Int. J. Electrochem. Sci., 8 **(2013)** 5121 - 5135

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Preparation and Characterization of Iminated Polyacrylonitrile for the Removal of Methylene Blue from Aqueous Solutions

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Received: 23 December 2012 / *Accepted:* 4 March 2013 / *Published:* 1 April 2013

Acrylonitrile (AN) was homopolymerized to polyacrylonitrile (PAN) using potassium persulphate as an initiator. The cyano groups of AN chains were iminated through treating AN with polyethyleneimine (PEI) in an aqueous solution. Iminated polyacrylonitrile (IPAN), characterized by chemical analysis, fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA) studies, was used as an adsorbent for the removal of Methylene Blue (MB) dye from its aqueous solutions. All factors affecting the adsorption of MB onto the adsorbent IPAN, like agitation duration, temperature, adsorbent dose and the initial concentration of dye solution were extensively studied. Two adsorption isotherm models, namely Langmuir model and Freundlich model were applied to the adsorption data. The adsorption data fitted well to both models. The Langmuir adsorption capacity (Q_o) was found to be 54 mg/g. Freundlish constants, K_F and n, were found to be 1.459 and 1.7, respectively. The results of the desorption study show that 92% of the adsorbed dye could be desorbed when shaking the dye-loaded adsorbent with distilled water for three hours at 40°C.

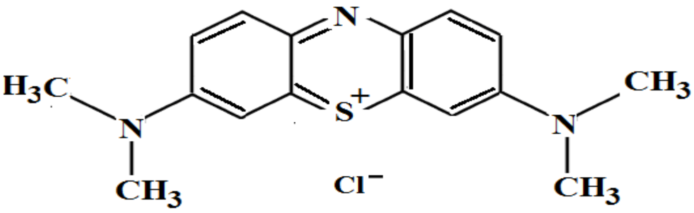
Keywords: Polyacrylonitrile, Polyethyleneimine; Methylene Blue, Adsorption, Dye removal, polymer, water treatment

1. INTRODUCTION

There has been an increase in effluents being disposed to natural water resources due to rapid industrialization. Major contaminants found in wastewater include biodegradable, volatile and recalcitrant organic compounds, toxic metals, suspended solids, plant nutrients, dyes, microbial pathogens and parasites [1-4]. Dyes are widely used in various industrial applications to impart color in several products like textiles, paper, plastics, leather, and so on. The main problem in discharging dyes to the water resources is that dyes which remain in waste effluents undergo chemical changes, consume dissolved oxygen, and destroy aquatic creatures. Moreover, the contamination of water with such dyes may cause suspected carcinogenic and genotoxic effects. However, the treatment of wastewaters contaminated with dyes via biological processes is very difficult and ineffective due to the large number of aromatic rings present in the dye molecules, which are very difficult to degrade to simpler compounds. Color is a characteristic effluent, which is easily detected and readily traced back to its source. Some dyes are stable to biological degradation and consequently, there is considerable need to treat colored effluents prior to their discharge into receiving waters [5-9]. The removal of such compounds at such low levels is a difficult problem. Physicochemical techniques such as coagulation [10], flocculation [11], ozonation [12], reverse osmosis [13] and adsorption on activated carbon, manganese oxide, silica gel and clays are among the methods employed [14-20]. Adsorption of dyes and heavy metals at the solid/liquid interface has been extensively studied during the last years [21-29]. One reason for this interest is the importance of adsorption on solid surfaces in many industrial applications in order to improve efficiency and economy. Adsorption techniques have proven success in removing colored organic species with activated carbon being the most widely used adsorbent due to its high capacity for the adsorption of organic materials [30-33].

PEI, a highly branched aliphatic polyamine, which is characterized by the repeating chemical unit denoted as $-(CH_2-CH_2-NH)-$. PEI is manufactured by the acid-catalyzed ring opening homopolymerization of ethyleneimine (or aziridine) monomer. The amine groups in PEI exist in primary, secondary and tertiary forms in the approximate ratio of 1:2:1 [34] with a branching site every 3–3.5 nitrogen atoms along any given chain segment. PEIs function as weak Lewis bases in aqueous environments. As the molecular weight of PEI increases, the polymer coils in solution and assumes a Gaussian conformation. This implies that there are charged nitrogen groups both on the surface and in the sterically protected interior of the molecule. It has been demonstrated in empirical studies that the attachment of the highly charged PEI molecule to anionic surfaces results in a near monolayer of polymer at the interface. In aqueous solution PEI exhibits a strong affinity to anionic materials such as polyanions and negatively charged organic and inorganic solids. PEIs are highly soluble in most polar materials including water, alcohols, glycols and certain organic solvents. The most prominent feature of PEI is its extremely high cationic charge density [35]. Therefore, PEI is widely used, for example, as an excellent brightener and retention aid for low-toxicity for paper [36], dispersant for toner compositions, densifying agents which improves H-bonding ability of fibers [37], cationic coagulant for heavy metal sequestering from effluent stream [37], adhesion promoters for pretreatment of nonwoven cellulosic fibers for improved wet strength, corrosion inhibitor for acid cleaning of metal and a retention aid for inorganic salts. PEI is one of the earliest known cationic flocculants and is often used in industrial effluent treatment. The capacity of branched PEI to bind several heavy metal ions has been evaluated [34, 38]. Extensive studies have also been carried out on the use of water soluble complexing polymers including PEI in membrane filtration [39, 40], however, the effect of PEI on dyes removal has not been studied. No attempts have been made to optimize the efficacy of polyelectrolytes in enhancing dye removal by modifying PEI with varying functional groups [41]. PEI which contains a large number of primary, secondary and tertiary amine groups in a molecule, exhibited good sorption ability for heavy metals when they were adsorbed or crosslinked on the adsorbent surface [42, 43]. The long PEI chains can stretch in solution and provide more active sites for the sorption of adsorbates. Sun et al. reported that aerobic granules exhibited excellent performance on metal ions adsorption, and after grafting with PEI, the adsorption capacity of aerobic granules could be definitely enhanced [44-46].

In this study AN was homopolymerized using conventional chemical initiation system, namely potassium persulphate to PAN. The cyano groups of PAN were iminated via reacting the latter with PEI to get IPAN. The changes in chemical, physical and morphological structure due to imination reaction were studied through FTIR, TGA, and SEM characterizations. IPAN was used for the removal of a dye, MB from aqueous solutions. The relevant parameters that affect dye removal like, initial dye concentration, adsorbent dose, adsorption temperature and adsorption duration were extensively studied. MB (Scheme 1) was selected as a model compound in this study because it has wide application range, which includes coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock, medical purpose, etc.[47-51]



Scheme 1. Chemical structure of MB dye.

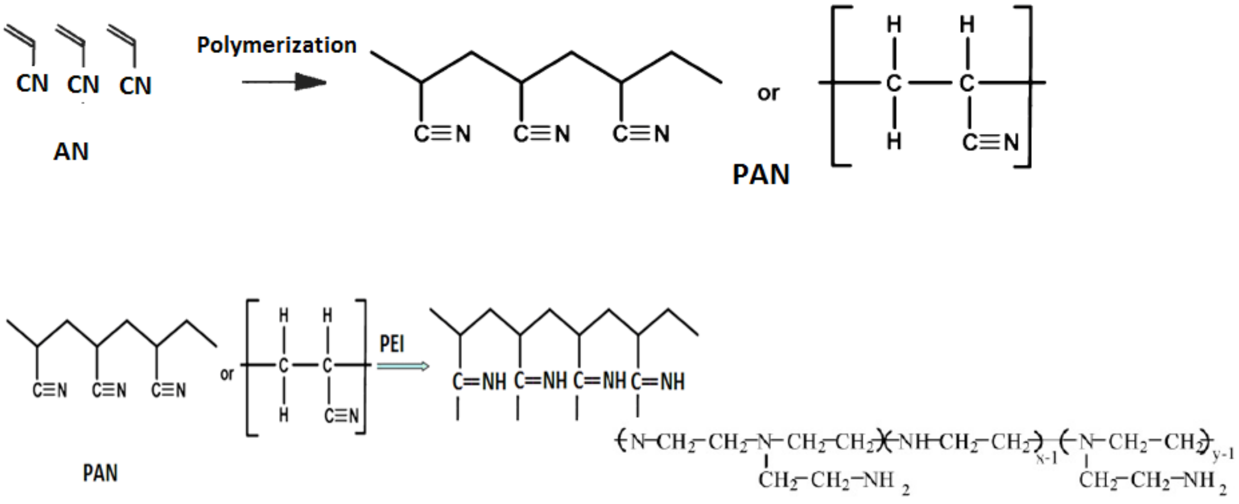
2. EXPERIMENTAL

2.1 Chemicals and materials

AN (99% purity) and potassium persulphate (purity = 99%) were supplied by BDH Chemicals Ltd (England). Absolute ethanol and PEI (99% purity) were supplied by Sigma-Aldrich Chemicals, Ltd. (Germany). MB was supplied by Techno Pharmchem (India). All other chemicals were laboratory grade reagents.

2.2 Preparation of PAN

AN was homopolymerized to PAN using potassium persulphate as an initiator. The polymerization reaction was carried out by dissolving 10% (v/v) AN in 0.01M potassium persulphate alcoholic solution (50/50 ethanol/water). The polymerzation process (Scheme 2) was conducted by stirring the polymerization solution in a thermostatic water bath at 55°C for 4 hrs. At the end of the predetermined reaction duration, PAN was separated from the polymerization liquor by filtration, washed repeatedly by 50/50 ethanol-water solution to get rid of unreacted monomer and initiator.



Scheme 2. Preparation and imination of PAN.

2.3 Imination of PAN

The cyano groups of PAN chains were iminated through treating PAN with 2% (v/v) PEI aqueous solution. The imination process (Scheme 2) was conducted by stirring PAN with PEI solution in a thermostatic water bath at 50°C for 3 hrs. At the end of the predetermined imination duration, IPAN was separated from the imination liquor by filtration, washed repeatedly by distilled water to get rid of unreacted PEI and finally dried for 24 hrs at 50°C.

2.4 Adsorption studies

The adsorbent was prepared by finely grounding the dried IPAN to pass through 200–400 mesh sieves. Stock solution of MB was prepared by dissolving 1.5 g of MB dye in certain volume of distilled water and then quantitatively transferring and diluting this solution to 1l in a volumetric flask to yield a solution containing 1500 mgL^{-1}. Definite volumes from the stock solution were properly diluted to obtain standard solutions of MB containing 50, 100, 200, 400, 600, 800, 900, 1000 mgL^{-1}Equal volumes (100 ml each) of the previously prepared dye solutions were placed in 125 ml Erlenmeyer flasks each of which containing 0.3 g of the adsorbent and the flasks were shaken at 40°C in a thermostatic water bath at 150 rpm for 3 hrs. At the end of agitation time, the dye solutions were separated from the adsorbent by filtration. Blank experiments were simultaneously carried out without the adsorbent and the extent of dye adsorption onto the IPAN was calculated mathematically by measuring the dye concentration in the blank and the exhausted solution spectrophotometrically.

2.5 Measurements and characterization

2.5.1 FTIR spectral analysis

The FTIR spectra of PAN and IPAN were recorded by means of Bruker, TENSOR Series FT-IR Spectrophotometer, Germany. Samples of 100 mg potassium bromide containing 2% of finely ground powder of each sample were prepared and subjected to analysis.

2.5.2 Scanning electron microscopy (SEM)

The surface morphology of PAN and IPAN were observed with SEM (JEOL GSM-6610LV) at an accelerated voltage of 25 kV. The fracture surfaces were vacuum-coated with gold for SEM.

2.5.3 Thermogravimetric analysis (TGA)

The thermal degradation behaviors of PAN and IPAN were studied with a thermogravimetric analyzer (TA Instruments, Q500 TGA, United States) in the temperature range from 20°C to 800°C under nitrogen at a flow rate of 40 ml/min and at a heating rate of 10°C/min.

2.5.4 Estimation of dye adsorbed onto IPAN

The estimation of the amount of dye adsorbed by the IPAN was carried out by using Perkin Elmer Lambda 35 UV/vis Spectrophotometer, USA at λ_{max} 665. A calibration curve was made by measuring the absorbance of properly prepared standard dye solutions having varying known concentrations. The concentration (mgL^{-1}) is linearly related to its absorbance value at the particular wavelength. By measuring the absorbance of the blank dye solutions and the exhausted dye solutions (after shaking with the adsorbent) and fitting them to the calibration curve, one gets the corresponding concentrations of these solutions.

3. RESULTS AND DISCUSSION

3.1 IR spectra

In this study, FTIR spectroscopy was used to prove the imination of PAN. This is done by recording and comparing the functional groups in the PAN structure before and after imination. Using this information, the modification mechanism of the cyano group of AN could be identified. The FTIR spectra of PAN and IPAN are shown in Fig. 1. It is clear from the spectra (curve A) that PAN exhibits strong absorption peak of a stretching vibration at 2241cm^{-1} (C≡N). This peak disappears completely in the spectra of IPAN (curve B). Another peak in curve b at 3641 and 1701 cm^{-1} were assigned to the flex vibration and bend vibration bands of the amine N–H group, respectively. This is in addition to the characteristics absorptions of bend vibration of C-N bond appearing at 1488 cm^{-1} and 1560 cm^{-1} and the C=N band at 1690 cm^{-1}. The appearance of these absorption bands shows clearly that PEI macromolecules have been introduced to the structure of PAN [52-53].

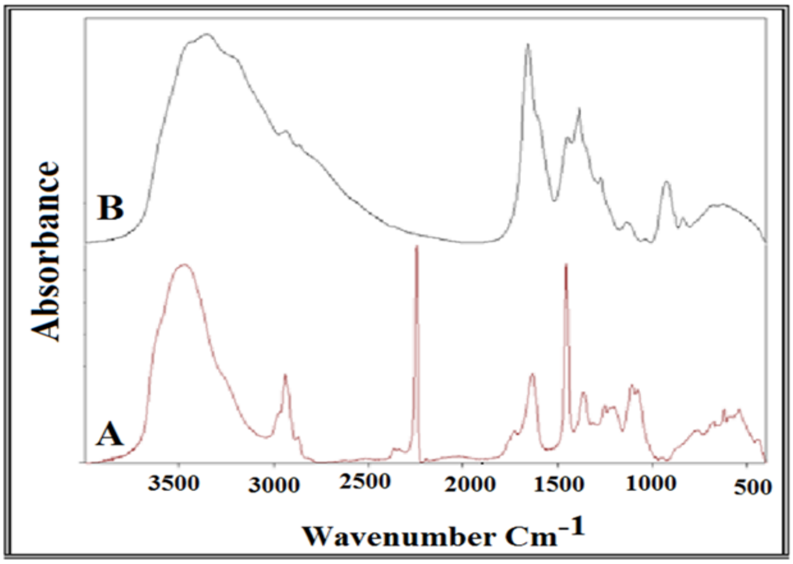


Figure 1. FTIR spectra of (A) PAN and (B) IPAN.

3.2 Scanning electron microscopy (SEM)

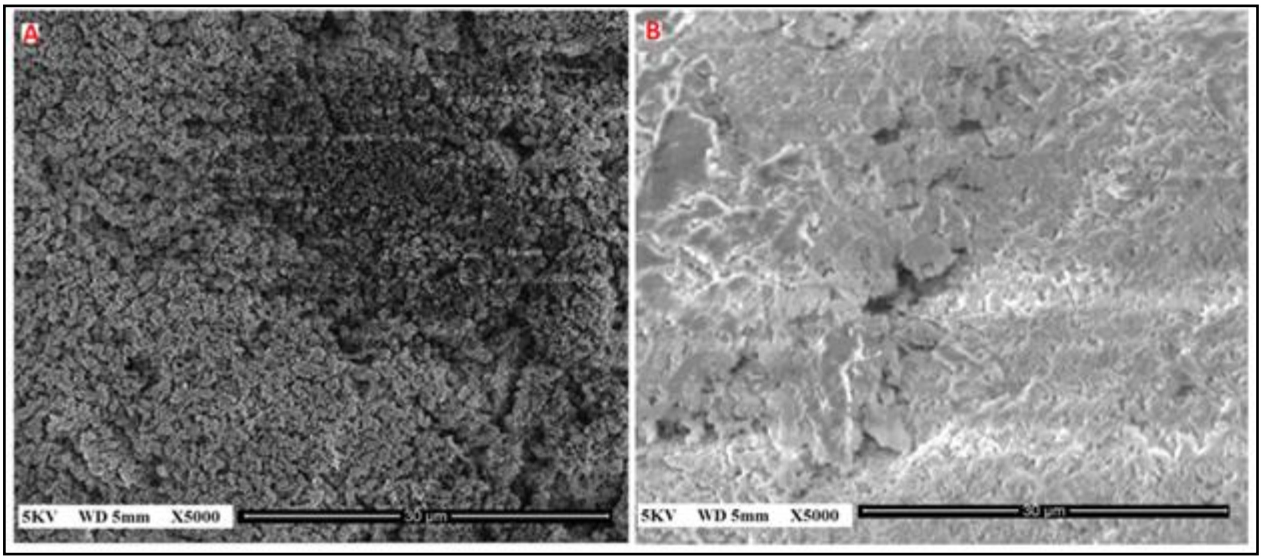


Figure 2. SEM micrographs of PAN (A) and IPAN (B).

For morphological characteristics changes due to imination, SEM of PAN (A) and IPAN (B) were carried out and micrographs are presented in Fig. 2. The SEM micrographs enable the direct observation of the changes in the surface microstructures and especially in the present study, SEM micrographs of PAN and IPAN reveal surface texture and porosity.

3.3 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) was used to analyze the thermal stability of IPAN compared to PAN. Thermal gravimetric analysis for PAN and IPAN was carried out by thermogravimetric analyzer in nitrogen atmosphere at a heating rate of 10°C/min. Fig. 3 shows the thermal degradation behavior of PAN (dashed line) and IPAN (solid line). The thermal degradation properties can be compared in terms of the T_{50}, which is the temperature needed for a substance to lose 50% of its original weight. It is clear from the two lines that T_{50} for IPAN is 785°C, while in case of PAN, the corresponding T_{50} value is 425°C, which implies that IPAN is thermally more stable than PAN.

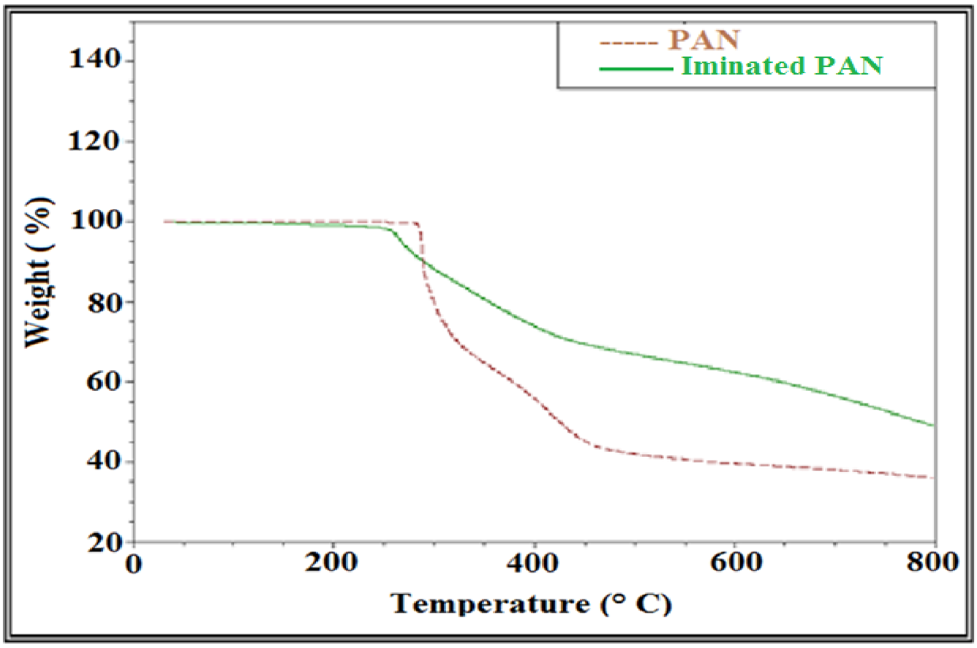


Figure 3. TGA thermographs of PAN (dashed line) and IPAN (solid line).

3.4 Adsorption studies

3.4.1 Effect of agitation time on MB removal

Fig. 4 shows the effect of agitation duration on MB percent removal due to adsorption onto IPAN. As shown in Fig. 4, the adsorption is quite rapid initially during the first 60 minutes. Nearly 66% of the ultimate adsorption occurred within 60 minutes of agitation, and then the adsorption slows down and then reaches the equilibrium. It is observed that the equilibrium is established within 120 minutes for a dye concentration of 150 mgL^{-1}. The curve is single and continuous indicating monolayer adsorption of MB onto the surface of IPAN. The uptake of dye molecules by the adsorbent, and the time required for establishment of equilibrium suggest the effectiveness of this material for wastewater treatment. The decrease in the amount of dye adsorbed with time more than 120 minutes may be due to aggregation of dye molecules around the adsorbent particles. This aggregation may hinder the migration of the dye, as the adsorption sites become saturated, and resistance to diffusion of dye molecules in the adsorbents increases.

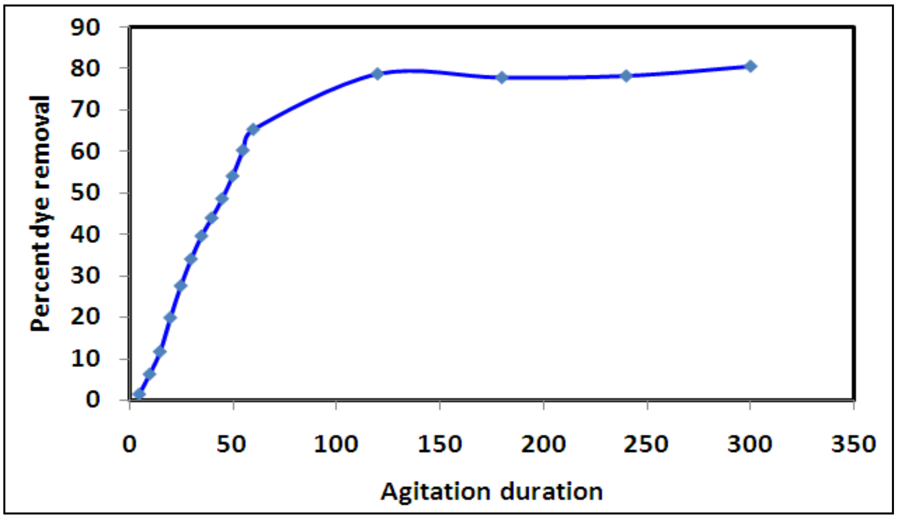


Figure 4. Effect of agitation duration on percent dye removal (0.3 g IPAN, pH 7, 40°C, 1500 mgL^{-1}).

3.4.2 Effect of Temperature

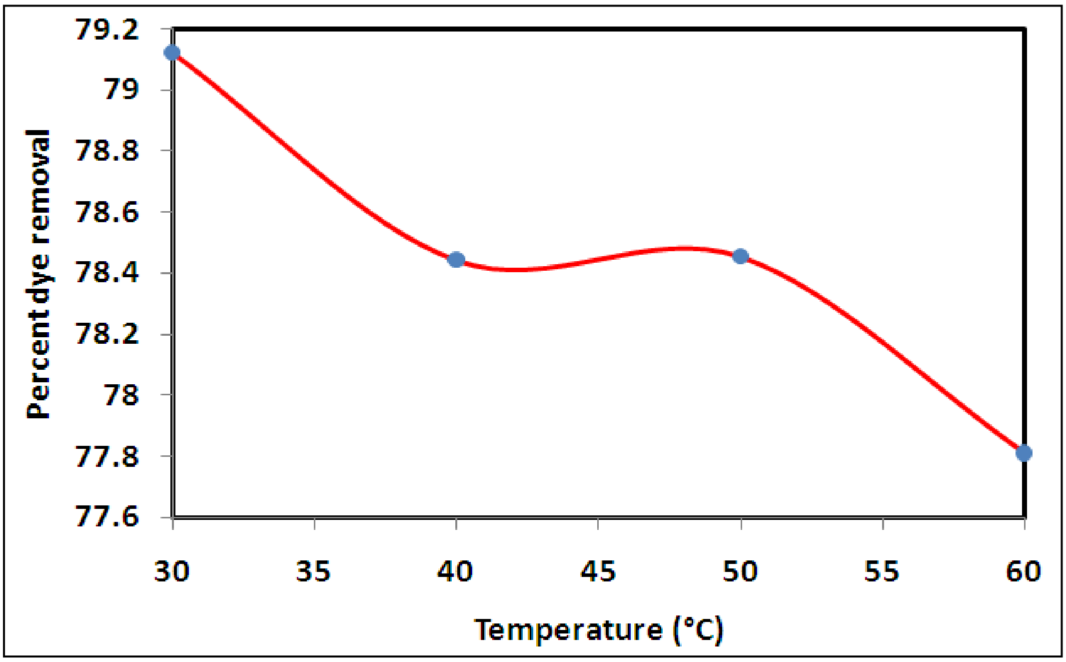


Figure 5. Effect of temperature on percent dye removal (0.3 g IPAN, pH 7, 3 h, 1500 mgL^{1}).

Adsorption of MB onto IPAN was carried out at four different temperatures, namely, 30°C, 40°C, 50°C and 60°C. The effect of temperature on the adsorption process is shown in Fig. 5, which shows that the percent dye removal decreases by increasing the temperature from 30°C to 60°C, i.e. the adsorption decreases with increase in temperature. This indicates the exothermic nature of the adsorption process and the decrease in the adsorption may be due to the tendency of dye molecules to migrate from the solid phase to aqueous phase as the solution temperature increases.

3.4.3 Effect of adsorbent dose

The effect of varying the adsorbent concentration on the percent removal of MB was studied by varying the adsorbent dose from0.05 gL^{-1} to3 gL^{-1} as illustrated in Fig. 6. The adsorption experiments with varying adsorbent doses were carried out at fixed dye concentration of 50 mgL^{-1} and fixed temperature of 30°C. It is clear from Fig. 6 that the adsorbent dose has great effect on the amount of dye adsorbed or percent dye removal. The enhancement in adsorption with increasing the adsorbent dose is most probably due to a stronger driving force and larger surface area available for adsorption. Higher porosity of the adsorbent as illustrated from the scanning electron microscopy (Fig. 2) may have allowed better diffusion of the larger sized dye molecules into the inner matrix resulting in its higher adsorption capacity.

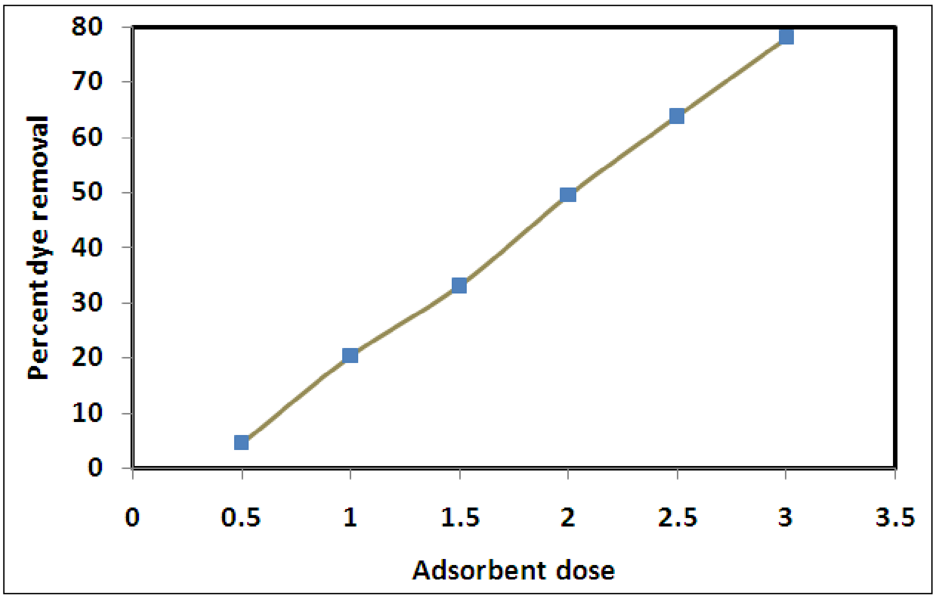


Figure 6. Effect of adsorbent dose on percent dye removal (40°C, pH 7, 3 h, 1500 mgL^{-1}).

3.4.4 Effect of initial dye concentration

The adsorption isotherm indicates how the adsorbate molecules are distributed between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes [54]. To determine the effect of initial dye concentration on the adsorption process, the initial concentration of MB was varied from 100 mgL^{-1} to 1500 mgL^{-1} at a fixed pH and fixed temperature of 40°C. Adsorption data for a wide range of adsorbate concentrations is the most conveniently described by adsorption isotherms, such as Langmuir or Freundlish isotherm, which relate adsorption density, q_e (dye uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk of liquid phase, C_e.

Fig. 7 shows the relationship between the equilibrium dye concentration in the liquid phase (C_e) and the dye uptake per unit weight of adsorbent (q_e). The amount of dye adsorbed per unit mass of adsorbent increases from 7.76 mg/g to 39 mg/g by increasing the initial dye concentration from100 mgL^{-1} to 1000 mgL^{-1}. This is in accordance with results reported by other researchers [55-60]. The increase in the adsorption capacity is probably due to greater interaction between the adsorbate and adsorbent. The higher amount of dye adsorption at higher concentrations is probably due to increased diffusion and decreased resistance to dye uptake. However, increasing the dye concentration above 1000 mgL^{-1} was found not to causes any increase in the dye uptake, indicating saturation of the adsorption sites.

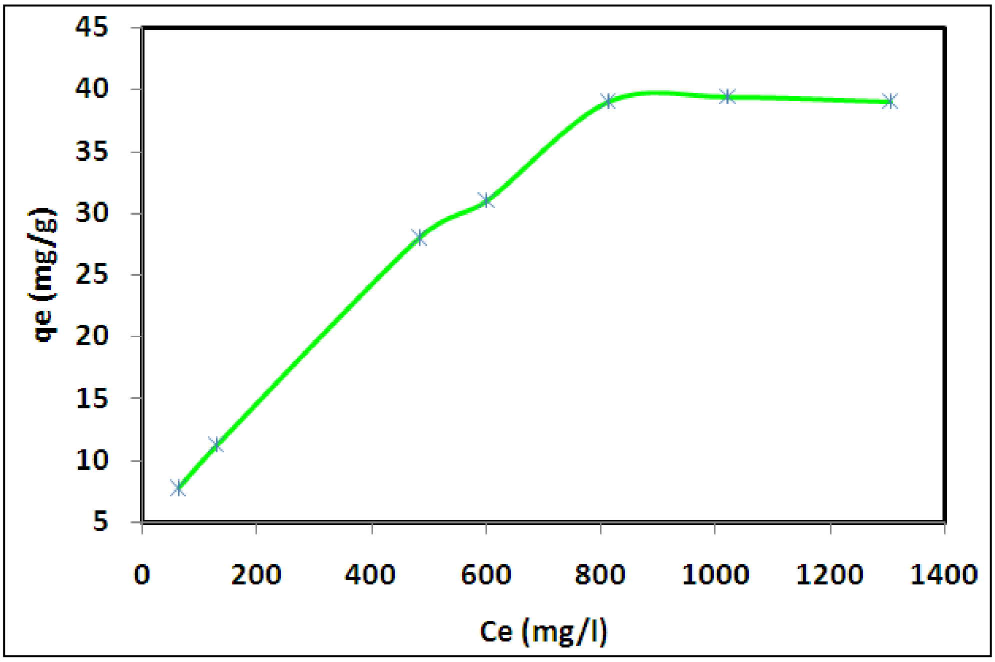


Figure 7. Effect of initial dye concentration on the dye uptake (40°C, 3 h, Ph 7, 0.3 g IPAN).

3.4.5 Adsorption isotherm

3.4.5.1 Langmuir isotherm

Langmuir equation [61] was applied to adsorption equilibrium of MB onto IPAN as an adsorbent. The Langmuir treatment is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant, and there is no transmigration of adsorbate in the plane surface. The linear form of Langmuir isotherm is given by equation 1

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o{*}b} \qquad (1)$$

where C_e is the equilibrium concentration of the adsorbate (mgL^{-1}), q_e is the amount of dye adsorbed (mg/g adsorbent) and Q_o and b are Langmuir constants related to maximum adsorption capacity (mg/g) and energy of adsorption (l/mg), respectively. Langmuir equilibrium constant, K_L is obtained from equation 2

$$K_L = Q_o{*}b \qquad (2)$$

The equilibrium constant K_L may be used to determine the enthalpy of adsorption, ΔH.

When (C_e/q_e) was plotted against C_e, straight line with slop $1/Q_o$ and intercept $1/(Q_o{*}b)$ was obtained. Fig. 8 shows the Langmuir adsorption isotherm of MB onto IPAN. The Langmuir constants, Q_o and b were calculated from the straight line equation and K_L constant can be calculated from equation 2. The values of Langmuir constants for MB adsorption onto IPAN at 30°C are given in Table 1.

Table 1. Langmuir for MB adsorption onto IPAN at 30°C.

Langmuir constants			
R^2	K_L (l/g)	b (l/mg)	Q_o (mg/g)
0.9768	0.127	$2.34x10^{-3}$	54

The essential characteristics of Langmuir can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which describes the type of isotherm [62] and is defined by,

$$R_L = 1/(1+bC_o) \qquad (3)$$

Where b (l/mg) is the Langmuir constant and C_o (mg/l) is the initial concentration of dye solution.

The parameter, RL shows the shape of isotherm. It is unfavorable if RL>1, linear if RL=1, favorable if 0 <RL <1 and irreversible if RL = 0. The values of R_L for adsorption using different initial concentrations of MB are given in Table 2. The R_L values were between 0.8062 and 0.2217. All these values lay between 0 and 1 indicating the favorable adsorption of MB onto IPAN. Correlation coefficient, R^2 value for adsorption of MB onto IPAN was found to be 0.97, indicating that this adsorption process is fitted well on Langmuir isotherm (obey the Langmuir isotherm).

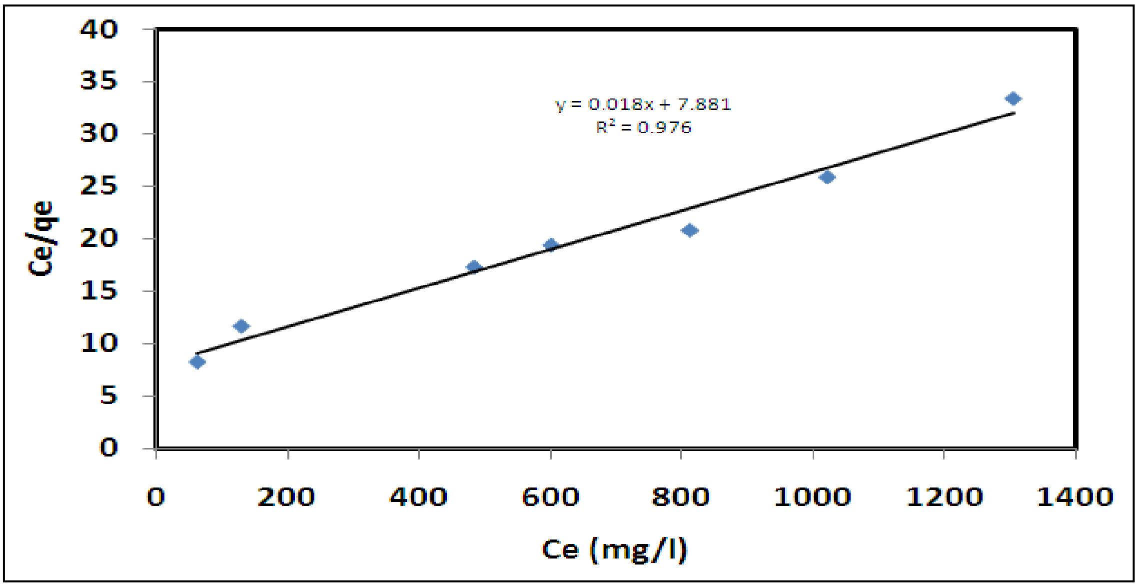


Figure 8. Langmuir isotherm of MB adsorption onto IPAN.

Table 2. R_L values based on Langmuir equation for adsorption of MB onto IPAN at 30°C

R_L values	Dye initial concentration (mg/l)
0.8062	102.7
0.6953	187.2
0.4060	625
0.3608	757
0.2977	1008
0.2595	1219
0.2217	1500

3.4.5.2. Desorption study

In order to regenerate the adsorbent and recovery the adsorbed compounds, desorption process is necessary to be studied. Also desorption study help to explain the adsorption mechanism. Desorption rate is proportional to the driving force and desorption kinetics is very important for the contaminant transport modeling [64-66]. Desorption process usually done by mixing a suitable solvent with the dye-saturated substrate and shaking together for fixed time, until the dye is completely extracted from the adsorbent and transferred to the solvent. Then filtration is used to separate the adsorbent from the desorbed dye in the solvent. The desorbed dye is then determined spectrophotometerically [67]. Desorption of the loaded dyes was carried out at pH 7 and the results shows that 92% of the adsorbed dye could be desorbed when shaking the dye-loaded adsorbent with distilled water for three hours at 40°C.

4. CONCLUSION

Acrylonitrile was homopolymerized to polyacrylonitrile using potassium persulphate as an initiator. The cyano groups of polyacrylonitrile chains were iminated through treating polyacrylonitrile with polyethyleneimine in an aqueous solution. The so prepared polyacrylonitrile and iminated polyacrylonitrile were characterized by doing infrared spectroscopy, thermogravimetric analysis and scanning electron microscopy for both samples and comparing the results. Infrared spectroscopy could prove the success of the imination process that by investigating the spectra of polyacrylonitrile, one easily notices a strong absorption peak of a stretching vibration at 2241cm^{-1} (C≡N). This peak disappeared completely in the spectra of iminated polyacrylonitrile and instead of it; new peaks at 3641 cm^{-1} and 1701 cm^{-1} were assigned to the flex vibration and bend vibration bands of the amine N–H group, respectively. This is in addition to the characteristics absorptions of bend vibration of C-N bond appearing at 1488 cm^{-1} and 1560 cm^{-1} and the C=N band at 1690 cm^{-1}. Thermogravimetric analysis showed that iminated polyacrylonitrile is thermally more stable than polyacrylonitrile. Scanning electron micoscopy micrographs enable the direct observation of the changes in the surface microstructures which reveal surface texture and porosity.

Iminated polyacrylonitrile was used in adsorption and removal of Methylene Blue dye from its aqueous solutions. All factors affecting adsorption of Methylene Blue onto iminated polyacrylonitrile, like agitation duration, temperature, adsorbent dose and dye initial concentration were studied. Adsorption isotherm models were applied to the adsorption data, namely Langmuir model and the adsorption data fitted well to both model. The results of the desorption study show that 92% of the adsorbed dye could be desorbed when shaking the dye-loaded adsorbent with distilled water for three hours at 40°C.

ACKNOWLEDGEMENT
The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding this work through research group no RGP - VPP - 201.

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