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SYNTHESIS AND THERMAL ANALYSIS OF AMBERLITE XAD-2 FUNCTIONALIZED WITH SULPHANILIC ACID

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ABSTRACT

The amberlite series XAD-2 resin was functionalized with sulphanilic acid. Selctive method diazo spacer technique (-N=N-) was used for the fictionalizations of amberlite XAD-2 and the product was abbreviated as SA-N=N-AXAD-2. Intermediates designed in reaction were characterized by FTIR study and final product were characterized by FTIR as well as TGA methods. Thermal decomposition of the functionalized polymer has been studied by thermogravimetric analysis. Thermokinetic parameters such as activation energy (Ea), Free energy change (ΔG) and entropy change (ΔS) of the degradation were resolved by Freeman-Carroll (FC) and Sharp-Wentworth (SW) method. The key advantage of FC method is to calculate both energy of activation (Ea) and order of reaction (n) in a solitary stage by keeping the heating rate constant. The energy of activation (Ea) and order of reaction (n) gained by the FC method was further confirmed by SW method. Thermal activation energy (Ea) calculate by these methods was found to be in close agreement with each other.

KEYWORDS: Amberlite XAD-2; Diazo spacer; Functionalization; Resin; Thermal degradation.

INTRODUCTION

In the recent years, synthesis and thermal degradation study of polymers has become a theme of interest. Now a day polymeric resin has received much attention and importance due to their wide range of industrial applications. The versatility of polymeric resin increases its use in several domains of life. Variously designed phenol-formaldehyde resins have a large number of practical application.[1-3]

Amberlite XAD series resin has efficient support for the anchoring chelating legands due to their high surface area, good porosity, uniform pore size and excellent physical and chemical properties. Amberlite XAD-2 and XAD-4 were found to be more ideal for the functionalization based on their surface area and porosity.[4-6]

The literature survey reveals that the two methods have been often used to design various functionalized chelating resine. First method involved the sorption of chelating legands on to the polymeric matrics and another is based on covalently coupling of a legand with polymer backbone via the several spacer arm, generally azo (-N=N-), methylene (-CH_2-) and SO_2 linkage.[7-10]

Thermal decomposition of the polymer has been studied by thermogrvimetric analysis. Thermal degradation study of polymer resolves the thermal stability of polymer.[11-14] Thermal study of the resin was studied wisely with minute details. Synthesis and thermo-gravimetric analysis, thermal degradation and various kinetic parameters such as Ea, ΔS, ΔG, frequency factor (A) and order of reaction (n) was studied by using Freeman-Carroll and Sharp-Wentworth method.[15-22]

The present work reports the synthesis of functionalized amberlite XAD-2 resin with sulphanilic acid, its thermokinetic parameters were studied by following methods.

A) Freeman–Carroll (FC) Method

Thermokinetic parameters are determined by following expression

$$\frac{\Delta \log(\frac{dw}{dt})}{\Delta \log W_r} = \left[-\frac{E_a}{2.303R}\right] \times \frac{\Delta(1/T)}{\Delta \log W_r} + n$$

Where-

dw/dt - rate of change of weight with time in min.

W_r – difference between weight loss at the completion of reaction at time (t)

E_a – activation energy

n – order of reaction

B) Sharp-Wentworth (SW) method

Thermokinetic parameters were further confirmed by SW method.

$$\log \frac{(d\alpha/dt)}{(1-\alpha)^n} = \log \frac{A}{\beta} - E_a/2.303RT$$

Where-

dα/dt - fraction of weight loss with time

n - order of reaction

A - frequency factor

β - linear heating rate

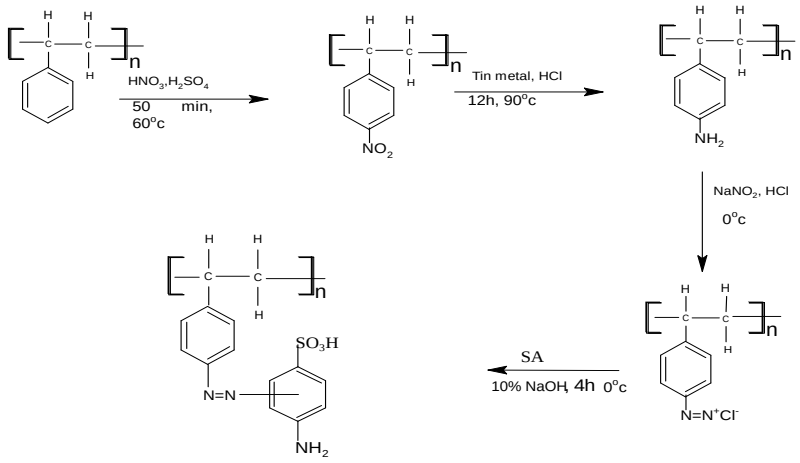
α - fraction of amount of reactant

Experimental Section

Instrumentation: Digital oil bath (Bio Techniques India, Model no. BTI-38) with silicon oil was used for the synthesis. Infrared spectra (4000-400 cm^{-1}) were recorded on FTIR spectrometer(Bruker Alpha- 12228734). Thermogravimetric analysis (TGA) was carried out on a Perkin Elmer Ddiamond TGA thermal analyzer.

Reagents and solutions: Chemical used in this synthesis were pure analytical grade. Amberlite XAD-2 resin (surface area 330 m^2g^{-1}; pore dimeter 9 nm; bead size 20-60 mesh) was procured from Sigma-Aldrich, sulphanilic acid, conc. HCl, HNO_3 and conc. H_2SO_4 were procured from Merck, SD fine chemicals, India Ltd.

Synthesis of functionalized amberlite XAD-2 resin: Amberlite XAD-2 beads in the form of powder (5gm) were crushed finely and nitrated with nitrating mixture (25 ml conc. H_2SO_4 and 10 ml HNO_3) for 30 min. at 50^0C. The reaction mixture was pored in ice cold distilled water and nitrated resin (NO_2-AXAD-2) was collected by filtration. The intermediate product was washed with distilled water until free from acid and dried in air. In a second phase nitrated resin wsa reduced by refluxing it for 12 hrs. with a tin metal in conc. HCl (45 ml) and ethanol (50 ml). The improved aminated resin (NH_2-AXAD-2) was then filtered and repeatedly washed with distilled water and dried. Aminated resin was reacted with 100 ml of 2M HCl for 30 min. which was then filter and wash with distilled water. It was then suspended in 200 ml of ice cold water and then diazotized with 1 M HCl at 0 to -5^0C until the reaction mixture changes the colour of iodided paper tu violet. The diazotized resin was filtered, washed with ice cold water and reacted with sulphanilic acid (15 gm taken in 200 ml of 10% NaOH solution) the resulting product was filtered and washed with distilled water followed by dil. NaOH to remove unreacted sulphanilic acid, then it washed with dil. HCl and finally washed with distilled water. The final product was dried and stored in vacuum desiccator. The overall reaction scheme is shown below.



Scheme. 1: Synthesis of SA-N_2-AXAD-2.

RESULTS AND DISCUSSION

FTIR Spectra: Infrared spectra of pure amberlite XAD-2 resin and intermidiate products obtained in every phase of reaction was studied by FTIR spectrum. FTIR of pure AXAD-2 polymer is shown in figure I. Nitrated resin NO_2-AXAD-2 was confirmed by two prominent peaks at 1525 and 1347 cm^{-1} which were attributed to N-O symmetric and asymmetric stretching vibration (Figure II). The NH_2-AXAD-2 was confirmed by absorption peak at 3371 cm^{-1} for N-H stretching for prinary amine (Figure III). Absorption peak appired at 2124 cm^{-1} is due to -N=N- stretching (Figure IV). A very broad band in the reagion at 3400 cm^{-1} is assigned to the streching of hydroxyl group exhibiting intermolecular hydrogen bonding, peaks at 796 and 758 cm^{-1} is due to $–CH_2$- bending, peak at 2924 cm^{-1} is due to C-H streatching of aromatics, absorption band at 1446-1265 cm^{-1} shows thepreseance of Ar-CH_2-Ar bridge. A peaks observed at 1605 cm^{-1} is due to aromatic ring present in SA-N_2-AXAD-2, absorption at 890 cm^{-1} suggest $–CH_2$- wagging. (Figure V).

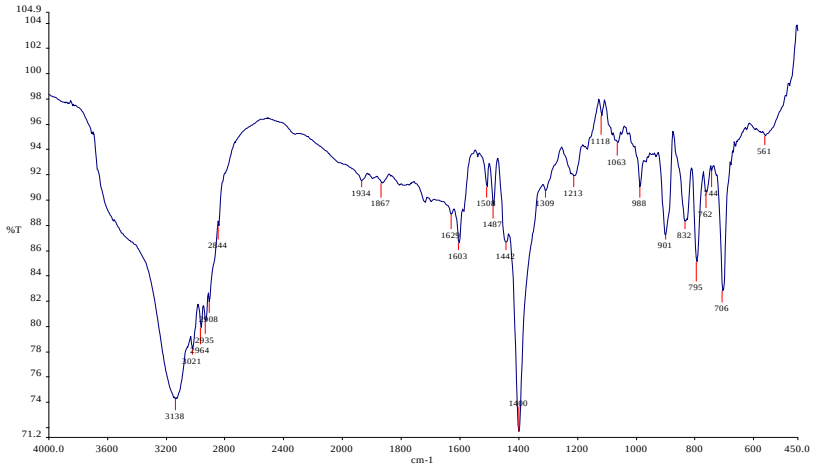


Fig. I FTIR Spectrum of Pure AXAD-2 resin.

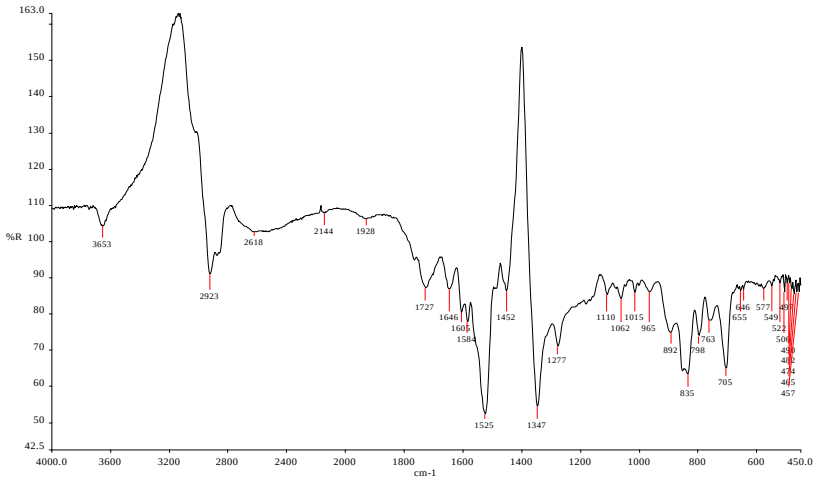


Fig. II FTIR Spectrum of NO_2-AXAD-2.

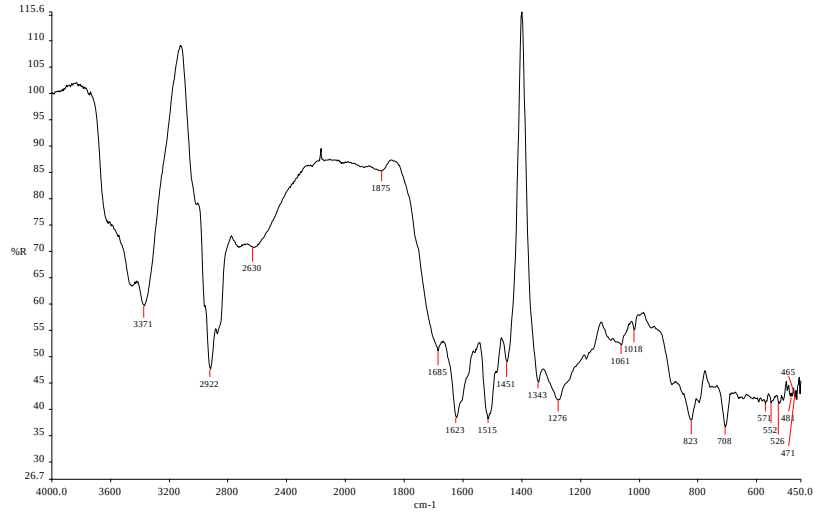


Fig. III FTIR Spectrum of NH_2-AXAD-2.

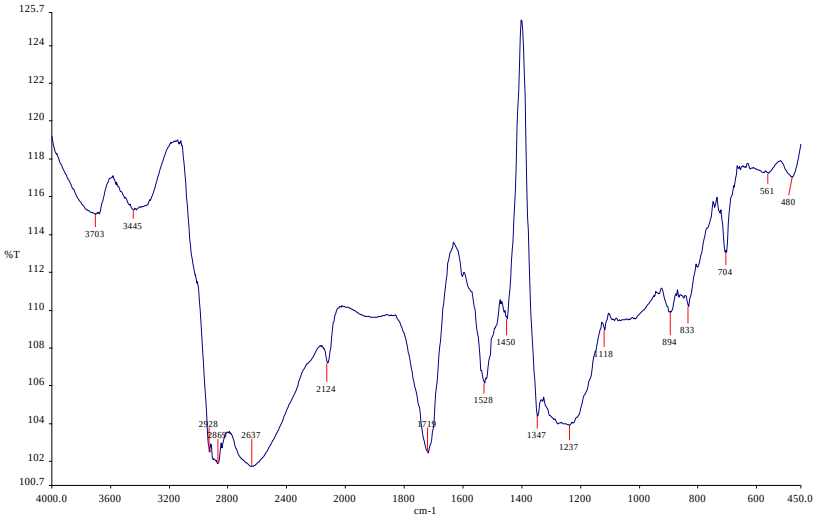


Fig. IV FTIR Spectrum of Cl^-N2^+ -AXAD-2.

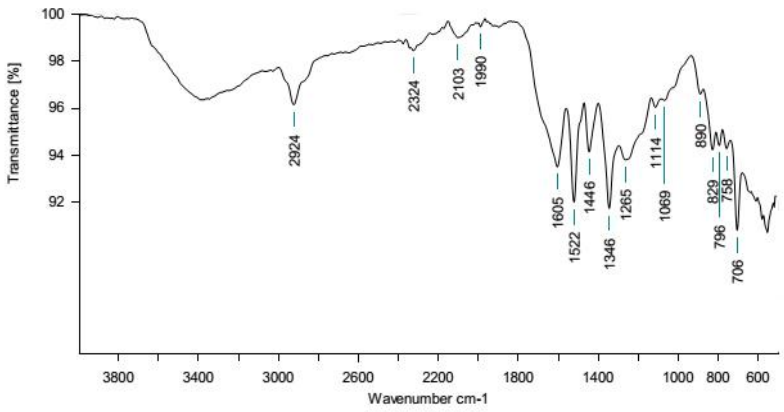


Fig. V FTIR Spectrum of SA-N_2-AXAD-2.

Thermogravimetric analysis (TGA): Thermogravimetric analysis (TGA) of SA-N=N-AXAD-2 was carried out at the Department of Material Science, Vishvesharaya National Institute of Technology (VNIT), Nagpur (M.S.) India.

Thermogram of modified resin SA-N=N-AXAD-2 **(Fig.VI)** was scaned up to 1000^0C by Perkin Elmer Diamond TGA analyzer in the argon environment at a linear heating rate 10^0C min^{-1}. Various thermokinetic parameters were determined by FC and SW methods. Order of reaction (n) and activation energy (Ea) was calculeted by FC method. Loss in weight of product up to 387^0C was due to water in the resin. Major degradation due to dissociation of chemically immobilized moiety start from 410^0C. The order of reaction was found to be 2.0 as obtained from FC plot **(Fig.VII)** which was further confired by SW method **(Fig.VIII)**. The various properties of SA-N=N-AXAD-2 like activation energy (Ea), free energy change (ΔG) and entropy change (ΔS) shown in **table I**.

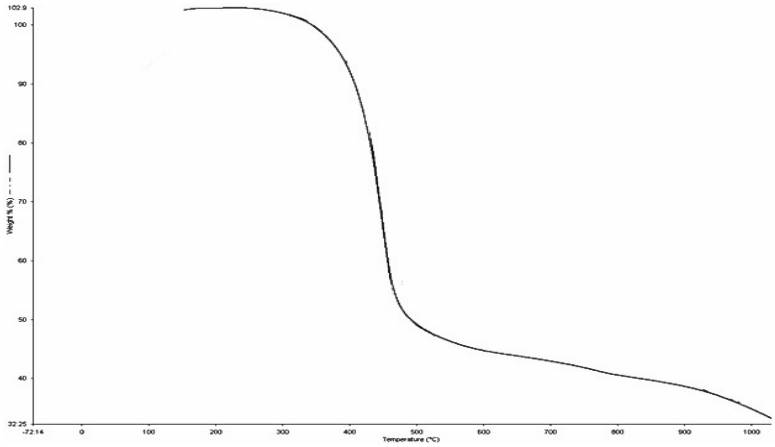


Figure. VI - TG Curve of SA-N=N-AXAD-2.

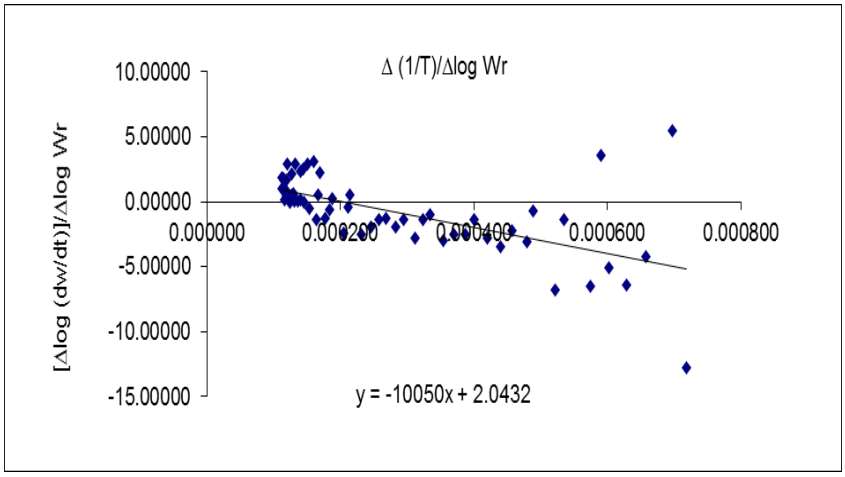


Figure. VII: Freeman-Carroll plot of SA-N=N-AXAD-2.

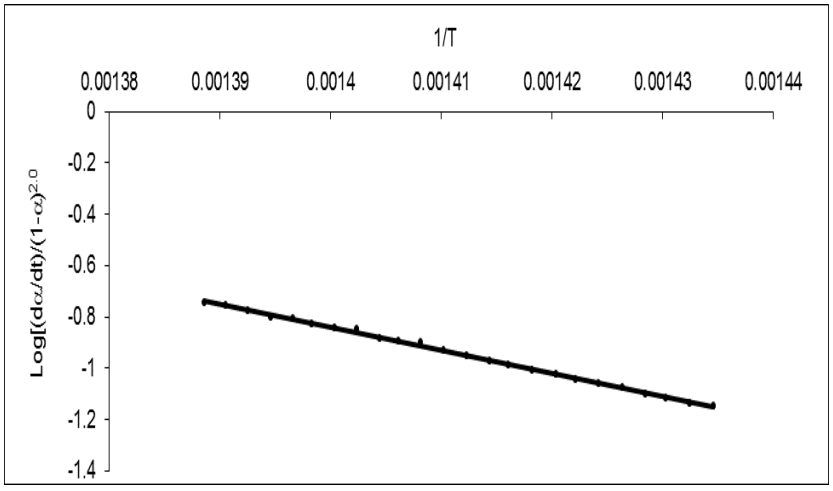


Figure VIII Sharp-Wentworth plot of SA-N=N-AXAD-2.

Table. I: Thermokinetic Thermokinetic parameters of SA-N=N-AXAD-2.

Resin	Parameter	Freeman-Carroll (FC) method	Sharp-Wentworth (SW) method
SA-N=N-AXAD-2	Temperature range (^{0}C)	410-480	410-480
	Activation energy Ea (kJ)	189.9588	119.9377
	Frequency factor A (min^{-1})	5.50 x 10^{12}	6.02 x 10^{11}
	Entropy ΔS (JK-1)	8.237	7.486
	Free Energy ΔG (kJ)	195.817	178.031
	Order of Reaction(*n*)	2.0	2.0

CONCLUSION

From the FTIR studies the proposed structure of the product SA-N_2-AXAD-2 has been determined. Thermogram of SA-N_2-AXAD-2 polymer resin shows activation energy (Ea), calculated by the Freeman–Carroll (FC) and Sharp-Wentworth (SW) methods are in good agreement with each other. The intermediates and final product shown in reaction scheme

were confirmed with the aid of FTIR data which was found to be in good agreement with standard values of FTIR. Various thermokinetic parameters such as entropy (ΔS) and free energy (ΔG) were determined by both (FC and SW) methods are in good agreement . The value of frequency factor (A) and entropy (ΔS) suggest the slow degration rate. The resin undergoes degradation at the high temperature implies that the resin under study are thermally stable at elevated temperature.

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REFERENCES

1. H. Kimura, Y. Murata, A. Matsumoto, K. Hasegawa, K. Ohtsuka, A. Fulkuda, J. Apply. Polym. Sc., 1999; 74: 2273.
2. H. Sahebalzamania, S. Ghammamy, K. Mehrania, F. Salimi, Der Chemica Sinica, 2010; 1: 67-72.
3. P. K. Rahangdale, W. B. Gurnule, L. J. Paliwal, R. B. Kharat, Synth. React. Inorg.Met.Org Chem., 2003; 33: 1205.
4. A. M. Thakre, V. V. Hiwase, A. B. Kalambe, J. Chem. Pharm. Res., 2013; 5: 18-23.
5. Z. Y. Xu, Q. X. Zhang, J. L. Chen, L. S. Wang, G.K. Anderson, Chemosphere, 1999; 38: 2003.
6. R. Kunin, Pure Appl. Chem., 1976; 46: 205.
7. C.W. McLeod, A. Otsuki, K. Okamoto, H. Haraguchi, K. Fuwa, Analyst, 1981; 106: 419-428.
8. T. Akagi, H. Haraguchi, Analytical Chemistry, 1990; 62: 81-85.
9. L. Elci, S. Saracoglu, Talanta, 1998; 46: 1305-1310.
10. A.M.Thakre,V.V. Hiwase,A.B. Kalambe, Der Pharma Chemica, 2013; 5: 244-250.
11. H.K. Kohli, World Journal of Pharmacy and Pharmaceutical Sciences, 2015; 4: 1163-1170.
12. Zhao Hong, Wang Yu-Zhang, Wang Xui-Li and Yang Ke-Ke, Polym Deg Stab., 2002; 80: 135.
13. A. S. Aswar, K. N .Munshi, J. Indian ChemSoc, 1992; 69: 544.
14. K. A. Nandekar, J. R. Dontulwar, W. B. Gurnule, RASAYAN J. Chem., 2012; 5: 261-268.

15. R. N. Singru, J. Chem. Pharm. Res., 2012; 4: 46-53.
16. K. M. Khedkar, V.V. Hiwase, A. B. Kalambe, S. D. Deosarkar, E-Journal of Chemistry, 2012; 9: 1911-1918.
17. A.N. Gupta, V.V. Hiwase, A. B. Kalambe, Der PharmaLettre, 2013; 5: 105-112.
18. S. K. Kapse, V. V. Hiwase, A. B. Kalambe, Der PharmaChemica, 2012; 4: 460-467.
19. S. K. Kapse, V. V. Hiwase, A. B. Kalambe, J.D. Kene, Res. J. Chem. Sci., 2014; 4: 81-86.
20. P. U. Belsare, A. B. Zade, Chem Sci Trans., 2013; 2: 1136-1147.
21. A. D. Kushwaha, V. V. Hiwase, A. B. Kalambe, Der Chemica Sinica, 2012; 3: 794-799.
22. N. Rathore, Mat. Sci. Res. India, 2013; 10: 93-100.