KINETICS AND REDOX COPOLYMERIZATION OF ACRYLONITRILE GRAFTED PALM SEED POWDER AFTER CHEMICAL MODIFICATION WITH HYDROXYLAMINE AS ADSORBENTS FOR METHYLENE BLUE REMOVAL

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ABSTRACT
In this research the potentials of palm seeds powder (PSP) as an alternative and environmental friendly adsorbent for the treatment of dye-methylene blue (MB) in waste water was explored. Also, the copolymerization of acrylonitrile (AN) onto palm seeds powder (PSP), using sodium persulphate (SPS) and potassium persulphate (KPS) as initiators were successfully carried out via redox copolymerization method under optimum conditions. The optimum conditions of grafting efficiency and grafting yield were achieved within 2 h and 40°C reaction time. Afterwards, grafted product was chemically modified using hydroxylamine hydrochloride in order to convert the nitrile into oxime functional group. The characterization of poly(AN-*g*-PSP) and amidoxime – modified (AN-*g*-PSP) were done using: Fourier Transform Infrared (FT-IR) Spectroscopy, Thermal Gravimetric Analysis (TGA) and Scanning Electron Microscope (SEM) . All the results from the characterization techniques shows that the copolymerization of PSP onto PAN and subsequently modification of poly(AN-*g*-PSP) using hydroxylamine hydrochloride were successfully carried out. The influence of pH, contact time and initial metal concentration towards adsorption of MB onto amidoxime-modified poly(AN-*g*-PSP) were investigated via the atomic absorption spectroscopy (AAS). The optimum removal of MB onto amidoxime-modified poly(AN-g-PSP) was found to be 97% (16.03 mg/g). Kinetic and thermodynamic studies were investigated, pseudo second-order was observed to be the most suitable that describes the adsorption process R^2 (0.998). Values obtained from thermodynamic analysis shows that the adsorption process is endothermic, spontaneous and chemisorptions in nature.

Keywords: Adsorption, Palm Seed, Methylene Blue, Polyacrylonitrile, hydroxylamine hydrochloride, modification

1.0 INTRODUCTION

The presence of industrial dyes in the effluent has released a voluminous amount of toxicity into the water system that has affected human beings as well as the vegetation and wildlife.
Dyes are used extensively in various industries such as textiles, rubber, plastics, printing, leather, cosmetics, etc., and also in the colouring of different products. About 7×10^5 dyes are produced annually in the global market (Siphiwe *et al*., 2012). It is estimated that about 2% of these dyes are discharged into aquatic inhabitant with most of the sources generated from textile industries. Dyes impede the penetration of sunlight into water bodies and thus interfere with the growth of bacteria, which hinders photosynthesis in aquatic plants. It poses serious threat to mankind and water quality in general, thus, it has become a major environmental concern. In addition, human exposure to dyes may cause acute and chronic effects, such as allergy, dermatitis, skin irritation, cancer, mutation. (Eren, 2009; Eren and Afsin, 2007). There are various treatment methods for dye pollution, such as photo-catalytic degradation, sono-chemical degradation, Fenton biological treatment, biodegradation, integrated chemical-biological process, electrochemical process, adsorption process, chemical coagulation flocculation degradation process, and so on. The aforementioned methods have all been explored in the remediation of dyes in waste-water. Among the various techniques available for its remediation, adsorption technique has been proven to be most effective. Adsorption is preferred over other processes due to its possible regeneration, sludge free operation and recovery of the sorbent.

The dyes both cationic and basic readily dissolve in water producing coloured solutions. They contain substituted aromatic groups in their structure and therefore considered as toxic materials. Cationic dyes are highly visible with very high brilliance and intensity of colours (Mishra and Tripathy, 1993). Examples of cationic dyes include methylene blue (MB), crystal violet (CV) and basic basic blue 41. MB is widely used in textile dyeing and has been studied for adsorption by various authors, such as Wanyonyi *et al.,* (2013) on Eichhornia crassipies and Gupta *et al.,* (2012a) on Ashoka leaf powder.

The distinguishing feature of anionic or acid dye is their water solubility and ionic substituents *Salleh et al.,*(2011). They depend mainly on negative ions, which are in varieties, such as direct dyes, anionic azo dyes and reactive dyes (Hunger, 2003; Tyagi *et at.,* 2002). Acid dyes are mainly used with wool, silk, polyamide, modified acrylic acid and polypropylene fibres. The presence of aromatic and sulphonic groups makes acid dye harmful to humans and other microoganisms (Attia *et al.,* 2006). Examples of anionic dyes include congo red, indigo carmine and red reactive 141. Chanzu (2012) has modeled congo red removal from wastewater on spent brewery grains, on ball-milled sugarcane bagasse by Zhang *et al.,* (2011) and on waste by Mittal *et al.,* (2009).

Adsorption is a unit operation process which refers to attachment of molecules onto their surfaces. It is based on the fact that some solid preferentially adsorb other solute from the solution onto their surfaces. Dyes are particularly removed using various adsorbents, including natural sources adsorbents. Examples of such adsorbents, include orange peel, oil cakes, date palm, olive

shell, charcoal etc. however, activated carbon has shown higher removal properties with respect to other adsorbents. It is a versatile adsorbent with high porosity and surface area. Further, palms seeds powder has also been utilized selectively for the removal of methylene blue dye in various textile industries.

Palm trees are regarded as international socio-economic plants (Dewir *et al.,* 2011). The palms belong to the Arecaceae sub-group, which are a botanical family of perennial shrubs, and trees commonly known as palm trees. They are flowering plants, the only family in the monocot order Arecaceae and mostly restricted to tropical and warm temperate climates. Most palms are distinguished by their large, compound, evergreen leaves arranged at the top of un-branched stems.

However, many palms are exceptions, and in fact exhibit an enormous diversity in physical and morphological characteristics (Rafatullah *et al.,* 2013). A variety of common products and foods are derived from palms, such as palms are also widely used in landscaping due to their exotic appearance, making them one of the most economically viable plants. However, not much attention has been given to the seeds aspect of palm, especially in water treatment applications. Only a little information has been documented on the utilization of the palm seeds for this application. This has prompted us to evaluate the potentials of palm seeds as alternative adsorbent in wastewater. Hence, the basic objectives of our study is to observe the characteristics properties of the palm seed powder and find the influence of process parameters such as pH, adsorbent dosage, contact time and adsorbate concentration on the removal capacity of methylene blue.

2.0 MATERIAL AND METHOD

2.1 Chemicals, Reagents and Asorbent
The palm seeds (PS) were bought locally in one of the Nigerian market and acrylonitrile was purchased from (Merck Co., United Kingdom, 99%). Aluminium Oxide (Al_2O_3) (Merck Co., Germany) was used to purification of acrylonitrile. Potassium persulphate (KPS) (Systerm Chemical, Malaysia, analytical reagent) and sodium persulfate (SPS) (Systerm Chemical, Malaysia, analytical reagent) were used as initiators. Hydroxylamine hydrochloride (Systerm Chemical, Malaysia, 98%) was used as modification agent of poly(AN-*g*-PSP). Sodium hydroxide (NaOH) solution (Systerm Chemical, Malaysia) and hydrochloric acid were used to regulate the pH of the solution. Methanol (Systerm Chemical, Malaysia), ethanol (Systerm Chemical, Malaysia) was used as solvents and double deionized water was used as reaction medium.
Methylene blue (MB) (Hamburg chemicals, Germany) of analytical grades was used as contaminant in this study.

2.2 Preparation of palm seeds powder
Palm seeds were washed thoroughly with deionised water to remove the surface impurities. It was then dried under the sun for at least 48 h before further drying in a vacuum oven at 50 °C 2 h eliminate the moisture content. The palm seeds were crushed using mortar mill and further sieved to obtain a desirable size. The final product was then stored in a plastic container and placed in a silca gel desiccant for further experimental use.

2.3 Synthesis of poly(AN-*g*-PSP)
About 10 g of dried palm seeds (PSP) and 200 mL of deionized water were mixed in a three necked round bottomed flask fitted with a water condenser flask under nitrogen gas and stirred for 1 h. The acrylonitrile (AN) monomer was added followed by SBS and KPS. The graft copolymerization was performed at different condition parameters. KPS and SBS were used as initiators. The reaction time was 2 h and the reaction temperature was 50 °C under nitrogen atmosphere with constant stirring at 250 rpm. The reaction was terminated by pouring the product into 50 mL of methanol and left to precipitate for 1 h. The grafted copolymer was then filtered and washed with 50 mL of methanol and 100 mL of deionized water. The polymer was dried in a vacuum oven at 50 °C until a constant weight obtained. Homopolymerpolyacrylonitrile (homoPAN) was using the same procedure.
The removal of the homoPAN from poly(AN-*g*-PSP) was accomplished by stirring the poly(AN-*g*-PSP) at 200 rpm in 25 mL dimethyl sulfoxide (DMSO) for 24 h to dissolve the homoPAN. The poly(AN-*g*-PSP) was then filtered on a butcher filter paper and the polymer was washed with 50 mL of methanol and 100 mL of deionized water. The purified poly(AN-*g*-PSP) was dried in vacuum oven at 50 °C until a constant weight was obtained. The PSP was purified with the same way as well.

2.4 Modification of poly(AN-*g*-PSP)
About 2.0 g of poly (AN-*g*-PSP), 25 mL of methanol and about 3.0 g of hydroxylamine hydrochloride were added into a 250 mL three-necked round bottomed flask fitted with a reflux condenser. The mixture was stirred at room temperature for 2 h. In order to neutralize the HCl in $NH_2OH.HCl$, 6 mL of sodium hydroxide solution (6 M) was added to the reaction mixture and the pH was adjusted to 8. The reaction was allowed to proceed for 6 h at 70 °C under constant stirring. The amidoxime-modified poly(AN-*g*-PSP) was then filtered and washed thoroughly with 50 mL of ethanol and 100 mL deionized water. The polymer was then allowed to dry in a vacuum oven at 50 °C till a constant weight was obtained (Jamil *et al.,* 2015).

2.5 Characterization of the modified and un-modified adsorbent

2.5.1 Fourier transform infrared (FT-IR) spectroscopy
Molecular analysis of the samples was performed by FT-IR using ATR, with the FT-IR Series 100 Perkin Elmer spectrophotometer (United State of America). Since molecules have different vibration frequencies; this analysis could determine the molecular bonding in polymer materials. Proceeding to the analysis, samples were placed on diamond disk; light was passed through to obtain the molecular bonding vibrations of the sample. The spectra were obtained in the range of 4000–400 cm^{-1}. For the purpose of comparison and analysis, the spectra of PSP, poly(AN-*g*-PSP) and amidoximed-modified poly(AN-*g*-PSP) were recorded as well in the same conditions.

2.5.2 Thermogravimetric analysis (TGA)
Thermogravimetric analysis is considered as one of the most vital method used to characterize materials by measuring physical and reactive properties as a function of temperature (Jamil *et al.,* 2007). The thermal analysis of the polymer samples were carried

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out on Mettler Teledo TGA/SDTA851ᵉ from Switzerland. ∼12 mg of polymer powder was used for this characterization in order to establish the relationship of temperature with weight loss and degradation behaviour of the polymer.

2.5.3 Scanning electron microscopy
The micrograps of polymer were obtained by using scanning electron microscope (SEM) (JSM 6400 JEOL, Japan). The polymer was placed on a copper grid using carbon adhesive and mounted on double-sided tape before coated with gold by ion sputtering method. The micrographs were captured at different magnification using 15 KV accelerating voltage.

2.6 Batch scale adsorption
Batch experiment was performed at room temperature in order to establish the sorption capacity towards MB by mixing the sorbent with 100 mL of MB solution in a 250 mL conical flask. The mixture was magnetically stirred at 200 rpm for 2 h. 5 mL was withdrawn from the bulk solution and filtered using membranes filter. The initial and final concentrations of metal ions were analysed using atomic absorption spectrometer (AAS). The percentage removal of the MB was computed using the following equation.

$$Removal\ efficiency = (C_o - C_e)/C_o\ x\ 100 \qquad (1)$$

where C_o and C_e are the initial and the equilibrium concentrations (mg.L^{-1}) respectively. The adsorption capacity at equilibrium q_e (mg.g^{-1}) was calculated using equation (3.4).

$$q_e = \frac{C_o - C_e}{m} x\ V \qquad (2)$$

where V corresponds to volume of the aqueous phase and m is the mass of the adsorbate (mg).

3.0   RESULTS AND DISCUSSIONS
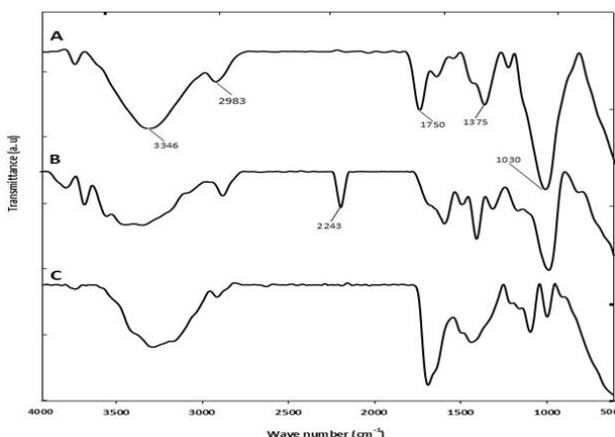
3.1.1 Infrared spectra analysis (FTIR)

Figure 1: FT-IR spectra of (a) PSP (CS) (b) poly(AN-*g*-PSP) & (C) amidoxime- modified poly(AN-*g*-PSP)

The IR spectra of PSP, poly(AN-*g*-PSP) and amidoxime-modified poly(AN-*g*-PSP) are shown in Figure 1(a, b and c). The IR spectrum of PSP Figure 1(a) shows characteristic absorptions at 3346, 2983 and 1750-1655 cm^{-1} which correspond to –OH, C-H

and C=O functional groups respectively. While the IR spectra of poly(AN-*g*-PSP) in Figure 1(b) showed characteristic absorption peaks at 2243 and 1461 cm^{-1} which correspond to the absorption of C≡ N and C=N . These observations confirmed the successful graft copolymerization of PSP onto AN. In the case of amidoxime-modified poly(AN-*g*-PSP) (Figure 1(c)), the band at 2243 cm^{-1} that corresponds to the C≡N absorption is completely disappeared and new band was formed at 1655 cm^{-1} and 968 cm^{-1} which corresponds to the vibrational stretching of C=N and N-OH bands respectively. Furthermore, the characteristic peak of the amine group (NH₂), in the range 3400-3300 cm^{-1} was not observed, this might be due to overlapping of the NH₂ and OH stretching vibration. The band observed at 980 cm^{-1} was assigned to the stretching vibration of the =N-O bond from the oxime group. The IR spectrum of modified poly(AN-*g*-PSP) confirms the chemical modification of poly(AN-*g*-PSP) with hydroxylamine hydrochloride was achieved (Jamil *et al.,* 2015).

3.1.2 Thermogravimetric analysis
The thermograms of PSP, poly(AN-*g*-PSP) and amidoxime-modified poly(AN-*g*-PSP) are illustrated in Figure 2 (a), (b) and (c) respectively. The TG curve of PSP shows two stages of weight loss that correspond to two different types of degradation (Figure 2 (a)). The TG curve of PSP shows 10% weight loss in the first stage (35–100 ᵒC), which was attributed to vaporisation of moisture. The second stage (280–500 ᵒC) shows a sharp DTG peak revealing that the weight loss was fast with the maximum weight loss of 68% which was due to the decomposition of lignocellulosic of the PSP. However, in the case of poly(AN-*g*-PSP), four stages of degradations were observed (Figure 2 (b)). The TG curve of poly(AN-*g*-PSP) shows a small weight loss of 5% at the initial stage (40–100 ᵒC) which was attributed to water evaporation and the second stage shows a weight loss of 12% in the temperature at range 230–290 ᵒC. The third stage (298–334 ᵒC) shows a sharp DTG curve revealing a maximum weight loss of 20%, which was attributed to degradation of poly(AN-*g*-PSP). The sharp and intense DTG curve at the third stage shows that all reactions occurred during the treatment of poly(AN-*g*-PSP) that took place concurrently and that molecular fragmentation is generally favoured, leading to weight loss in poly(AN-*g*-PSP). In the case of amidoxime-modified poly(AN-*g*-PSP), three-stage decomposition patterns were observed (Figure 2(c)). It is clear that the first stage (60–100 ᵒC) is caused by water vaporisation, accounting for about 9% weight loss. On the other hand, the maximum weight loss of 34% which corresponds to the degradation weight of amidoximed-modified poly(AN-*g*-PSP) in the 200–280 ᵒC temperature range which happens to be in the second stage. The third stage produced 18% weight loss at temperature of 360–400 ᵒC. As the sample were heating up to 600 °C, the chair yield were recovered for the PSP (21%), poly(AN-*g*-PSP) (52%) and amidoxime-modified poly(AN-*g*-PSP) (57%). Similar observation was reported by (Athawale and Lele, 2000) where two-step characteristics TG curve for PSP were observed where its major weight loss (75%) was found to take place in the second step within the 243–378 ᵒC of temperature range.
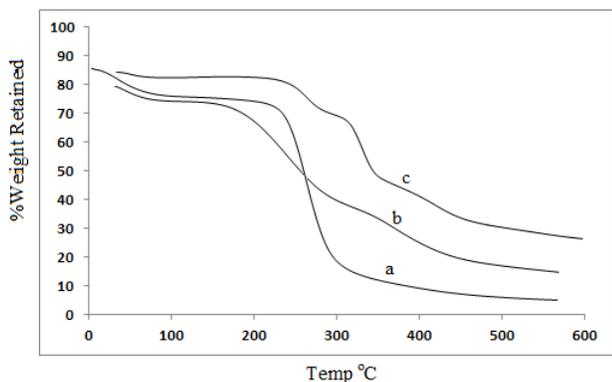
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Figure 2: TG and DTG curves of (A) PSP (B) poly(AN-*g*-PSP) and (C) amidoxime-modified poly(AN-*g*-PSP).

3.1.3 SEM images
The surfaces morphologies of PSP, poly(AN-*g*-PSP) and modified poly(AN-*g*-PSP) are shown in Figure 3 (a), (b) and (c) respectively. As shown in Figure 3 (a), the micrograph of PSP granules was spherical, irregular shape and varied particle sizes with flat and smooth surface (Lanthong *et al.,* 2006). However, the granular structure completely disappeared in the case of poly(AN-*g*-PSP) and amidoxime-modified poly(AN-*g*-PSP) Figure 3 (b). The surface of poly(AN-*g*-PSP) are rough with small and irregularly distributed pores. Meanwhile, the micrograph of amidoxime-modified poly(AN-*g*-PSP) in Figure 3 (c) appeared as small agglomerated particles. The changes of the SEM micrograph is one of the way to indicate that the grafting of PSP onto PAN system (Figure 3 (b)) and chemical modification of poly(AN-*g*-PSP) with hydroxylamine hydrochloride (Figure 3 (c)) were successful (Nair and Jyothi, 2014).
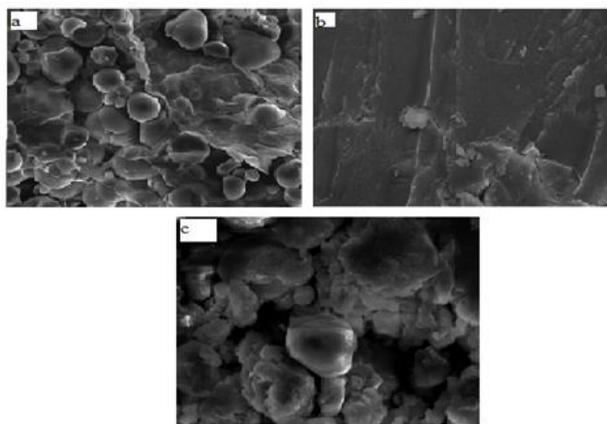

Figure 3: SEM images of (a) PSP (b) poly(AN-*g*-PSP) and (c) Amidoxime-modified poly(AN-*g*-PSP)

3.2 Kinetics of Adsorption
Kinetic models are used to fit experimental data in order to gain a better understanding of the adsorption process. According to Feng *et al.,* (2012) and Ugurlu (2009) the adsorption process and mechanism depends on the physical and/or chemical characteristics of the adsorbent, mass transfer of dye molecules to adsorbent surfaces, diffusion of dye molecules into the interior pores of adsorbent and equilibrium dye attachment. The kinetics of methylene blue adsorption process was investigated using the pseudo-first and second order kinetics.

3.2.1 Pseudo-first order kinetics
The Lagergren (Singh *et al.,* 1998) pseudo-first order kinetics model is presented as:

$$dqt \quad / \quad dt \quad = \quad k^1(q_e \quad - \quad qt) \quad (1)$$

$$\ln(q_e \quad - \quad qt) \quad = \quad \ln q_e \quad - \quad k^1 t \quad (2)$$

Where qe = equilibrium amount of dye adsorbed per unit mass of adsorbent (mg/g)
qt = amount of dye adsorbed per unit mass of adsorbent at time t (mg/g)
K^1 = pseudo-first order adsorption rate constant (min-^{1})
t = time (min).
This model is based on the assumption that the rate of change of adsorbed solute with time is directly proportional to the difference in equilibrium adsorption capacity and the adsorbed amount (Nandi *et al.,* 2009). A linear plot of ln(q_e - qt) against time t, gives the equilibrium adsorption capacity qe (mg/g), as intercept while the slope gives the pseudo-first-order rate constant, K^1. If a system follows pseudo-first-order kinetics, then the experimental equilibrium adsorption capacity qe,exp. (mg/g), and the calculated equilibrium adsorption capacity qe,cal. (mg/g), must be in agreement with high values for the correlation coefficient R².

Table 1: The pseudo First-order kinetics plot for the sorption of methylene blue dye onto amidoxime-modified poly(AN-*g*-PSP)

Concentration	Time (min)	qt (mg/g)	ln(q_e - qt)
100ppm	10	15.38	-0.1805
	20	15.59	-0.3467
	30	15.92	-0.9208
	40	16.03	-2.0
25ppm	10	3.50	2.5284
	20	3.61	2.5201
	30	3.78	2.5063
	40	3.90	2.4916

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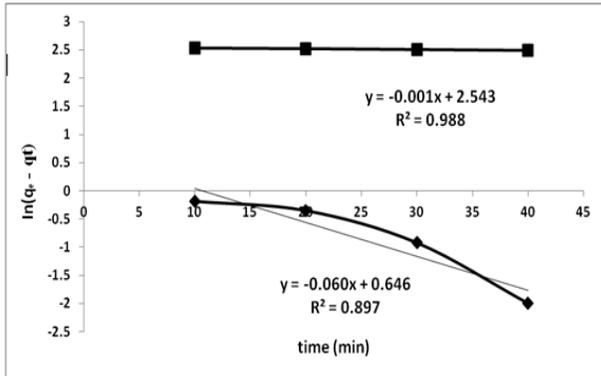
Figure 4: The Pseudo first-order kinetics plot for the sorption of methylene blue dye onto amidoxime-modified poly(AN-*g*-PSP).

Table 2: Kinetic parameters for adsorption of MB on to amidoxime-modified poly(AN-*g*-PSP)

Initial concentration (ppm)	Pseudo first order kinetics			
	q_e mg/g (exp)	K_1 (min^{-1})	q_e mg/g (cal)	R^2
25	3.96	0.06033	1.9081	0.897
100	16.03	0.00126	12.7197	0.988

As shown in Table 1, the experimental equilibrium adsorption capacity, q_e, experiment (mg/g) and calculated equilibrium adsorption capacity, qe,cal (mg/g) values differ greatly hence the adsorption of methylene Blue onto amidoxime-modified poly(AN-*g*-PSP) follow not the pseudo-first order kinetics.

3.2.2 Pseudo-second order kinetics
The linear form of the Lagergren pseudo-second order kinetics model as described by Ho and Mckay, (1999) is given as:
$t/qt = 1/k2q_e{}^2 + t/qt$ (3)
This model assumes that the rate limiting step during adsorption of solute onto adsorbent is based on chemisorptions (Qin *et al.*, 2009). The linear plot of sorption against time t, gives the slope as equilibrium adsorption capacity, qe (mg/g) and intercept pseudo-second-order rate constant K^2. If adsorption process follows pseudo-second-order kinetics, then the experimental equilibrium adsorption capacity qe,exp. (mg/g), and the calculated equilibrium adsorption capacity qe,cal. (mg/g), must be in agreement with high values for the correlation coefficient R^2 (0.998).

Table 3: The pseudo second-order kinetics plot for the sorption of methylene blue dye onto amidoxime-modified poly(AN-*g*-PSP).

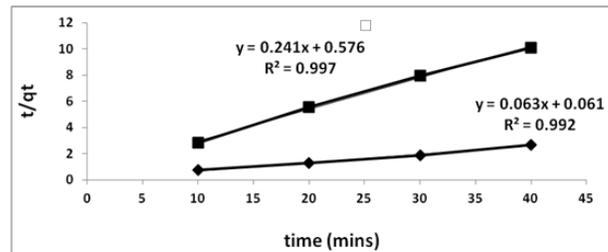| Concentration	Time (mins)	t/qt
100ppm	10	0.7502
	20	1.2829
	30	1.8844
	40	2.6613
25ppm	10	2.8571
	20	5.5401
	30	7.9365
	40	10.101

Figure 5: The pseudo second-order kinetics plot for the sorption of methylene blue dye onto amidoxime-modified poly(AN-*g*-PSP).

Table 4: Kinetic parameters for adsorption of MB onto amidoxime-modified poly(AN-*g*-PSP)

Initial concentration (ppm)	Pseudo first order kinetics			
	q_e mg/g (exp)	K_1 (min^{-1})	q_e mg/g (cal)	R^2
25	3.96	0.1006	4.15	0.992
100	16.03	0.00126	15.79	0.997

According to Table 4 above, the adsorption of MB dye onto amidoxime-modified poly(AN-*g*-PSP) was found to follow pseudo-second order kinetics. This is because the experimental equilibrium adsorption capacity, qe,exp (mg/g) and calculated equilibrium adsorption capacity qe,cal (mg/g) are in agreement with high correlation coefficients R^2 0.988 to 0.993. Hence, the rate-controlling step during MB adsorption is a chemisorptions process dependent on concentration of dye molecules and surface active site (Qin *et al.*, 2009).

Table 5: Comparison of Different Adsorbants for Methylene Blue Dye Adsorption Capacity

Raw materials	C_o initial concentration (mg/l)	Q_e mg/g	Reference
Our study (amidoxime-modified poly(AN-g-PSP)	100	16.03	-
Coconut (hair dust)	100	15.25	Aygu A. Vnising karakas
Banana	100	4.67	Kavith A.D. Namasivayan
Walnut shell	100	3.53	Mecedo J.S. Junior, N.B. Almedia I.g

3.3 Thermodynamic Properties

The thermodynamic properties of amidoxime-modified poly(AN-g-PS) for MB adsorption were investigated at varying reaction temperature. The following were employed to elucidate the mechanism of MB removal by PSP:

$K = C_a/C_e$

$lnK = lnA – Ea/RT$

$lnK = \Delta S/R - \Delta H/RT$

Where, T, R, K are represented as the temperature (K), gas constant (8.314 J/mol K), and equilibrium constant respectively. Where K can be obtained from:

$\Delta G = - RTlnK$

$\Delta G = \Delta H - T\Delta S$

INITIAL CONCENTRATION 100ppm

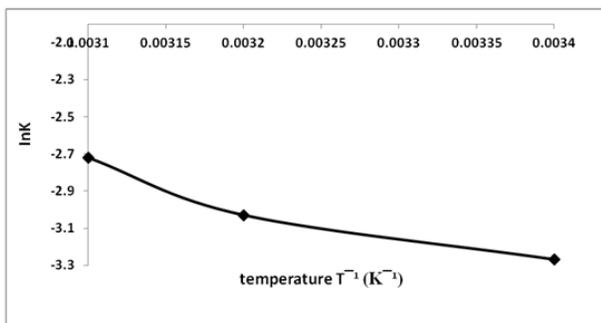| ADSORBANCE	C_o mg/l	C_e mg/l	ln (k)	T^{-1} (K^{-1})
25°C	0.385	96.19	3.81	3.228	0.00336
35°C	0.487	95.25	4.79	2.999	0.00324
45°C	0.667	93.41	6.59	2.650	0.00314

Figure 6: Temperature effect on the adsorption of methylene blue onto amidoxime-modified poly(AN-g-PSP) (Volume of the MB dye solution: 50 ml, Adsorbent dosage: 0.3g, Temperature: 298 K, 308 K, 318 K, Initial concentration of MB 100 ppm, pH: 6.5, Particle size: 75-300

Table 7: Thermodynamic parameters for the adsorption of MB onto amidoxime-modified poly(AN-g-PS)

Initial concentration 100ppm	ΔS Jmol$^-$K	ΔH kJmol$^-$^{1}	ΔG kJmol^{-1}		
			25°C (298K)	35°C (308K)	45°C (318K)
100	0.021855	14.49013	-7.990	-7.679	-7.006

The adsorption of MB dye was studied at different temperatures in the range of 25°C to 45°C using amidoxime-modified poly(AN-g-PS) as an adsorbent for an initial MB dye concentration of 100ppm is shown in Figure 7. The experimental result shows that the removal of MB dye decreased with increase in the solution temperature from 35°C to 45°C. This indicates that the adsorption of MB dye onto amidoxime-modified poly(AN-g-PSP) is endothermic in nature. The decrease in the removal of MB dye with increase in temperature may be due to weakening of the adsorptive forces between the MB dye molecules and the active sites of amidoxime-modified poly(AN-g-PSP) and also between the adjacent molecules of the adsorbed phases. The variation in the extent of the adsorption of MB dye onto amidoxime-modified poly(AN-g-PSP) with temperature has been explained on the basis of the adsorption thermodynamic parameters such as change in free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS); they were estimated from table 7. The estimated values for (ΔG) were -7.99, -7.679 and -7.006 kj/mol at 298, 308 and 318 K, respectively, which are rather law, indicating that spontaneous process occurred.

It was observed from the results that the K values decreased with an increase in temperature, which results in the shift of equilibrium to the left, i.e., desorption of the adsorbed MB dye molecules from amidoxime-modified poly(AN-g-PSP) is favored at high temperatures. The negative values of ΔG confirm the feasibility and the spontaneous nature of the adsorption process. The values of ΔH and ΔS were obtained from the slope and intercept of the plot of lnK versus T^{-1} (Figure 6), and the values of these parameters are listed in Table 6. The negative values of ΔH at different temperatures showed the endothermic nature of the adsorption process. The low enthalpy values such as $\Delta H < 20$ KJmol^{-1} indicate that physical adsorption is involved in the adsorption process. The positive $\Delta S°$ is an indication of increased randomness at the solute- amidoxime-modified poly(AN-g-PS) interface (Vadivelan *et al.*, 2005).

3.4 Effect of ionic strength on methylene blue adsorption

The effect of ionic strength on methylene blue adsorption is shown in Figure 8. Industrial wastewater contains varying quantities of metal ions which affects adsorption process significantly. Higher metal ions concentration therefore leads to increase in ionic strength. In other to alter the concentration of Na^+ and Cl^- ions in solution in this study, the volume of 0.1M NaCl and distilled water were varied. Thus, ions interact with dissociated dye molecules compete in order to be adsorbed on the surfaces of the adsorbent hence altering the dye adsorption

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Table 8: The influence of ionic strength on Methylene blue (MB) adsorption onto amidoxime-modified poly(AN-*g*-PSP)

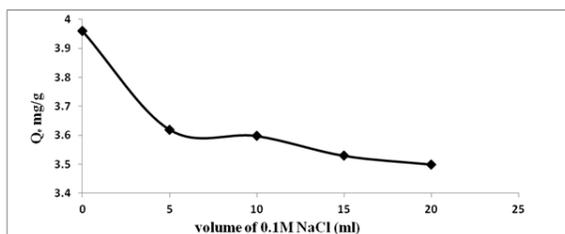| Volume of 0.1m NaCl	Volume of distilled water (ml)	Adsorbance	C_e (mg/l)	q_e (mg/g)	% removal
0	20	0.129	1.28	3.96	94.88
5	15	0.331	3.27	3.62	86.92
10	10	0.345	3.41	3.59	86.64
15	5	0.389	3.85	3.53	84.60
20	0	0.402	3.98	3.50	84.08

Figure: 7 Effect of Ionic Strength on Methylene Blue Adsorption onto amidoxime-modified poly(AN-*g*-PSP)

4.0 Conclusion

The synthesis of poly (AN-*g*-PSP) and its chemical modification with hydroxylamine hydrochloride to form amidoxime-modified poly(AN-*g*-PSP) were demonstrated in present work. The optimum condition for the graft copolymerization of poly(AN-*g*-PSP) were; 40 °C reaction temperature, 2 h reaction time. For the removal of MB from solution, amidoxime-modified poly(AN-*g*-CS) was used as adsorbents. Various experimental parameters were found to influence the adsorption ability of the adsorbent such, initial pH, and initial MB concentration. The optimum MB removal by poly(AN-*g*-PSP) was observed to occur at pH 6. It was established that the adsorption capacity of MB increases with increasing initial concentration of MB. The optimum removal for MB was recorded as 97.5% (16.03 mg/g). This was achieved at a very low adsorbent dosage of 0.3 g in an acidic pH 6. The isotherm and kinetic studies showed that the adsorption of amidoximed-modified poly(AN-*g*-PSP) follows Langmuir isotherm and pseudo-second-order kinetics. The estimated values for (ΔG) were -7.99, -7.679 and -7.006 kj/mol at 298, 308 and 318 K, respectively, which are rather law, indicating that spontaneous process occurred. The enthalpy changes and entropy of adsorption were 14.49 Kj/mol and 0.022 J/molK, respectively.

The results obtained from thermodynamic analysis shows that the adsorption process is endothermic, spontaneous and chemisorptions in nature

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