



Synthesis of environmental friendly chelating biopolymers for the selective adsorption of metal ions to be used in effluent treatment

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ABSTRACT

Chemical modification of naturally occurring polysaccharide, guaran has been made by incorporating 5-aminosalicylic hydroxamate moiety to improve its selectivity and capacity for heavy metal ions. 5- Amino salicylic acid hydroxamate derivative of guaran (ASAH-G) was synthesized, characterized and its adsorption behavior with Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), U(VI), W(VI), Cr(VI) and Ca(II) metal ions was studied at equilibrium in terms of molar distribution coefficient values (K_d). The metal adsorption ability of the resin was compared with the hydroxamate derivative of dialdehyde guaran (HADA-G). Separation of a mixture of Fe(II) and Co(II) was achieved using column chromatography.

Keywords: 5- Amino salicylic acid hydroxamate, Selective metal adsorption, Guarant.

INTRODUCTION

During the past few decades, increase in both industrial activities and urbanization has led to huge increase in the amount of various wastes including heavy metal inputs into the environment (1). Most of them are toxic and represent a serious threat to human population as well as flora and fauna. Chelating resins find great applications as selective ion-exchanger in separation and pre-concentration of metal ions (2-4). Chelating resins have been found to be more useful than chelating agents because they combine the advantageous properties of the polymer backbone and the functional group both.

Guaran (5), a naturally occurring polysaccharide having linear chains of β -(1 \rightarrow 4) - D - mannopyranose units with α -D- galactopyranosyl units attached by a (1 \rightarrow 6) linkage, possesses excellent flocculating properties (Fig.1).

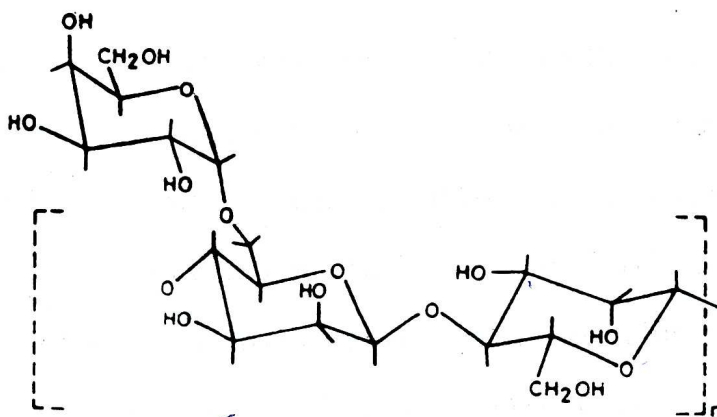


Fig. 1 . Structure of Guarant

It is cheap, hydrophilic, easy to get structurally modified and biodegradable. Incorporation of chelating groups into the guaran polymer provides required selectivity for the separation of metal ions.

Therefore, in continuation of our work on naturally occurring chelating biopolymers and their adsorption behavior (6-8), we report here the synthesis of 5- amino salicylic acid hydroxamate derivative of guaran (ASAH-G), its adsorption behavior and comparison of its adsorption ability with hydroxamic acid derivative of dialdehyde guaran (HADA-G).

MATERIALS AND METHODS

2.1. Reagents

Guaran Powder (200 mesh size) was obtained from the local guar gum industry. 5- Amino salicylic acid, hydroxylamine hydrochloride, epichlorohydrin, metal salts and all the reagents were analytical grade chemicals.

2.2. Physical measurements

Infrared spectra of the synthesized resins were recorded on the Shimadzu IR-400 spectrophotometer using KBr pellets. A Perkin Elmer-2380 atomic absorption spectrophotometer was used for the quantitative determination of metal ions. Nitrogen analysis was done by Vario EL III CHN analyzer. The resin characteristics, viz., bulk density, moisture content and total ion-exchange capacity were determined by the standard methods.

2.3. Synthesis of Guaran-5- Amino salicylic Acid Hydroxamate (ASAH-G) Resin

Guaran was cross linked with epichlorohydrin into epoxyether of guaran (9) which was further used for derivatization. Synthesis was carried out in following three steps:-

2.3.1. Preparation of methylester of 5- amino salicylic acid

0.1 mol of acid was taken in a round bottom flask. To the acid, excess of methanol was added and then dry HCl gas was passed into the mixture until the saturation was complete. The reaction mixture was refluxed for 3 hrs. The methyl ester of 5- amino salicylic acid was thus formed.

2.3.2. Preparation of hydroxamate of 5- aminosalicylic acid

0.05 mol of methylester prepared in step (2.3.1) and methanolic solution of hydroxylamine hydrochloride (0.05 mol) were stirred on magnetic stirrer for 5 hrs at 30°C. The pH of the reaction mixture was adjusted by sodium ethylate to 9.2 - 9.3. The hydroxamate of 5-aminosalicylic acid was formed which was filtered and washed with 80% methanol solution.

2.3.3. Incorporation of hydroxamate of 5-aminosalicylic acid in guaran.

0.02 mol of hydroxamate of 5-aminosalicylic acid was taken in 10 ml methanol and stirred at 45°C for 5 hrs. During the process of stirring 0.01 mol of epoxyether of guaran was added. The product formed was filtered and the resin was successively treated with 0.1 N HCl, 0.1 N NaOH and 0.1 N HCl and was finally suspended in 200 ml 0.1 N HCl. Supernatant liquid was decanted and resin was washed 5-6 times with 80% methanol to remove the suspended impurities. Washing was continued till the supernatant liquid was clear from acid. Lastly, the product was washed with absolute alcohol and dried in vacuum (Fig 2).

2.4. Analysis for metal uptake

The molar distribution coefficient values (Kd) of metal ions viz., Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), W(VI), and Cr(VI) with the resin were determined by batch method in the pH range 3.5 -7. Estimation of U (VI) was done by thiocyanate method using UV spectrophotometer at 380 nm.

2.5. Column Separations

Ion exchange method is often used for removing a certain ion from a solution or for replacing it by another ion. Most of the ion-exchange separations are carried out in columns. We have attempted the separation of a mixture of Fe(II) and Co(II) ions on ASAH-G resin on the basis of large difference in their distribution coefficient values by column chromatography.

60 cm long glass column of uniform diameter was used. ASAH-G resin was swelled in DMF and the swollen resin was poured down the column wall and was allowed to settle in order to form a homogeneous layer. The resin was washed with the buffer of pH 6. The mixture of two metal ions (20 ml each) was poured onto the column at a flow rate of 1+0.2 ml/min. The loaded metal ions were eluted using 0.1N HCl eluent. The quantity of individual metal ions in the eluent was then determined by atomic absorption spectrophotometer.

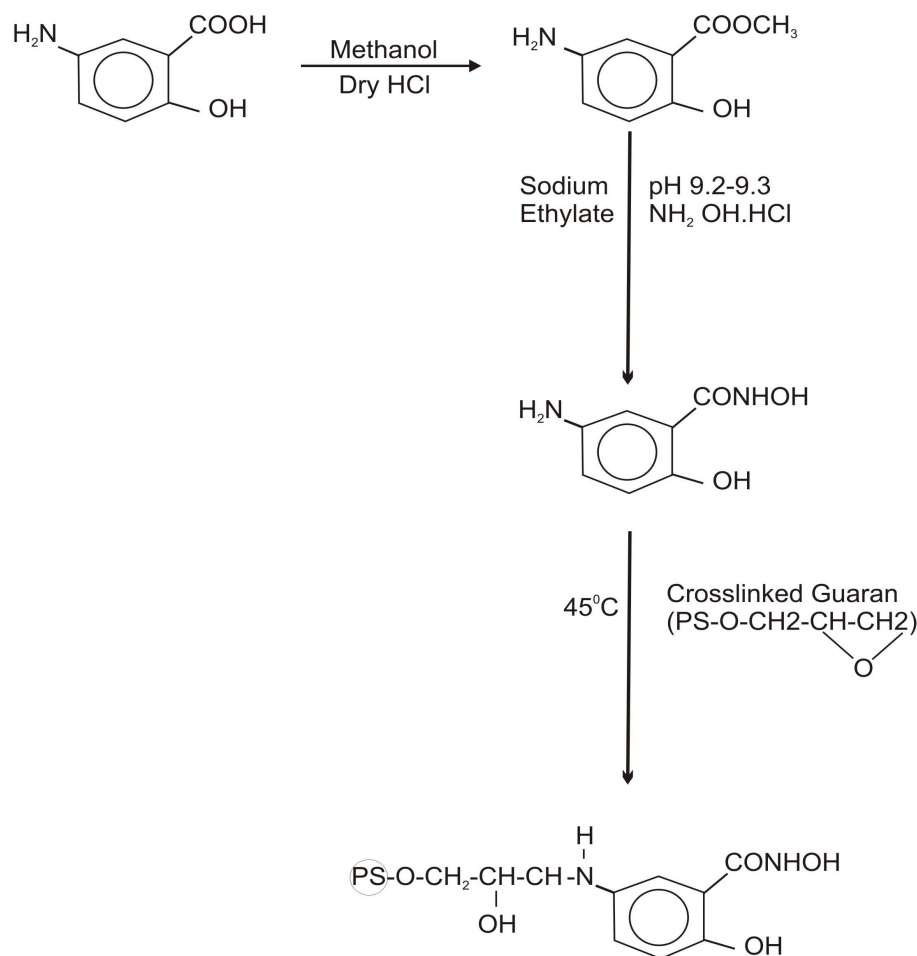


Fig. 2. Synthesis of 5- Aminosalicyclic acid Hydroxamate in Guaran (ASAH-G)

RESULTS AND DISCUSSION

The resin characteristics viz. bulk density, nitrogen content, moisture content and total ion exchange capacity are given in Table 1.

Table 1: Resin Characteristics

Resin	Moisture Content (%)	Bulk density (g/cm ³)	Nitrogen Content (%)	Total Ion Exchange Capacity (meq/gm)
ASAH-G	16.54	0.714	1.45	0.718

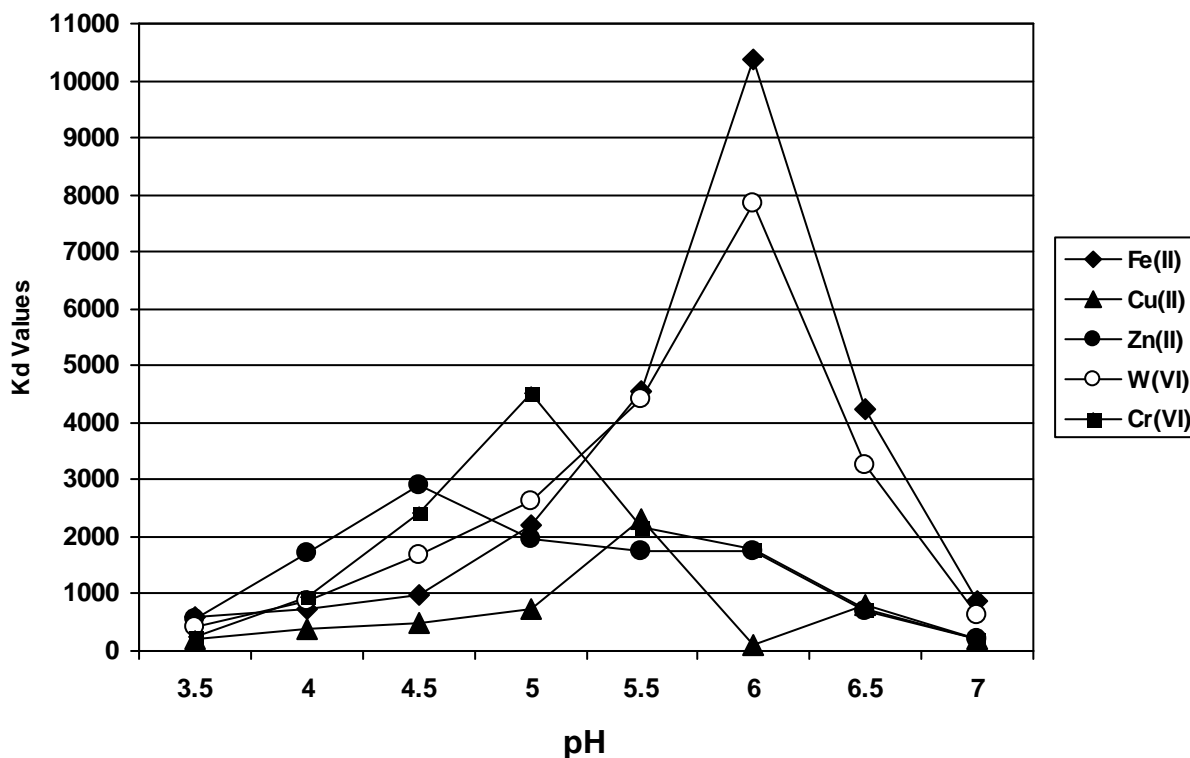
Two bands due to N-H stretching vibrations of amine group at 3550 and 3460 cm⁻¹ transformed into a single medium band at 3360 cm⁻¹ in the infrared spectra of ASAH-G resin. The \square (C=O) peak present in the spectra of carboxylic acid near 1700 cm⁻¹ shifted near 1680 cm⁻¹ in the spectra of hydroxamate resin. A band present at 3600 cm⁻¹ region was attributed to phenolic (O-H) stretching vibrations.

3.1. Adsorption of Metal Ions by the Resin

The molar distribution coefficient (K_d) values of different metal ions on ASAH-G resin are represented in Table 2 while Fig 3 shows that the adsorption ability of resin for iron, copper, zinc, tungsten and chromium metal ions is higher in comparison to other metal ions.

Table 2: K_d Values of Different Metal Ions on ASAH-G Resin

pH	K_d Values									
	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	U(VI)	W(VI)	Cr(VI)	Ca(II)
3.5	580	-	-	210	570	242	-	420	240	74
4.0	727	252	180	369	1734	438	370	892	962	163
4.5	970	456	340	493	2892	590	506	1682	2420	40
5.0	2210	646	545	723	1971	687	580	2620	4530	25
5.5	4540	856	676	2320	1761	873	778	4430	2160	-
6.0	10371	424	726	1210	1742	1046	2102	7840	1780	-
6.5	4233	147	329	820	706	748	674	3256	736	-
7.0	880	-	119	225	221	680	310	636	210	-

Fig. 3. K_d Values of Different Metal Ions on ASAH - G Resin

The order of adsorption of metal ions on (ASAH-G) resin at the pH of their maximum adsorption is :

Fe(II) > W(VI) > Cr(VI) > Zn(II) > Cu(II) > Cd(II) > Co(II) > Ni (II) >> Ca(II).

The results clearly indicate that iron, nickel, uranium, tungsten and cadmium are adsorbed maximum at pH 6, cobalt, copper at pH 5.5, chromium at pH 5, zinc at pH 4.5 and calcium at pH 4.0 on ASAH-G resin. A perusal of data indicates higher chelating ability of the resin for iron and tungsten at pH 6. Fe (II) ($K_d=10371$) can be separated from cobalt ($K_d=424$), nickel ($K_d=726$), copper ($K_d=1210$) and zinc (1742) at pH 6 (Fig.4). Cadmium ($K_d=590$), a toxic metal can be separated from zinc ($K_d=2892$) at pH 4.5 with which it is must of the times associated (Fig.5).

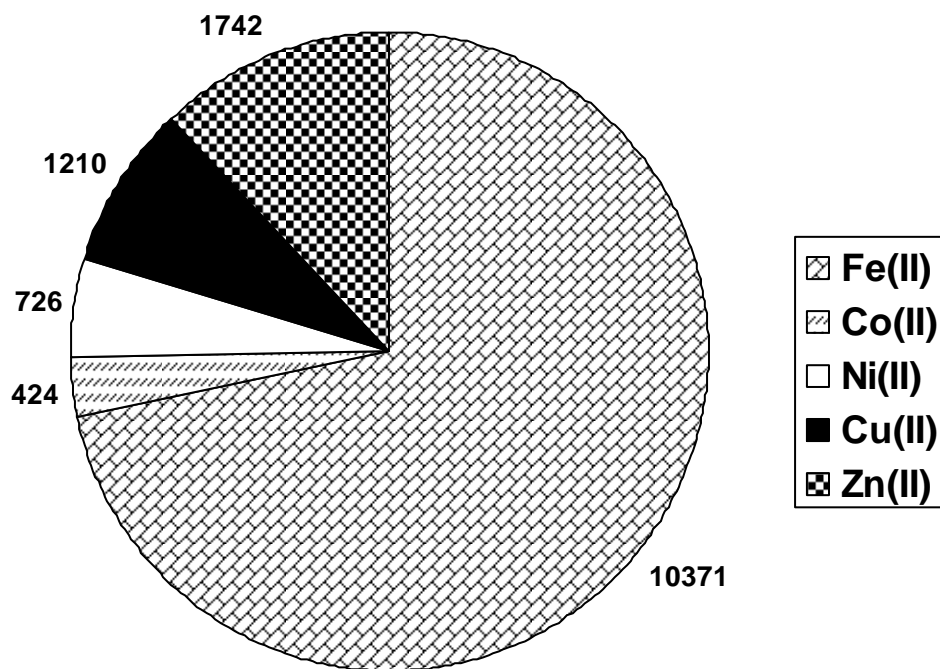
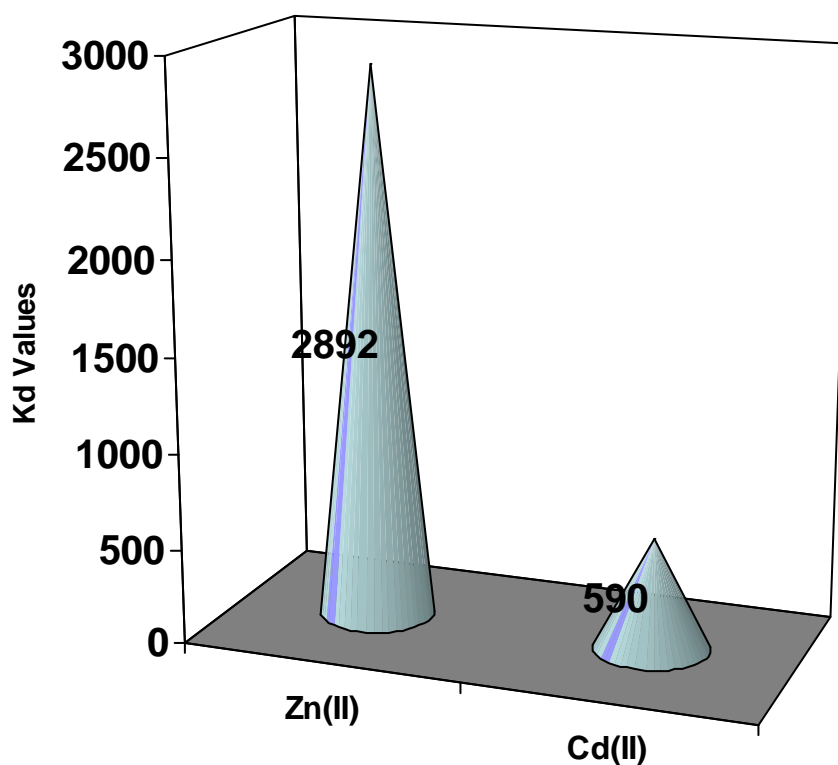
Fig. 4. Comparison of K_d Values of some metal ions at pH 6

Fig. 5. Adsorption Ability of Zn (II) – Cd (II) at pH 4.5

The use of chromate in metal plating and as corrosion control agent makes the effluent water coming from these industries in abundance of chromium (10) which is toxic and needs to be removed from the waste water before it is discharged into the main streams. This resin exhibits high efficiency for chromium and it can be separated from waste water at pH 5.

All the metal ions can be easily separated from alkaline earth metals i.e. calcium as seen from the Fig 3. The resin is very efficient for transition and heavy metal ions as compared to alkaline earth metals. Hydroxamate group present in the resin provides required selectivity to the resin for Fe(II) and other transition metal ions (11). Recently, Ying Lin & co-workers (12) also reported the selectivity of the hydroxamic acid group towards Fe(II) ions. Metal complexes are formed via the hydroxamide functional group of hydroxamate and therefore there is considerable covalency in the bonds formed (compared with the ionic characteristic of the bonds formed with the carboxylic group) and this contributes to the high selectivity of the hydroxamate interaction with metals.

The effect of the resin backbone on the separation efficiency is seen by comparing the K_d values of resin for different metal ions at pH of their maximum adsorption and at the same pH in the case of hydroxamic acid derivative of dialdehyde guaran prepared by Mathur *et. al.* (13) (Table 3). It is evident from the table that 5-amino salicylic acid hydroxamate of guaran has more adsorption ability for metal ions as compared to the HADA-G resin. This comparison confirms that monohydroximate of hydroxy acids are more efficient than HADA-G resin.

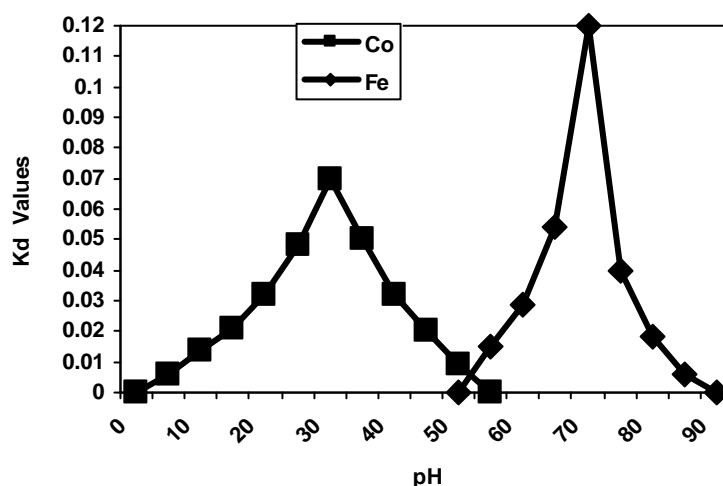
Table 3. Comparison of K_d Values of ASAH-G and HADA-G Resins for Different Metal Ions at pH of their Maximum Adsorption

Metal Ions	pH	K_d Values	
		ASAH-G	HADA-G
Fe(II)	5.5	4540	473
	6.0	10371	210
Cu(II)	5.5	2320	273
	6.5	820	403
Co(II)	5.5	856	140
	6.0	424	351
Ni(II)	6.0	726	339
W(VI)	6.0	7840	2452
Ca(II)	4.0	163	116

3.2. Separation of metal ions by the resin

A study of distribution coefficient values of various metal ions indicates that there are separation possibilities for a large number of metal ions on this resin. However, the difference in the K_d values between Fe (II) and Co(II) at pH 6 are large enough to permit their good separation on columns. Cobalt ions being less strongly held by the resin moved down the column more rapidly and were collected before iron (Fig.6).

Fig 6 Column Separation of Fe (II) and Co (II)



CONCLUSION

Therefore, we can conclude that this naturally occurring environmental friendly resin can be utilized for toxic & heavy metal ion separations from effluents of different industries.

Acknowledgements

Financial assistance from the UGC (File No. F. 41-338/2012(SR) dated 13.07.2012 New Delhi is gratefully acknowledged.

REFERENCES

- [1] Leyden D E, Patterson T A, Alberto J J, *Ana. Chem*, **1975**, 47, 733.
- [2] Sengupta S, Sengupta A K, *React Funct Polym*, **1997**, 35, 111.
- [3] Beauvais R A, Alexandratos S D, *React Funct Polym*, **1998**, 36, 113.
- [4] Sun S, Wang Li, Wang A, *J Hazardous Mater*, **2006**, B 136, 930.
- [5] Ahuja M, Rai A K, *Carbohy Polym*, **1997**, 33, 57.
- [6] Ahuja M, Rai A K, Mathur P N, *Talanta*, **1996**, 43, 1955.
- [7] Ahuja M, Rai A K, Mathur P N, *J Polymer Materials*, **1996**, 13, 211.
- [8] Ahuja M, Gupta S, Mathur P N, *J Polymer Materials*, **1995**, 12, 257.
- [9] Bohra S, Mathur P N, *J Polymer Materials*, **1992**, 9, 319.
- [10] Schmuhl R, Krieg H M, Keizer K, *Water SA*, **2001**, 27, NO.1, 1.
- [11] Ying Liu C, Tsungchang H, Jiun Vang L, *J Anal Chem*, **1987** 328, 61.
- [12] Fuerstenau D W, Pradip, *Mineral Flotation with Hydroxamate Collectors," Reagents in the Mineral Industry*, The Institution of Mining and Metallurgy, London,, **1984**, pp 161.
- [13] Bohra S, Mathur R, Mathur N K, *J. Polymer Materials*, **1992**, 9, 101.