



# Thermal Stability Studies of Cd(II) Ion Imprinted Interpenetrating Polymer Networks

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## Abstract

The relative thermal stabilities, decomposition patterns and the kinetic parameters of decomposition of the imprinted, non-imprinted and Cd(II) ion bound polymer networks were followed by thermogravimetric analysis. Cd(II) ion bound polymer-network showed higher thermal stability compared to Cd(II) ion desorbed polymer

Key words; Thermal stability, Ion imprinted polymer, Alginic acid

## 1.INTRODUCTION

Thermal studies of metal ion imprinted polymers can reveal the thermal stability of metal ions bound polymers<sup>1</sup>. The thermal stability varies with metal ions and the structure of metal ion imprinted polymers. The thermal stabilities depend on the characteristics of functional polymers and the bound metal ion<sup>2</sup>. Naturally occurring biopolymers like alginate, extracted from algae exhibit excellent adsorption ability for metal ions<sup>3</sup>. The thermal degradation and kinetics of biodegradable polymers is very much important. The present paper describes the thermal decomposition behavior of the Cd(II) ion imprinted interpenetrating polymer networks prepared from alginic acid and crosslinked polyacrylamide.

## 11.EXPERIMENTAL

The Cd(II) ion imprinted and non-imprinted interpenetrating polymer networks were prepared by using alginic acid and functional monomer acrylamide, NNMB as crosslinker in presence of initiator potassium persulphate. Fourier transform infrared (FTIR) spectra of the metal ion imprinted, non-imprinted, and the Cd(II) ion bound polymers were recorded between 4000-400 cm<sup>-1</sup>, using a Perkin Elmer 400 FTIR spectrophotometer. TG curves were recorded on a Shimadzu D-740 thermal analyzer at a heating rate of 10°C/min from 30-900°C under nitrogen atmosphere.

## 111. RESULTS AND DISCUSSIONS

The Cd(II) ion imprinted, non-imprinted and their metal bound polymers were subjected to thermo analytical studies. The major decomposition was used for the kinetic analysis. The kinetic parameters for the thermal decomposition of metal ion desorbed imprinted and bound polymers were evaluated by the reported integral<sup>4</sup> and approximation<sup>5</sup> methods using the least square method. The integral equation was used in the form

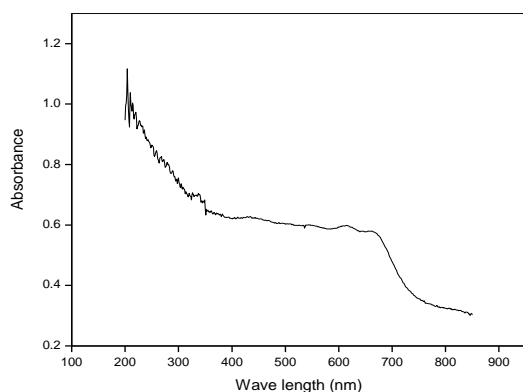
$$\ln \frac{g(\alpha)}{T^2} = \ln \left[ \frac{AR}{\beta Ea} \left( 1 - \frac{2RT}{Ea} \right) \right] - Ea/RT \longrightarrow (1)$$

and the approximation equation as:

$$\ln \frac{g(\alpha)}{T^{1.921}} = \ln \left( \frac{AE}{\beta R} \right) + 3.772050 - 1.921503 \ln E - 0.120394 (E/T) \longrightarrow (2)$$

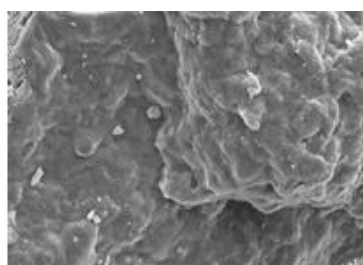
### 3.1.UV-vis. Spectra

MIP showed bands at  $15243\text{cm}^{-1}$  is shifted to  $15082\text{ cm}^{-1}$  after adsorption of Cd(II) ion MIP showed band at  $16200\text{ cm}^{-1}$  and  $18382\text{cm}^{-1}$  is shifted to  $16051\text{cm}^{-1}$  and  $18518\text{cm}^{-1}$  after binding of Cd(II) ion. These shifts indicate  $E_g \rightarrow T_{2g}$  transition. Thus it indicates the presence of tetragonal geometry.

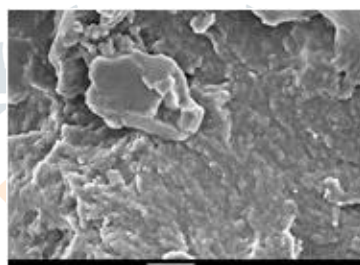


**Figure1.** U V visible spectra of Cd(II) bound MIP

### 3.2 Scanning Electron Microscopy



(a)



(b)

**Figure 2.** SEM images (a) MIP and (b) Cd(II) bound MIP

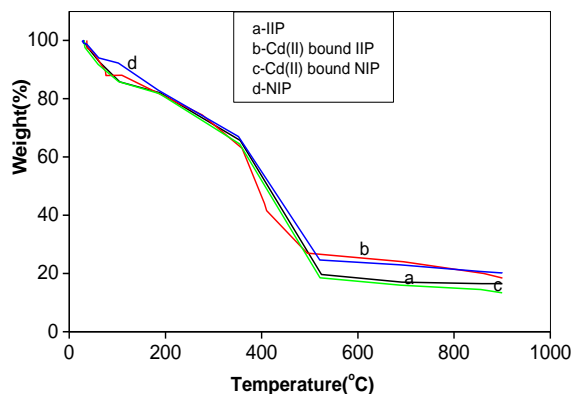
Scanning Electron Microscopy was employed to determine the surface properties of MIP, NIP and Cd(II) bound sample. SEM images show the difference in surface morphology. After binding with Cd(II) ion the surface became smooth and edges became rigid.

### 3.3 FTIR Spectra

FTIR spectrum of the IPN is different from those of the pure polymers because in interpenetrating polymer network there will be inter molecular interactions. FTIR spectra of Cd(II) ion imprinted polymer networks showed absorption at  $1643.36\text{cm}^{-1}$ , which is assigned to  $-\text{COOH}$  group of Alginic acid, is shifted to  $1634.4\text{ cm}^{-1}$  in Cd(II) bound polymer network. This result revealed that  $-\text{COOH}$  group of alginates is participated in adsorption process. MIP showed bands at  $2923.69\text{ cm}^{-1}$  and NIP showed bands at  $2953\text{cm}^{-1}$  due to C-H stretching vibrations. Both MIP and NIP showed bands at  $1516\text{cm}^{-1}$  due to various C-H bending vibrations.

### 3.4 Thermal studies

Thermogravimetric analysis of imprinted, non-imprinted and the corresponding Cd(II) ion bound interpenetrating polymer networks reveals the variation of thermal stability with Cd(II) ion binding (Fig.3). The decomposition of ion imprinted and non-imprinted polymers occur at three stages and their corresponding Cd(II) ion bound polymer networks required two stages. In all the cases, the first stage decomposition corresponds to decomposition of the carboxylate group or uncomplexed ligands. The second stage is the major decomposition in which polymer chain breaks and leaving only the metallic residue. Thermogravimetric analysis of Cd(II) ion desorbed imprinted polymer showed 15% weight loss at about  $80\text{-}120^\circ\text{C}$ , which is ascribed to the removal of carboxylate group or uncomplexed ligands. During the second stage of decomposition from  $300\text{ to }400^\circ\text{C}$ , 50% weight loss is observed which is attributed to the decomposition of interpenetrating polymer networks. While in Cd(II) ion bound polymer the decomposition was in the range  $150\text{-}500^\circ\text{C}$ , resulting a mass loss of 55%. Non-imprinted polymer networks also decompose in a similar manner. The temperature for maximum weight loss ( $T_{\text{max}}$ ) for imprinted polymer, Cd (II) ion bound polymer networks were  $310$  and  $390^\circ\text{C}$  respectively. Also it is clear that thermal stability of Cd(II) bound interpenetrating polymer networks are much higher than that of uncomplexed polymers. The major decomposition was used for the kinetic analysis. The kinetic parameters for the thermal decompositions of metal ion imprinted and bound polymers were evaluated by the reported integral<sup>4</sup> and approximation<sup>5</sup> methods using the least square method.



**Fig . 3. TGA curves of Cd(II) ion imprinted, non-imprinted and S Cd(II) ion bound polymers**

The phenomenological data is given in Table. I. The activation energy, pre-exponential factor, entropy of activation and correlation coefficient are given in Table II. For Cd(II) ion imprinted polymer the temperature range is from 266 to 486°C with a temperature interval of 202°C. The activation energy obtained according to equations 1 and 2 for imprinted polymer are 10.33 and 13.1 kJmole<sup>-1</sup> respectively. For Cd(II) ion bound polymer the temperature range is from 277 to 444°C with a temperature interval of 167°C. The activation energy obtained according to equations 1 and 2 for imprinted polymers are 13.12 and 14.1 kJmole<sup>-1</sup> respectively. The activation energy increases on metal ion binding. This is due to the fact that the thermal stability increases in metal bound polymers and more energy is required for the decomposition. The entropy of activation is negative for all polymers. The high entropy values of bound polymers than unbound polymers indicate that during metal ion binding reaction distortion of the polymer chain takes place from their normal position and hence randomness increases. The activation energy of non-imprinted polymers is lower than that of ion imprinted polymer, suggesting lower thermal stability. Also for metal bound non-imprinted polymers activation energy decreases from the corresponding metal bound imprinted polymer due to the absence of H-bonding. The entropy of activation of metal bound imprinted polymers is higher than that of the corresponding non-imprinted metal bound polymer. The higher entropy value is due to lower metal content.

**Table I Phenomenological data for the second stage of decomposition of Cd(II) ion imprinted polymers**

Polymer	Decomposition temperature range in TG		Peak temperature DTG (°C)	Mass loss (%)
IIP	272	474	406.02	53.9
NIP	277	477	398.18	54.5
Cd(II) IIP	277	444	408.19	44.5
Cd(II)NIP	237	437	398.00	23.5

**Table II. The kinetic parameters of Cd(II) ion imprinted polymers**

	Equation I				Equation 2			
	E (kJmole <sup>-1</sup> )	A (S <sup>-1</sup> )	ΔS (J)	R	E (kJmole <sup>-1</sup> )	A S <sup>-1</sup>	ΔS (J)	R
A	9.03	8.8x10 <sup>-4</sup>	-311	0.99	7.4	7.18x10 <sup>-4</sup>	-312	0.99
B	10.33	4.7x10 <sup>-2</sup>	-315	0.99	13.1	1.89x10 <sup>-2</sup>	-299	0.99
C	11.29	6.1x10 <sup>-4</sup>	-310	0.99	10.4	9.60x10 <sup>-4</sup>	-309	0.99
D	13.12	1.567x10 <sup>-3</sup>	-306	0.98	14.1	9.84x10 <sup>-4</sup>	-308	0.98

A- non-imprinted polymer, B- imprinted polymer, C- Cd(II) ion bound non-imprinted polymer, D- Cd(II) ion bound imprinted polymer

## Conclusions

Cadmium ion imprinted and non-imprinted interpenetrating polymer networks were synthesized and characterized by FT-IR, UV-vis., SEM and TGA. Thermodynamic parameters were calculated using van't Hoff's equation and the sorption of Cd(II) ion on imprinted polymer network was spontaneous and endothermic in nature and entropy of sorption increases during the reaction. The activation energy of Cd(II) ion imprinted interpenetrating polymer network was found to be higher, indicates more thermal stability. It was found that on Cd(II) ion binding thermal stability of polymeric system increases. The extra stability of Cd(II) ion imprinted polymer network is due to the formation of stable ring structures of metal bound polymeric system. Higher value of entropy of activation suggests the distortion of the polymer chain from their normal position for complex with metal ions.

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