



Synthesis and thermal analysis of Amberlite XAD-4 functionalized with p-toludine

Abhishek M. Thakre¹, Vinay V. Hiwase² and Ashok B. Kalambe¹

¹Department of Chemistry, Institute of Science, Nagpur, (MS) India

²Department of Chemistry, Arts, Commerce and Science College, Arvi, Wardha, (MS) India

ABSTRACT

Amberlite XAD-4 resin was functionalized by coupling through the $-N=N-$ group (azo spacer arm) with p-toludine. Resulting intermediate products were characterized by FTIR method. The functionalized resin was characterized by elemental analysis and FTIR. Thermokinetic parameters were determined by Freeman-Carroll (FC) and Sharp-Wentworth (SW) methods. Activation energies of the degradation were found to be 27.28 kJ (FC method) and 25.60 kJ (SW method). Free energy change (ΔG) and entropy change (ΔS) of the 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 zero which was further confirmed by SW method.

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

INTRODUCTION

Amberlite XAD series resins with a polystyrene-divinyl benzene copolymer matrix have efficient support for anchoring chelating ligands due to their good porosity, uniform pore size distribution, high surface area, and excellent chemical and physical stability. Amberlite-XAD resins have superior physical properties like durability and chemical stability towards harsh environments [1]. These resins, including XAD-2 and XAD-4 have been ideal for the preparation of functional resins based on their porosity and surface area [2-3]. Styrenic resins are excellent substrates for the preparation of functional polymers and recently more attempts have been made to modification of amberlite XAD-4 (AXAD-4) as per industrial importance by using various preconcentration methods such as ion-exchange, liquid-liquid extraction, coprecipitation, solid-phase extraction (SPE) and flotation [4-14].

Two methodologies have been frequently adopted for designing such chelating functionalized amberlite XAD resins. First involves physical sorption of ligands onto a matrix and other is based on covalent coupling of a ligand with polymer backbone through a spacer arm, generally $-N=N-$ or $-CH_2$ group. Recently, amberlite XAD resins functionalized with allyl phenol [15], chronotropic acid [16], pyrocatechol [17]. styrene-divinylbenzene copolymers are the most popular sorbents for trace enrichment purposes [18]. Modified amberlite resins shows improved ion-exchange properties, thermal resistance properties, electrical conductivity properties and good storage stability [19]. Beiraghi *et al* were used functionalized amberlite resin to extract beryllium in water sample using micelle-mediated extraction and determined by inductively coupled plasma-atomic emission spectrometry [20]. Al-Blaty *et al* used N-methylfluorohydroxamic acid as the complexing agent and amberlite XAD-4 as the adsorbent for the sorption of insoluble metal complexes in water [21].

Thermo gravimetric studies of polymer provide information about the degradation pattern during heating and thermal stability. Polymer degradation occurs throughout the life of the polymer both by oxidative and thermal degradation [22]. Degradation generally takes place by way of two major competing mechanisms: peeling-off,

which consists of the removal of monomers or oligomers, one at a time, and the random scission of the polymer backbone [23]. In general, the quality and quantity of ashes and the levels of off-gas during pyrolysis are significantly affected by the degree of cross-linking of the resins [24-25] and the environments of air or nitrogen gas [26, 27-30].

Herrera *et al* reported major species evolving from thermal degradation of polyamides and a kinetic study of the thermal degradation under dynamic conditions using discrimination method [31]. Simister *et al* studied thermal degradation rates and effect of different counter ions on the polystyrene-divinylbenzene ion exchange resins under the simulated conditions : temperature and high purity water [32]. Thermal analysis of functionalized amberlite XAD resins with nitrosonaphthol were studied by Memon and co-workers [33]. Kapse *et al* have reported thermodynamic parameters and order of thermal stabilities of terpolymers by using TGA [34]. Many co-workers determined various kinetic parameters such as ΔS , ΔF , Z , S^* and G^* by using Freeman- Carroll and Sharp-Wentworth method [35,36]

The present paper reports the synthesis of functionalized amberlite XAD-4 resin with p-toludine and its thermokinetic parameters of thermal degradation of resin using following methods [37-41].

A) Freeman-Carroll Method (FC)

In this method thermokinetic parameters are determined by following expression (1)

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

Where

dw/dt = rate of change of weight

W_r = difference between weight loss at the completion of the reaction and at time t

E_a = activation energy

n = order of reaction

B) Sharp-Wentworth method (SW)

Following expression (2) has been used to evaluate the kinetic parameters.

$$\log \frac{d\alpha / dt}{(1 - \alpha)^n} = \log \frac{A}{\beta} - \frac{E_a}{2.303RT} \quad \text{-----} \quad (2)$$

Where

$d\alpha/dt$ = 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

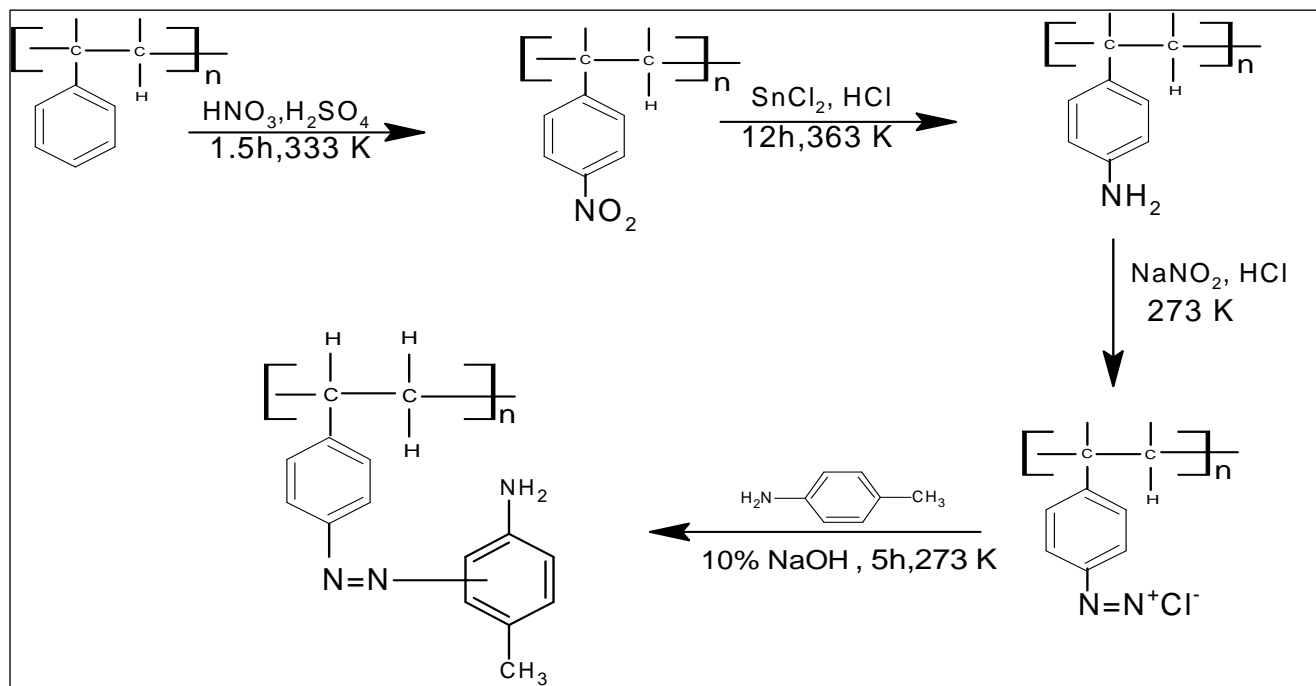
Materials

Chemicals used for the synthesis were pure and of analytical grade. Amberlite XAD-4, p-toludine, conc. HCl, conc. HNO₃, conc. H₂SO₄ and NaOH were procured from Merck, SD Fine Chemicals, India Ltd.

Functionalization of Amberlite XAD-4 resin

Amberlite XAD-4 (AXAD-4) was nitrated with the help of nitrating mixture by refluxing the mixture at 333 K for 1.5 hrs. Reaction mixture was poured in ice cold water and nitrated resin (NO₂-AXAD-4) was collected by filtration. The product was repeatedly washed with water and dried. In second step product was reduced with the help of SnCl₂, conc. HCl and ethanol at about 363 K for 12 hrs. Aminated resin (NH₂-AXAD-4) was obtained and purified by washing with water to remove excessive HCl. Aminated resin was boiled with conc. HCl so as to form amine hydrochloride. The amine hydrochloride of resin was poured into ice cold water and then it was treated slowly with 1M NaNO₂ solution. Diazotized resin (Cl-N=N-AXAD-4) quickly filtered and washed with ice cold water repeatedly. Diazotized resin was coupled with p-toludine in presence of 10% NaOH at 273 K with constant stirring for 5-6 hrs. The final product, functionalized amberlite XAD-4 with p-toludine (p-TLND -N=N-AXAD-4) so obtained was washed with water followed by dilute NaOH solution to remove unreacted p-toludine impurity then it

was washed with dilute HCl and getting yellowish brown colored product. It was repeatedly washed with water dried in air and stored in vacuum desiccator. The complete reaction scheme shown below.



Scheme. Synthesis of p-TLDN-N=N-AXAD-4

RESULTS AND DISCUSSION

Elemental analysis of p-TLDN-N=N-AXAD-4 (C, H, N)

Elemental analysis of functionalized Amberlite XAD-4 was carried out at Central Institute of Mining and Fuel Research (C.I.M.F.R.), Nagpur (M.S.) India. Elemental analysis data given in following Table 1.

Table 1: Elemental analysis of p-TLDN-N=N-AXAD-4

	C	H	N
Found (%)	81.14	7.29	11.57
Calculated (%)	81.89	7.08	11.03

FTIR Spectra

Product obtained in each step of synthesis was characterized by FTIR spectrum. NO₂-AXAD-4 was confirmed by the prominent peaks at 1550 and 1349 cm⁻¹ which were attributed to N-O asymmetric and N-O symmetric stretching vibration respectively (Fig.1). The NH₂-AXAD-4 was identified with IR absorption peaks at 3356, 3203 cm⁻¹ for N-H stretching. Peaks at 1623 and 1306 cm⁻¹ N-H bending, C-N stretching respectively (Fig.2). Cl-N=N-AXAD-4 was confirmed by the prominent peak at 1524, 1487 cm⁻¹ which is attributed to the presence of -N=N- (Fig. 3). Formation of p-TLDN-N=N-AXAD-4 was confirmed by peaks at 3600, 3610 cm⁻¹ (doublet) N-H stretching in NH₂ group and C-N Stretching at 1347 cm⁻¹ for aromatic primary amine. The strong peak at 2929 cm⁻¹ was due to aliphatic C-H stretch. The peaks obtained at 2000-1700 cm⁻¹ was assign to overtone and combination bands. 1022, 1082 cm⁻¹ C-H bend (in plane) and 710 cm⁻¹ C-H bend (out of plane).

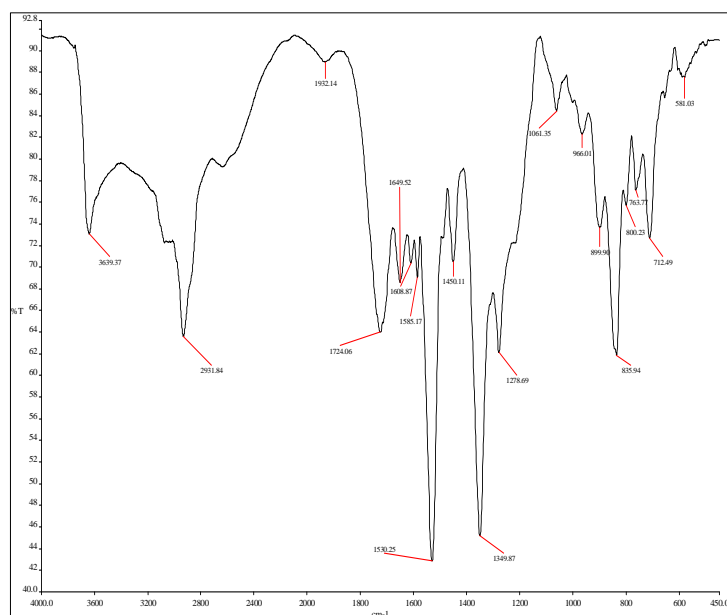
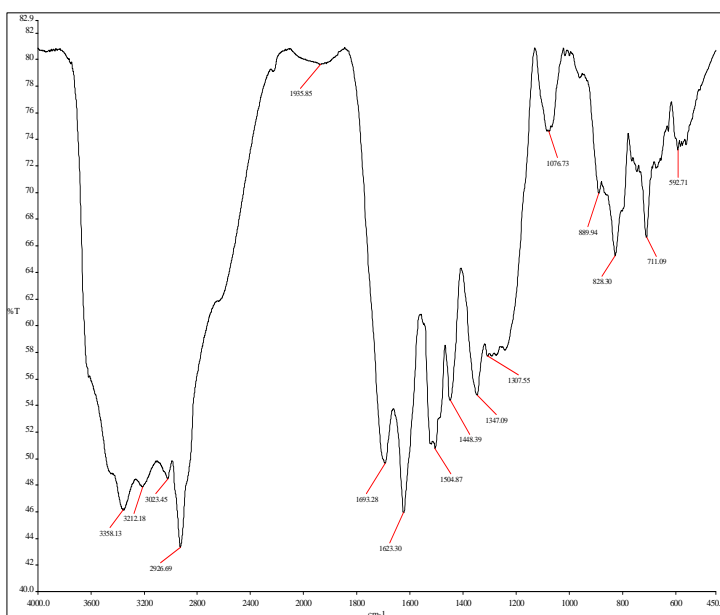
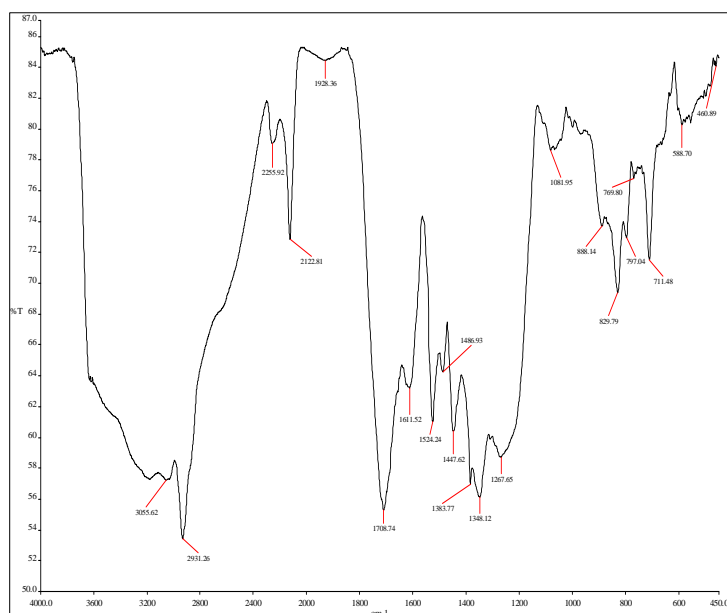
Fig. 1 - FTIR Spectrum of NO₂-AXAD-4Fig. 2 - FTIR Spectrum of NH₂-AXAD-4

Fig. 3 - FTIR Spectrum of Cl-N=AXAD-4

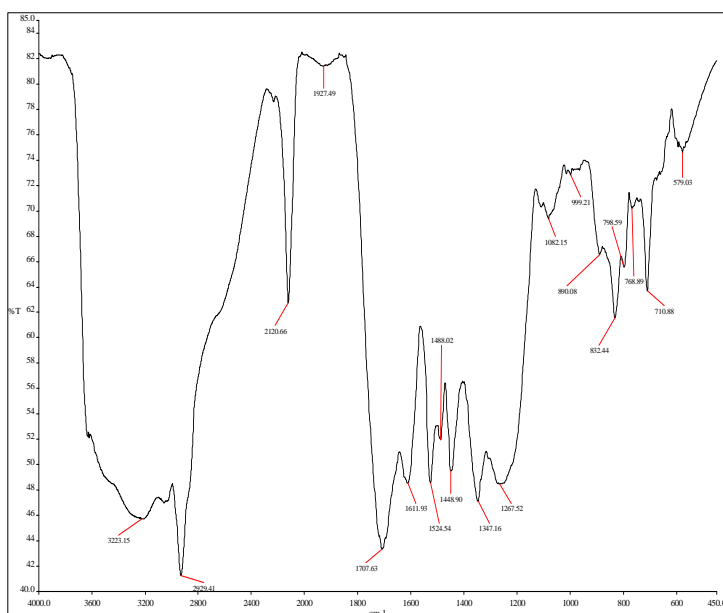


Fig. 4 - FTIR Spectrum of p-TLDN-N=N-AXAD-4

Thermogravimetric analysis (TGA)

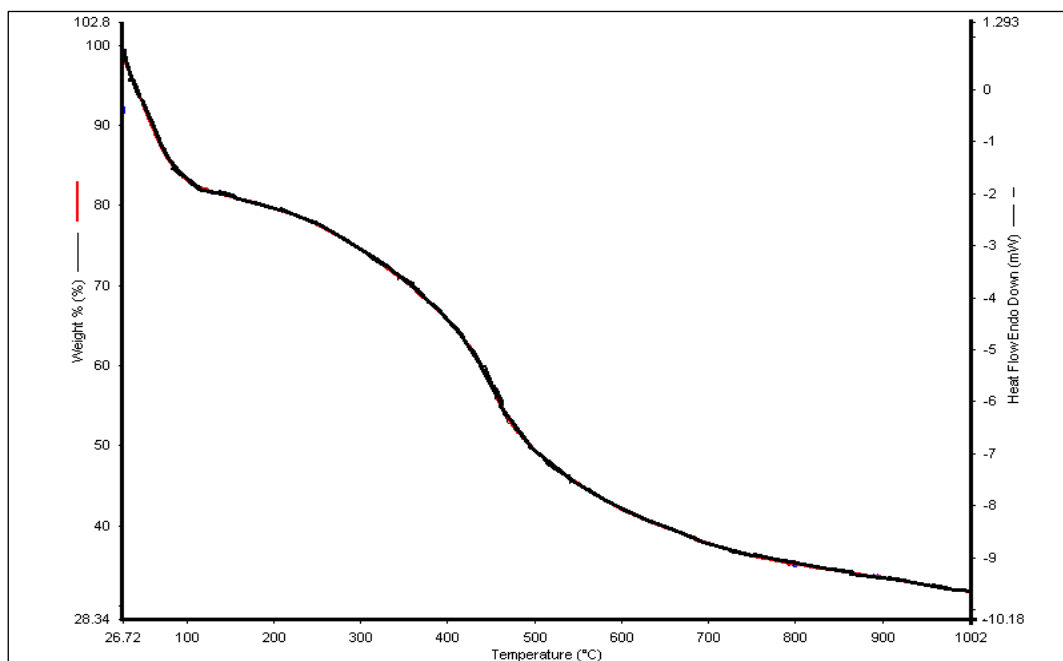
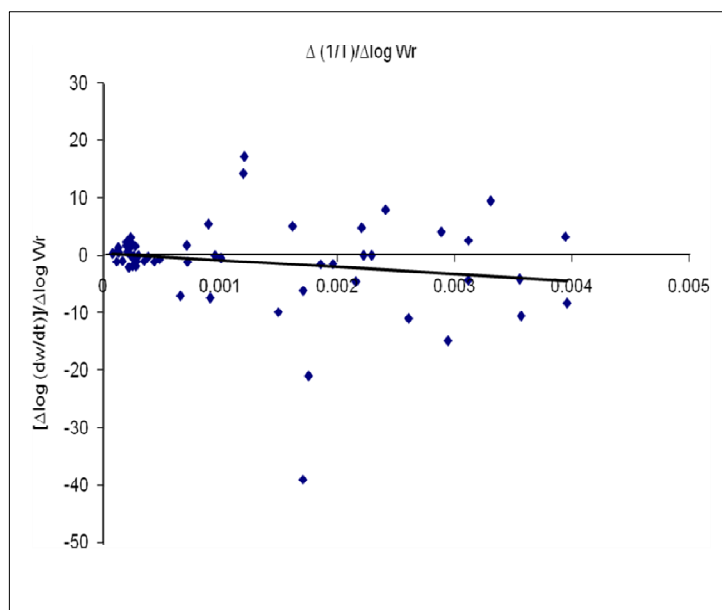
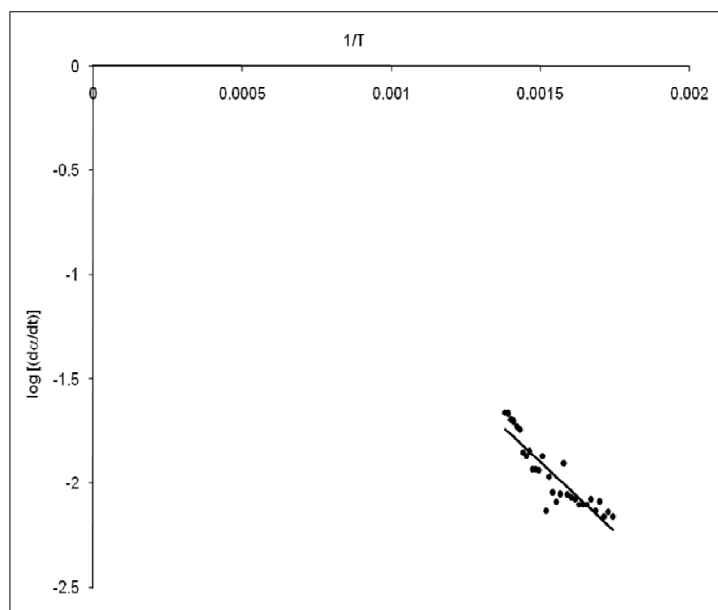
TGA analysis of p-TLDN-N=N-AXAD-4 was carried out at the Department of Material Science, Vishveshwaraya National Institute of Technology (V.N.I.T.), Nagpur (M.S.) India.

Thermogram of p-TLDN-N=N-AXAD-4 (Fig. 5) was scanned up to 1273 K by Perkin Elmer Diamond TGA/DTA analyzer in argon environment at linear heating rate 283 K min⁻¹. The thermokinetic parameter were determine by FC and SW methods. Activation energy and order of reaction have been calculated simultaneously by FC method.

Weight loss up to 453 K was due to the water molecule in polymer. Major degradation starts from 638 K is due to the dissociation of chemically immobilized moiety and polymeric matrix. The order of degradation was found to be zero which was obtained from FC plot (Fig. 6a) further confirmed by SW method. SW plot shown in Fig. 6b. Thermokinetic parameters of resin in temperature range 543-823K shown in Table 2.

Table 2: Thermokinetic parameters of p-TLDN-N=N-AXAD-4 by different methods

Resin	Parameters	Freeman-Carroll method	Sharp-Wentworth method
p-TLDN-N=N-AXAD-4	Temperature range	543-823 K	543-823 K
	Activation energy E_a (kJ)	27.28	25.60
	Frequency factor A (min^{-1})	14.26	14.32
	Apparent entropy ΔS (JK^{-1})	-271.60	-271.64
	Free energy ΔG (kJ)	218.42	216.75
	Order of reaction n	0.0	0.0

**Fig. 5 - TG Curve of p-TLDN-N=N-AXAD-4****Fig. 6(a) - Freeman-Carroll plot of p-TLDN-N=N-AXAD-4****Fig. 6(b) - Sharp-Wentworth plot of p-TLDN-N=N-AXAD-4**

CONCLUSION

Functionalized amberlite XAD-4 product (p-TLDN-N=N-AXAD-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 p-toluidine 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 energies, entropy change (ΔS), free energy change (ΔG) and frequency factor (A) obtained by FC and SW method are in good agreement.

Acknowledgment

Authors are thankful to the Director and Head, Dept. of Chemistry, Institute of Science, Nagpur (M.S.) India for providing necessary facility. We are thankful to the Director, CIMFR, Nagpur, India (M.S.) India for analysis of samples.

REFERENCES

- [1] SD Cekic; H Filik; R Apak. *Analytica Chimica Acta*, **2004**, 505, 15-24.
- [2] ZY Xu; QX Zhang; JL Chen; LS Wang; GK Anderson. *Chemosphere*, **1999**, 38(9), 2003-2012.
- [3] R Kunin. *Pure and Appl. Chem.*, **1976**, 46, 205-211.
- [4] J Dumont; M Cote; J Hubert. *Applied Spectroscopy*, **1989**, 43(7), 1132-1135.
- [5] J Kubova; V Nevorál; V Streko. *J. Anal. At. Spectrom*, **1994**, 9(3), 241-243.
- [6] PL Malvanker; VM Shinde. *Analyst*, **1991**, 116(10), 1081-1084.
- [7] CW McLeod; A Otsuki; K Okamoto; H Haraguchi; K Fuwa. *Analyst*, **1981**, 106(1261), 419-428.
- [8] T Akagi; H Haraguchi. *Analytical Chemistry*, **1990**, 62(1), 81-85.
- [9] L Elci; S Saracoglu. *Talanta*, **1998**, 46(6), 1305-1310.
- [10] C Frigge; E Jackwerth. *Analytica Chimica Acta*, **1991**, 242, 99-105.
- [11] S Kagaya; Y Araki; K Hasegawa. *Fresenius Journal of Analytical Chemistry*, **2000**, 366(8), 842-845.
- [12] S Kagaya; ZA Malek; K Hasegawa. *Analytical Sciences*, **2002**, 18(8), 923-926.
- [13] RE Santelli; M Gallego; M Valcarcel. *Analytical Chemistry*, **1989**, 61(13), 1427-1430.
- [14] K Cundeava; T Stafilov; G Pavlovska. *Spectrochimica Acta Part B*, **2000**, 55(7), 1081-1087.
- [15] MN Nezhati; HA Panahi; E Moniri; SR Kelahrodi; F Assadian; M Karimi. *Korean J. Chem. Eng.*, **2010**, 27(4), 1269-1274.
- [16] PK Tewari; AK Singh. *Analyst*, **1999**, 120, 1847-1851.
- [17] PK Tewari; AK Singh. *Talanta*, **2001**, 53, 823-833.
- [18] GA Junk; IH Suffet; M Malayiandi. *Organic Pollutants in Water*, eds., ACS Symp.; Washington D.C. 201, **1987**, 214.
- [19] JH Chen; YY Kao; CH Lin. *Separation Science and Technology*, **2003**, 38(15), 3827-3852.
- [20] A Beiraghi; S Babae. *Analytica Chimica Acta*, **2008**, 607(2), 183-190.
- [21] IA Al-Biaty; JS Fritz. *Anal. Chim. Acta*, **1983**, 146, 191-200.
- [22] JR Stahlbush; RM Strom. *Reactive Polym*, **1990**, 13(3), 233-240.
- [23] LR Van loon, MA Glaus. *J. Environ. Polym. Degrad.*, **1997**, 5(2), 97-109.
- [24] B Elvers; S Hawkings; M Ravenscroft; G Schuiz. *Ion exchangers*, in: *Ullmann's Encyclopedia of Industrial Chemistry*, VCH Publishers, New York, **1989**, A14, 394-410.
- [25] JW Neely. *Carbon*, **1981**, 19, 27-36.
- [26] UK Chun; K Choi; KH Yang; JK Park; MJ Song. *Waste Manage*, **1998**, 18(3), 183-196.
- [27] S Pettersson; G Kemmier. *Waste Management Arizona Board of Regents*, **1984**, 2, 223-225.
- [28] M Matsuda; K Funabashi; H Yusa. *J. Nucl. Sci. Technol.*, **1987**, 24, 124-128.
- [29] M Matsuda; K Funabashi; T Nishi; H Yusa; M Kikuchi. *Nucl. Technol.*, **1986**, 75, 187-192.
- [30] MA Dubois; JF Dozol; C Nicotra; J Serosé; C Massiani. *J. Anal. Appl. Pyrolysis*, **1995**, 31, 129-140.
- [31] M Herrera; G Matuschek; A Kettrup. *Chemosphere*, **2001**, 42, 601-607.
- [32] C Semister; F Caron; R Gedye. *Journal of Radioanalytical and Nuclear Chemistry*, **2004**, 261(3), 523-531.
- [33] SQ Memon; MI Bhangar; SM Hasany; MY Khuhawar. *Talanta*, **2007**, 72(5), 1738-1745.
- [34] SK Kapse; VV Hiwase; A. B. Kalambe. *Der Pharma Chemica*, **2012**, 4(1), 460-467.
- [35] RN Singru; VA Khati; WB Gurnule; AB Zade; JR Dontulwar. *Anal. Bioanal. Electrochem.*, **2011**, 3(1), 67-86.
- [36] DN Urade; VV Hiwase; AB Kalambe. *J. Chem. Pharm. Res.*, **2012**, 4(1), 732-740.
- [37] ES Freeman; DA Anderson. *J. Polym. Sci.*, **1961**, 54(159), 253-260.
- [38] JH Sharp; SA Wentworth. *Anal. Chem.*, **1969**, 41(14), 2060-2062.
- [39] AD Kushwaha; VV Hiwase; AB Kalambe. *Der Chemica Sinica*, **2012**, 3(4), 749-799.
- [40] KM Khedkar; VV Hiwase; AB Kalambe; SD Deosarkar. *E-Journal of chemistry*, **2012**, 9(4), 1911-1918.
- [41] AM Thakre; VV Hiwase; AB Kalambe. *Arch. App. Sci. Res.*, **2012**, 4(2), 1150-1154.