International Journal of
Life Sciences
International Peer Reviewed Open Access Refereed Journal

Special Issue A 12: March 2018 :29-34
UGC Approved Journal No 48951

Original Article | Open Access

Removal of Chlorpyrifos pesticide from wastewater using RPHF-I

Maskey Sudhirkumar M

Yashwantrao Chawhan College, Lakhandur-441803, India
Email: sudhirchem1717@gmail.com

Manuscript details:

Available online on
http://www.ijlsci.in

ISSN: 2320-964X (Online)
ISSN: 2320-7817 (Print)

Editor: Dr. Arvind Chavhan

Cite this article as:
Maskey Sudhirkumar M (2018) Removal of Chlorpyrifos pesticide from wastewater using RPHF-I, *Int. J. of. Life Sciences*, Special Issue, A12: 29-34.

ABSTRACT

In the pesticide especially chlorpyrifos is currently one of the most widely applied pesticides in the all over the India. In this article, the copolymer RPHF-I using for effective adsorbents of chlorpyrifos pesticide from wastewater. Chlorpyrifos (CPS) pesticide may appear as pollutants in water sources, having undesirable impacts to human health because of their toxicity, carcinogenicity and bioaccumulation to tissue. The aim of the present study is an attempt to synthesize new group of copolymer RPHF-I with higher efficiency of chlorpyrifos removal from aqueous solution. In batch method experiment is carried out to remove the chlorpyrifos. The adsorption capacity of the copolymer was studied as the function of solution pH, concentration of chlorpyrifos and contact time of adsorption. The adsorptive applicability of copolymer was tested by Langmuir isotherm and Freundlich isotherm. The adsorption capacities were found to be 92.23% for pesticide removal. The copolymer RPHF-I can be successfully used as an efficient material for removal of pesticide from aqueous environments and can have a variety of potential environmental pollution control.

Keywords: Chlorpyrifos Pesticide, Copolymers, Batch Experiments, Adsorption, Environmental Pollution.

INTRODUCTION

As India is a tropical country, it suffers severe losses in agriculture due to pests. This necessitates the use of pesticides to protect our crops against the attack of several pests. Pesticides are the chemicals that kill or destroy the pests (Aktar et al. 2009). They are also poison chemicals have adverse effect to human, animal and microorganism by accumulating in food and water. As per an estimate, worldwide nearly 10,000 deaths occur annually, owing to the use of chemical pesticides. At present, India is the largest producer of pesticides in Asia and ranks twelfth in the world for the use of pesticides with an annual production of 90,000 tons (Tijani et al. 2007). In the pesticide especially chlorpyrifos

(O,O-Diethyl O-3,5,6-trichloropyridin-2-yl phosphoroth-ioate) is hazardous to humans, they affect the central nervous system, the cardiovascular system, and the respiratory system(Muller et al. 2000). It was introduced in 1965 by Dow Chemical Company. According to Dow, chlorpyrifos is registered for use in nearly 100 countries and is annually applied to approximately 8.5 million crop acres (Rathod et al. 2017). Chlorpyrifos exposure may lead to acute toxicity at higher doses. Persistent health effects follow acute poisoning or from long-term exposure to low doses, and developmental effects appear in fetuses and children even at very small doses (Rauh et al. 2017).) For this study is an attempt to synthesize and characterize new copolymer with chlorpyrifos adsorbent properties for their removal from environment, specifically chlorpyrifos from contaminated water. In the present investigation, copolymer RPHF-I was synthesized by using resorcinol (R), Phenylhydrazine (PH) and Formaldehyde (F) in 1:1:2 molar ratios of the reacting monomers. The new copolymer was characterized by Elemental analysis, NMR, TGA and SEM. The newly obtained copolymer have been proved to be a very good adsorbent which can be successfully used for removal of Chlorpyrifos contaminated water which can then be used for safe potable purpose.

MATERIALS & METHODS

All chemicals used were of analytical grade. Resorcinol, Phenylhydrazine, Formaldehyde (37%) procured from Merck, India. Double distilled water was used for all the experiments.

Synthesis and Purification of RPHF–I Copolymer:
The copolymer (RPHF-I) was synthesized employing the method published earlier (Rahangdale et al. 1993; Maskey et al. 2015). The purity of newly synthesized and purified copolymer sample has been tested and confirmed by TLC. The yield of Copolymer resin was found to be 82%. The proposed structure of RPHF-I with reaction scheme has shown in fig.1**.**

Characterization of copolymer:
Characterization of surface modified copolymer was carried out by techniques like Elemental Analysis, NMR, SEM and TGA. The scanning was carried out at Sophisticated Analytical Instrumental Facility (SAIF) Punjab University, Chandigarh and SAIF Cochin.

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

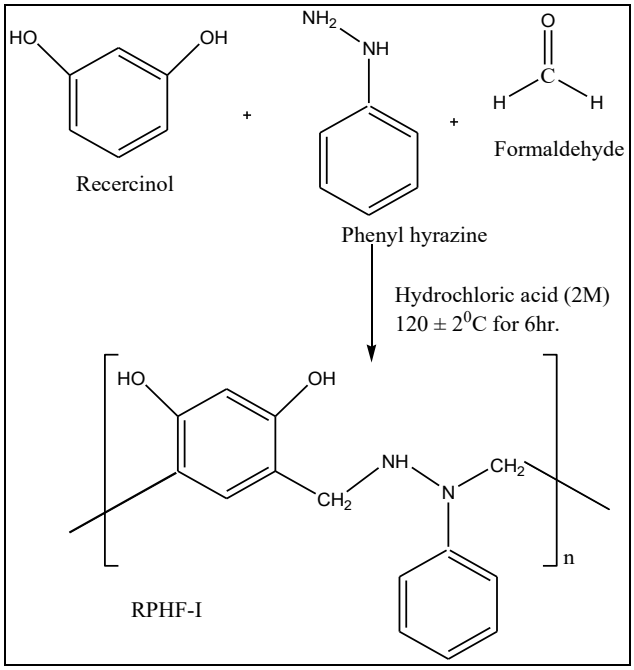

Fig.1:Reaction Scheme and Structure of Copolymer (RPHF-I)

RESULTS AND DISCUSSION

Elemental analysis was analyzed the percentage of carbon, hydrogen, nitrogen and oxygen content in Copolymers. Elemental analysis data of Copolymers are shown in table 1, it is found that the determine values of the percentage elements are in good agreement with the calculated values. The elemental analysis data suggest the empirical formula and the empirical formula weight for the repeating unit of Copolymers (Campbell et al. 1989).

The ^{1}H NMR spectrum of RPHF-I Copolymer is reprented in **fig.2**. The chemical shifts (δ) ppm observed have been assigned on the basis of the literature (Pretsch et al. 2000). The signals in the region at 6.2-7.2

(δ) ppm may be assigned to the protons in the aromatic ring. The medium singlet at 2.5 (δ) ppm may be due to methylene proton of Ar–CH_2 bridge. A singlet observed in the region 3.5(δ) ppm is corresponding to methylene proton of Ar–CH_2–N moiety. A signal observed at 4.1 (δ) ppm is attributed to proton of amines i.e. Ar-NH moiety. A singlet observed in the region 1.2(δ) ppm may be due to the protons in–NH linkage. The signal at 8.1(δ) ppm is assigned due to phenolic–OH group involved inintramolecular hydrogen bonding.

Table 1:- Results of elemental analysis of Copolymers

Name of Copolymer	Carbon (%)	Nitrogen (%)	Oxygen (%)	Hydrogen (%)	Empirical formula of repeated unit	Empirical formula weight
RPHF-I	59.80 (Cal.)	9.96 (Cal.)	11.29 (Cal.)	4.94 (Cal.)	C14H14N2O2	242
	59.10	9.12	11.29	4.12		

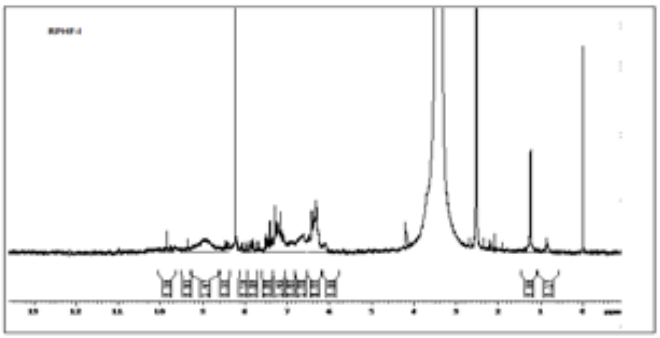

Fig. 2: ^{1}H NMR spectrum of RPHF-I

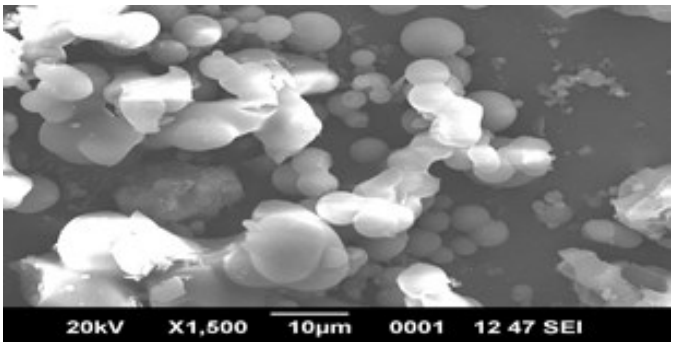

Fig.3: SEM image of RPHF-I

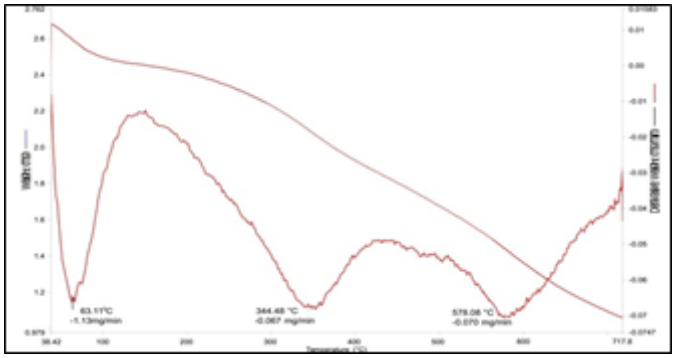

Fig. 4:- TGA of RPHF-I

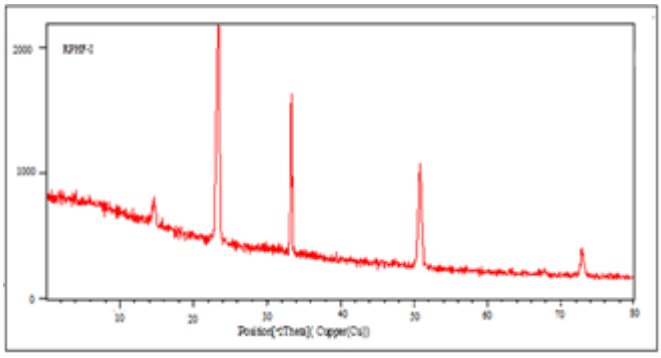

Fig.5:-XRD of RPHF-I

Fig.3 indicates the SEM images of RPHF-I obtained using an accelerating voltage of 20 KV at (x 1500, x10000) magnification. At such magnification, SEM images clearly revealed that wide variety of microspheres are presents on the surface RPHF-I. Microspheres were formed in the form of large beads with uniformity and monodispersity (Lai et al. 2007). The microspheres are globular size with diameter 2.86 µm, 1.98 µm and 2.86 µm. The image also showed RPHF-I is crystalline states. The microspheres presented in the Copolymer surface may be responsible for the swelling behavior and reactivity of active sites buried in the polymer matrix and also responsible for better adsorption of metal ion (Wang et al. 2007).

The TGA curve of RPHF-I shown in fig.4. it can be seen from figure that three consecutive weight loss steps were observed in RPHF-I. The first weight loss was about 50 to 150^{0}C. The derivative peak observed at temperature 63.11^{0}C with a weight loss of 4 %which may be due to the removal of water molecule (Learmonth et al. 1964). When temperature was raised

to the range 300-350^{0}C,the second derivative peak appeared at 344.480C with 20 % weight loss of material which may be due to the elimination of –OH groups attached to the aromatic nucleus of polymeric sample. In the third stage, the weight loss in the temperature range of 500 to 700^{0}C.The derivative peak observed at temperature 578.08^{0}C with a weight loss of 48 % which may be due to the elimination of $-CH_2$ bridges and the aromatic nucleus (Horowitz et al. 1963). After 700^{0}C, the TGA curve almost flatten due to the only residue remains behinds.

The X-ray diffractograph of RPHF-I has shown in fig.5. In this spectrum a high intense sharp peaks at 2θ= 21^0,33^0 and 50^0 show crystalline nature of Copolymer. The spectrum also contains low intense peaksat 2θ= 15^{0}and 72^0 indicate semicrystalline nature. Thus it can be concluded that RPHF-I Copolymer exhibits crystalline and semicrystalline nature (Cullity et al. 1978; Klug et al. 1974).

Adsorption of Chlorpyrifos (CPS) on RPHF-I

Effect of pH on Chlorpyrifos removal:
The adsorption capacities of RPHF-II towards Chlorpyrifos were determined using various pH values of solution in the range of 1.0 to 10. From **fig.6**. It is evident from this figure that maximum at pH 5 the adsorbents i.e. RPHF-I remove 93.23% of Chlorpyrifos ion.

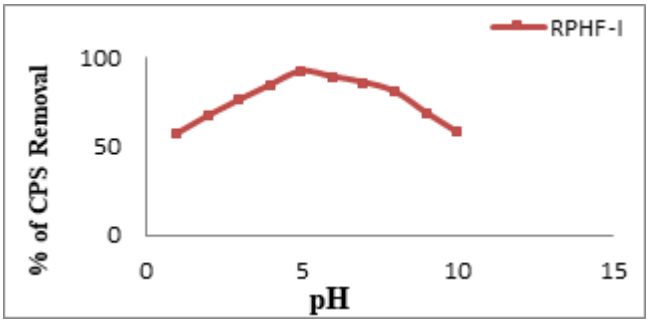

Fig.6: Effect of pH on CPS removal

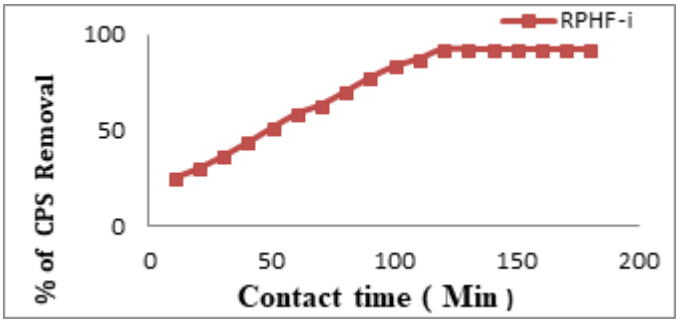

Fig.7: Effect of Contact time on CPS removal

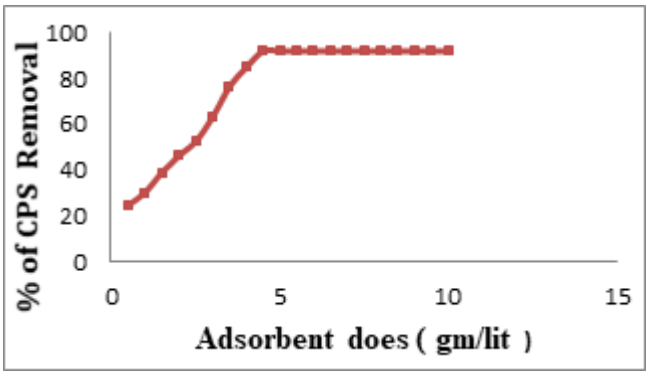

Fig.8: Effect of Adsorbent dose on CPS removal

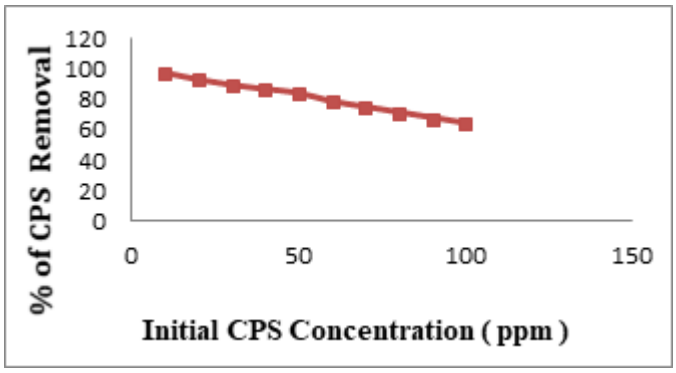

Fig. 9: Effect of initial concentration of CPS removal

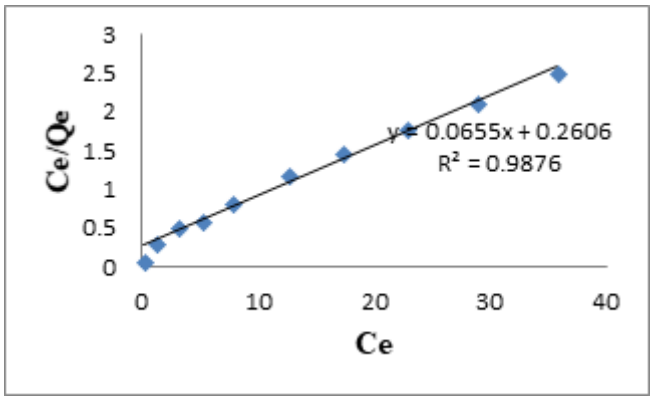

Fig 10: Langmuir isotherm for the adsorption

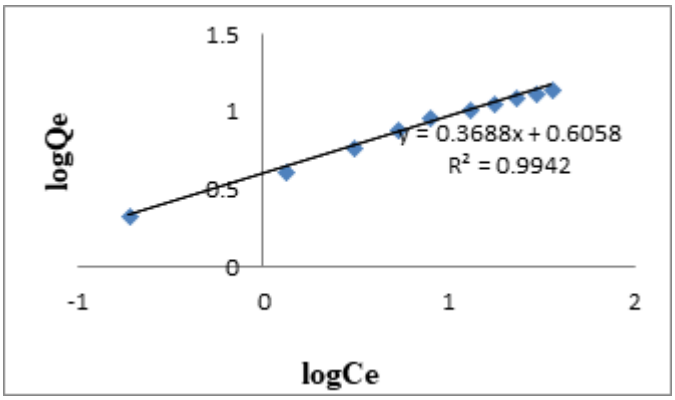

Fig . 11: Freundlich isotherm for the adsorption

Effect of contact time on Chlorpyrifos removal:
From fig.7 It can be seen that Chlorpyrifos removal efficiency of RPHF-I increased from 20% to 93.23% when contact time was increased up to 140 min. Thus optimum contact time for RPHF-I was found to be 140 min.

Effect of Adsorbent dose on Chlorpyrifos Removal: From **fig.8** the RPHF-I dose increased from 0.5 to 7.0 gm/lit, there was increased of removal efficiency of Chlorpyrifos from 21.30 % to 93.23% It is also seen from the figure that a further increase of RPHF-I i.e. 7.0 gm/lit does not affect the percentage of Chlorpyrifos removal. The optimum dose of RPHF-I for the maximum removed percentage of Chlorpyrifos was 7.0 gm/lit.

Effect of initial Chlorpyrifos Concentration:
The percentage of adsorption with different Chlorpyrifos concentration was studied by varying Chlorpyrifos ion concentration from 10 to 100 mg/lit keeping other parameters such as pH of solution, adsorbents dose, contact time optimum. The results are show in **fig.9.** From the figure, it is observed that percentage of Chlorpyrifos removal was found to decrease from 93.23% to 58.45% as initial concentration started from 10 to 100 mg/lit for RPHF-I.

Adsorption Isotherm
In order to establish the most appropriate correlation for the equilibrium data in the design of adsorption system, two common isotherm models were tested Freundlich and Langmuir models.

Langmuir isotherm:
The isotherm data have been linearized using the Langmuir equation and is plotted between Ce/Qe versus Ce shown in fig.10. . The Langmuir constant 'Qm' which is measure of the monolayer adsorption capacity of RPHF-I is obtained as 15.38. The Langmuir constant 'b' which denotes adsorption energy, is found to be 0.250. The high value (0.987) of regression correlation coefficient (R2) indicates good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of Cr(VI) onto the RSF-I. The dimensional parameter 'RL' which is a measure of adsorption favorability is found to be 0.091(0< RL < 1) which confirms the favorable adsorption process for Chlorpyrifos on RPHF-I adsorbent (Khattri et al. 1999).

Freundlich isotherm:
The Freundlich equation suggests multilayer adsorption. Sorption energy exponentially decreases on completion of the sorption centers of and adsorbent. Therefore, the parameters of k_f and 'n' were be estimated from the intercept and slope of the plots between $\log Q_e$ against $\log C_e$. Freundlich isotherms are shown in fig.11. The k_f value of both the adsorbents i.e. RPHF-I was found to 4.0271 mg, which indicate that dominance of adsorption capacity. The Freundlich exponent 'n' was 2.717 for RPHF-I which is reflects the favourable adsorption. The value of R2 was found to 0.994 for RPHF-I (Arivoli et al. 2007).

CONCLUSION

Copolymer RPHF-I successfully synthesized with using monomers Resorcinol Phenylhydrazine and Formaldehyde in the molar ratio of 1:1:2 in the presence of 2M HCl as a catalyst. RPHF-I copolymer has been characterized using elemental analysis, NMR, TGA, SEM and XRD. This copolymer is proved to be an excellent adsorbent for Chlofirofis pesticide. The optimum parameters for efficient application of the RPHF-I copolymer under present investigation are adsorbent dose 7.0 g, pH 5 and contact time is 140 min. The adsorptive applicability of copolymer was tested by Langmuir isotherm and Freundlich isotherm. The adsorption capacities were found to be 92.23% for pesticide removal.

Acknowledgement:
Authors are highly thankful to Principal, Science College, Congress Nagar, Nagpur for providing necessary laboratory facilities. Authors are also thankful to Director SAIF Punjab University, Chandigarh and SAIF Cochin University, Kerala for their help in scanning of material.

Conflicts of interest: The authors stated that no conflicts of interest.

REFERENCES

Aktar MW, Paramasivam M (2009) Impact of Pesticide Use in Indian Agriculture-Their Benefits and Hazards, http://www. shamskm.com/ env/ impact-of-pesticide-use-in-Indian-agriculture.html.

Tijani AA, Osotimehin KO (2007) Res. J. Agric. Biol. Sci.3-129.

Muller, Franz (2000). Agrochemicals: Composition, Production, Toxicology, Applications. Toronto: Wiley-VCH. p. 541. ISBN 3-527-29852

Rathod, AL, Garg RK (April 2017) "Chlorpyrifos poisoning and its implications in human fatal cases: A forensic perspective with reference to Indian scenario". *Journal of forensic and legal medicine*. 47: 29–34. doi:10.1016/j.jflm.2017.02.003. PMID 28259020.

Rauh H, Virginia A, Frederica P, Megan K (2012) Brain anomalies in children exposed prenatally to a common organophosphate pesticide". *PNAS*. 109 (20): 7871–7876.

Rahangdale PK., Gurnule WB, Paliwal L.J and Kharat R.B(1993) *J. Appl. Polym. Sci*.89 787.

Maskey SM, Burghate PD and Rahangdale PK (2015) Carcinogenic Cr(VI) removal using RPHF-I Copolymer. Sevadal Mahila Mahavidyalaya, Nagpur. *Material Science* – NCRTS 2015ISSN 2347 – 517X

Campbell D, Pethrick RA, White JR (1989) Polymer Characterization Physical Techniques. Chapman and Hall, p. 11-13.

Pretsch E, Buhlmann P (2000) Structure determination of organic compounds. Springer, New York

Lai J, Yang M, Niessner, R (2007) Molecularly imprinted microspheres and nanospheres for di(2-ethylhexyl) phthalate prepared by precipitation polymerization. *Analytical and Bioanalytical Chemistry*, 389, 405–412.

Wang Y, Liu Q, Rong, F (2011) facile method for grafting of bisphenol A imprinted polymer shells onto poly(divinylbenzene) microspheres through precipitation polymerization. *Applied Surface Science*, 257, 6704–6710.

Learmonth GS, Wilson T (1964) Thermal degradation of resins. *J. Appl. Polym. Sci*. 8, pp. 2873-2881;

Horowitz HH, Metzger GA. (1963) New analysis of thermogravimetric traces. Anal Chem. 35, pp. 1464-146

Cullity BD (1978) Elements of X-ray diffraction. 2nd ed. Addison-Wesley, Reading, Mass.

Klug HP (1974) Alexander. X-ray diffraction procedures for polycrystalline and amorphous materials. 2nd ed. Wiley, New York

Khattri SD, Singh MK (1999) *Indian J. Chem. Technol*, 3, 114

Arivoli S, Venkatraman B.R, Rajachandrasekhar T (2007) Res. J. Che. Environ.,17,70

.