



## Removal of methylene blue dye from aqueous medium by nano poly acrylonitrile particles

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### ABSTRACT

This article concerns the removal of Methylene Blue (MB) dye using nano-poly Acrylonitrile (PAN) and hydroximated nano-poly Acrylonitrile (HPAN) particles prepared by precipitation polymerization technique. The effect of the process variables including contact time, pH, initial dye concentration and temperature on the adsorption characters for PAN and HPAN was studied. The removal percentage varied from 100% to 60% with MB concentration ranged from 5 to 50 ppm. A significant difference was observed at 15–20 ppm where the removal percentage was found 70% and 90% for PAN and HPAN, respectively. No significant effect was observed of variation adsorption temperature from 30°C to 70°C or pH variation from 5 to 9. On the other hand, the polymerization and hydroximation processes of Acrylonitrile were studied. The conversion yield (%) was affected significantly by initiator concentration and polymerization temperature and varied from 2% to 80%. Particle size increased from 130 to 210 nm as a result of hydroximation process. Additional proves for occurrence of hydroximation process was obtained from thermo gravimetric analysis (TGA) and infrared spectrometer analysis (FT-IR). Irregular shape of polymer particles was indicated by scanning electron microscope (SEM) photographs.

*Keywords:* Nano-polyacrylonitrile; Precipitation polymerization; Dye removal; Adsorption; Methylene blue; Polymer functionalization

### 1. Introduction

The effluents from textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are important sources of dye pollution [1]. The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [2]. Mankind has used dyes for thousands of years [3]

and the earliest known use of a colorant is believed to be by Neanderthal man about 180,000 yr ago. However, the first known use of an organic colorant was much later, being nearly 4000 y ago, when the blue dye indigo was found in the wrappings of mummies in Egyptian tombs [4]. Till the late nineteenth century, all the dyes/ colorants were more or less natural with main sources like plants, insects and mollusks were generally prepared on small scale. It was only after 1856 that with Perkin's historic discovery [5] of the first synthetic dye,

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mauveine, that dyes were manufactured synthetically and on a large scale. However, wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents [6,7]. During the past three decades, several physical, chemical and biological decolorization methods have been reported; few, however, have been accepted by the paper and textile industries. Amongst the numerous techniques of dye removal, adsorption using different adsorbents is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials [8–10]. PAN fibers known with their dye ability towards cationic (basic) dyes [11–13]. S. Rosenbaum studied dyeing of PAN with cationic dye (Malachite Green) [11,12] and monitoring the diffusion rates and models. T.M.A. Hossain et al. [13] reviewed the diffusion of cationic dyes into PAN. Recently, D. Şuteu et al. [14] presents new results about efficiency of wastes based on hydrolyzed Poly Acrylonitrile textile fibers (HPAN) as sorbents in removal of some dyes from textile effluents. The effect of some experimental variables such as initial dye concentration, sorbent mass, pH, temperature, and contact time were investigated. The sorbent–dye sorption systems are described using Freundlich, Langmuir and Dubinin-Radushkevich isotherm models. The laboratory experimental results performed using the textile fibres wastes indicate the good removal of dyes from aqueous medium, suggesting that these textile solid wastes correspond to the actual tendency of using non-conventional sorbent materials to reduce the overall cost of sorbent preparation. The surface area of the adsorbent materials is a determined factor. Nano adsorbents with high surface area are the optimum choice to have efficient adsorption process. Nano PAN particles have been prepared using different techniques [15–18]. L. Boguslavsky et al. [15] prepared PAN nanoparticles in sizes ranging from approximately 35–270 nm by dispersion/emulsion polymerization of acrylonitrile in a continuous aqueous phase in the presence of potassium persulfate as initiator and various alkyl-sulfate and sulfonate surfactants. T. Biswal et al. [16] synthesis PAN nanoparticles under the catalytic effect of in situ developed Co (II)/EDTA complex with ammonium persulphate as initiator, in the absence of emulsifier. Later on the same authors developed the process under simple microwave conditions [18]. Jung-Min Lee et al. prepared poly(acrylonitrile-co-itaconic acid-co-methylacrylate) nanoparticles by aqueous dispersion polymerization using hydrophilic PVA in a water/N,N-dimethylformamide mixture media.

The aim of this article is to remove MB from synthetic dye solution using nano polyacrylonitrile particles and nano PAN particles functionalized with

oximic groups. The article presents an advantage of using emulsifier free polymerization system. The conditions of polymerization and amidooximation processes were optimized and the formation hydroxymated polymer was verified through FT-IR, TGA, SEM and PSA analysis.

## 2. Material and methods

### 2.1. Materials

Chemicals for polymerization process; Potassium persulfate extra pure (KPS) from (LOBA Chemie), Acrylonitrile 99% (AN) from Aldrich, Germany and Ethanol absolute from Adwic, Egypt were perused.

For hydroximation process of nano PAN Hydroxylamine hydrochloride (H.A) and Sodium hydroxide from Adwic, Egypt were perused.

Finally, MB from Aldrich, Germany was used in preparation of synthetic dye solution.

### 2.2. Preparation of basic dye solution

MB, C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl<sub>3</sub>H<sub>2</sub>O, stock dye solution was prepared by dissolving 0.01 g of MB in 1000 ml distilled water. The dye concentration in the supernatant and residual solutions was determined by measuring their absorbance in 1 cm light-path cell at Max wave length 660 nm using spectrophotometer (Jenway 6305).

### 2.3. Preparation of poly acrylonitrile nanoparticles

In reaction vessel, 50 ml volume, a predetermined weight of KPS was dissolved first in Water: Ethanol equal mixture to have 0.1% concentration, then selected volume of AN was added to have 8% final concentration. The whole mixture was stirred well to have a homogenous solution. The polymerization vessel was thermo-incubated at 65°C temperature and the polymerization reaction was conducted for 4 h. After completion the polymerization time, the PAN was collected after successive washing with Water: Ethanol equal solution to remove un-reacted AN after centrifugation at 14,000 rpm for 30 min using ultra speed centrifuge. The formed polymer was then dried at 80°C for 24 h before weighted. The degree of monomer conversion to polymer was calculated according to the following formula:

$$\text{Conversion (\%)} = \left[ \frac{W_1}{W_0} \right] \times 100 \quad (1)$$

where  $W_0$  is the weight of AN monomer and  $W_1$  is the weight of PAN.

#### 2.4. Poly acrylonitrile amidooximation

To have amidooxime functionalized PAN, 1 g of PAN was reacted with 50 ml of 2% HA at 50°C for 4 h. After completion of the functionalization reaction time, the HPAN was filtered and washed with distilled water to remove un-reacted HA, then treated with 1% NaOH solution at room temperature for 1 h. The modified polymer was then successively washed with distilled water to remove excess of sodium hydroxide and finally dried at 80°C for 24 h before used in the MB adsorption experiments.

#### 2.5. Batch MB adsorption experiments

Definite weight of PAN or HPAN (0.2 g) was mixed with 50 ml of MB dye of definite concentration at 200 rpm. The adsorption experiments were conducted at selected pH and temperature for selected time.

The dye removal percent was calculated according to the following formula:

$$\text{Removal (\%)} = \left( \frac{C_0 - C}{C_0} \right) \times 100 \quad (2)$$

where  $C_0$  and  $C$  (both in  $\text{mg l}^{-1}$ ), are the initial concentration and the concentration at any time, respectively.

#### 2.6. Ion exchange capacity

The ion exchange capacity (IEC) of HPAN particles was determined using acid–base titration. Weighed samples were immersed in 20  $\text{cm}^3$  of a 2 M NaCl solution for at least 12 h at R.T. The solution was then titrated with a NaOH solution of known concentration. IEC was calculated as follows:

$$\text{IEC (m eq}^{-1}\text{)} = \frac{n \text{ (mm d)}}{(\text{cm}^3)} \times \frac{v \text{ (cm}^3\text{)}}{w \text{ (gm)}} \quad (3)$$

where  $n$ ,  $v$ , and  $w$  are the concentration of the NaOH solution, the volume of the NaOH solution, and the weight of the sample, respectively [19].

#### 2.7. SEM morphology examination

Morphology characterization of the synthesized PAN and HPAN nanoparticles adsorbent was carried out by SEM (JEOL JSM 6360LA, Japan).

#### 2.8. Particle size analysis

Particle size distribution was performed using Sub-micron Particle Size Analyzer (Beckman Coulter—USA) through dispersed polymer sample in water, at a temperature 20°C, of viscosity 1.002 cP and refractive index 1.33.

### 3. Results and discussion

#### 3.1. Characterization of adsorbing materials

The amidooximation of PAN nano-particles has been verified using FT-IR and TGA analysis. Morphology characters and particle size of both types of particles, PAN and HPAN, have been examined and the results are mentioned below.

##### 3.1.1. Fourier transforms infrared spectroscopy (FT-IR)

The FT-IR spectrum of PAN (Fig. 1A), modified PAN with 1% HA (Fig. 1B) and 5% HA (Fig. 1C), respectively were measured using Fourier Transform Infrared Spectrophotometer (Jasco-4100). The pattern of PAN shows a broad band at 3527  $\text{cm}^{-1}$  for (O-H) water. Also there is band at 2245  $\text{cm}^{-1}$  attributed to (C≡N), band at 1709  $\text{cm}^{-1}$  for (C=C) and band at 2936  $\text{cm}^{-1}$  for (C-H).

Modified Polymer (B) pattern shows significant broad band corresponding to (NH<sub>2</sub>) groups at 3537.7  $\text{cm}^{-1}$  and there is also band at 1626  $\text{cm}^{-1}$  corresponding to (C=N) bond due to reaction with hydroxyl amine. Also there is a band at 2245  $\text{cm}^{-1}$  attributed to (C≡N) with intensity less than native polymer (A) which indicates of incomplete conversion of Nitrile groups into oximic ones. At 2936  $\text{cm}^{-1}$  there is a band corresponding to (C-H) with less intensity than native polymer (A).

As a result of higher modification degree, polymer (C) shows a broad band at 3442  $\text{cm}^{-1}$  assigned to formation of more (NH<sub>2</sub>) with higher intensity than (B), an absorption band at 1629  $\text{cm}^{-1}$  (C=N) with intensity higher than (B) and an absorption band at 2245  $\text{cm}^{-1}$  (C≡N) was appeared with less intensity than (B) due to reaction of more (C≡N) groups with hydroxyl amine.

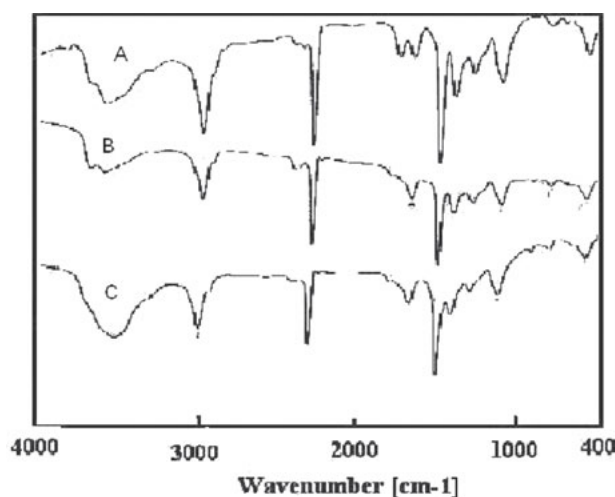


Fig. 1. FT-IR spectra of PAN (a), HPAN obtained with 1% HA (b) and HPAN obtained with 5% HA (c).

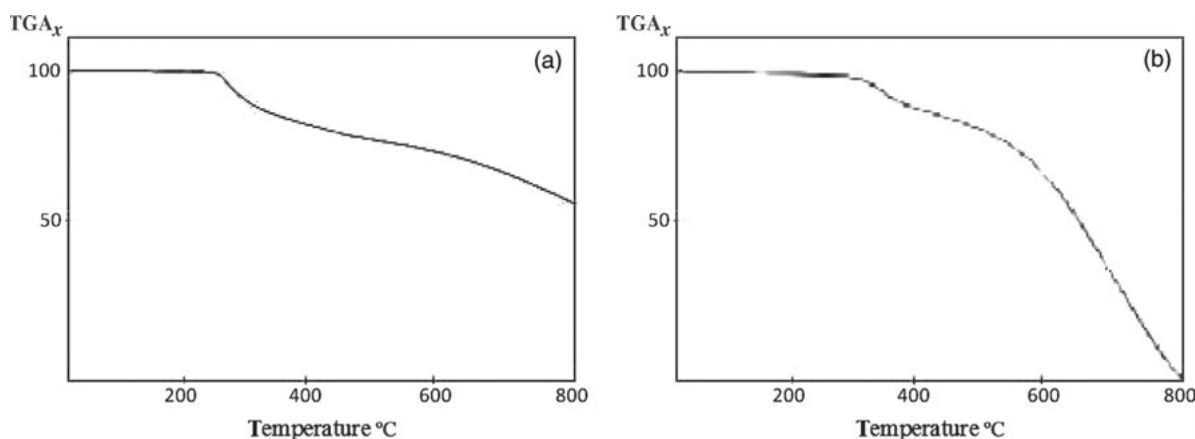


Fig. 2. Thermo-gravimetric patterns for PAN (a) and HPAN (b).

### 3.1.2. Thermo gravimetric analysis

The thermal stability of the PAN (Fig. 2A) and HPAN (Fig. 2B) was evaluated by Thermo Gravimetric Analyzer TGA-50 Shimadzu. TGA curve (a) of PAN shows the main step began at 196.46°C and end at 287.85°C with weight loss 7.836% and another step began at 287.85°C and end at 799.73°C with weight loss 40.193%. Curve (b) shows the TGA pattern of HPAN which contained two main steps. The first step began at 167.78°C and ended at 363.98°C with weight loss 10.76%, second degradation step starts at 364.31°C and end 799.06°C with weight loss 85.474%. The double weight loss at 800°C of HPAN indicates the acquired hydrophilic nature which is a result of Nitrile groups' conversion into oximic ones.

### 3.1.3. SEM morphology examination

Examination of morphology structure of PAN and HPAN nanoparticles with different Amidooximation functionalization degree is presented in Fig. 3. From inspection the figure it is clear that PAN nanoparticles has irregular structure. Amidooximation treatment results in kind of changes the structure to rod like. The effect is clearer with samples treated with 5% HA. This is an indication of possible coagulation of PAN with increase of their hydrophilicity through amidoxime groups induced into its structure.

### 3.1.4. Particle size analysis (PSA)

Analysis of PAN particles size show that amidooximation reaction has a positive effect on enlarge the size of the particles from 130 nm to about 200 nm with samples reacted with 5% HA (Table 1). This result is in agreements with observations from SEM photographs. The presence of a new amidoxime groups in the structure of PAN increase the distance between the polymers chains especially with alternation of matrix to charged one.

## 3.2. Preparation of poly acrylonitrile (PAN)

### 3.2.1. Effect of monomer concentration

The effect of variation monomer concentration on the conversion yield percentage and MB removal percentage was investigated in Fig. 4. The conversion yield (%) was found to increase with monomer concentration increase until reach a maximum value (48%) at 10% monomer concentration. Further increase of AN concentration to 12% has no effect on the conversion yield (%). The obtained results are in agreement with previous published results [20]. This behavior may attribute to the limitation of produced free radicals from initiator thermal decomposing. The MB removal percentage of PAN and HPAN was also investigated as show in Fig. 4. In general, the removal percentage was found follow the same behavior as conversion yield where increases with polymers prepared using 2–6% monomer concentration. Using further higher concentration of monomer has no effect on the removal percentage. At the same time, the HPAN has higher removal percentage. This may be due to the extra exchange sites produced onto polymers particles generated from oximic groups. Table 2 summarized the IEC which confirming our explanation. The adsorption character of PAN has been refereed to some exchange sites introduced during the polymerization process by persulfate [13].

### 3.2.2. Effect of initiator concentration

Fig. 5 illustrates the effect of variation initiator concentration on the conversion yield (%) and MB removal percentage. The conversion yield (%) was found to increase from 2.8% to 79.4% with increase potassium persulfate concentration from 0.02% to 0.4%. This is expected behavior due to increase the number of produced free radicals. The adsorption capacity of produced polymers has been evaluated. From the figure, it is clear that moderate effect of variation the used initiator concentration



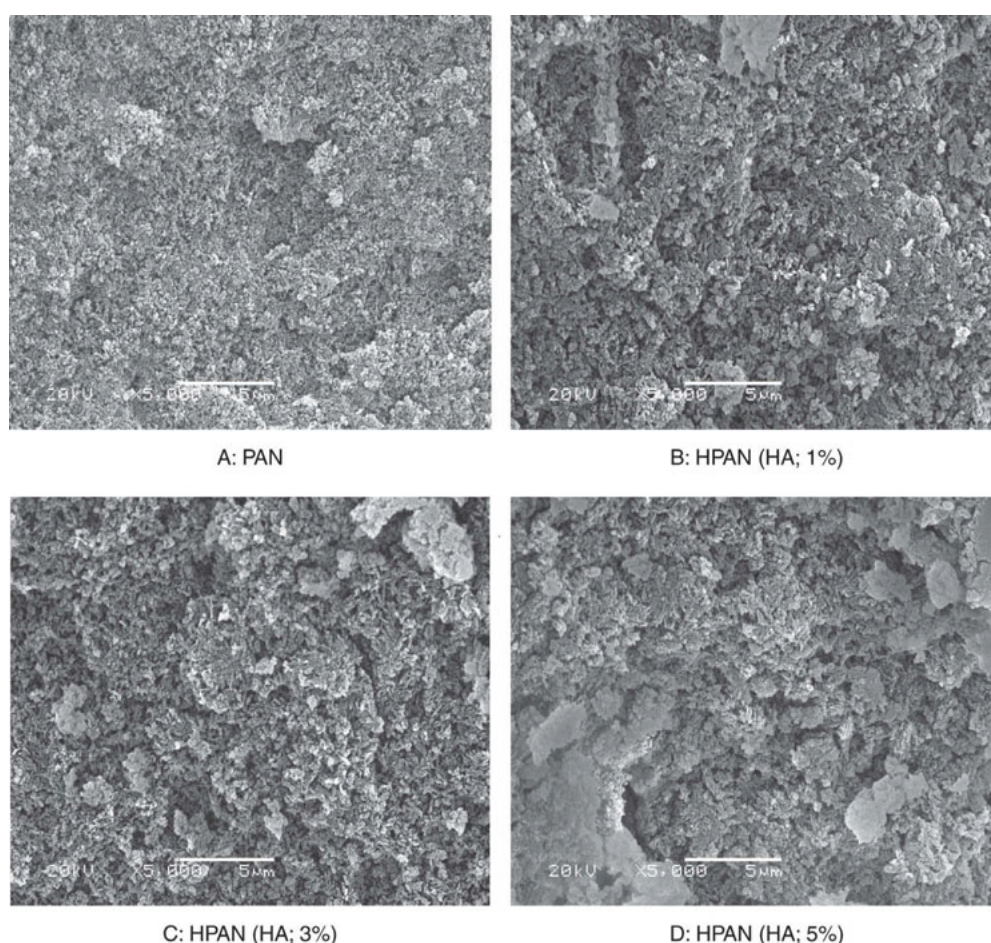


Fig. 3. SEM photographs of polymer particles (a) PAN, (b) HPAN; HA 1%, (c) HPAN; HA 3%, (d) HPAN; HA 5%.

Table 1  
Effect of amidooximation process on particle size

HA (%)	0	1	3	5
PS (nm)	51	129	195	208

Table 2  
Effect of monomer concentration on IEC of HPAN

AN (v/v%)	IEC (meq g <sup>-1</sup> )
4	0.05
6	0.07
8	0.09
10	0.09
12	0.09

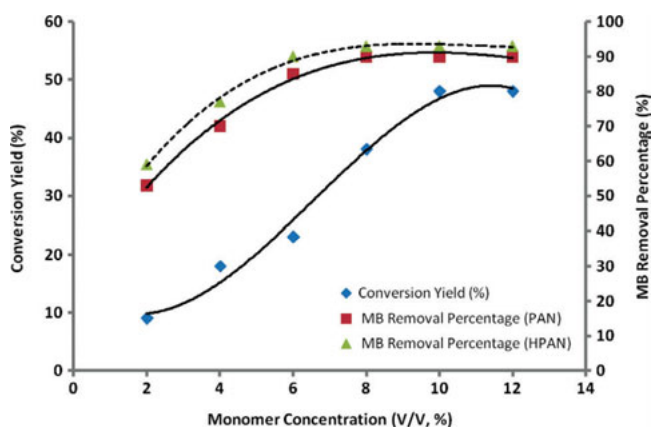


Fig. 4. Effect of monomer concentration on the conversion yield (%) and MB removal percentage (%).

on MB removal percentage was observed. HPAN as usual has a slightly higher MB removal percentage due to presence of oximic charged groups. Table 3 shows the IEC of HPAN which reinforces our explanation.

### 3.2.3. Effect of polymerization time

Fig. 6 shows the effect of variation polymerization time on conversion yield (%) and MB removal percentage of PAN and HPAN. It could be observed from the figure that the conversion yield (%) increased as

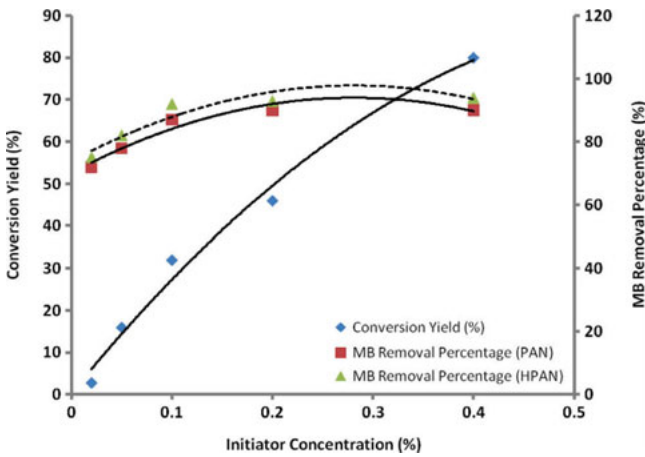


Fig. 5. Effect of initiator concentration on the conversion yield (%) and MB removal percentage.

Table 3  
Effect of initiator concentration on IEC of HPAN

Initiator (%)	IEC (meq g <sup>-1</sup> )
0.05	0.07
0.1	0.09
0.2	0.1
0.4	0.12

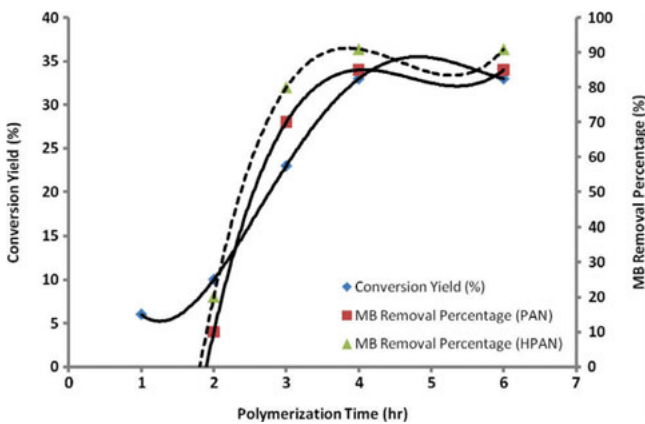


Fig. 6. Effect of polymerization time on conversion yield (%) and MB removal percentage (%).

polymerization time increases from 1 to 4 h; 5.7–33%. Further increase of polymerization time has no effect although more than 65% of monomer is still available. This may be due to adsorption of free radicals formed on the precipitated PAN particles which leads to higher termination step rate over the rate of polymerization step. This result is in agreement with other published

Table 4  
Effect of polymerization time on IEC of HPAN

Time (h)	IEC (meq g <sup>-1</sup> )
2	0.03
3	0.05
4	0.09
6	0.09

results [21]. The same effect of polymerization time on MB removal percentage of PAN and HPAN was found. Again, MB removal percentage of HPAN is higher than that of PAN. Table 4 presents the IEC of HPAN which explains the adsorption behavior.

### 3.2.4. Effect of polymerization temperature

Fig. 7 illustrates the effect of variation polymerization temperature on the conversion yield (%) and MB removal percentage (%) of PAN and HPAN. The extent of conversion was found to increase from 3.7% to 80.64% with temperature increase from 55°C to 75°C. This behavior is referred to increase the dissociation rate of initiator. Further increase of temperature to 85°C has no effect. This is may be due to dissociate all the available initiator so no further free radicals could be generated over raising temperature. The variation of polymerization temperature has a slight significant effect on MB removal percentage of both PAN and HPAN. The MB (%) removal increased from 82% to 90% for PAN and from 84% to 92% for HPAN. The small variation of IEC of HPAN may explain this behavior; Table 5.

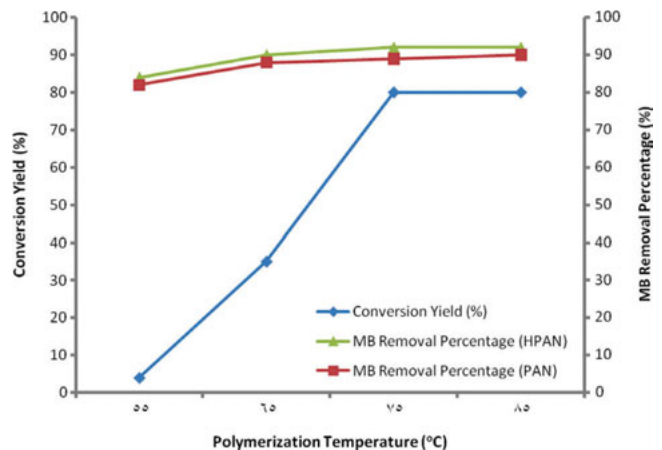


Fig. 7. Effect of polymerization temperature on conversion yield (%) and MB removal percentage (%).

Table 5  
Effect of polymerization temperature on IEC of HPAN

Temperature (°C)	IEC (meq g <sup>-1</sup> )
55	0.05
65	0.07
75	0.09
85	0.09

### 3.2.5. Effect of polymerization solvent composition

Fig. 8 demonstrates the effect of variation polymerization solvent composition on conversion yield (%) and MB removal percentage (%) of PAN and HPAN. The extent of conversion was found to decrease continuously with increase the ethanol volume from 25% to 75%. This may be explained by the insolubility of the initiator in Ethanol which leads to decrease the availability of initiator in the polymerization medium and consequently reduce the rate of polymerization although AN is soluble in Ethanol.

MB removal percentage was found correlated to the behavior of conversion yield (%). MB removal percentage of HPAN is higher than that of PAN. The variation of IEC for HPAN may explain this behavior (Table 6).

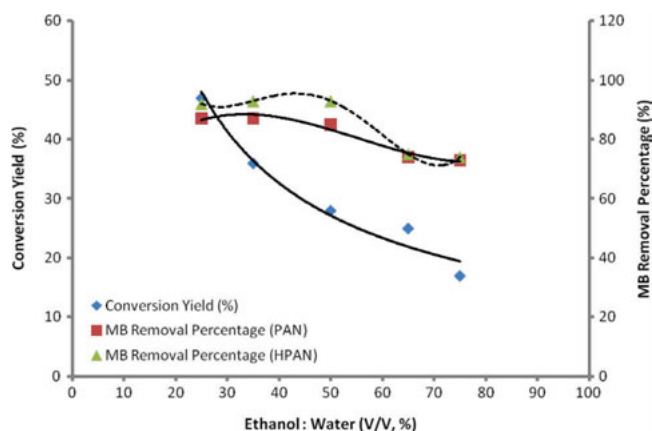


Fig. 8. Effect of polymerization solvent composition on conversion yield (%) and MB removal percentage (%).

Table 6  
Effect of polymerization solvent composition on IEC of HPAN

Ethanol (%)	IEC (meq g <sup>-1</sup> )
25	0.09
33.3	0.09
50	0.09
66.6	0.07
75	0.05

### 3.3. Functionalization of poly acrylonitrile

#### 3.3.1. Effect of HA concentration

Fig. 9 illustrates the effect of variation HA concentration on MB removal percentage and IEC of HPAN. From the figure it is clear that with variation of HA concentration from 1% to 5% the MB removal percentage was increased almost linearly from 80% to about 100%. This behavior explained by progressive formation of more oximic exchangeable sites on the expense of Nitrile groups of PAN surface and pores interiors as a result of increase of concentration gradient between the aqueous phase and polymer phase as proved by variation of IEC.

#### 3.3.2. Effect of amidooximation time

The effect of variation functionalization time with HA on MB removal percentage and IEC of HPAN was investigated as shown in Fig. 10. The MB removal

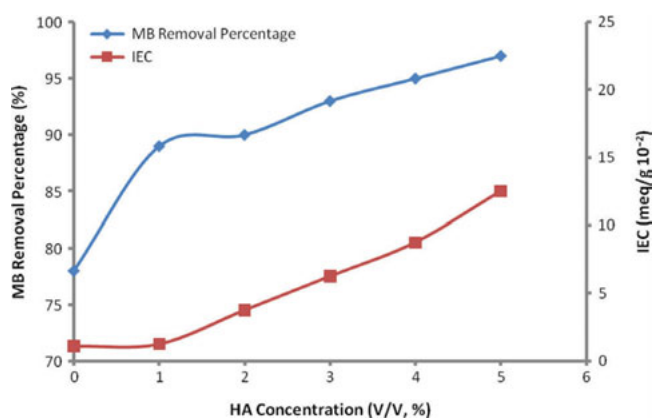


Fig. 9. Effect of HA concentration on MB removal percentage (%) and IEC of HPAN.

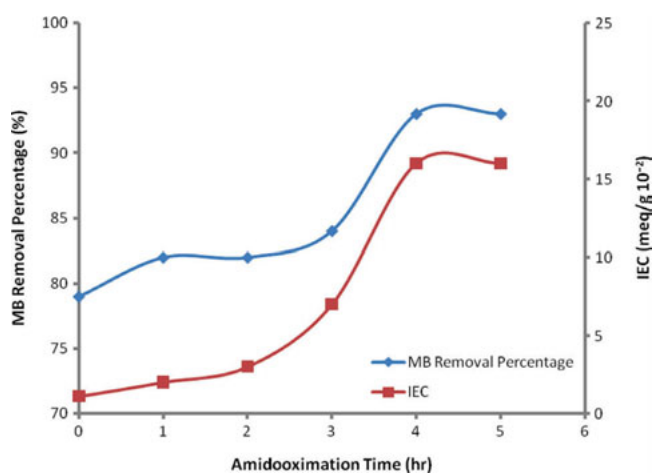


Fig. 10. Effect of amidooximation time on MB removal percentage (%) and IEC of HPAN.



percentage was found to increase from 80% to 95% with increase reaction time up to 5 h with HA to reach maximum after 4 h. Further increase of the reaction time above 4 h has no significant effect. This result is strongly correlates with the IEC values which shows the same behavior.

### 3.3.3. Effect of the amidooximation temperature

The effect of variation functionalization temperature on the MB removal percentage and IEC of HPAN was investigated as shown in Fig. 11. No significant increase of the MB removal percentage was observed with variation temperature from 30°C to 70°C although the IEC has been varied significantly. This may be explained by the limitation of MB which more than 90% has been removed by HPAN samples prepared with 30°C.

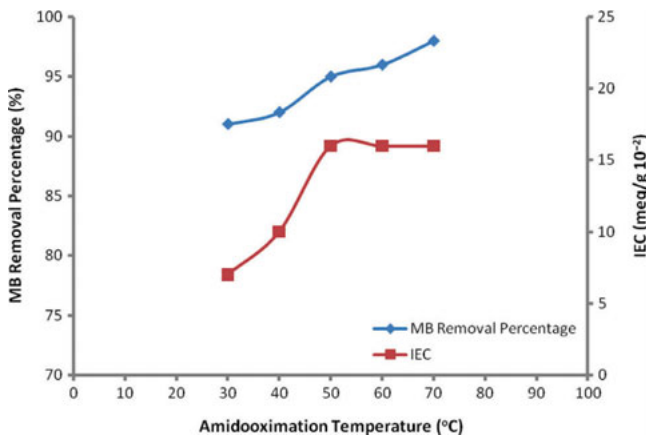


Fig. 11. Effect of amidooximation temperature on MB removal percentage.

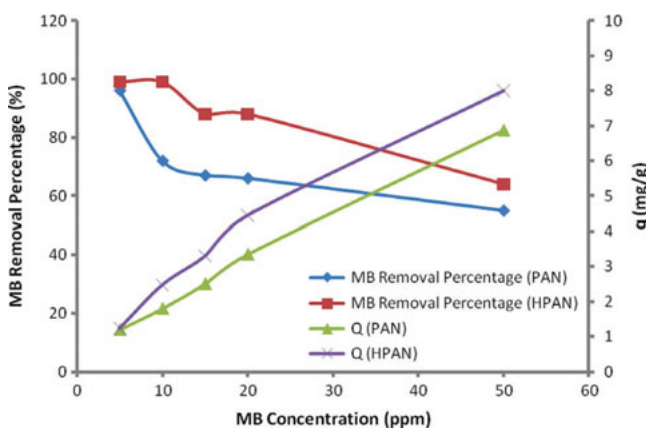


Fig. 12. Effect of initial dye concentration on MB removal percentage and adsorption capacity ( $Q_e$ ).

## 3.4. Batch absorption experiments

### 3.4.1. Effect of MB concentration

It is observed from Fig. 12 that the MB removal percentage is inversely proportional to the initial dye solution concentration. The MB removal percentage decreases from 96% to 56% on increasing the initial dye concentration from 5 to 50 ppm for PAN and from 98% to 64% for HPAN. This may be attributed to the increase of dye molecules adsorption onto the external surface, increases significantly the local dye concentration, giving rise to the formation of aggregates of the dye on the polymers particles which consequently reduce the concentration gradient, the driving force for dye adsorption. On the hand, the adsorption capacity of PAN and HPAN increase linearly with MB concentration. The capacity of HPAN is higher than that of PAN. The significant difference between PAN and HPAN particles appeared in MB concentration ranged between 15 and 20 ppm. This result is in agreement with other published results [22,23].

### 3.4.2. Effect of contact time

The effect of variation contact time on MB removal percentage was investigated as shown in Fig. 13. From the figure it can be seen that the MB removal percentage of HPAN has been slightly affected by increasing contact time over 15 min. Very fast equilibrium has been achieved due to large amount of available exchange sites. For PAN, the removal percentage increases from 60% to 86% with increase time from 5 to 30 min. Beyond 30 min adsorption time, slight increase of removal percentage was observed. This behavior may be referred to the reduction of the concentration gradient between the liquid phase and the adsorbent surface [23].

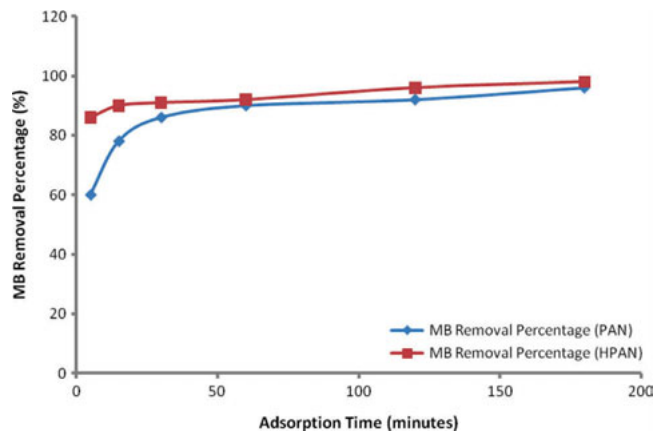


Fig. 13. Effect of contact time on MB removal percentage (%) of PAN and HPAN.



### 3.4.3. Effect of adsorption temperature

Fig. 14 shows the effect of variation adsorption temperature over wide range, from 30°C to 70°C, on the MB removal percentage for both polymers. Slight decrease of removal percentage has been observed. The obtained results are considered an advantage since the process of dye removal does not need any additional heating and or other extra cost. This behavior may be referred to acceleration effect of temperature on the adsorption of dye molecules on the surface of both PAN and HPAN particles. This fast initial step reduces the concentration gradient between the liquid phase and the solid surface phase of the particles. Limiting the MB concentration and high concentration of exchange sites over the particles surface contributes significantly to obtain this behavior. The absence of pore diffusion process also eliminates the effect of temperature.

### 3.4.4. Effect of adsorption pH

The effect of variation pH of the dye solution on the MB removal percentage was studied by varying the initial pH under constant process parameters as shown in Fig. 15. The removal percentage after an adsorption period of 60 min was increased from 84% to 93% between pH values 5–9 for PAN and from 90% to 96% for HPAN. The lower adsorption of MB at acidic pH could be attributed to the presence of excess H<sup>+</sup> ions that competed with the dye cation for adsorption sites. As the pH of the system increased (pH > 7), the number of positively charged available sites decreased while the number of the negatively charged sites increased. The negatively charged sites favored the adsorption of dye cation due to electrostatic attraction. The obtained result is in agreements with other published results [24].

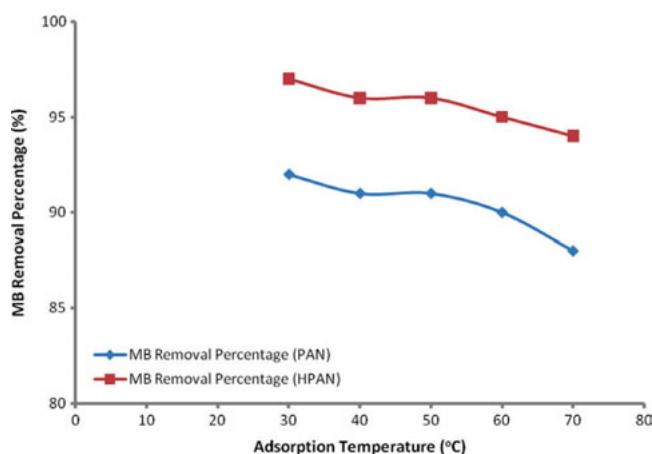


Fig. 14. Effect of adsorption temperature on MB removal percentage (%).

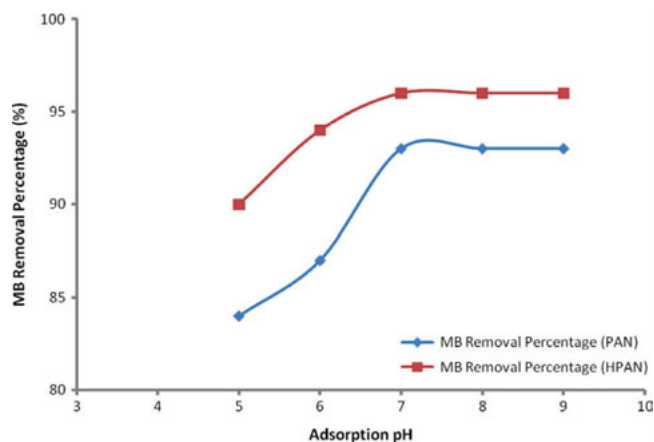


Fig. 15. Effect of adsorption pH on MB removal percentage (%) of PAN and HPAN.

## 4. Conclusions

Nano PAN polymer has been prepared by precipitation polymerization technique. PAN has been functionalized with hydro-oximic groups (HPAN) using reaction with hydroxyl amine hydrochloride. The particle size of the polymer was affected by the functionalization process where increased from 130 up to 210 nm. Both polymers, PAN and HPAN, were tested in removal of MB from aqueous solution. Study the effect of some process variables including contact time, pH, initial dye concentration and temperature on the adsorption process were carried out. Only initial dye concentration shows a determining effect. 30 min of contact time at pH range from 5 to 9 was found enough to remove over 90% of 10 ppm MB at room temperature. HPAN shows advantages over PAN in adsorption of high MB concentration with higher rate of adsorption.

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