

Spectrophotometric study of Aniline blue dye adsorbed on the surface of new cross link polymer

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Abstract

This research is including of a new polymer from reaction between poly vinyl alcohol and acryl amide then study some of it's physical properties also study thermodynamic adsorption for aniline blue dye on polymer surface. The raw materials used in our experiments are available as commercial products. PVA, AM ,benzoyl peroxide, potassium persulfate, ferrous sulfate and ethylene glycol were used without further purification. The synthesis of polymer was done in aqueous solution and in ethylene glycol /water mixture (70/30). To determine the synthesis condition, took gravimetric ratio PVA, AM and benzoyl peroxide or redox system (potassium persulfate /ferrous sulfate as initiators were used. PVA was dissolved in water or ethylene glycol/ water mixture at (60-70)C°, solution were obtained, then the adequate quantity of acryl amide and initiator were introduced under continuous stirring in reaction vessel. Further, the temperature was raised and maintained at 85-90C° for 5 hours. The obtained products were dried at 60C° for 72hours to avoid hydration. The evidence of grafting was obtained by comparing FTIR spectra analysis of PVA, AM and grafted polymer as shown in section three . Adsorption studies were carried out to investigate the effect of different parameters such as: (contact time, adsorbent weight, pH, initial dye concentration and temperature effects). The results showed that the adsorption of anilin blue dye at initial concentration (30 ppm) was rapid at the first minutes of contact time until reached to the equilibrium time at (30)min for polymer. This percent removal (20ml) of anilin blue was at the equilibrium time for all the adsorbent also at the optimum weigh which were (0.9)g for polymer. The equilibrium adsorption isotherm has been examined by applying the Langmuir and Frenlich isotherms. The optimum experimental results were described by the frendlich isotherm. Thermodynamic parameters such as the change of free energy, enthalpy and entropy were also evaluated. The results indicated that the adsorption of the anilin blue dye onto the polymer was an endothermic, decrease disorder and spontaneity of the adsorption process.

Introduction

Polymers are the giant molecules of chemistry. Chemists also call them macro-molecules. The small building-block molecules are called monomers.

Synthetic polymers are a mainstay of modern life, but nature also makes polymers; they are found in all living matter⁽¹⁾.

Poly(vinyl alcohol) with varying physical properties can be obtained from poly(vinyl acetate) by varying the solvent and temperature used in the vinyl acetate polymerization⁽²⁾.

It has been widely utilized in polymer modifications as it is readily available, it is inexpensive and it has hydroxyl groups present.

Graft copolymer from poly(vinyl alcohol) have been prepared especially by irradiation techniques.

PVA with grafted methyl methacrylate has been studied as membrane for hemodialysis⁽³⁾.

Graft copolymer consisting of 50% PVA, 25% poly(vinyl acetate) and 25% grafted ethylene oxide units have been used to prepare capsules for drugs which do not require any additional plasticizers⁽⁴⁾.

Acrylamide or (is a with the Chemical formula C_3H_5NO Carbon /Hydrogen/Nitrogen/ Oxygen Its IUPAC name is prop-2-enamide. It is a white odorless Crystallin solid, soluble in Water_(molecule), /Ethanol, Diethyl_ether, and Chloroform. Acrylamide decomposes in the presence of acids, bases, oxidizing agents, iron, and iron salts.

Experimental

Determination of λ max and calibration curve:

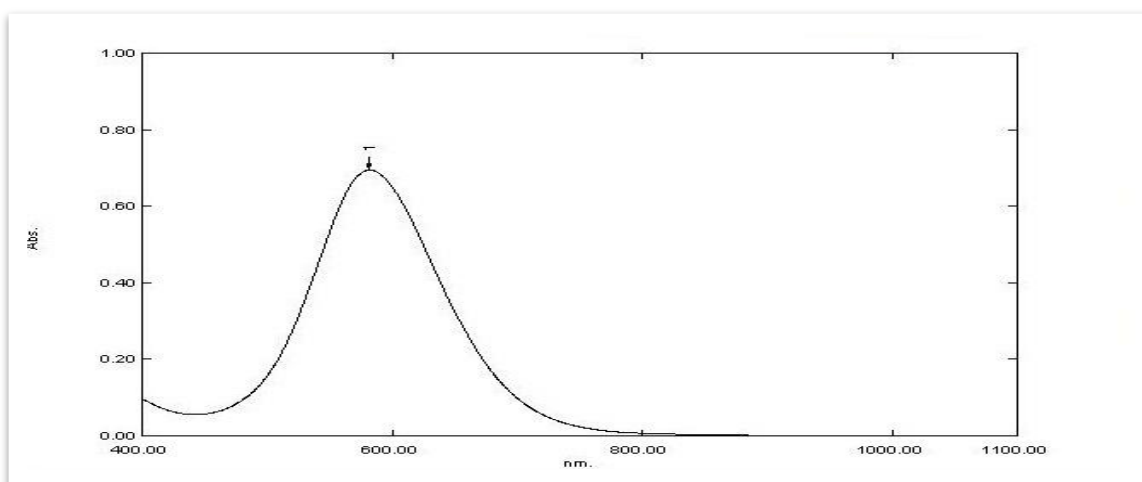
To determine the wave length at maximum adsorption, adsorption

Acrylamide is prepared on an industrial scale by the hydrolysis of Acrylonitrile by Nitrile_hydratase Nitrate hydratase.

Most acryl amide is used to synthesize Polyacrylamide, which find many uses as water-soluble. These include use in Wastewater treatment, Gel electrophoresis SDS-PAGE Papermaking, Ore processing, tertiary oil recovery, and the manufacture of Permanent press fabrics. Some acryl amide is used in the manufacture of Dye and the manufacture of other Monomers⁽⁵⁾.

The aim of the study is synthesis a new cross linke polymer made from PVA and acrylamide, then measuring the new polymer by F.T.I.R. technique, then study of some physical properties of it such as solubility, swelling behavior and make adsorption on the new polymer by use aniline blue dye and measuring the effects of various experimental parameters on adsorption process such as weight of adsorbent, pH, contact time, initial concentration of aniline blue dye, contact time and temperature, than study of the thermodynamic parameters such as ΔS , ΔH , ΔG .

spectrum for dye by using UV-Vis has been recorded in the range (200-1000) by using cell (cuvette) of 1cm thickness (path length). The spectra are shown in figures (1-1).



figures (1-1). Maximum wavelength for (A.B) dye.

The calibration curve was determined by fixing the λ_{max} at (586 nm) and a specific concentrations that obeys the (Lambert beer's law) prepared for (A.B) dye, after that, the absorption has been recorded and a calibration

curve was plotted absorbance vs. concentration, the best line between points has been drawn using least square method. The spectra are shown in figure (1-2).

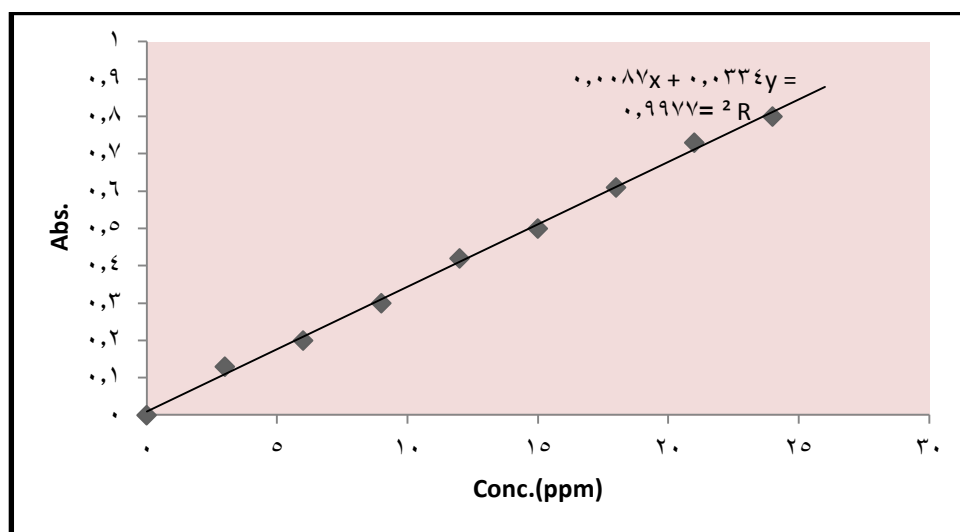


Figure (1-2) Calibration curve for (A .B)dye at λ max (586 nm).

Results and discussion

The mechanism of the new polymer is show in this scheme:

The obtained polymers were characterized by FTIR spectroscopy In figs.(1-3) and (1-4), FTIR spectra of poly vinyl alcohol-grafted with acryl amide unmodified poly vinyl alcohol and acryl amid, were presented.

The specific absorption bands at 1676 cm^{-1} corresponding to C=O group (amide band 1) and 1600 cm^{-1} , corresponding to NH group (amid band 2)⁽⁶⁻⁷⁾.

The synthesis polymer was identified with FT.IR, Figure (1-5) demonstrated appearance of stretching vibration band at 3490cm^{-1} due to the stretching vibration of (OH) group, also showed disappearance of the two absorption bands at (3338cm^{-1}) and (3371cm^{-1}) were due to the stretching vibrations of $(-\text{NH}_2)$ group of acryl amide. and also expressed of medium to strong bands of aliphatic (C-H), (C-C) group at $2943, 2883\text{cm}^{-1}$, and

appearance of stretching vibration band of amid at 1668cm^{-1} due to the stretching vibration of $(\text{C}=\text{O})$, also the disappearance of $(\text{C}=\text{C})$ group at 1429cm^{-1} ⁽⁷⁾. also appearance absorption band at 1082cm^{-1} due to medium band of $(\text{C}-\text{N})$ group, finally appearance of strong band at 1043cm^{-1} for $(\text{C}-\text{O})$ group.

All the absorption bands that had been mentioned were good evidence for preparation of the new polymer.

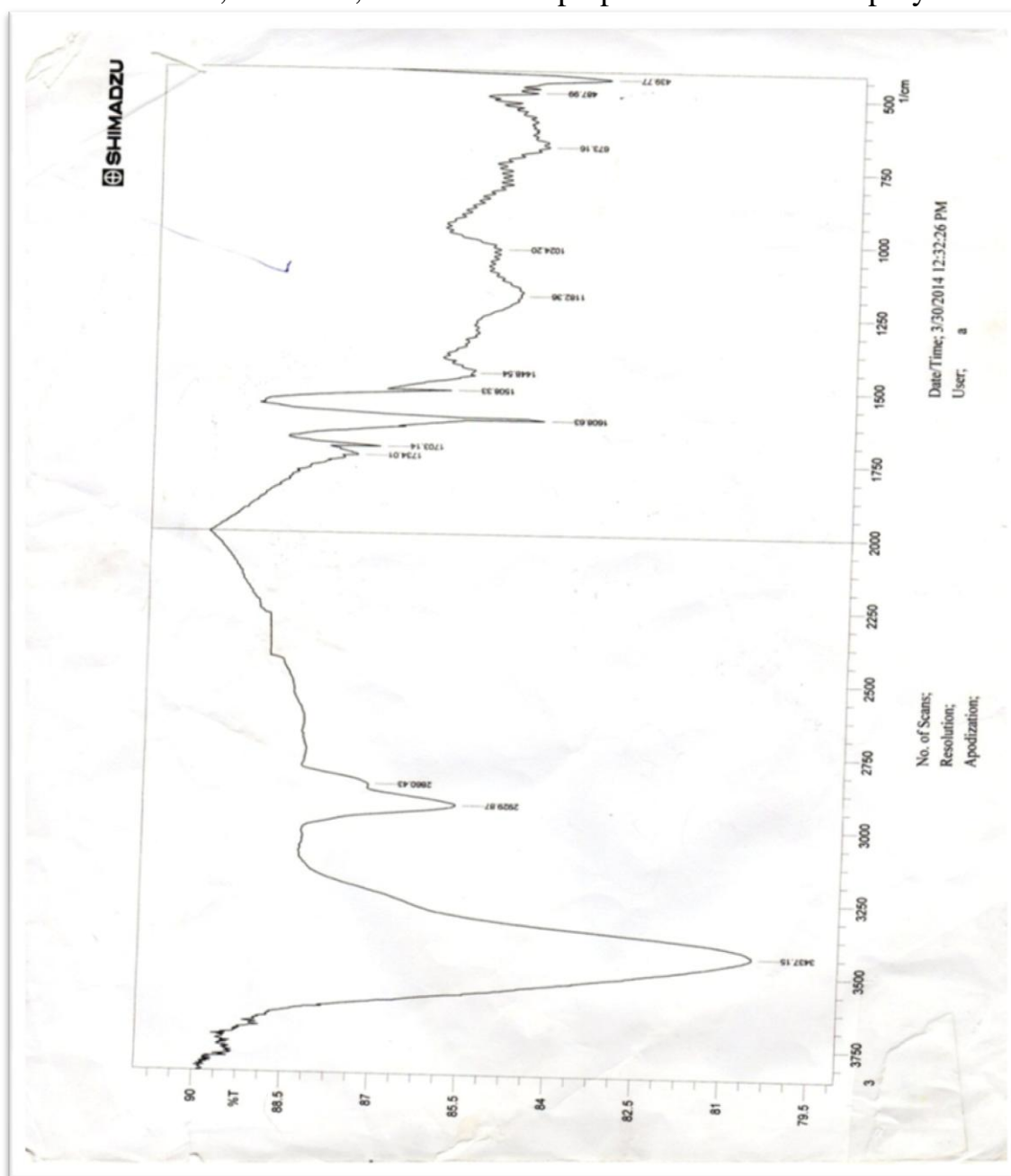


Figure (1-3) Fourier Transform Infrared for poly vinyl alcohol.

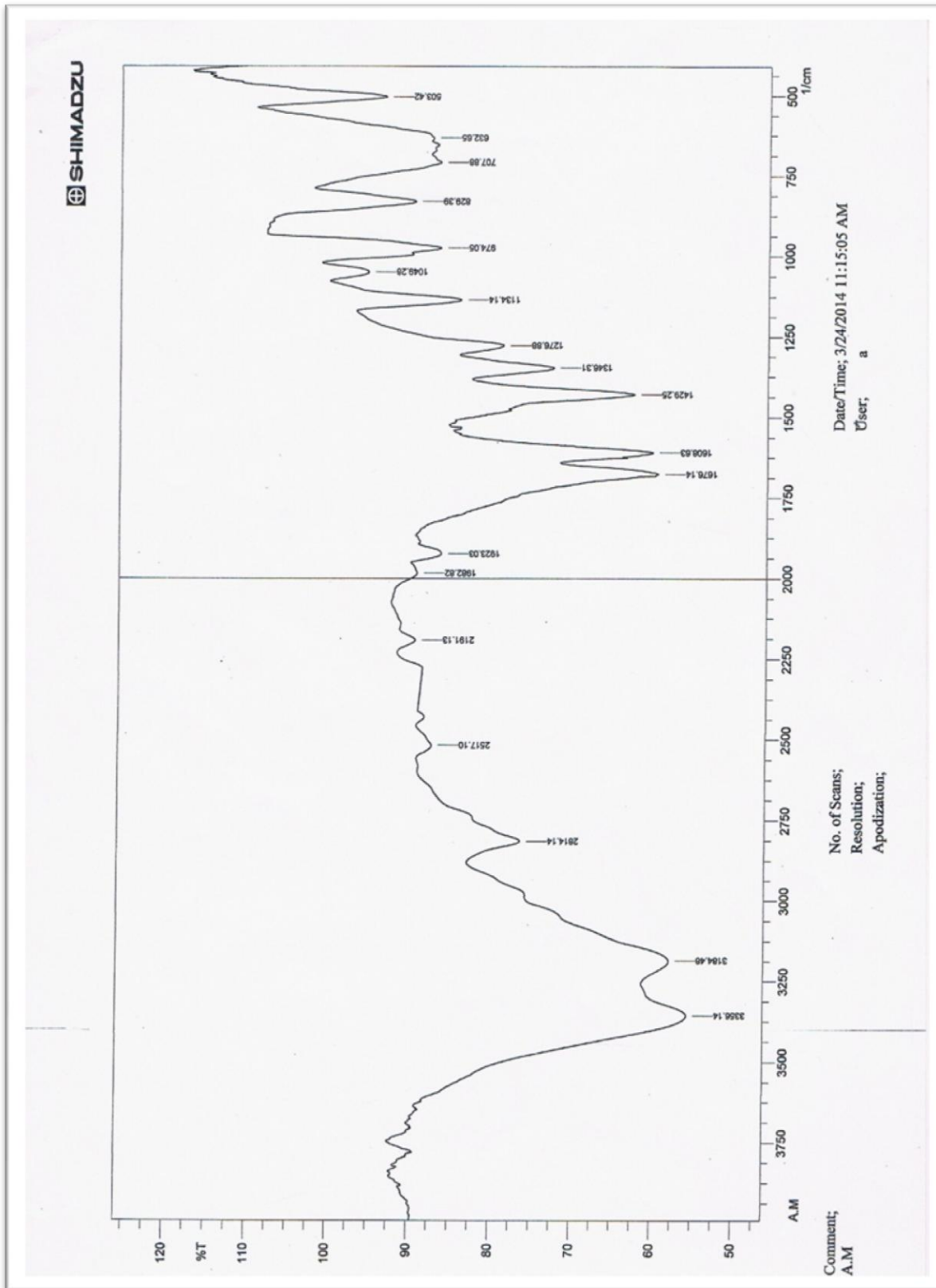


Figure (1-4) Fourier Transform Infrared for acryl amide.

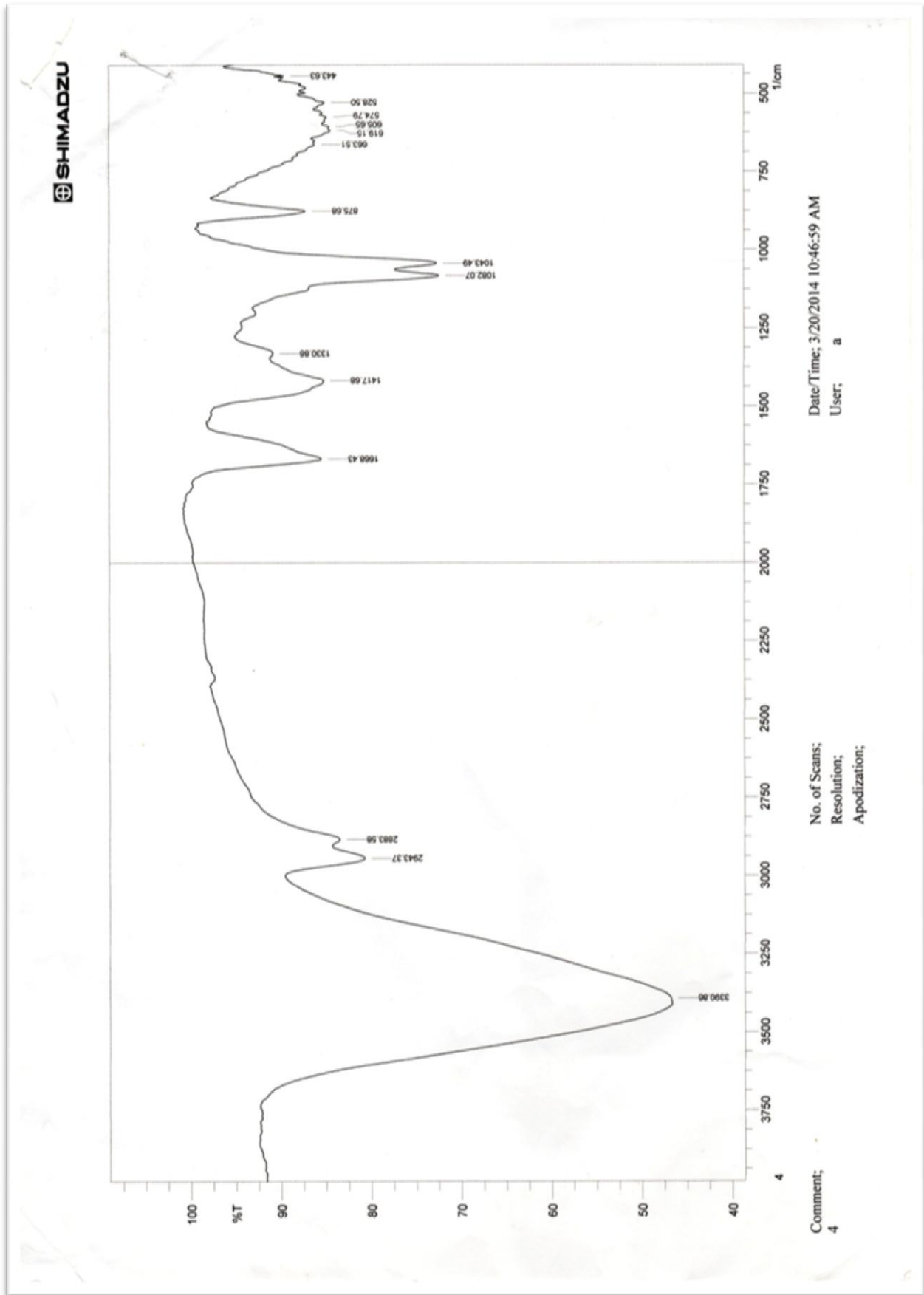


Figure (1-5) Fourier Transform Infrared for New Polymer.

Physical properties solubility

The polymer was dissolved in DMS, DMSO because it's a good solvent with high polarity that make it easy to dissolve the polymers also was dissolve in (0.05N) of HNO₃.

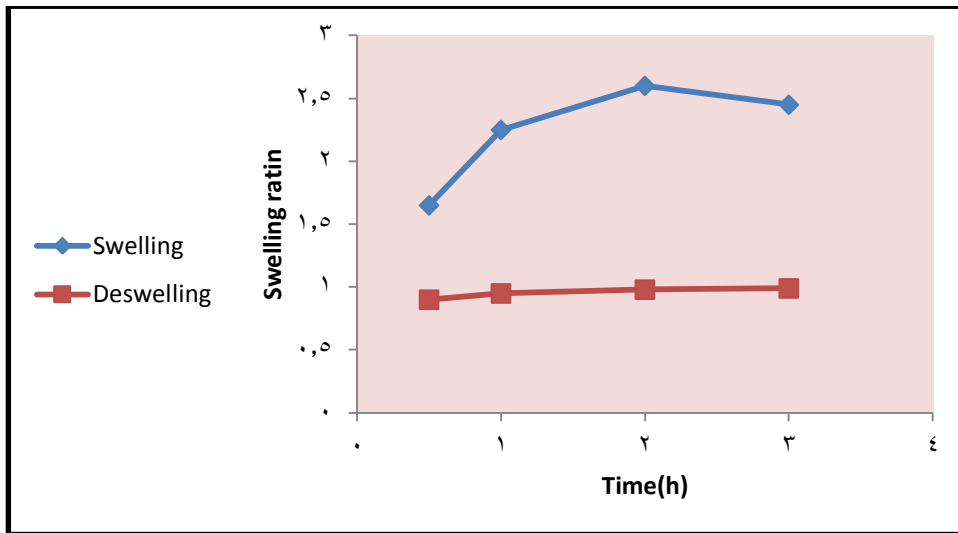
Swelling and deswelling studies as a function of time

The swelling ratio (Q) as a function of time at room temperature of the prepared hydrogel is show in fig.(1-6). Presented swelling ratio of (1.3)g of dried polymer that immersed in distilled water at (25)°C revealed that the swelling ratio (Q) was increased with

increase of time. An increase in the swelling ratio (Q) will be more than twice. the low values of these parameters were due to the fact that after water immersion and swelling, the polymer was divided in to several fragments; it was partially dissolved and its weight decreases, thus weighing errors at determining swelling behavior were noted . From the data presented we noticed that in the case of redox initiated polymer, the swelling characteristics were better. To prevent the division of the synthesized polymer in to fragments, it must be cross-linked with adequate cross-linking agents(8).

Table(1-1): show swelling in distilled water of synthesized polymer at 25 °C and the deswelling at 50 °C.

No.	Time(h.)	Swelling	Deswelling
1	0.5	3.445	0.930
2	1.0	4.225	0.950
3	2.0	4.680	0.980
4	3.0	4.485	0.990



Figure(1-6): Show swelling in distilled water of synthesized polymer at 25°C and the deswelling at 50°C.

Effect of Adsorbent weight on A.B dye adsorption

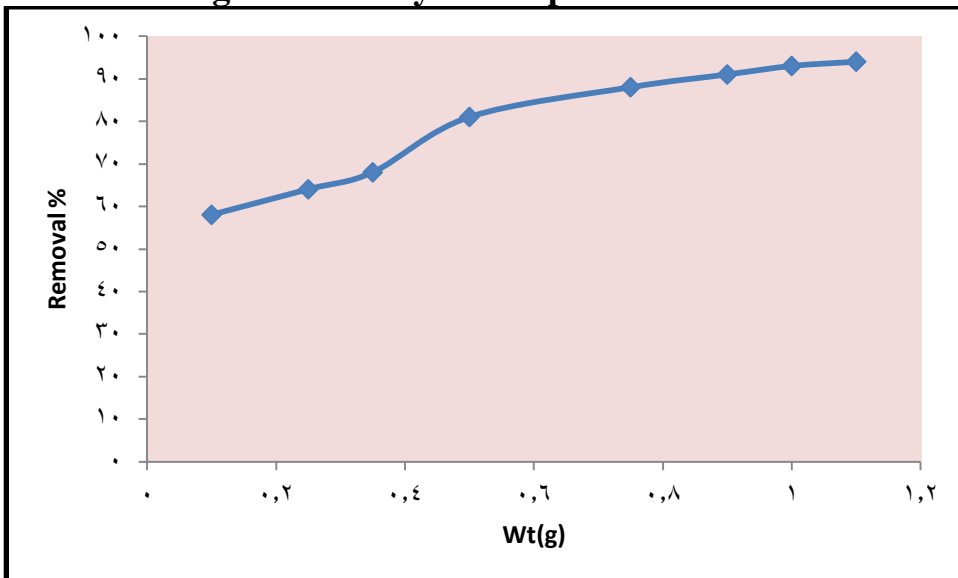


Figure (1-7): Effect of adsorbent weight(0.1-1 g) on adsorption of (20 ml) A.B dye concentration (30 ppm) at 35°C.

From the above figure, it is clear that adsorbent weight for the best adsorption is (0.9g). Beyond these weights, there is no increase in the adsorption. With increase in the adsorbent weight the

percentage removal of A.B dye increase. That attributed to increased adsorbent surface area and availability of more adsorption site⁽⁹⁾.

Effect A.B dye concentration on the adsorption:

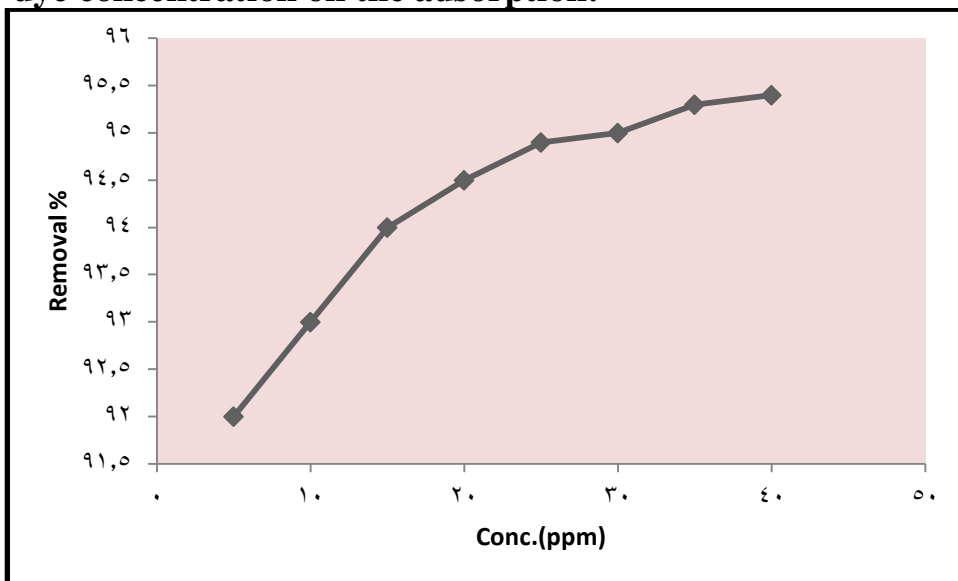
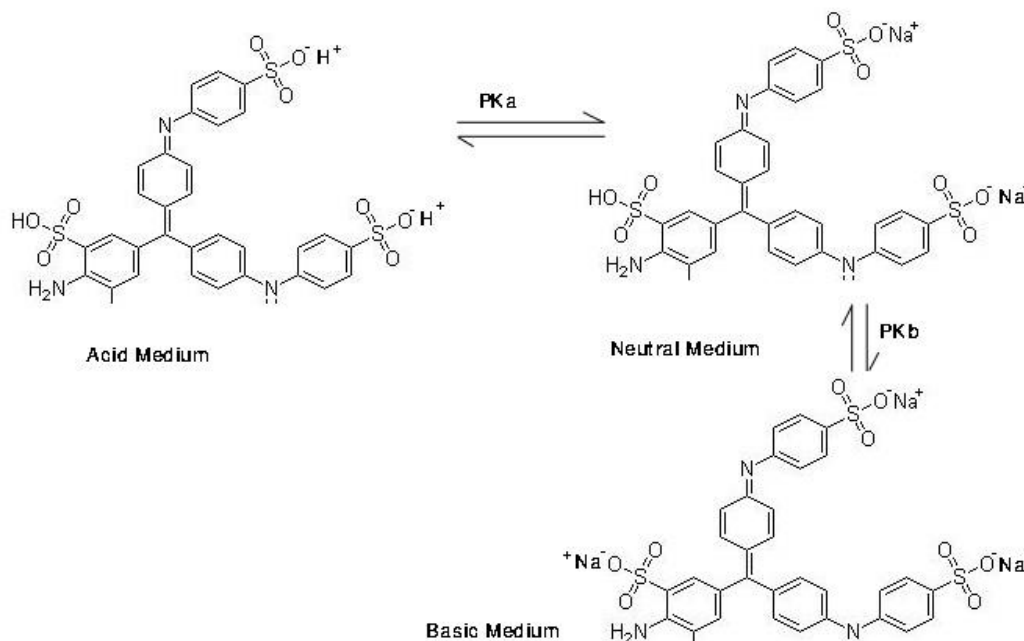


Figure (1-8): Effect of concentration(5-40 ppm) adsorbent weight(0.9 g) on adsorption at (20 ml) A.B dye at (35°C).

That due to increasing the driving force between adsorbent and dye solution. after (30 ppm) of dye concentration the removal percentage

were remain constant. therefore (30 ppm) dye concentration was chosen as the optimum dye concentration. ⁽¹⁰⁾

Effect of pH solution on A.B dye adsorption



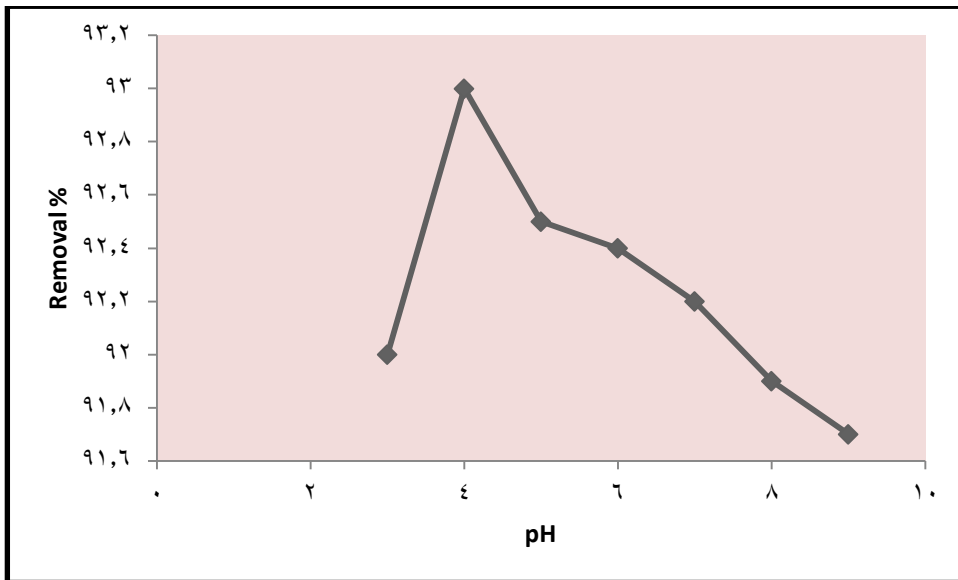


Figure (1-9):)pH effect of adsorption with (20ml) A.B dye concentration (30 ppm) on(0.9g) polymer at (35°C).

The maximum adsorption of dye onto polymer at the pH(4) .

Effect of Contact Time on A.B dye adsorption

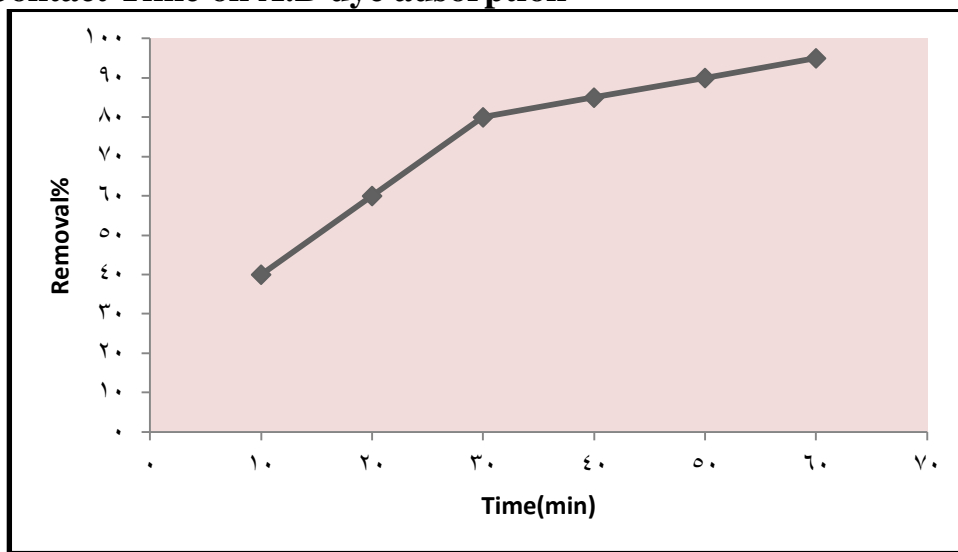


Figure (1-10): Effect of Contact Time at pH (4) with (20 ml) A.B dye concentration (30 ppm) on (0.9g) polymer at (35°C).

It can be estimated that the equilibrium is reached after (30 min).

Effect of temperature on A.B dye adsorption

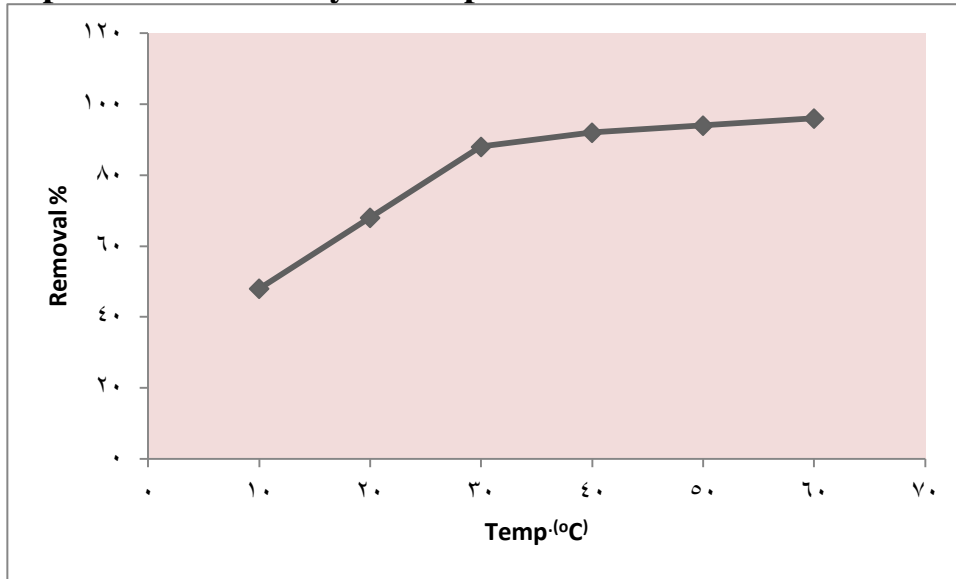


Figure (1-11): Effect of temperature(10-60 °C) at pH (4) with (20 ml) A.B dye concentration (30 ppm) on (0.9g) polymer for (30m).

The figure (1-11) exhibit an increase in the adsorption of A.B dye on the polymer with increase the temperature that due to presence of pores on the surface of adsorbent and Then exhibit decrease the adsorption of A.B dye on the polymer with increase the temperature that due to when temperature increasing that

when temperature increasing that lead to increase the kinetic energy for dye molecules and enter inside the pores thus increase the adsorption with increasing the temperature.⁽¹¹⁾ lead to increase the kinetic energy for adsorbing molecules on the adsorbent surface which may increase the probability of molecule desorbed.⁽¹²⁾

Adsorption isotherm of A.B dye on polymer

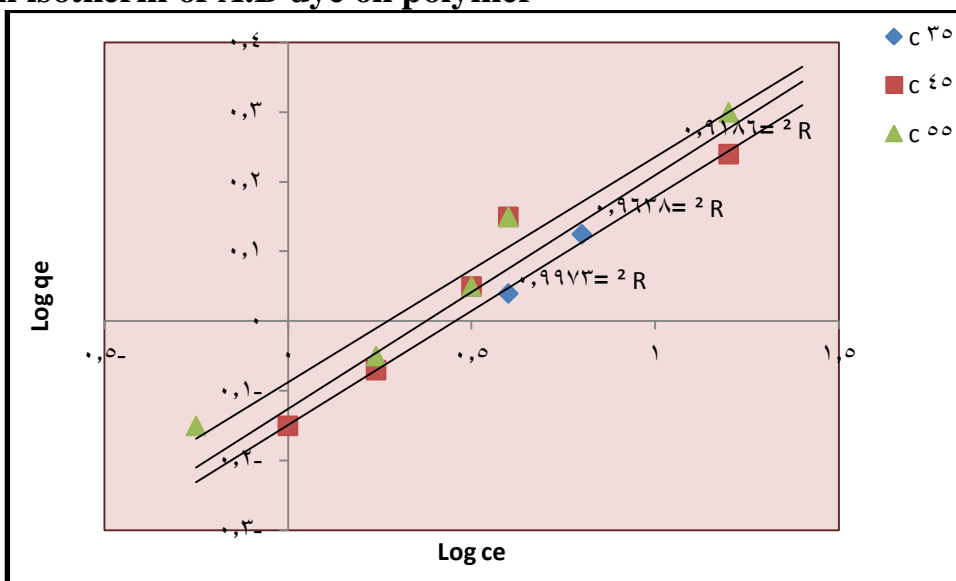


Figure (1-12): Freundlich isotherm for A.B dye on polymer (35, 45, 55)°C.

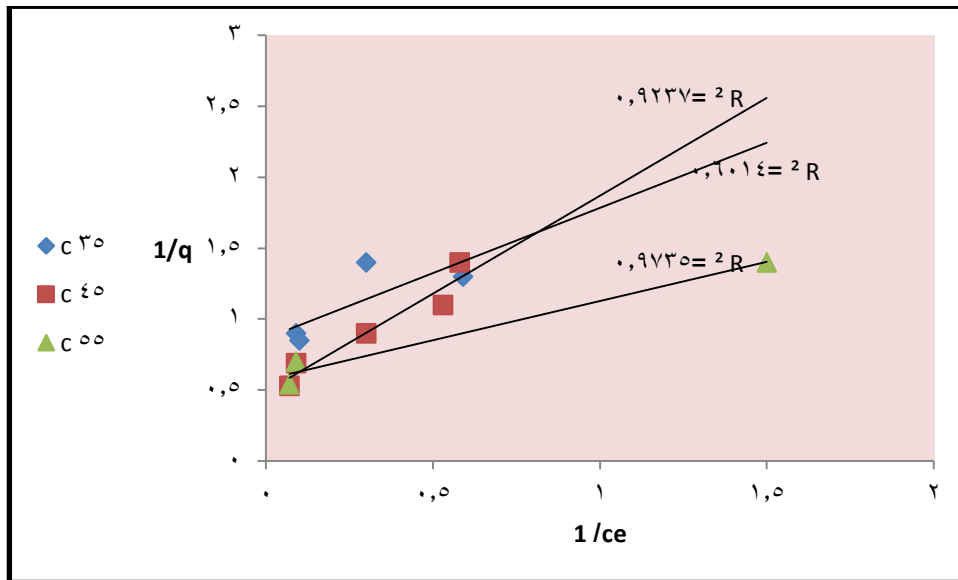


Figure (1-13): Langmuir isotherm for A.B dye on polymer at (35, 45, 55)°C.

The fig. show the straight lines of freundlich and Langmuir isotherm for B.B dye solution at different

temperatures (35, 45, 55)°C. which indicate the adsorption isotherm for A.B dye solution is freundlich isotherm.

Thermodynamic parameters of adsorption of A.B dye on the polymer

The thermodynamic parameters were calculated based on the following equations:

$$\Delta G = -RT \ln K_f \tag{2-4}$$

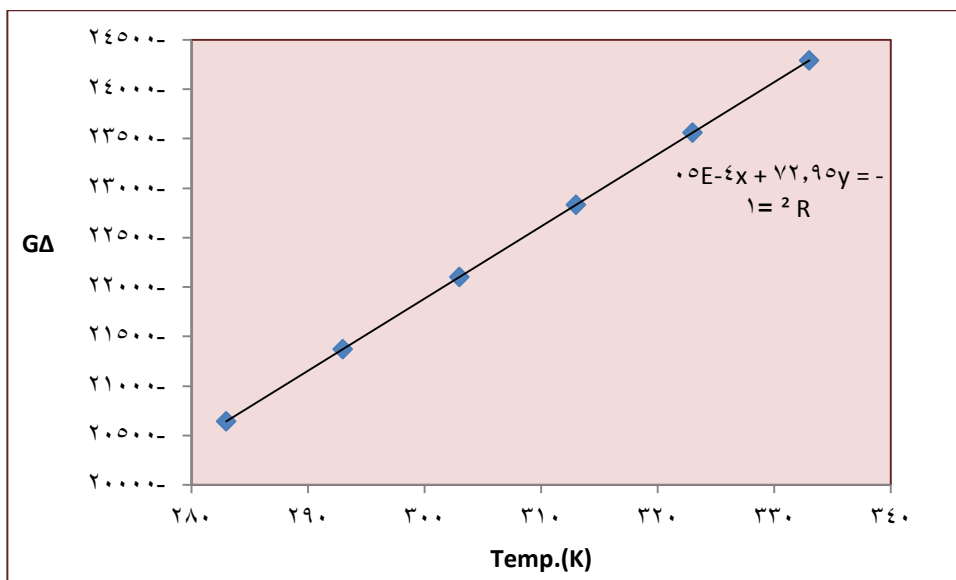
$$\frac{\Delta G}{T} = \frac{\Delta H}{T} - \Delta S \tag{2-5}$$

$$T\left(\frac{\Delta G}{T}\right) = T\left(\frac{\Delta H}{T} - \Delta S\right)$$

$$T\left(\frac{\Delta G}{T}\right) = \Delta H \frac{T}{T} - \Delta S T$$

$$\Delta G = \Delta H - T\Delta S \tag{2-6}$$

where K_f is the equilibrium constant, R is the universal gas constant (8.314 J/mol K), and T is the temperature (K)⁽¹³⁾.



Figure(1-14): Shows the values for the ΔG parameters that is calculate in different temperatures.

Table (1-2): Thermodynamic parameters of adsorption of A.B dye on polymer.

No.	Temp.(K)	ΔG J.mol ⁻¹	ΔH k J.mol ⁻¹	ΔS J.mol ⁻¹ K ⁻¹
1	283	-20644.990		0.733
2	293	-21374.495		3.197
3	303	-22104.000		5.500
4	313	-22833.504	-20.4375	7.654
5	323	-23563.009		9.676
6	333	-24292.514		11.576

Reference :

1- Miles D. C. and Briston J.H.,(1996),"Polymer Technology".

Harris H.E. and Pritchard J.G, (1964), "J. Plym. Sci."A2,3673.

3- Hochst A.G.,(1975), "Neth Appl.74" ,362.

4- Sun-Yi H., David W. L., Raymond S. F.,(2001), "Encyclopedia Of Polymer Science and Technology".

5- Linga A.C., Lraoj., Reddy B.C. and Veera K.B.,(2007)," Thermal and IR studies on copper doped polyvinyl alcohol".

2- Yamashita S., Takakura K. , Imay Y. and Masahura E.,(1978),"Kobunshi Ronbunshu 35",283.

6- Skoog D.A., James H.F., Crouch S.R. (2007)" Principles of Instrumental Analysis".

7- Habibe Y., Guliz A.K. and Senay H.S., (2012) "Removal of Hazardous Food Dye, 8-Brilliant Blue FCF from aqueous solution by Magnetic crosslinked chitosan Beads", Hacettepe J. Bio.& Chem. 40,(1), p 111- 117.

8- Lin J.; Huang Y.; Xiong G. and Dong H., (2001) Polymer preprint, 42 (1) , 695.

9- Fauzy Y. W., (2008) MSc Thesis, A Thermodynamic Study of the Adsorption of Industrial Pollution Dyes in Al-Hilla Textile factory on Sawdust Wood Surface college of education, University of kufa,.

10- Anderson S., Clegg W. and Anderson H. L., (1998). "Crystal

Structure of an Azo dye Rotaxane", Pergamon Press, Oxford, p 37,.

11- Liu Y., and Liu Y. J., (2008) Biosorption isotherms, kinetics and thermodynamics, Separation and Purification Technology, 61,p229–242,.

12- Tamez, U. M., Akhtarul I. M., Shaheen M. & Rukanuzzaman M., (2009). "Adsorptive Removal of Methylene Blue by Tea Waste", J. Haz.Mater., 164,p 53–60,.

الملخص

يتضمن هذا البحث تحضير بوليمر جديد من المواد الاساسية (poly vinyl alcohol و amidacryl) ودراسة بعض من الخواص الفيزيائية ومن ثم دراسة حرارية الامتزاز لصبغة الانيلين الازرق على سطح البوليمر. المواد الخام المستخدمة في التجربة هي مواد متوفرة تجارياً. (benzoyl peroxide، AM، PVA، ethylene glycol ، ferrous sulfate، potassium persulfate) هذه المواد استخدمت بدون تنقيته اضافيه. تخليق البوليمر الجديد تم بوسط مائي بوجود خليط الماء/ ethylene glycol . لمعرفة ظروف التفاعل تم اخذ نسب وزنيه من acryl amide / poly vinyl alcohol و benzoyl peroxide او نظام الأكسدة والاختزال (ferrous sulfate و potassium persulfate) كبادئ للتفاعل. تم اذابة (poly) vinyl alcohol في خليط الماء و (ethylene glycol) في درجة حرارة (60-70) C⁰ . تم انتاج المحلول بعدها اضيفت كمية من acryl (amide) والبادئ مع التحريك المستمر. بعدها تم رفع درجة الحرارة (85-90)C⁰ لمدة (5hr). المادة الناتجة تم تجفيفها بدرجة حرارة (60C⁰) لـ(72h) ساعه لتجنب الهدرجة. تمت دراسة البوليمر المحضر بواسطة تقنيه مطيافية الأشعة تحت الحمراء (FTIR) مع المواد الاساسية (poly vinyl alcohol و acryl amide). ثم أجريت دراسة الامتزاز لإيجاد تأثير كل من (وزن المادة المازة ، تركيزالصبغة ، الدالة الحامضية ، زمن التماس ، تركيز الصبغة وتأثير درجة الحرارة). وإن النتائج التي تم الحصول عليها كانت تدل على ان إمتزاز صبغة الانيلين الأزرق عند تركيز (30ppm) يزداد بزيادة زمن التماس حتى يصل الى حالة التوازن عند (30 min). إن نسب الإزالة (R%) هذه تم الحصول عليها عند زمن الاتزان لكل سطح كذلك عند أفضل وزن من المادة المازة الذي بلغ (0.9 g) للبوليمر.

ومن خلال رسم النتائج تبين انها تتبع آيزوثيرم لانكماير ، كذلك تم حساب الدوال الترموديناميكية

التغيرات في الطاقة الحرة لجبس والتغيير في الانتالبي وكذلك التغير في الانتروبي ($\Delta S - \Delta H - \Delta G$) ،
ومن خلال النتائج التي تم الحصول عليها تبين ان عملية الامتزاز لصبغة الانلين الازرق (A.B) على سطح
البوليمر المحضر و المستخدم ماص للحراره ، وان التفاعل كان تلقائيا من خلال قيم ΔG التي تم الحصول عليها ،
وهناك نقصان واضح في قيم الانتروبي نتيجة حالة الامتزاز الحاصل على سطح البوليمر المستخدم .