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Synthesis and Thermokinetic parameters of Amberlite XAD-4 functionalized with Hydroquinone

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ABSTRACT

Amberlite XAD-4 resin was functionalized by coupling it through an –N=N- group with hydroquinone. The resulting intermediate products were characterized by FTIR method. The functionalized resin was characterized by elemental analysis and FTIR. The Thermokinetic parameters were determined by Freeman-Caroll (FC) and Sharp-Wentworth (SW) methods. The activation energies of degradation were found to be 41.61KJ (FC method) and 40.56KJ (SW method). The free energy and entropy of degradation was calculated by both of these methods were found to be in good agreement. The order of degradation obtained by FC method was found to be 0.85 which was further confirmed by SW method.

Keywords:- Resin, Functionalization, Amberlite XAD-4, Thermal degradation, Thermokinetic parameters.

INTRODUCTION

Functionalization of commercial available resins such as Amberlite XAD-2, XAD-4, IRC-718 are the boon for analysts and chemists which has been widely used for the purpose of preconcentration and solid phase extraction of valuable metal ions [1-4]. Chelating resins have been frequently used SPE's (Solid phase extraction) as they provide good stability, high sorption capacity for metal ions and good flexibility in working conditions. Researchers have frequently used two of the amberlite resins, XAD-2, XAD-4, as the matrix for the preparation of functional resins. Much of the work treated these resins as standard polystyrene resins, with no mention of the presence of vinyl group. In 1962, Rohm and Haas announced the preparation of macroreticular (macroporus) resin [3].

In 1967, the first of the amberlite adsorbents became commercially available. The styrenic based one were developed as high surface area non polar adsorbents with application in the pharmaceutical and water-treatment industries[4].One of the most frequently used resin is Amberlite XAD-4[5-6].

Two methodologies have been frequently adopted for designing such chelate functionalized Amberlite XAD resins. First involves sorption of ligand onto a matrix. The second one based on covalent coupling of a ligand with polymer back bone through a spacer arm, generally –N=N- or $–CH_2-$ group. Recently, Amberlite XAD-4 functionalized with quinoline-8-ol [7]. In1981, deMunck and coworkers conducted extensive research on Amberlite XAD-2 and XAD-4 [8]. Faber and coworkers modified XAD-2 and XAD-4. They found by transmittance infrared spectroscopy that XAD-2 was composed of styrene, divinylbenzene and ethylvinylbenzene, whereas XAD-4 was composed of divinylbenzene and ethylvinylbenzene[9].

Zuo and Muhammes used XAD-2 and XAD-4, and other styrenic resin to prepare coordinating resins [10]. The styrene units were chloromethylated, aminated with hexamethylenetetramine and then converted to the polymer-bound thiourea functionality by reaction with NH_4CN. Fritz and coworkers used XAD-4 as a matrix for the preparation of many modified resins. One modification involved first acetylation, followed by hydrolysis to the benzyl alcohol functionality, then esterification with thioglycolic acid to produce a resin with thioglycoloylmethyl groups[11].Various hydroxamic acid resins have been prepared from XAD-4. The first step involved acetylation followed by oxidation of the acetophenone groups to carboxylic acid groups. The carboxyl groups were then converted to acid chloride (chloroformyl) groups by reaction with thionyl chloride. The addition of various hydroxyl amines to the acid chloride groups formed hydroxamic acid group.The surface characteristics of XAD-4 were also altered by modification [12-14]. Functional groups such as $-C(CH_3)_3$, $-CH_2OH$, $-COCH_3$, $-COCH_2CH_2COOH$, and $-CH_2CN$ were added using Friedel-Crafts methods. The modified resin showed differences as chromatographic materials due to difference in their hydrophilicity. Armer studied the effects on sorptive properties by modification of XAD-4 [15-16]. Functional groups which were incorporated included: alkanes, ketone, amines, sulphonamides, fluorocarbons, polyglycols with or without methylcapping, benzyl alcohol, chloromethyl, bromopentafluorophenyl, and phosphonic acid.

MATERIALS AND METHODS

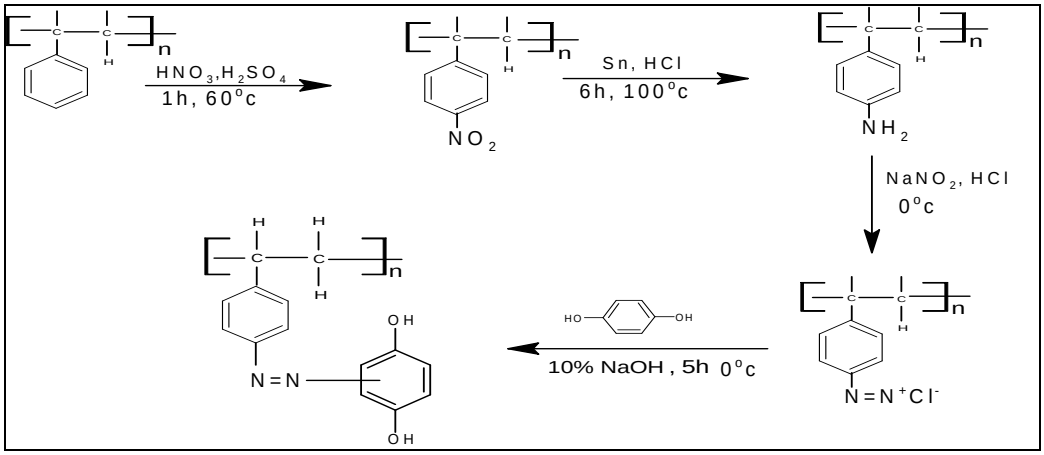
Material

The chemicals used for the synthesis were chemically pure and analytical grade.

Amberlite XAD-4, Hydroquinone, Conc.HCl, Conc.HNO_3, Conc. H_2SO_4 and NaOH were obtained from Merck, SD-Fine Chemicals, India Ltd.

Functionalization of Amberlite XAD-4 resin

Amberlite XAD-4 (7g) was nitrated with the help of nitrating mixture (21ml conc.HNO_3 and 63ml conc. H_2SO_4) by refluxing the mixture at 60^{o}c for 1.5 hrs. The reaction mixture was poured in ice cold water. The nitrated resin was collected by filtration; the product was repeatedly washed with water and dried. In second step the product was reduced with the help of tin and HCl at about 90^{o}c for 6 hrs. The aminated resin was obtained which was purified by washing with water to remove excessive HCl. The aminated resin was boiled with conc. HCl so as to for amine hydrochloride. The amine hydrochloride of resin was poured into ice cold water and then it was treated slowly with 65ml of 1M $NaNO_2$ solution. The diazotized resin quickly filtered and washes with ice cold water repeatedly. The diazotized resin was coupled with hydroquinone in presence of 10% NaOH at 0^{o}c with constant stirring for 5-6 hrs. The product so obtained was washed with water followed by dilute NaOH solution to remove unreacted hydroquinone impurity then it was washed with dilute HCl to get yellowish brown colored product. It was repeatedly washed with water dried in air and stored in vacuum desiccator. The reaction scheme shown below.



Scheme 1: Synthesis of HQ-Amberlite-XAD4

RESULTS AND DISCUSSION

Elemental analysis (CHN):

The elemental analysis of functionalized Amberlite XAD-4 was carried out at Central Institute of Mining and Fuel Research, Nagpur. The elemental analysis data are given in following table 1.

Table1: Elemental analysis of HQ-XAD-4

	C	H	N
Found (%)	80.29	8.12	7.51
Calculated (%)	80.21	8.02	7.48

IR Spectra:

The product obtained in each step of synthesis was characterized by FTIR spectrum. The nitrated amberlite XAD-4 is confirmed by the prominent peaks at 1550 and 1349 cm^{-1} which are attributed to N-O asymmetric and N-O symmetric streching vibration respectively (Fig.1). The NH_2-XAD-4 was identified with IR absorption peaks at 3358, 3210, 1623 and 1306 cm^{-1} for N-H stretching, N-H bending, C-N stretching respectively (Fig.2). The diazotized XAD-4 product was confirmed by the prominent peak at 1525, 1487 cm^{-1} attributed to the presence of –N=N- (Fig. 3). Formation of HQ-XAD-4 was confirmed by the prominent peak 3214 cm^{-1}(broad), 2928, 1238 and 831 cm^{-1} corresponding to H bonded phenolic –OH, C-H stretch, C-O stretching vibration and p-disubstituted aromatic ring respectively (Fig.4)[18-21].

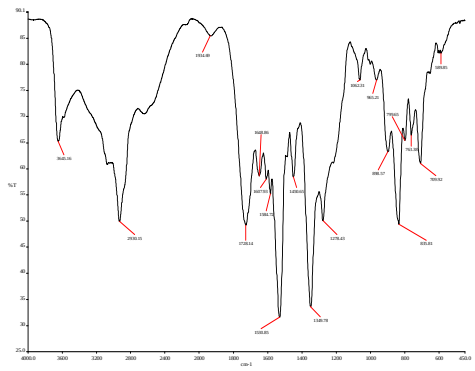


Fig.1: FTIR Spectrum of NO2-XAD-4

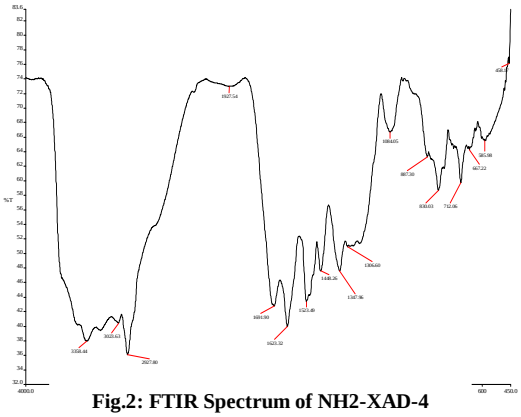


Fig.2: FTIR Spectrum of NH2-XAD-4

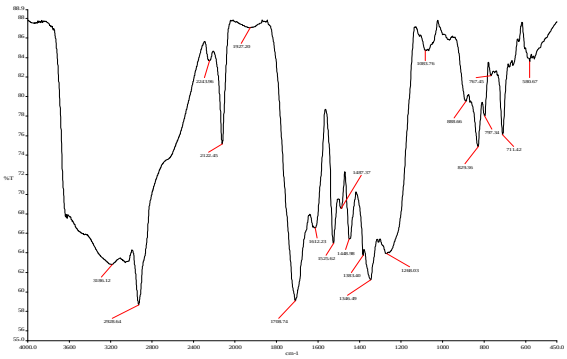


Fig.3: FTIR Spectrum of Cl-N=N-XAD-4

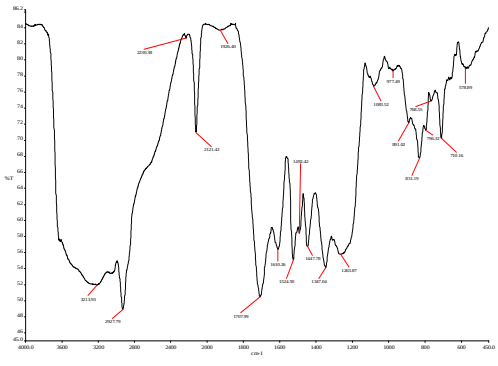


Fig.4: FTIR Spectrum of HQ-XAD-4

Thermogravimetric Analysis:

The TGA Analysis of HQ-XAD-4 was carried out at Department of Material Science, VNIT, Nagpur. Thermogram of HQ-XAD-4 resin was scanned up to 1000°c by perkin Elmer Diamond TGA/DTA analyzer in argon environment. The weight loss up to 150°c was due to the water molecule in polymer. Major degradation starts from 315°c (Fig- 5). The order of degradation was found to be 0.85, obtained by Freeman-Carroll method further confirmed by Sharp-Wentworth method [22-26]. The thermokinetic parameters of resin in temperature range 315-455°c are shown in following table (Table 2),

Table 2: Thermokinetic Parameters

Resin	Parameters	Freeman-Caroll method	Sharp-Wentworth method
HQ-XAD-4	Temperature range	588-728 K	588-728 K
	Activation energy, kJ	41.61	40.56
	Frequency factor, Z (min-1)	172	354.7
	Apparent entropy, ΔS (JK-1)	-209.17	-203.15
	Free energy, ΔG (kJ)	186.63	181.41
	Order of reaction, n	0.85	0.85

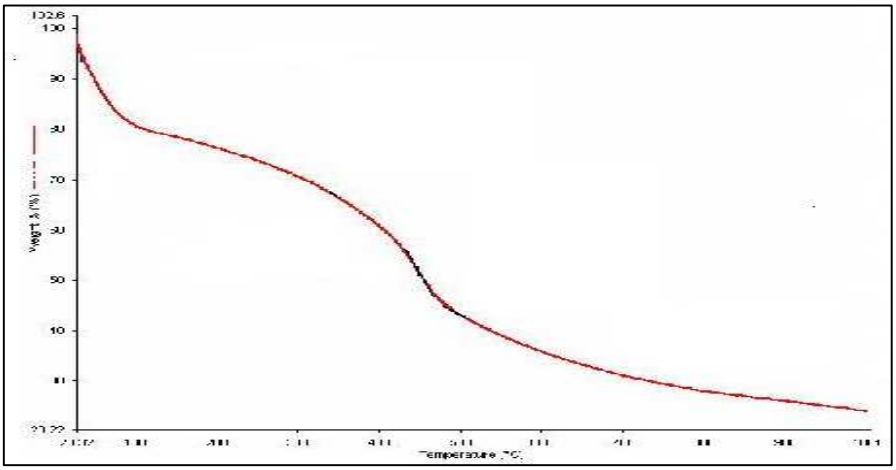
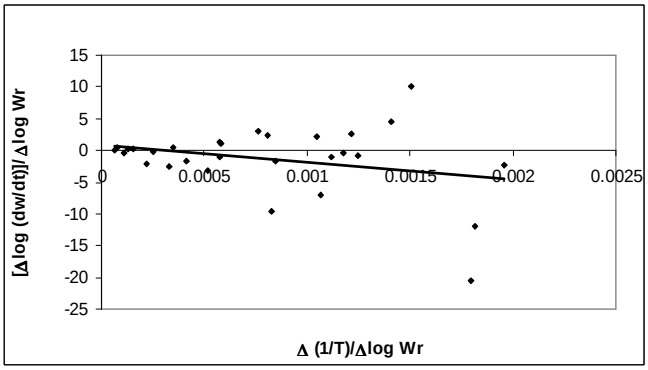


Fig.-5 : TG Curve of HQ-XAD-4



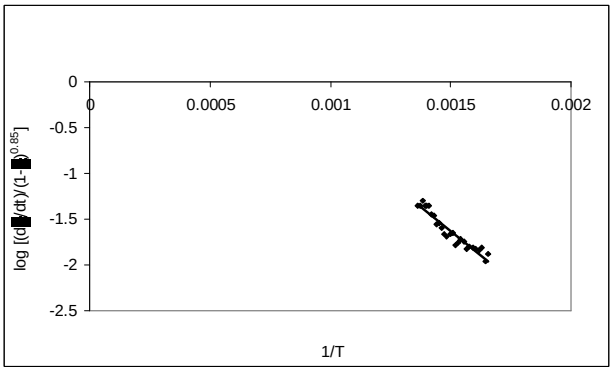


Fig 6:- (a): Freeman-Caroll plot of HQ-XAD4 resin
(b): Sharp-Wentworth plot of HQ-XAD4 resin

CONCLUSION

The functionalized Amberlite XAD-4 product (HQ-Amberlite XAD-4) is confirmed by elemental analysis, FTIR spectra and thermogravimetric analysis is in good agreement with the reaction scheme shown above. However the position of attachment of hydroquinone to the resin via azo group to the polymer matrix is not clear as per finger print region of FTIR spectrum. Low value of frequency factor suggests the slow degradation of resin. The values of activation energy, free energy and entropy obtained by FC and SW method are in good agreement. The fractional order of degradation is attributed to solid state thermal degradation.

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