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Research Article

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Synthesis and thermal analysis of amberlite XAD-2 functionalized with 5-Sulfosalicylic acid

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ABSTRACT

The amberlite XAD-2 resin was functionalized with 5-sulfosalicylic acid. Selective method diazo spacer technique (-N=N-) was used for the functionalization of amberlite XAD-2 and the product was abbreviated as 5-SSA-N=N-AXAD-2. Intermediates formed in the reaction were characterized by FTIR method and resulting product was further characterized by FTIR and TGA. Thermo-kinetic parameters were determined by Freeman-Carroll (FC) and Sharp-Wentworth (SW) methods. Activation energy (Ea), free energy changes (ΔG) and entropy change (ΔS) of degradation were calculated by both FC and SW methods. Results were found to be in good agreement. The order of degradation (n) obtained by the FC method was finally confirmed by SW method.

Key words: Amberlite XAD-2; diazo spacer; functionalization; resin; thermal degradation

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INTRODUCTION

Since last three decades, functionalized and thermally stable polymeric materials have attracted much attention of analysts, modern chemists and environmentalists owing to the cheap cost, durability, ease of synthesis, analysis at elevated temperatures, regeneration and handling [1].

Functionalized chelating resins as ion exchangers is focused attractive analytical tool outstanding to the improvement in selectivity for hazardous metal ions. The two means for attaching ligands to polymer matrix are impregnation and functionalization. Impregnation involves physical adsorption while functionalization implicates chemical bonding based on the covalent coupling of the ligand with polymer backbone through a diazo spacer arm (-N=N-) [2]. Recently, the amberlite XAD resins functionalized with various ligands such as Pyrocathecole, organophosphrus extractants, Cyanex-272, 2-Mercaptobenzimidazole, 1-(2-pyridylazo)-2-napthol are popularly used for the functionalization[3-7].

Polymer degradation occurs throughout the life of the polymer by oxidative as well as thermal degradation. In previous studies, thermo gravimetric analysis of polymer provides information about the degradation pattern and thermal stability. [8-9]. Thermodynamic parameters and order of thermal stabilities of polymers have been studied by using TGA[10]. Synthesis and thermo gravimetric analysis, thermal degradation kinetics and various kinetic parameters such as, Ea, ΔS, ΔG, frequency factor(A) was studied using Freeman – Carroll (FC) and Sharp-Wentworth (SW) method by researcher the world over[11-15]. Freeman-Carroll method is much more helpful than

any other method since it provides information about activation energy and order of thermal degradation at one single time. Latter that can be confirmed by Sharp-Wentworth method. [16-22]

Amberlite XAD series resin have efficient support for anchoring chelating legands due to their good porosity, uniform pore size distribution, high surface area, and excellent physical and chemical properties. Amberlite XAD-2 and XAD-4 have been ideal for the functionalization based on their porosity and surface area [23-30].

The present paper report the synthesis of functionalized amberlite XAD-2 resin with 5-sulfosalicylic acid and its thermo-kinetic parameter were studied by FC and SW method.

1.1. Freeman-Carroll Method (FC)

Thermo-kinetic parameters were determined by following expression

$$\frac{\Delta \log(\mathrm{d}w/\mathrm{d}t)}{\Delta \log W_r} = \left[-\frac{E_a}{2.303R}\right] \times \frac{\Delta\left({}^{1}/_{T}\right)}{\Delta \log W_r} + n$$

Where;

d*w*/dt - Rate of change of weight with time in min

W_r -Difference between weight loss at completion of reaction and at time *t*

E_a -Activation energy

n -Order of reaction

1.2. Sharp-Wentworth method (SW)

In this method thermo-kinetic parameters were determined by using following expression.

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

Where;

dα/dt -Fraction of weight loss with time

n -Order of reaction

A -Frequency factor

A -Fraction of the amount of reactant

EXPERIMENTAL SECTION

2.1. Materials and Methods

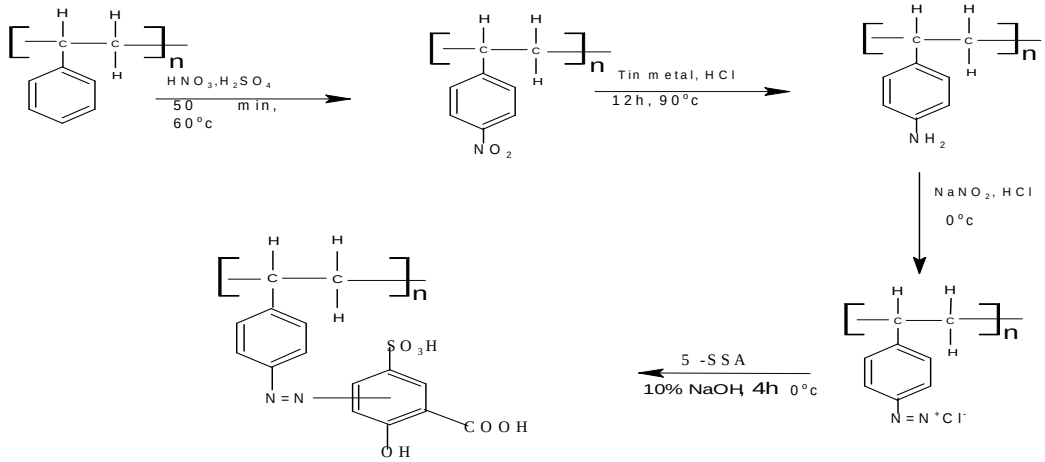
Chemicals used in the synthesis were pure analytical grade. Amberlite XAD-2 resin (surface area, 330 $m^2 g^{-1}$; pore diameter 9 nm; bead size 20-60 mesh was procured from Sigma-Aldrich (USA). 5- Sulfosalicylic acid (Sigma Aldrich), conc. HCl, conc. HNO_3 and conc. H_2SO_4 were procured from Merck, SD Fine Chemicals, India Ltd.

Digital oil bath (Bio Techniques India, Model BTI-38) with silicon oil was used for the synthesis. Infrared (IR) spectra were recorded on a Nicolet FT-IR spectrometer. Thermo-gravimetric analysis (TGA) was carried out on a Perkin Elmer Diamond TGA thermal analyzer.

2.2. Synthesis of functionalized amberlite XAD-2 resin

Amberlite XAD-2 beads (5 gm) were crushed and nitrated with 10 ml of concentrated HNO_3 and 25 ml of concentrated H_2SO_4 (nitrating mixture) for 30 min. at 50^0C. The reaction mixture was poured in ice cold water and nitrated resin (NO_2-AXAD-2) was collected by filtration. The intermediate product was repeatedly washed with distilled water until free from acid and dried. On further nitrated resin was reduced by refluxing for 12 hours with tin metal in conc. HCl (45 ml) and ethanol (50 ml). The modified aminated resin (NH_2-AXAD-2) was filtered and repeatedly washed with distilled water until free from acid. Aminated resin was treated with 100 ml of 2M HCl for 30 min. filter and washed with distilled water. It was then suspended in 200 ml of ice-cold water and then diazotized with 1M $NaNO_2$ and 1M HCl at 0 to -5^0C until the reaction mixture started change in colour of iodide paper from white to violet. The diazotized resin was filtered, washed with ice cold water and reacted with 5-sulfosalicilyc 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 5-Sulfosalicylic acid then it was washed with dil. HCl and finally again

washed with distilled water. Final product was dried and stored in vacuum dessicator. The complete reaction presented in(scheme 1).



Scheme 1: Synthesis of 5-SSA-N_2-AXAD-2

RESULTS AND DISCUSSION

3.1. FTIR Spectra

Infrared spectra of pure AXAD-2 polymer and intermidiate products obtained in each step of synthesis was characterized by FTIR spectrum. FTIR of pure AXAD-2 polymer is shown in (Figure 1) NO_2-AXAD-2 was confirmed by the prominent two peaks at 1525 and 1347 cm^{-1} which were attributed to N-O asymmetric and symmetric stretching vibration (Figure 2). The NH_2-AXAD-2 was confirmed by IR absorption peak at 3371 cm^{-1} for N-H stretching of primary amine (Figure 3). Peak appeared at 2124 cm^{-1} is due to –N=N- stretching (Figure 4). A very broad band seen in the region 3504 cm^{-1} is assigned to the stretching vibration of the hydroxyl group exihibiting intermolecular hydrogen bonding, peak at 832 cm^{-1} shows tetra-substituted aromatic ring, peak at 795 and 763 cm^{-1} is due to $–CH_2$- bending, peak observed at 2922 cm^{-1} is due to C-H streatching of aromatics, absorption band at 1452-1250 cm^{-1} suggest the preseance of Ar-CH_2-Ar bridge. A peak appeared at 1604 cm^{-1} is due to aromatic ring present in 5-SSA-N_2-AXAD-2, absorption at 892 cm^{-1} suggest $–CH_2$- wagging. (Figure 5).

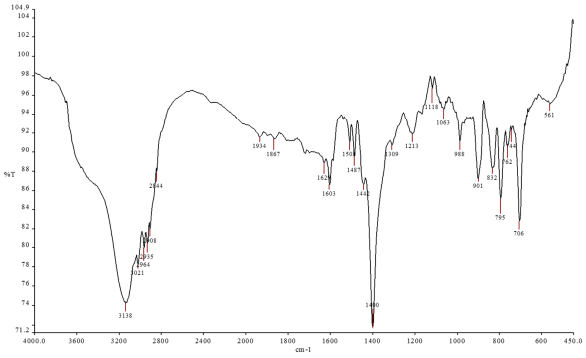


Figure 1 FTIR Spectrum of pure-AXAD-2 resin

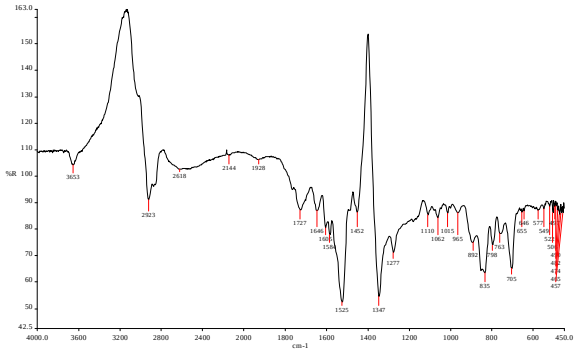


Figure 2 FTIR Spectrum of NO_2-AXAD-2

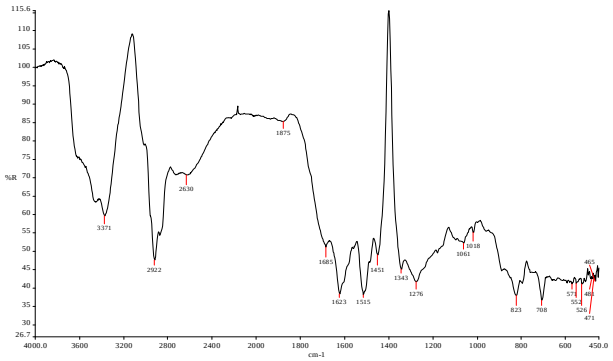


Figure 3 FTIR Spectrum of NH_2-AXAD-2

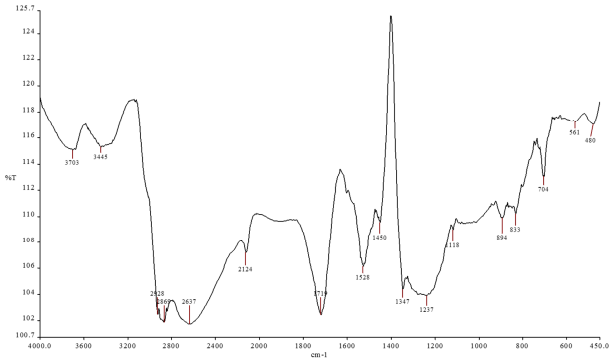


Figure 4 FTIR Spectrum of Cl N_2-AXAD-2

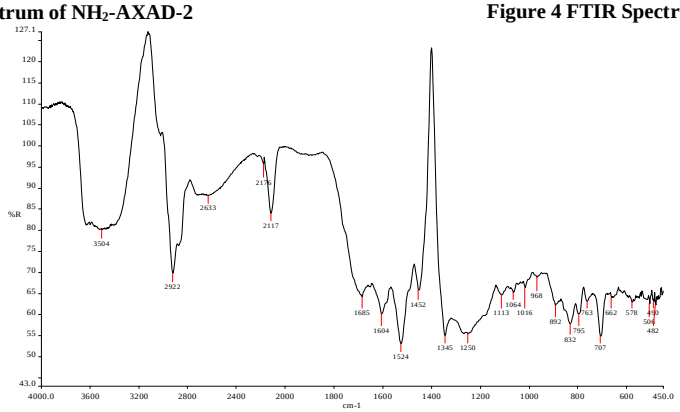


Figure 5 FTIR Spectrum of 5-SSA-N_2-AXAD-2

3.2. Thermogravimetric analysis(TGA)

TGA analysis of 5-SSA-N=N-AXAD2 was carried out at Department of Material Science, Vishvesharaya National Institute of Technology (V.N.I.T.), Nagpur (M.S.) India. Thermogram of 5-SSA-N=N-AXAD2 (figure 6) was scaned up to 1000^0C by Perkin Elmer Diamond TGA analyzer in argon environment at linear heating rate 10^0C min^{-1}. Related thermokinetic parameters were determined by FC and SW methods. Order of degradation and activation energy was calculated by FC method. Weight loss up to150^0C was due to water in polymer. Major degradation start from 405^0C is due to the dissociation of chemically immoblized moiety and polymeric matrix. The order of reaction was found to be 0.5 obtained from FC plot (figure7) which was further confirmed by SW method. SW plot shown in (figure 8). The various properties of 5-SSA-N=N-AXAD2 like aactivation energy (Ea), free energy changes (ΔG) and entropy change (ΔS) shown in (Table 1).

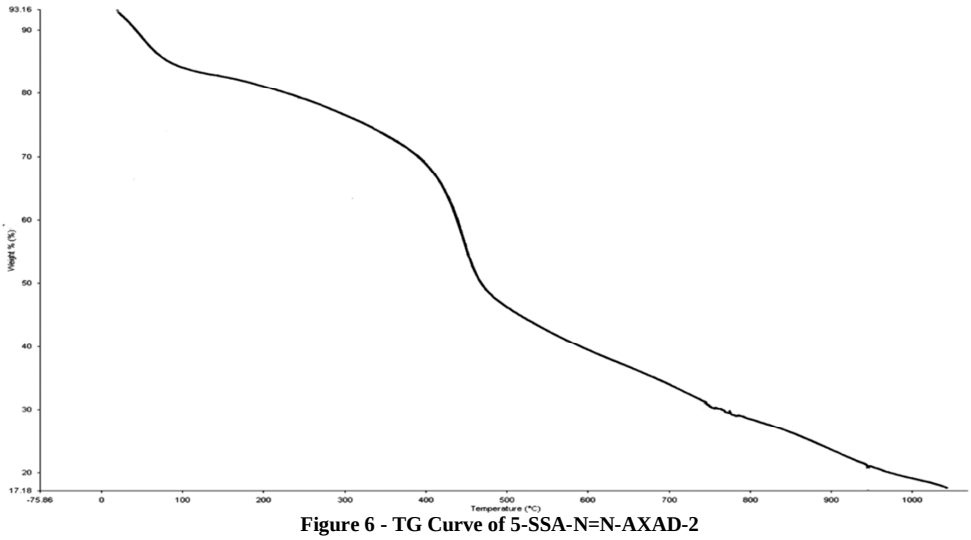


Figure 6 - TG Curve of 5-SSA-N=N-AXAD-2

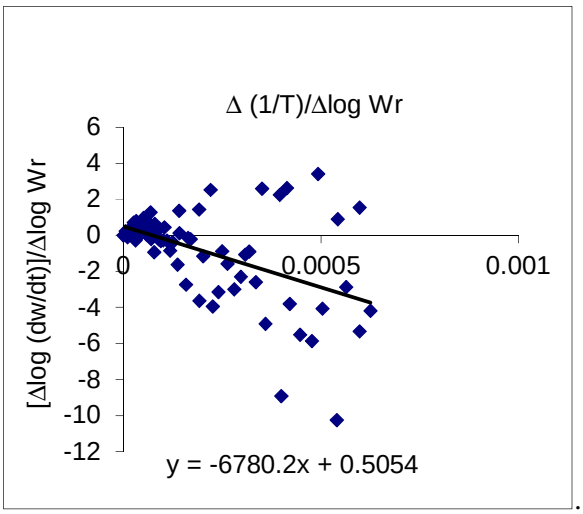


Figure 7 Freeman-Carroll plot of 5-SSA-N=N-AXAD-2

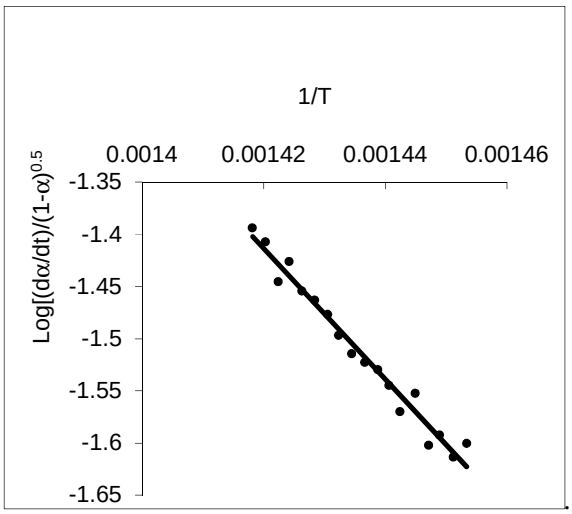


Figure 8 Sharp-Wentworth plot of 5-SSA-N=N-AXAD-2

CONCLUSION

Modified amberlite XAD-2 product (5-SSA-N=N-AXAD2) is conformed by FTIR spectra and thermogravimetric anaysis which is in good aggrement with the reaction scheme shown above. Position of attachment of 5-SSA to the resin via diazo spacer is not clear as per fingerprint region of FTIR spectrum. Low value of frequency factor suggest slow degradation of resin. Activation energy (Ea), free energy changes (ΔG) and entropy change (ΔS) of degradation was calculated by both FC and SW methods and excellent analytical results were predicted from study.

Table-1 : Thermokinetic parameters of 5-SSA-N=N-AXAD-2

Resin	Parameter	Freeman-Carroll method (FC)	Sharp-Wentworth method (SW)
5-SSA-N=N-AXAD-2	Temprature range (^{0}C)	405-480	405-480
	Activation energy Ea (KJ)	124.32	119.94
	Frequency factor A (min^{-1})	4 x 10^8	3.034 x 10^8
	Entropy ΔS (JK^{-1})	-87.07	-89.83
	Free Energy ΔG (KJ)	186.68	184.27
	Order of reaction (*n*)	0.5	0.5

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