

Synthesis, Characterization and Application of New Terpolymeric Resin**VILAYATKAR N.D.¹,**S.S. Jaiswal College,
Arjuni/Morgoan-441701, India**RAHANGDALE P.K.²,**Bhawabhuti College,
Amgoan-441902, India**GADEGONE S.M.³**Kamla Nehru College,
Nagpur-440024, India**ABSTRACT**

4-HAPHF terpolymeric resin has been prepared by condensation of 4-HydroxyAcetophenone (4-HA), Phenyl Hydrazine(PH) and Formaldehyde(F) in 1:1:2 molar ratio using 2M HCl as a catalyst and was proved to be a good adsorbent for removal of Cr(VI). The newly prepared terpolymer was characterized and its structural elucidation was confirmed by elemental analysis, TGA, XRD, FTIR and ¹H-NMR spectral studies. The metal removal properties of the terpolymer were studied by batch equilibrium method. The effects of various parameters like contact time, initial adsorbate concentration, pH and 4-HAPHF doses have also been studied and reported. The adsorption data were found to fit well with the Langmuir model. The percent removal of Cr(VI) was found to be increased with increasing adsorbent doses from 1 to 4gm. and maximum efficacy was found at 4gm. At optimum conditions nearly 91% abatement of Cr(VI) has been noted using 4-HAPHF. The results revealed that the terpolymeric resin as adsorbent reported in this article is effective for removal of Cr(VI) from wastewater and thus can be successfully used for control of chromium pollution.

Keywords: *Resinous terpolymer, wastewater treatment, Langmuir isotherm, chromium toxicity*

Introduction

In recent years significant research has been done on enhancing the properties of newly synthesized terpolymeric resins for the treatment of waste water and pollution control. Chromium is one of the toxic metal to living society. Most common forms of chromium are trivalent and hexavalent i.e. Cr(III) and Cr(VI) respectively, which are commonly used in various industrial processes. Cr(VI) is used in various industries such as electroplating, glass, ceramics, fungicides, rubber, fertilizer, tanning, mining, metallurgical etc¹⁻³. Cr(VI) is highly mobile and considered to be acute toxic, carcinogenic and mutagenic to living organisms and hence more hazardous than other heavy metals⁴⁻⁸. Therefore it is necessary to remove Cr(VI) from environment, in order to prevent the deleterious impact of Cr(VI) on ecosystem and public health. The usual methods for removal of Cr(VI) from aqueous effluents include chemical reduction⁹, nano-filtration¹⁰, bioaccumulation¹¹ and ion exchange¹². However these approaches are not cost-effective and difficult to implement in

developing/undeveloped countries. Bio-sorption a technically feasible and economical process has gained increased creditability during recent years¹³. The necessity to reduce the amount of heavy metal ions pollution in wastewater streams has led to an increasing interest in terpolymers¹⁴⁻¹⁹. Therefore, attempt has been made to synthesize the new terpolymer and study its properties with special reference to Cr(VI) abatement.

Materials and Methods

All the chemicals used were of analytical or chemically pure grade. Distilled water was used throughout the investigation.

Synthesis of terpolymer

A mixture of 4-HydroxyAcetophenone, Phenyl Hydrazine and Formaldehyde in 1:1:2 molar ratio in the presence of 200ml 2M HCl as a catalyst was taken in 500 ml round bottom flask fitted with water condenser and heated in an electrically operated oil bath at $123 \pm 2^\circ\text{C}$ for 5 hrs. with occasional shaking. The temperature of the oil bath was controlled with the help of dimmer stat. The resinous mass obtained was removed as soon as the reaction period was over. The solid product obtained was repeatedly washed with hot water followed by methanol to remove unreacted monomers. The resinous product was then dried in air and powdered. The powder was washed many times with petroleum ether in order to remove HydroxyAcetophenone-formaldehyde copolymer which may be present with the terpolymer. The product so obtained was further purified by reprecipitation technique. The terpolymer was dissolved in 8% NaOH solution, filtered and reprecipitated by drop wise addition of ice cold 1:1 (v/v) conc. HCl / distilled water with constant stirring. The precipitated resin product was filtered off, washed with hot water until it was free from chloride ions. The purified polymer sample was dried in vacuum at room temperature, powdered and stored in air tight bottles. The reaction scheme and most probable structure of newly obtained terpolymer has been presented in figure 1, while elemental analysis data are given in table1.

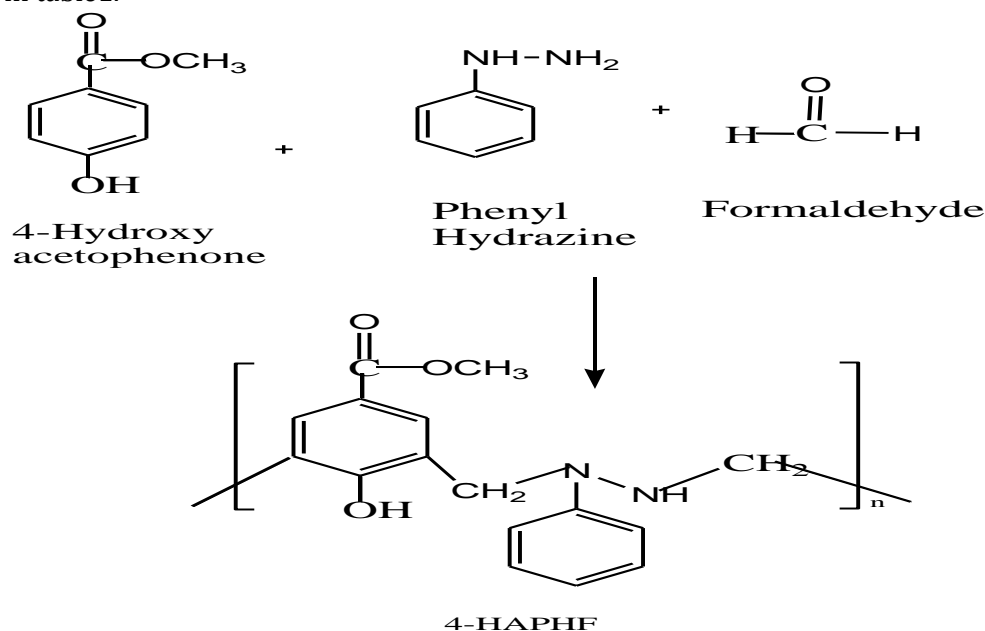


Fig.1 Reaction scheme and structure of 4-HAPHF Terpolymeric Resin

Name of terpolymeric resin	Carbon (%)	Nitrogen (%)	Oxygen(%)	Hydrogen (%)	Empirical formula of repeating unit
4-HAPHF	71.64(Cal.)	10.44(Cal.)	11.94(Cal.)	5.97(Cal.)	C ₁₆ H ₁₆ N ₂ O ₂
	70.76(Fnd.)	10.34(Fnd.)	11.47(Fnd.)	5.59(Fnd.)	

Table No.1 Elemental analysis data of 4-HAPHF Terpolymeric resin

Preparation of Cr (VI) solution

A Cr(VI) stock solution having 1000 mg^l-1 concentration was prepared by dissolving 2.8287 g of potassium dichromate in 1000ml of distilled water. This solution was diluted to proper proportions to obtain various standard solutions ranging their concentrations 10-100mg^l-1. pH adjustment was done using 0.5N HCl and 0.5N NaOH solution.

Batch Experiment

Batch equilibrium studies were conducted with different parameters such as pH, agitation time, initial concentration of Cr(VI) solution and effect of adsorbent doses. The systems were agitated on rotary shaker at 200 rpm, filtered through Whatmman no.42 filter paper and filtrates were analyzed for Cr(VI) concentration using UV-Visible Spectrophotometer. From experimental data, the applicability of Langmuir model was judged. Linear regression coefficient (R²) and isotherm constant values were determined from the model.

Characterization of 4-HAPHF terpolymeric resin

FTIR Studies of 4-HAPHF

FTIR spectrum of 4-HAPHF terpolymeric resin is shown in **Fig.2**. The broad band at 3397cm⁻¹ indicates presences of stretching vibration of phenolic hydroxyl (-OH) group. The methylene bridges²⁰ associated with 4-HydroxyAcetophenone can be identified by the peak at 2929cm⁻¹. The adsorption peak at 1660cm⁻¹ indicate -C=O carbonyl stretching. The peaks appeared at 1167 and 749cm⁻¹ are due to methylene bridges coupled with aromatic ring.²¹ The tetra substitution in the benzene ring is established by presence of medium band at 837cm⁻¹ which is attributed to (C-H) bending vibration.²² A peak at 1495 cm⁻¹ may be ascribed to N-H bending of secondary amide group. The peak at 1360 cm⁻¹ indicate -C=C- stretching in aromatic vibration.²³

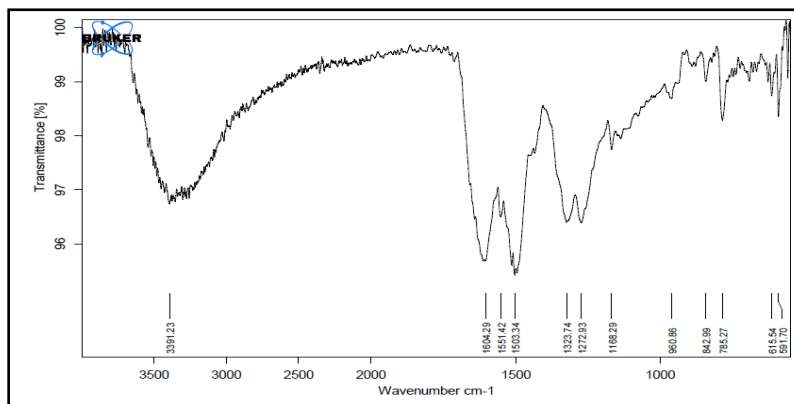


Fig. 2-FTIR spectrum of 4-HAPHF

XRD Studies of 4-HAPHF

Fig. 3 illustrates the X-ray diffractograph of 4-HAPHF. This terpolymer exhibit very broad diffraction peaks and the absence of a sharp peak reveals a predominantly amorphous structure. Thus it can be concluded that 4-HAPHF terpolymer is amorphous in nature.

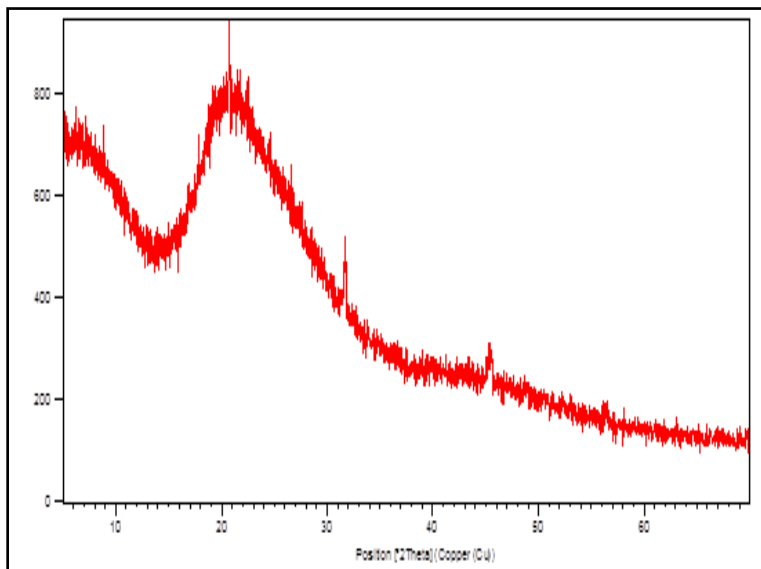


Fig. 3 - XRD spectrum of 4-HAPHF

^1H NMR- Studies of 4-HAPHF

^1H NMR spectrum of 4-HAPHF terpolymeric resin has shown in **Fig.4**. The signal at 2.2(δ) ppm is attributed to $-\text{NH}$ -bridge. The $\text{Ar}-\text{CH}_2$ protons are assigned at 3.63(δ) ppm. The $\text{Ar}-\text{CO}-\text{CH}_3$ protons are assigned due to signal at 2.7(δ) ppm. ^1H NMR spectrum of 4-HAPHF terpolymer resin shows unsymmetrical pattern in the region 6.8-7.6(δ) ppm which is characteristic of aromatic protons ($\text{Ar}-\text{H}$). The protons of $\text{Ar}-\text{OH}$ group involved in proton exchange reaction shows peak at 8.3(δ) ppm²⁴.

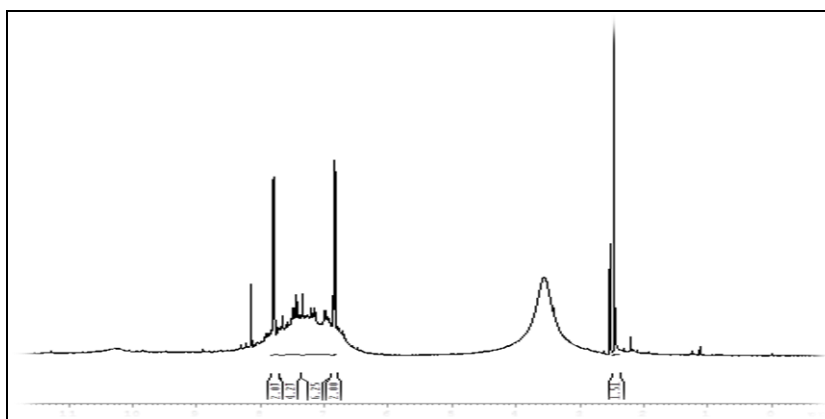


Fig. 4 ^1H NMR spectrum of 4-HAPHF

TGA studies of 4-HAPHF

Fig.5 shows TG curves of 4-HAPHF. The first derivative peak at temperature was 68°C with a weight loss of 2% up to 160°C which may be due to the removal of water molecule present in the terpolymer. The second and third peak temperature was 299°C with 22% and 380°C with 44% of weight loss and this loss may be due to the elimination of -OH groups attached to the aromatic nucleus. 66% weight loss occurred at temperature 600°C may be due to the elimination of -CH₂ and the aromatic nucleus²⁴.

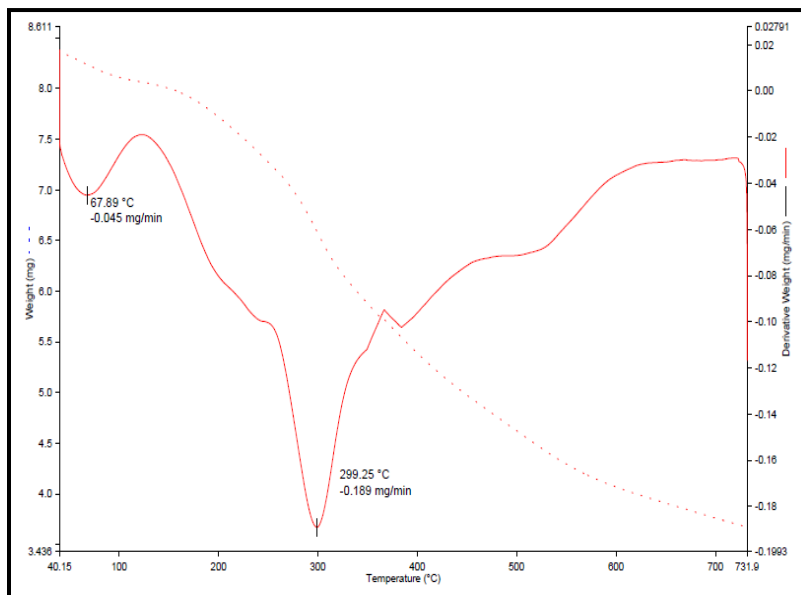


Fig.5- TGA spectrum of 4-HAPHF

Results and Discussion

Effect of pH on adsorption

Effect of pH on Cr(VI) adsorption using 4-HAPHF as an adsorbent has been studied in the pH range 1 to 10 and presented in Fig.6. It is noticed that solution pH plays a very important role in the adsorption of Cr(VI). The percentage removal increases steadily from 74 to 87% when pH is increased from 1 to 4 and slowly decreases on further increases in pH.

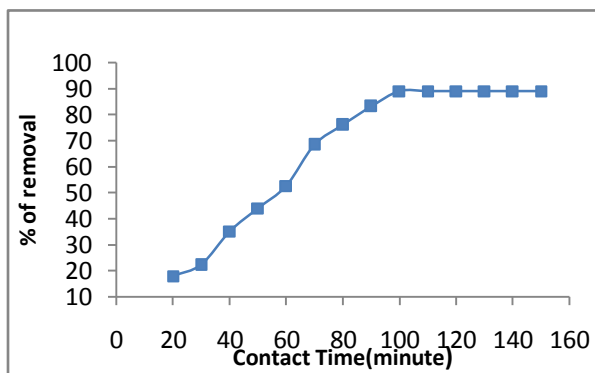
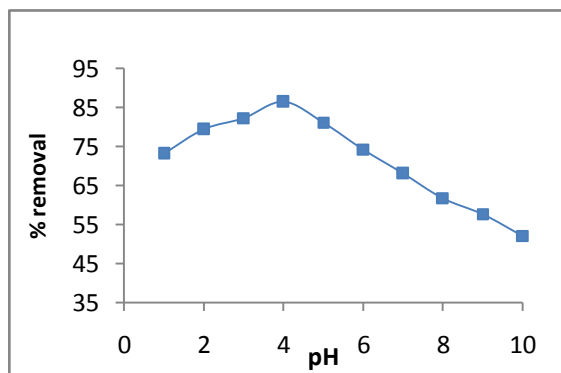


Fig.6 Effect of pH on Cr(VI) removal by HAPHF Fig. 7 Effect of Contact time on Cr(VI) removal by 4-HAPHF

Effect of contact time on adsorption

Adsorption experiments were conducted as a function of contact time and results have shown in Fig.7. The rate of Cr(VI) binding with adsorbent was greater in the initial stages then gradually increases and remains almost constant near about 90%, after optimum period of 100 min.

Effect of adsorbent doses

The effect of adsorbent (4-HAPHF) doses on percent removal of Cr(VI) in the range 1 to 10gm is represented in Fig.8. The initial Cr(VI) concentration was taken to be 30ppm. However after certain adsorbent dose it becomes constant and it is treated as an optimum adsorbent dose, which is found to be 4gm/lit. for the 4-HAPHF adsorbent.

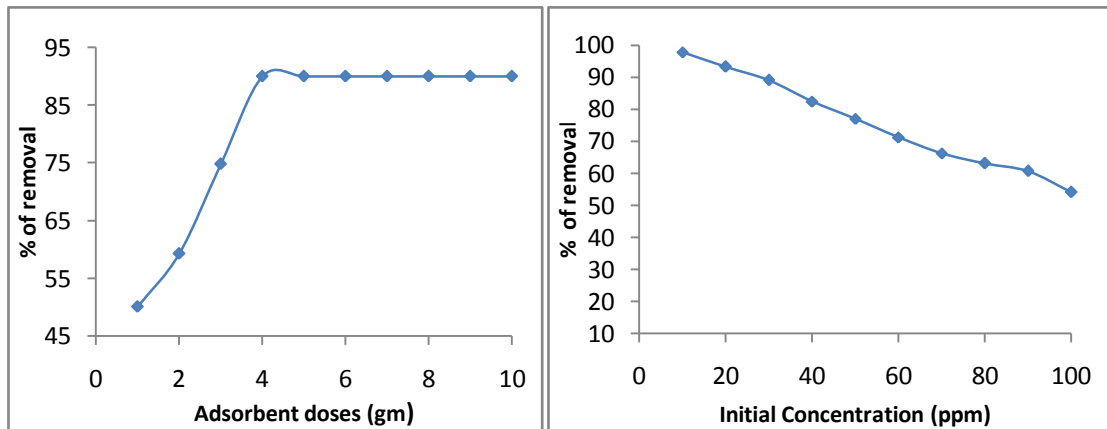


Fig.8-
Effect of

adsorbent doses on Cr(VI) adsorption Fig. 9 -Effect of initial concentration on Cr(VI) adsorption

Effect of the Initial concentration of Cr(VI) solution.

The Experimental studies were carried with varying initial concentration of Cr(VI) ranging from 10 to 100 ppm using 4 gm/lit. of adsorbent dose. The results have been shown in Fig. 9. The results demonstrate that at a fixed adsorbent dose the percentage of Cr(VI) removal decreases with increasing concentration of adsorbate.

Adsorption Isotherm

The isotherm data have been linearized using Langmuir equation and is plotted between C_e/q_e versus C_e . The Langmuir constant q_m , which is measure of the monolayer adsorption capacity of 4-HAPHF, is obtained as 11.54. The Langmuir constant 'b' which denotes adsorption energy is found to be 0.250. The high value (0.9880) of regression correlation coefficient (R^2) indicates good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of Cr(VI) onto 4-HAPHF. The dimensional parameter ' R_L ' which is measure of adsorption favorability is found to be 0.1170 ($0 < R_L < 1$) which confirms the favorable adsorption process for Cr(VI) on 4-HAPHF adsorbent.

Conclusion

Utilization of 4-HAPHF for the removal of Cr(VI) from the industrial waste-water is investigated. 4-HAPHF is found to be better adsorbent for removal of Cr(VI). The maximum percentage (91%) for removal of Cr(VI) is noticed at pH 4 with contact time 100 min. The percentage removal decreases with increase in initial Cr(VI) concentration. At 4 gm/lit of optimum adsorption dose maximum removal efficacy has been noticed. The adsorption data are best fitted with Langmuir isotherm

model which confirms the monolayer adsorption of Cr(VI) onto 4-HAPHF. Thus the resinous terpolymer reported in this research article can be successfully used for abatement of toxic hexavalent chromium from contaminated water and hence it is applicable in pollution control.

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Reference

- 1) C. Namasivayam and R.T.Yamuna, 1995, Adsorption of Chromium(VI) by a Low-Cost Adsorbent: Biogas Residual Slurry, *Chemosphere* 30, pp.561–578.
- 2) L.R. Radovic, 2000, Chemistry and physics of Carbon, *Marcel Dekker Inc.* 27, pp. 227–405.
- 3) E. Malkoc and Y. Nuhoglu, 2007, Potential of tea factory waste for Chromium(VI) removal from aqueous solutions: Thermodynamic and kinetic studies, *Sep. Purif. Technol.* 54, pp. 291–298.
- 4) R.A. Goyer and M.A. Mehlman, 1977, Toxicology of Trace Elements, *John Wiley & Sons Inc., New York.*
- 5) B.L.Carson et al., 1986, Toxicology and Biological Monitoring of Metals in Humans, *Lewis Publishers, Chelsea, MI*,18.
- 6) E. Alvarez-Ayuso et al., 2007, Adsorption of Cr(VI) from synthetic solutions and electroplating wastewaters on amorphous aluminium oxide, *J. Hazard.Mater.* 142, pp.191–198.
- 7) S.S. Baral et al., 2007, Chromium(VI) removal by calcined bauxite, *Biochem. Eng. J.*, 34, pp.69–75.
- 8) S. Srivastava et al., 2007, Removal of chromium and pentachloro -phenol from tannery effluents, *Bioresour. Technol.* 98, pp.1128–1132.
- 9) S.S. Chen et al., 2007, Reduction of chromate from electroplating wastewater from pH 1 to 2 using fluidized zero valent iron process. *J.Hazardous Materials*, 142: pp. 362-367.
- 10) M.T. Ahmed et al., 2006, Nano filtration process applied to the tannery solution. *Desalination*, 200: pp. 419- 420.
- 11) B. Preetha and T. Viruthagiri, 2007, Bioaccumulation of Cr(VI), copper(II) and nickel (II) ions by growing *Rhizopusarrhizus*. *Biochem. Engineering J.*34: 131-135.
- 12) S.A. Cvaco et al., 2007, Removal of chromium from electroplating industry effluents by ion exchange resin, *J Hazardous Materials*,144: pp.634-638.
- 13) M. X. Loukidouet al., 2004, Equilibrium and Kinetic modeling of chromium (VI) biosorption by *Aeromonascaviae*. *Colloids and surface A: Physiochemical and Engineering Aspect*, 242: pp.93-104.
- 14) A. A. Elassar et al., 2010, “Novel synthesis of poly (N1’,N3’-diacryloylmalonohydrazide): characterization, complexation, ion selectivity, thermogravimetry, swelling, morphology and biological activity,” *J. Polym. Res.* vol. 17, pp. 447–458.
- 15) S.D. Alexandratos et al., 1998, A mechanism for enhancing ionic accessibility into selective ion exchange resins, *Solv. Extr. Ion Exch.*, vol. 16(4), pp. 951–966.
- 16) A. Singh and S.K. Saraf, 2009, “Synthesis, characterization and ion-exchanging properties of a novel ion-exchange resin, part II,” *Int. J. Polym. Mater.*, vol. 58(10), pp. 499–508.

- 17) Michael Pratik et al., 2007, "Synthesis, characterization and thermal degradation of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer," *Eur. Polym. J.*, vol. 43, pp. 4995-5000.
- 18) O. Szabadka et al., 2003, Determination of protonation and metal complex stability constants for a chelating monomer and its immobilized in polymer resin, *Talanta.*, vol. 59, pp. 1081-1088.
- 19) Q. Rong-jun et al., 2004, Syntheses and adsorption properties of phenol-formaldehyde-type chelating resins bearing the functional group of tartaric acid, *Chinese J. Polym. Sci.*, vol. 22(5), pp. 469-475.
- 20) B.A Shah et al., 2007, Studies of chelation ion-exchange properties of copolymer resin derived from salicylic acid and its analytical applications, *Iranian Polym. J.*, 16(3), pp. 173-184.
- 21) S.S Baral et al. 2001, *J. Physical and Chemical Reference Data*, 30, pp. 187.
- 22) Ullah M.R. and Haque M. E., 2010, Spectrophotometric Determination of Toxic Elements (Cadmium) in Aqueous Media, *Journal of Chemical Engineering*, Vol., 25, pp.1-12.
- 23) H. Petrov et al., 1992, Adsorption of zinc, cadmium, copper and lead ions on oxidised anthracite. *Carbon*, 30, pp. 135.
- 24) W. B Gurnule and V. R. Bisen, 2014, Kinetics of Thermal Decomposition of Copolymer Resin-II Derived from 4-hydroxybenzaldehyde, Phenyl hydrazine and Formaldehyde. *Research Journal of Pharmaceutical, Biological and Chemical Sciences*, 5(4) Page No. 1283-1298