, plants, waste water material, such as peat, rice husk, sugar beet pulp, banana pith, sawdust, plant leaves, bark, coir, orange wastes, cotton fabric, etc., are causing scientist's interest in wastewater treatment due to broad availability and relative cheapness. Other adsorbents such as clays with higher surface areas are alternatives. Recent investigations have focused on the use of clays [14–19]. Another reason for this interest is the importance of adsorption on a solid surface in many industrial applications to improve the efficiency and economy of the treatment process. Cotton fabric is a cellulosic material (natural polymer) produced with a large amount of waste (byproduct) from textile industries. We choose cellulose because it is cheap, renewable, biodegradable, and the most abundant organic raw material in the world [20]. The aim of the present study is to develop amidoxime PAN-grafted cotton fabrics ions exchanger with the potential to adsorb methylene blue (MB) dye molecules from aqueous solution under different operational conditions.

2. Experimental

2.1. Materials

Cotton fabrics kindly supplied by ESTIA Co., Alexandria (Egypt). Potassium persulfate (KPS) (purity 99%) obtained from Sigma–Aldrich chemical Ltd (Germany). Hydroxylamine (HA) hydrochloride (purity 99%) obtained from Sigma–Aldrich Chemical (Germany). Acetone absolute (purity 99.9%) was obtained from El-Nasr Pharmaceutical Co., for Chemicals (Egypt). Sodium hydroxide (purity 99%) obtained from El-Nasr Pharmaceutical Co., for Chemicals (Egypt). Acrylonitrile (AN) and dimethyl formamide (DMF) (purity 99%) obtained from Fluka.

3. Methods

3.1. Preparation of alkali-treated cotton fabric

Cotton fabrics were scouring for 2 h at 50˚C using sodium hydroxide (0.5 M) as a purification step before grafting process according to K.M. Mostafa [21]. The excess alkali then removed by successive washing using distilled water until changes in washing water pH was no more detected. The fabrics were then dried at 50˚C overnight.

3.2. Grafting process

3.2.1. Treatment with potassium persulfate

To enhance the possibility of AN grafting over the formation of a homopolymer, the samples produced in the previous step were then treated with a solution containing KPS (1%) for 10 min at 50˚C using the material to liquor ratio of 1:20 with continuous shaking to induce free radicals over the cotton fabrics. After this treatment, the fabrics were washed and squeezed between two filter papers, then immersed in polymerization solution [22].

3.2.2. Graft polymerization

The treated cotton fabrics were carried out in a 50-ml stoppered Erlenmeyer flask. Polymerization was done under the following conditions: 8–16% AN, 0.0–1.5% KPS, acetone/water composition (20–80; v/v %) as a solvent, 45–65˚C, 1–6 h, and fabric liquor ratio of 1:20. At the end of the reaction period, the grafted cotton fabrics were thoroughly extracted by DMF to remove ungrafted PAN homopolymers, and then the grafted fabrics were dried at 60˚C to constant weight. Different parameters have been estimated to evaluate grafting process, namely: grafting percent (GP%), grafting efficiency (GE%), grafting conversion (GC%), and weight conversion (WC%) calculated as follows:

$$GP\% = [(B - A)/A] \times 100 \quad (1)$$

$$GE\% = [(B - A)/(C + H)] \times 100 \quad (2)$$

$$WC\% = [(C + H)/D] \times 100 \quad (3)$$

$$GC\% = [(B - A)/D] \times 100 \quad (4)$$

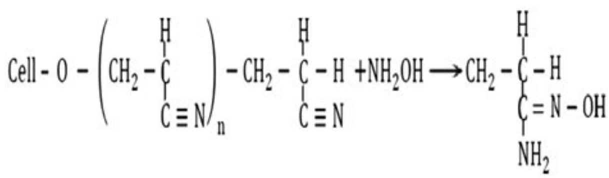
where A is the weight of the original cotton fabric, B is the weight of the grafted cotton fabrics, C is the weight of the grafted polymer after extraction of a homopolymer, H is the weight of the homopolymer, and D is the weight of the used monomer.

3.3. Amination process

The cyano-groups of grafted PAN branches onto the cotton fabrics were converted into hydroxime ones by reaction with HA [23,24] under the following conditions: HA concentration (2–10%), reaction time (1–6 h), and reaction temperature (40–60°C). The aminated grafted cotton fabrics were then alkali-treated with 1% NaOH for 2 h and material:liquor ratio (1:40). The samples were then washed repeatedly with distilled water to remove excess unreacted NaOH. The reaction between PAN´ nitrile groups and HA is presented in Scheme 1.

3.4. Batch adsorption experiments

The adsorption experiments were carried out in a batch process using MB aqueous solution [25,26]. The variable parameters, namely the initial MB concentration (10–300 ppm), the adsorbent amount (0.25–3.0 g), and the adsorption temperature (30–50°C) and pH (3–11) were studied. The MB adsorption studies were performed by mixing 1 g of hydroxime-grafted fabrics with 40 ml of MB solution. The mixture was agitated at 150 rpm at RT in a shaking water bath for 2 h. The dye concentration, before and after the adsorption, for each solution, was determined by measuring the absorbance at the maximum wavelength (λ_{max} = 660 nm) using UV–vis spectrophotometer. Dye removal percentage calculated according to the following formula:



Scheme 1. Amination process of PAN graft chains.

$$\text{Dye removal}\,(\%) = [(C_0 - C_t)/C_0] \times 100 \quad (5)$$

where C_0 and C_t (mg L^{-1}) are the initial concentration at zero time and the final concentration of MB at a definite time, respectively.

4. Matrices characterization

4.1. FT-IR spectroscopic analysis

FT-IR spectra analyzed the structure of cotton fabrics. Samples were mixed with KBr to make pellets. FT-IR spectra in the absorbance mode were recorded using FT-IR spectrometer (Shimadzu FTIR-8400 S, Japan), connected to a PC, and analysis of the data was done by IR Solution software, Version 1.21 [26].

4.2. Thermal characterization (TGA)

The thermal degradation behaviors of cotton fabrics were studied using Thermo Gravimetric Analyzer (Shimadzu TGA-50, Japan) instrument in the temperature range from 20 to 800°C under nitrogen at a flow rate of 20 ml/min and a heating rate of 10°C/min [26].

4.3. Morphological characterization (SEM)

The scanning electron microscope (SEM) images of the cotton fabrics were obtained by placing the particles onto carbon tape-attached aluminum SEM stubs after coating with gold to a few nanometer thicknesses under vacuum using scanning electron microscopy (Joel Jsm 6360LA, Japan) at an accelerated voltage of 20 kV [26].

4.4. Water uptake percentage

In the water uptake measurement, for ungrafted and grafted, cotton fabrics were previously immersed in distilled water at room temperature for 24 h and the samples were dried by wiping with filter papers.

The water uptake percent was calculated as follows:

$$W\% = [(B - A)/A] \times 100 \quad (6)$$

where B is the weight of the wet sample and A is the weight of the dry sample [27].

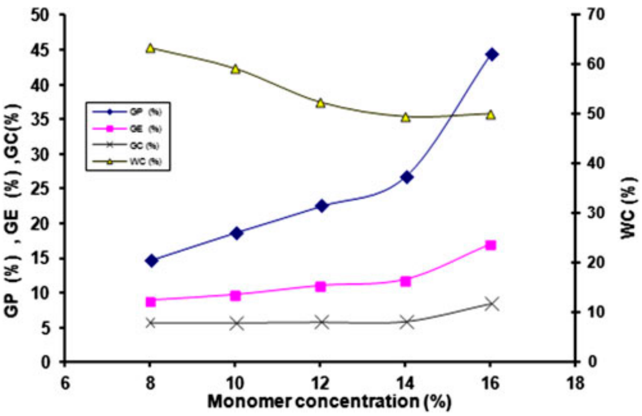


Fig. 1. Effect of monomer concentration on grafting parameters (1 g, 55˚C, 4 h, acetone:water 1:1, 1% KPS, solid:liquid 1:20, 20 ppm).

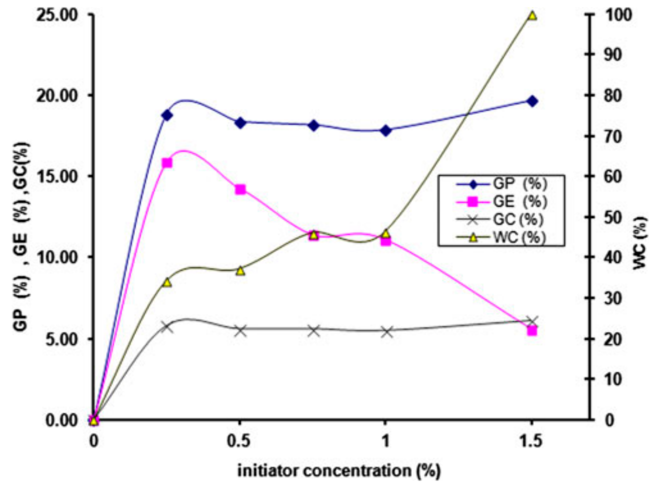


Fig. 2. Effect of initiator concentration on grafting parameters (1 g, 55˚C, 4 h, acetone:water 1:1, 10% AN, solid:liquid 1:20, 20 ppm).

5. Results and discussion

5.1. Grafting step

5.1.1. Effect of monomer concentration

Diffusion of the monomer into the polymer matrix has a great effect on the grafting process. The effect of variation in the monomer concentration on the grafting process parameters, grafting percentage, GE%, GC %, and total conversion is shown in Fig. 1. From the figure, it can see that all the parameters of the grafting process have been positively affected by the increase in AN concentration, except the total conversion. The grafting percentage increases successively by increasing the concentration of AN within the range studied. This increment is may be to the higher availability of monomer molecules in the proximity of cellulose macroradicals at a higher monomer concentration. It is understandable that cellulose macroradicals are immobile, and for grafting to occur, the monomer should be in the vicinity of the cellulose [28]. On the other hand, the effect of variation in the grafting percentage from 14 to 44% on the percentage removal of MB was explored. No significant effect observed where the MB removal percentages with a narrow range, 98.3–99.4%, obtained. This result may explain the limitation of available MB molecules. However, this is considered as an advantage where a minimum amount of grafted branches can be sufficient for the MB removal process within the studied range.

5.1.2. Effect of initiator concentration

Fig. 2 represents the effect of variation in the initiator concentration on the grafting parameters. From the figure, it is clear that the grafting percentage is not significantly affected by variation in persulfate concentration from 0.25 to 1.5%. This unchanged may explain why the primary radicals formed by initiator trigger not only the graft polymerization via hydrogen abstraction along the cellulose backbone but also the homopolymerization of vinyl monomers. The grafting of PAN chains starts first on the fabrics surface. This surface grafting will lead to the formation of hydrophobic barrier reducing the diffusion of further AN monomer units to graft the interior of the fabrics. Also, PAN homopolymers formed in the polymerization medium precipitate on the fabrics surface and create an additional barrier for AN monomer diffusion increasing the number of the regenerated radicals consumed in the formation of the homopolymer [29]. As a result, the GE% continuously decreased, and WC% increased with the increase in the initiator concentration. The removal of MB by the prepared fabrics at different initiator concentrations has not also been affected as the grafting percentage. This unchanged expected results since the adsorption process depend basically on the number of active ionic sites generated on aminated PAN graft chains to adsorb MB molecules that are constant numbers.

5.1.3. Effect of solvent composition

The effect of variation in the solvent composition (acetone:water) on the grafting process parameters is shown in Fig. 3. From the figure, it can observe that the grafting percent slightly increased from 18 to 20% with the acetone content increase from 20 to 50%. Further increase in the acetone content leads to a slight

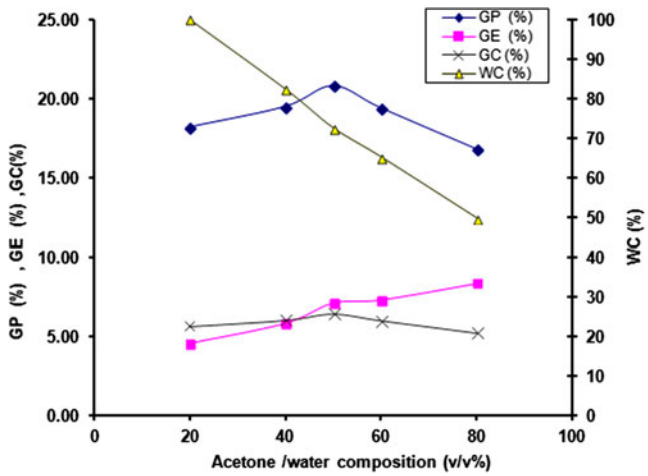


Fig. 3. Effect of solvent ratio composition on grafting parameters (1 g, 55˚C, 4 h, 10% AN, 1% KPS, solid:liquid 1:20, 20 ppm).

decrease in the grafting percentage. On the other hand, the results showed a decrease in WC with progressive increase in acetone content. Acetone plays more than one role here acting as a solvent for the AN monomer, swelling agent for the cellulose fabrics, and finally as a precipitating agent for the formed PAN. Moreover, the initiator used does not dissolve in the acetone; so, increasing the acetone content will limit the polymerization of AN to the water content in the solvent medium. This limitation consequently reduced the conversion degree. Since the MB removal percentage directly correlated to the amount of grafted PAN or the number of the available ionic active sites for the adsorption, so no significant change of the MB removal percentage was observed using the grafted samples prepared under the studied conditions.

5.1.4. Effect of polymerization time

The effect of variation in the reaction time from 1 to 6 h on grafting parameters was studied and recorded in Fig. 4. Maximum grafting percentage (28%) obtained during the first 2 hours of grafting time. Further, the prolongation of the grafting process reduces the grafting percentage gradually to reach minimum value (18%) after 5 h of grafting reaction. This decrement may be due to the post-grafting effect which is mainly responsible for the formation of PAN precipitation layers onto the fabrics surface. Consequently, this leads to the reduction in AN monomer diffusion to the cellulose bulk and limits only to the surface [30]. The correlation between the grafting percentage and the MB removal % was explored. The obtained results revealed that the MB removal % has its maximum value (97%) with the grafted fabrics of the highest grafting percentage of 28%. The sensitivity of the MB removal percentage to changes in the grafting percentage is not high since minimum grafting percentage, 18%, is enough to remove 94% of the MB molecules from the dye solution.

5.1.5. Effect of polymerization temperature

The effect of variation in the polymerization temperature on the grafting parameters is shown in Fig. 5.

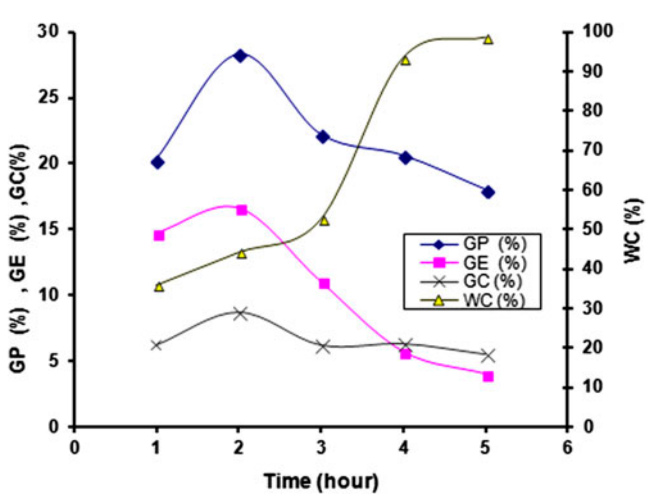


Fig. 4. Effect of polymerization time on grafting parameters (1 g, 55˚C, 10% AN, acetone:water 1:1, 1% KPS, solid: liquid 1:20, 20 ppm).

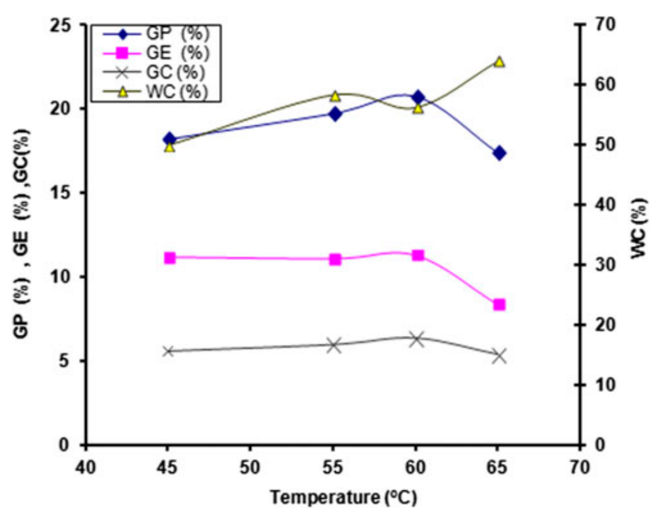


Fig. 5. Effect of polymerization temperature on grafting parameters (1 g, 10% AN, 4 h, acetone:water 1:1, 1% KPS, solid:liquid 1:20, 20 ppm).

It was observed that the grafting parameters changed slightly with a variation in the polymerization temperature from 45 to 65˚C. The WC% was increased from 50 to 65%. The grafting percentage was slightly increased from 18 to 21% with temperature increase from 45 to 60˚C and decreased to 15% at 65˚C. This decrease in the grafting percentage may be the result of the premature termination of growing grafted chains by an excess of produced persulfate radicals at 65˚C [31].

Correlation of the MB removal percentage with the cotton fabrics grafting percentage shows that the MB removal percentage increased from 94.8 to 96.8% with grafting percentage increase from 18 to 21%.

5.2. Functionalization step

Polyacrylonitrile hollow fiber membranes [23], nanofibers [24], and nanoparticles [25,26] were previously functionalized using HA for different applications. Different functionalization factors affecting the hydroximation process investigated, and its impact on the MB removal percentage and the adsorption capacity monitored.

5.2.1. Effect of HA concentration

Fig. 6 shows the effect of variation in the HA concentration on the amount of dye uptake on the grafted cotton. It is clear that increasing the HA concentration over 4% has a negligible effect. It can assume that all the available nitrile groups located onto the surface, so using 4% HA is enough to convert them into oxime ones. This behavior in agreement with our assumption about occurring the grafting onto the fabrics surface.

5.2.2. Effect of amination temperature

The effect of variation in the amination temperature on the amount of dye uptake is shown in Fig. 7. Upon increasing the temperature from 30 to 50˚C, the dye uptake increases from 240 to 330 μg/g. The dye uptake decreased to 290 μg/g at temperature 60˚C. The MB uptake increment stage results from enhancement of the aminoalkylation reaction between the nitrile groups and the HA molecules. According to our proposal that most of PAN graft chains located onto the fabrics surface, so increasing the temperature of the amination process up to 60˚C will create a high density of amino-hydroxyl groups on the fabrics surface. This induced fast adsorption of MB molecules on the fabrics surface which reduced the concentration gradient between the MB liquid phase and the fabrics solid phase and consequently the amount of the adsorbed MB.

5.2.3. Effect of amination time

The dependence of the amount of dye uptake on the amination time investigated. Evidently, the amount of dye removed was not affected by prolongation of the amination process time. This finding reinforced our proposal of locating the PAN graft branches onto the fabrics surface. This result is considered as an advantage since shortened the needed time to generate the amidoxime groups on the fabrics surface.

5.3. Dye adsorption step

The adsorption capacity at equilibrium for amidoxime cotton fabrics was studied under different

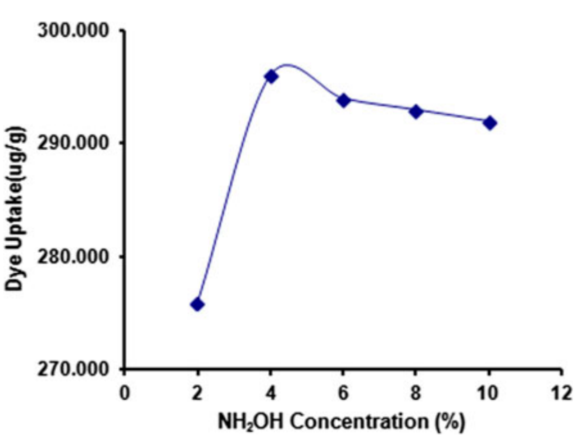


Fig. 6. Effect of hydroxyl amine concentration on dye removal (%) on the PAN-grafted cotton fabric (6 h, 60˚C).

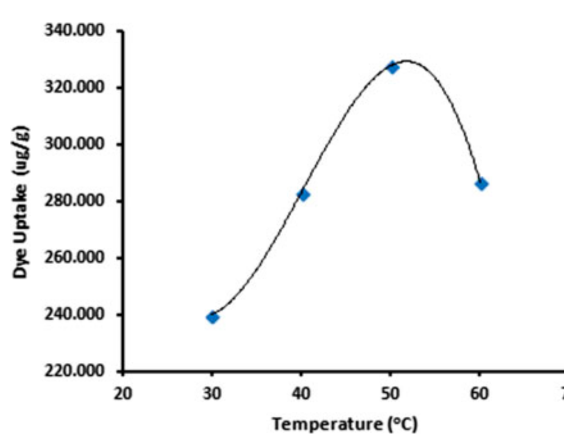


Fig. 7. Effect of amination temperature on dye removal (%) of the aminated PAN-grafted cotton fabric (10% HA, 6 h).

operational conditions such as dye concentration, adsorption temperature, and pH. Finally, the correlation between grafting percentage and adsorption capacity was explored, and the obtained results were compared to the results of ungrafted fabrics. In addition to the adsorption capacity, the MB removal % was also presented as a qualitative indicator of the efficiency of the adsorption process.

5.3.1. Effect of grafting percentage

Amidoxime-grafted fabrics with different grafting percentage used and the adsorption characteristics, MB removal %, and adsorption capacity, were illustrated in Table 1. From the table, it can abstract that the variation in grafting percentage above 7% has a neglectable effect on the adsorption characteristics of studied MB concentration. This trend may refer to the limitation of the available MB molecules where almost 95% of MB molecules adsorbed by amidoxime-grafted cotton fabrics with 7% grafting percentage. Such explanation was claimed by studying the effect of variation in the initial dye concentration on the adsorption characteristic.

5.3.2. Effect of initial dye concentration

To study the effect of initial MB concentration on the adsorption characteristics, varied MB concentrations (10–300 ppm) were used (Table 2). From the table, it is clear that the capacity of the amidoxime-grafted fabrics was positively affected which increased linearity from 0.38 to 11.16 mg/g, while the capacity of cotton fabrics increased with a lower rate from 0.31 to 6.72 mg/g. The MB removal percentage was varied from 93 to 98% for the amidoxime-grafted cotton fabrics compared with 76–56% of ungrafted cotton fabrics within MB studied range; Fig. 8. This behavior illustrated the positive effect of amidoximation modification of grafted cotton fabrics.

Table 1
Effect of grafting percentage on MB removal percentage and adsorption capacity of amidoxime-grafted cotton fabrics

G (%)	Dye removal (%)	*q* (mg/g)
0	77	0.27
7	95	0.37
14.7	96	0.38
18.7	98	0.38
22.5	98	0.38
35	98.5	0.38

5.3.3. Effect of adsorption temperature

As temperature increases, the rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of the adsorbent increased. Changing the temperature will change the equilibrium capacity slightly of the adsorbent for the particular adsorbate. Increasing the temperature of MB solution from 25 to 50°C has no effect on the MB removal percentage and capacity of the amidoxime-grafted cotton fabrics. This indeed confirmed our proposal about the location of the ionic adsorption sites only on the fabrics surface. This result is in agreement with our previous publication [25].

5.3.4. Effect of adsorbent dosage

As expected, the MB removal percentage increased from 20 to 99.4% with increasing dosage of adsorbent from 0.25 to 3.0 g. On the other hand, the capacity increased following the same trend and showed almost leveling off at adsorbent dose of 2 g due to the limitation of available MB concentration. The obtained results are in quite agreement with other published results [25,26] (Fig. 9).

Table 2
Effect of initial MB concentration on adsorption capacity of cotton fabrics and amidoxime-grafted cotton fabrics

Dye concentration (PPM)	Cotton fabrics *q* (mg/g)	Amidoxime-grafted cotton fabrics *q* (mg/g)
10	0.31	0.38
50	1.52	1.88
100	2.88	3.8
150	4.10	5.76
200	5.12	7.84
300	6.72	11.16

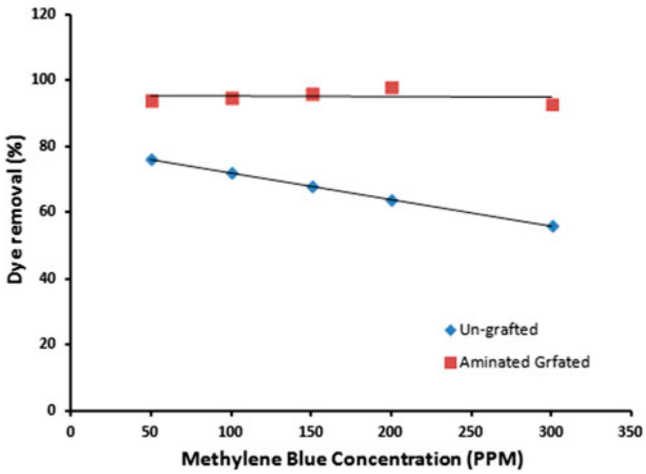


Fig. 8. Effect of initial methylene blue concentration on dye removal (%) of ungrafted and aminated PAN-grafted cotton fabrics.

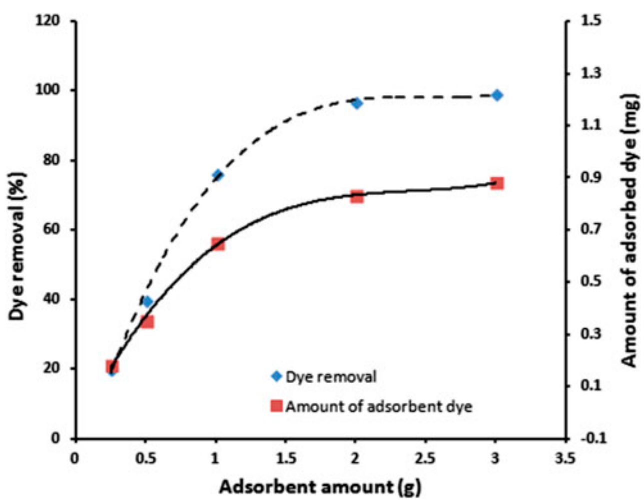


Fig. 9. Effect of adsorbent dosage on dye removal (%) (PH 7, 25˚C, initial concentration 20 ppm, V 50 ml, contact time 120 min).

5.3.5. Effect of adsorption pH

The data revealed that the dye removal (%) increased from 92% up to 98.5% with a pH increase from 3 to 11. The same trend noticed with the

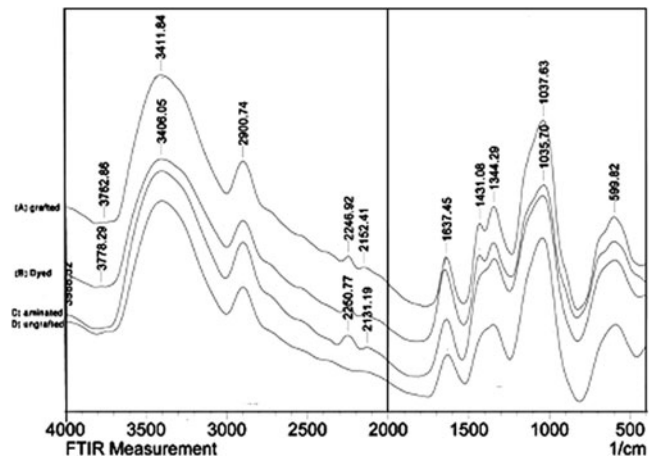


Fig. 10. FT-IR spectra of: (a) ungrafted, (b) grafted, (c) aminated grafted, and (d) dye-aminated grafted samples.

adsorption capacity that increased from 0.342 to 0.381 mg/g. This behavior presents an advantage where no need to adjust the pH of the dye solution. The obtained result is in agreement with other published results [25,32].

5.4. PAN-cotton fabrics graft copolymers characterization

5.4.1. Water uptake (%)

From Table 3, it can be noticed that the grafting process does not have a clear effect on the water uptake process even with the hydrophobic nature of the grafted PAN. The water uptake percentage of the amidoxime PAN-grafted sample increased twice the value of ungrafted or PAN-grafted samples that clarifies the occurrence and the importance of the amidoximation process in increasing the affinity of the amidoxime-grafted cotton fabrics to the MB solution that facilitate the contact between the MB molecules and the adsorption sites.

5.4.2. Infrared spectrophotometer analysis (FT-IR)

FT-IR study confirms the presence of –C≡N group as a result of PAN grafting with the appearance of

Table 3
Water uptake (W%) of ungrafted, grafted, and aminated grafted cotton fabrics

Samples type	Ungrafted sample (%)	Grafted sample (%)	Aminated sample (%)
Water uptake (%)	56	54	101.9

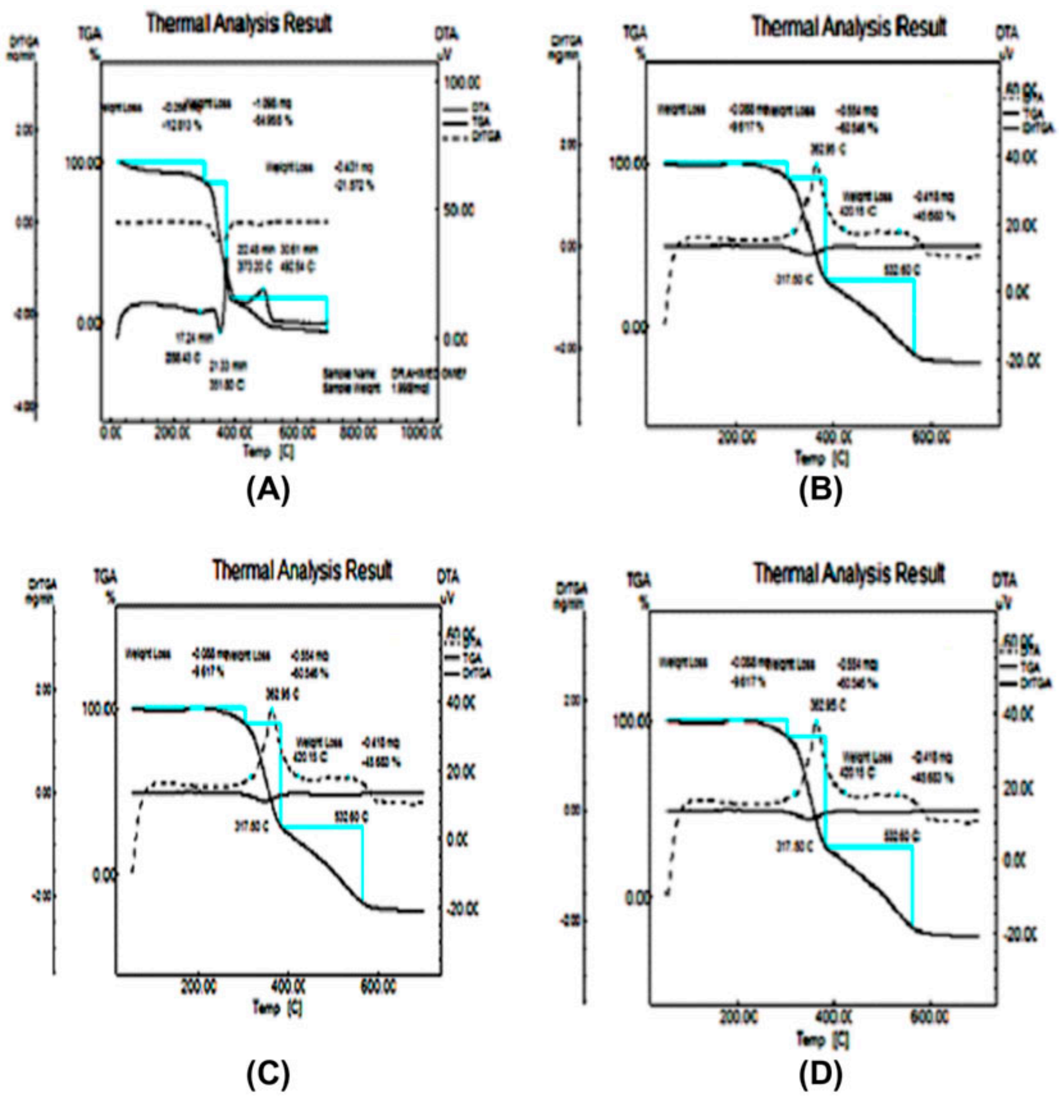


Fig. 11. TGA of: (A) ungrafted, (B) grafted, (C) aminated grafted, and (D) dye-aminated grafted samples.

peaks at 2,246.92 cm^{-1}. The –OH stretching vibration of untreated fabric occurs at 3,404 cm^{-1} and in grafted fabric, this band underwent a shift toward 3,411 cm^{-1}. We can also notice that the intensity of OH group increases after amidoximation due to the formed OH groups as a result of the amination step in addition to a band between 1,100 and 1,200 cm^{-1}; Fig. 10.

5.4.3. *Thermal gravimetric analysis (TGA)*

Fig. 11 shows the thermal gravimetric analysis of ungrafted, grafted, amidoxime-grafted, and dye-amidoxime grafted samples. From the shown thermograms, it can see that the weight loss in the case of ungrafted cotton fabrics occurs at 375˚C with a relative high rate where the sample lost about 85.0% of its original weight; Fig. 11(A). On the other hand, PAN-grafted cotton fabrics gained thermal stability and lost 70% of its weight at 375˚C due to the hydrophobic nature of the PAN-grafted chains [33]; Fig. 11(B). Further thermal stability was observed where the weight loss reduced to 66% at 375˚C which may be due to the formed hydrogen bonds; Fig. 11(C). Once more, further increase in the thermal stability was observed for dyed-amidoximated PAN-grafted samples due to the chemical structure of adsorbed MB molecules; Fig. 11(D).

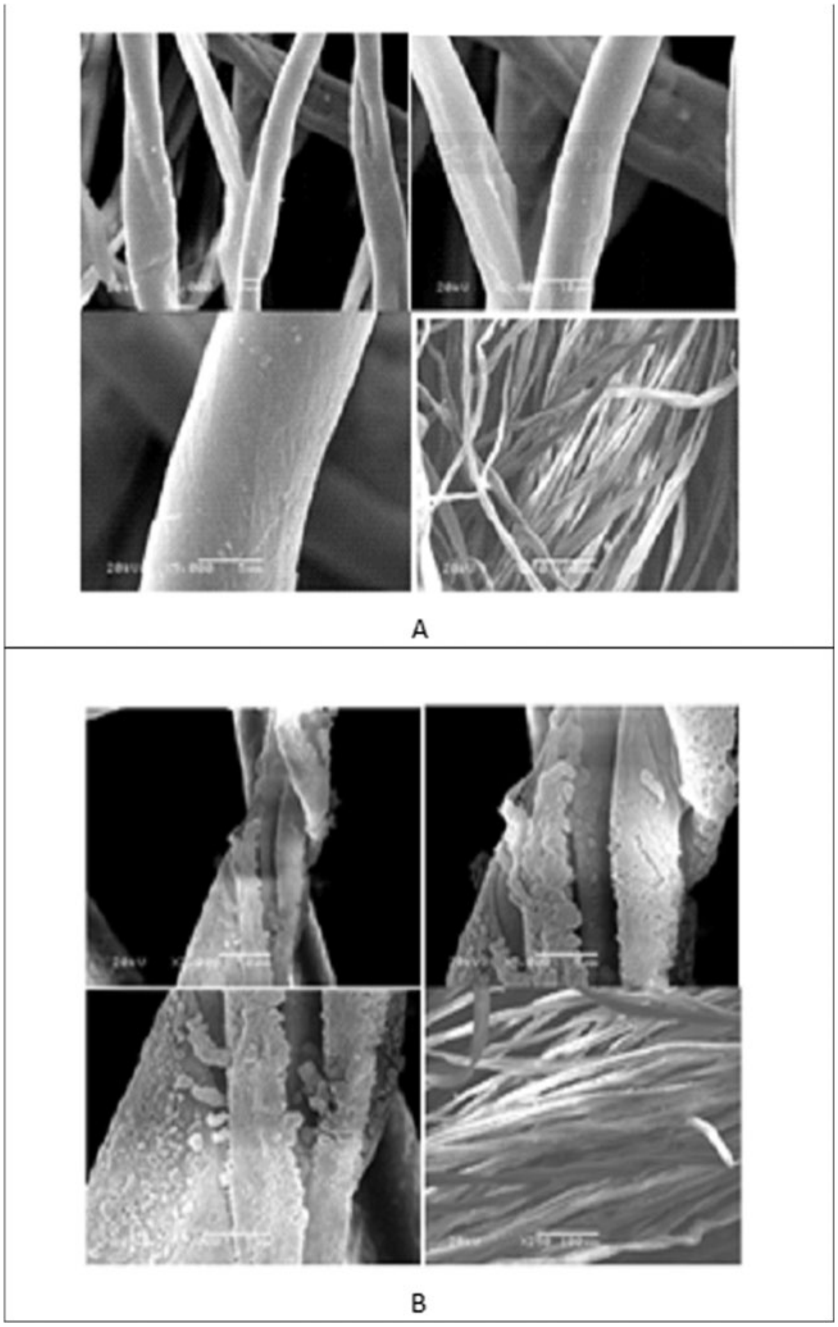


Fig. 12. SEM of (A) ungrafted and (B) grafted samples.

5.4.4. SEM analysis

As shown in Fig. 12(A) and (B), it is clear that ungrafted cotton fabrics are clear and smooth and the convolutions of the cellulose fibers are fairly visible. The surface of the PAN-grafted cotton fabrics appears to be bulkier, rougher, and the inter-fiber spaces reduced. Also, it can see that not all the fabrics surface grafted.

6. Conclusion

Amidoxime PAN-grafted cotton fabrics ions exchanger with the potential to adsorb MB dye molecules from aqueous solution was developed. The cotton fabrics were grafted first with polyacrylonitrile under different conditions. PAN-grafted cotton fabrics with grafted percentage ranged from 7 to 45% were obtained. The grafted PAN cyano-groups then converted into amidoxime ones through treatment with HA under different conditions. The amidoxime PAN-grafted cotton fabrics were then tested for the removal of MB molecules from synthetic dye solution at a concentration ranged from 10 to 300 ppm, temperature from 25 to 55°C, and at wide pH range of 3–11. The adsorption was found independent of solution pH or temperature which presents advantages. Twenty-two grams of the prepared adsorbent found enough to remove 300 ppm MB from 1 L.

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