Carcinogenic Cr(VI) removal using RPHF-I Terpolymer

[1]Maskey S.M.; [2]Burghate P.D. and [3]Rahangdale P.K*.
1Yashwantrao Chawhan College, Lakhandur-441803, India
2Shri Shivaji Science College, Nagpur-440012, India
3Bhawabhuti Mahavidyalaya, Amgaon-441902, India
*Corresponding Author; email: pralhadrahangdale@gmail.com contact: +91 9881010726

ABSTRACT

Presence of heavy metals in environment is a potential problem to water quality due to their high toxicity to plants and animals including human. Moreover, unlike organic pollutants, heavy metals cannot be destroyed chemically. This has motivated the scientific community to search for attractive treatment technologies for their removal. The hexavalent chromium is reported for its high toxicity and carcinogenicity. This study is an attempt to synthesize and characterize new terpolymer with heavy metal abetment properties for their removal, specifically Cr(VI), from contaminated water. In the present investigation, the terpolymer RPHF-I was synthesized by using resorcinol (R), phenyl hydrazine (PH) and Formaldehyde (F) in 1:1:2 molar ratios of the reacting monomers. This Terpolymer has been characterized using CHN estimation data and modern techniques like 1H-NMR, FTIR and XRD. The terpolymer under present investigation has shown excellent results towards uptake of Cr (VI) from contaminated water and, thus, can be successfully used as an efficient material for removal of dangerous Cr(VI) from industrial effluents and can have potential environmental applications.

Key words: Heavy metals, Toxicology, Hexavalent Chromium, Adsorption, Environmental contamination

INTRODUCTION

All human beings require fresh water for carrying out various activities. Unfortunately multifarious human activities for development and welfare lead to generation and release of objectionable materials into the fresh water bodies which make our life miserable and uncomfortable. Scarcity of pure drinking water is increasing due to presence of pollutants, such as surfactants, pesticides, dyes, persistent organic chemicals and heavy metals in the water, which has substantially raised the investigations into the decontamination of the impure water. Amongst the pollutants, heavy metals are very common toxic pollutants and the presence of heavy metals in environment is a potential problem to water quality due to their high toxicity to plants and animals including human.[1-3]

Out of 104 elements in the periodic table 80 are metals, in which 17 are toxic. Toxic metals include Be, Os, Pt, Hg, Ti, V, Te, Co, U, Se, Cd, Pb, As, Sb, Cr, Ni, Zn and Mn. Their toxicity varies with threshold limiting value (TLV) which is between $2\mu g/m^3$ to $5000\mu g/m^3$. Different metals have different degree of toxicity. Cr(VI) is highly soluble, reactive and considered to be acute toxic, carcinogenic and mutagenic to living organisms and hence more hazardous than other heavy metals.[4-8]

In animal studies, chromium was found to be accumulating mainly in liver, kidneys, spleen and bone marrow after both oral and parenteral administration of different Cr compounds and the distribution depends on the speciation. In humans, the highest concentrations are found in lymph nodes and lungs, followed by spleen, liver and kidneys. Recent studies show that Cr (VI) compounds have been shown to cause lung cancer in humans when inhaled. The report on carcinogens lists Cr (VI) compounds at the top.[9-10]

Chromium and its salts are used in the leather tanning industry, catalysts manufacture, pesticides, ceramic and glass industry, photography, pigments and paints, chrome alloy, chromium metal production, chrome plating, corrosion control and many more processings.[11-13] The present study is an attempt to synthesize and characterize the new terpolymer with heavy metal adsorbent properties for their removal, specifically Cr (VI), from contaminated water.[14-15] In the present investigation, RPHF-I terpolymer was synthesized by using resorcinol (R), phenyl hydrazine (PH) and Formaldehyde (F) in 1:1:2 molar ratios of the reacting monomers. This copolymer has been characterized using modern techniques like ^{1}H-NMR, FTIR and XRD. The terpolymer under present investigation has shown excellent results towards uptake of Cr (VI) from contaminated water and, thus, can be successfully used as an efficient material for removal of dangerous Cr(VI) from industrial effluents and can have potential environmental applications.

MATERIALs AND METHODs

Chemicals

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

Synthesis of RPHF –I Terpolymer

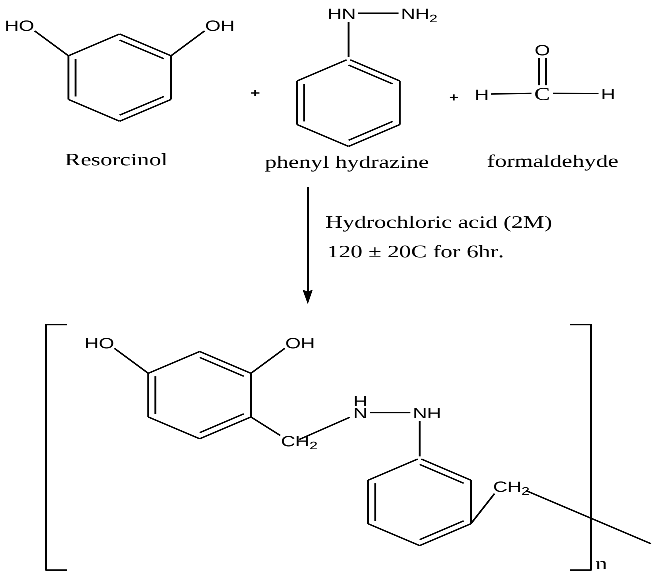
The terpolymer (RPHF -I) was synthesized by condensing Resorcinol, phenyl hydrazine with formaldehyde in molar ratio (1:1:2) in the presence of Hydrochloric acid (2M) as a catalyst. The reaction mixture was taken in 500ml round bottom flask fitted with water condenser and heated in an electrically operated oil bath at 120 ± 2^{0}C for 6hrs with occasional shaking. The temperature of the oil bath was controlled with the help of dimmer stat. The solid mass obtained was removed immediately as soon as the reaction period was over. The separated terpolymer product (RPHF-I) was filtered and purified.

Purification of terpolymer (RPHF-I)

The solid terpolymer product was repeatedly washed with hot distilled water followed by methanol to remove unreacted monomers. The resinous product was air dried and powdered. The powder was washed several times with petroleum ether in order to remove resorcinol-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% aqueous NaOH, filtered and reprecipitated by drop wise addition of 1:1 (v/v) conc. HCl / distilled water with constant stirring. The precipitated product was filtered off, washed with hot water until it was free from chloride ions, dried and powdered. The finely ground terpolymer was passed through a 300 mesh size sieve. The purity of copolymer was tested and confirmed by TLC. The yield of terpolymer resin was found to be 82%. The reaction conditions are presented inTable1 and proposed structure of RPHF-I with reaction scheme has shown in Figure1.

Table 1:-Reaction conditions for synthesis of RPHF-I Terpolymer

Terpolymer	Reactants			Molar ratios	Catalyst (2M HCL)	Reflux Temp. (^{0}C)	Time (hrs)	Yield (%)
	Resorcinol (R) (mol)	Phenyl hydrazine(PH) (mol)	Formaldehyde(F) (mol)					
RPHF-I	0.05 mol	0.05 mol	0.1 mol	(1:1:2)	200ml	120± 2	6	82%



RPHF-I

Fig1:-Reaction scheme and suggested structure of RPHF-I Terpolymer

Characterization of Terpolymer

Characterization of Terpolymer was carried out by CNH analysis andusing techniques like Fourier Transform Infra-Red (FTIR), Nuclear Magnetic Resonance (^{1}H-NMR) and X-Ray Diffraction (XRD) Analysis. The elemental analysis, FTIR, ^{1}H-NMR, and XRD were carried out at Sophisticated Analytical Instrumental Facility (SAIF) Punjab University, Chandigarh.

RESULTS AND DISCUSSION

The RPHF-I terpolymer was found to be soluble in solvents like NN-dimethylformamide, tetrahydrofuran, dimethylsulfoxide and aqueous NaOH/KOH solutions, but insoluble in other common organic solvents.

FTIR Studies

The FTIR spectrum of the RPHF-I terpolymer resin is shown in Figure 2, and the spectral data are presented in Table 3. A broad band appeared in the region 3726.93cm^{-1} may be assigned to the phenolic hydroxyl group intermolecular polymeric association.[16-17] A strong band at 1277.17 cm^{-1} is due to (C–N) stretching of (Ar–NH2).[16] The band appeared at 693,789, 1078cm^{-1} are indicative of 1,2,3,4-substitution of aromatic benzene ring.[19] The band appeared at 1595cm^{-1} may be due to aromatic –C=C bending and stretching.[18] The band appeared at 1499 cm^{-1} may be due to –NH bending vibration of secondary amine .The presence of –NH bridge in the copolymer is confirmed by the absorption band at 2793.48 cm^{-1}.[16] This band seems to be merged with a broad band of –OH group. A band appeared at 2833.41 and 1190.46 cm^{-1} may be attributed to –CH_2 linkage present in the copolymer resin.[20]

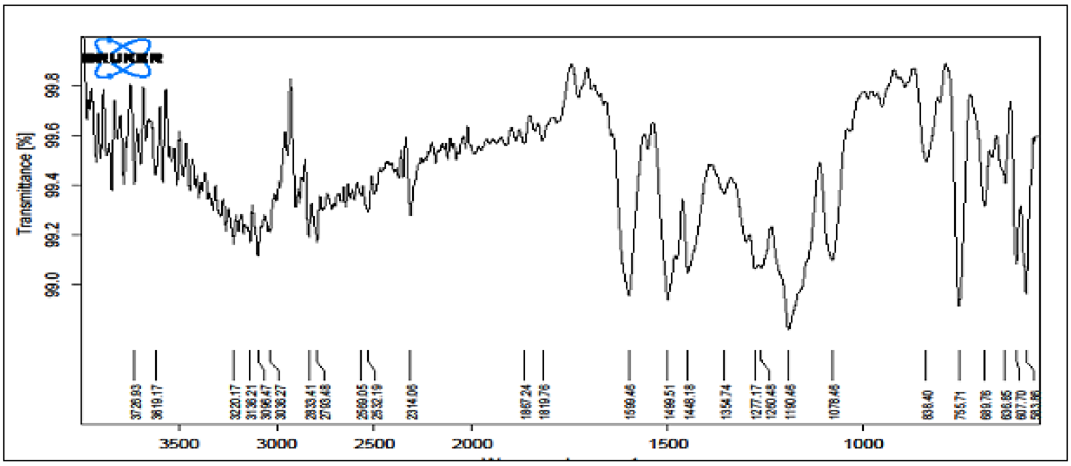


Fig 2:- FTIR Spectra of RPHF-I Terpolymer

Table 2: IR frequencies of RPHF-I Terpolymer

VIBRATION MODE	**FREQUNCY (cm^{-1})**	
	Reported	**Observed**
Phenolic (OH) group Intermolecular polymeric Association	3750-3150	3726.93
Starching methyl group-v (CH)	2910-2930	2833.41
-CH_2- Bridge	1158-1180	1190.46
aromatic –C=C bending	1600	1599
1,2,3,5-subtitude aromatic ring	1163-831	693,759,1078.48
-NH- bridge strong	3500-3200	3619.17
(C-N)Stretching	1250-1020	1277.17
N-H bending secondary amide	1500-1600	1499
Phenolic –OH in plane bending	1370-1385	1354.74

NMR Analysis

The ^{1}H NMR spectrum of RPHF-I terpolymer is depicted in Figure 3 and the spectral data are presented in Table 4. The chemical shifts (δ) ppm observed have been assigned on the basis of the literature.[18] 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 due to methylene proton of Ar–CH_2–N moiety. A signal observed at 4.1 (δ) ppm is due to proton of amines i.e. Ar-NH moity. A singlet observed in the region 1.2(δ) ppm may be attributed to the protons in –NH linkage. The signal at 8.1(δ) ppm is assigned due to phenolic–OH group involved in intramolecular hydrogen bonding. The signal at 9.87- 9.89(δ) ppm is assigned to Ar–CHO indicates the intramolecular hydrogen bonding between Ar–CHO groups in the terpolymer.[21] moiety. A signal observed at 4.1 (δ) ppm is due to proton of amines Ar-NH moity. A singlet observed in the region 1.2(δ) ppm may be attributed to the protons in –NH linkage. The signal at 8.1(δ) ppm is assigned due to phenolic –OH group involved in intramolecular hydrogen bonding. The signal at 9.87- 9.89(δ) ppm is assigned to Ar–CHO indicates the intramolecular hydrogen bonding between Ar–CHO groups in the terpolymer.[21]

Nature of proton assigned Expected	**chemical shift (δ)ppm**	**Observed Chemical Shift (δ)ppm**
Methylene proton of Ar-C**H2** moiety	2.35-2.99	2.50
Methylenic proton of Ar-C**H2**-N moiety	3.91	3.80
Proton of Ar–N**H** bridge	4.00	4.10
Aromatic proton Ar-**H**	6.50-7.50	7.20,6.20
Proton of phenolic-O**H** involved intramolecular hydrogen bonding	8.45	8.10
Proton of amines -CH_2-N**H**-	1-20	1.20

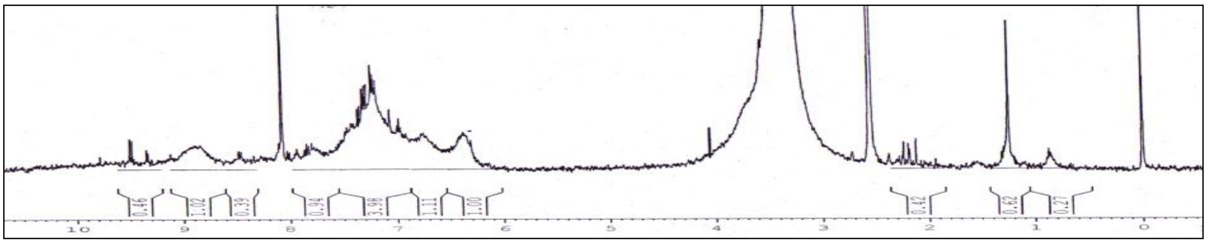


Fig 3:- ^{1}H-NMRSpectra of RPHF-I Terpolymer

XRD Analyses

The **figure 4** depicts the XRD pattern of the **RPHF-I** Terpolymer. A broad diffused peaks and absence of well defined peak clearly points out the amorphous nature[22] of the terpolymer.

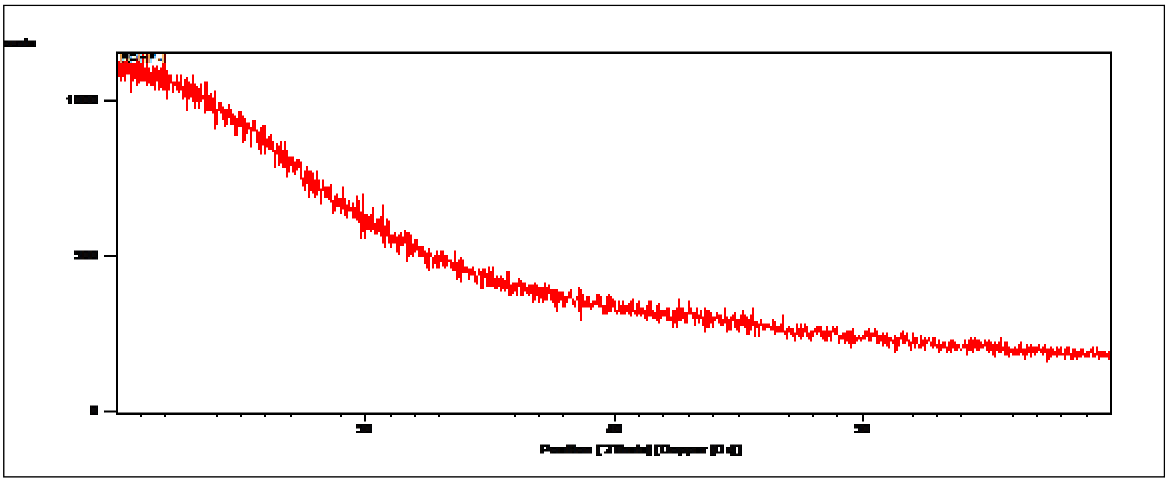


Figure 4:- XRD Spectra of RPHF-I Terpolymer

Removal of Cr (VI) by Terpolymer

Atomic Absorption Spectrophotometer (AAS) was used to determine Cr(VI) concentration in aqueous solution before and after the treatment. The removal of Cr (VI) by RPHF-I as an adsorbent was carried out at the pH 5.5. The initial metal ion concentration taken was 2.5 mg/lit and adsorbent dose was 6 gm/lit. The results have been presented in Table5/Figure5.

Table 4. Effect of contact time on removal of Cr (VI) by RPHF-I Terpolymer (pH = 5.5, adsorbent dose 6.00 gm/lit)

Contact Time (in min)	20	40	60	80	100	120	140	160	180	200
% of removal of Cr (VI)	42	49	55	63	71	79	83	83	83	83

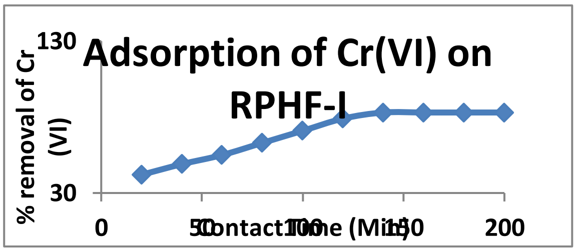


Figure 5.Effect of contact time on adsorption of Cr(VI) on RPHF-I

It can be noted fromTable5/Figure 5 that the removal of Cr (VI) increased with increase in contact time. It is evident that RPHF-I material is effective for maximum removal of Cr (VI) when the contact time is 140 min. No significant change in chromium removal efficacy was observed beyond 140 min. Thus the optimum treatment time is 140 min.

Conclusions

- RPHF-I terpolymer could be successfully synthesized with a good yield based on condensation reaction of resorcinol and phenyl hydrazine with formaldehyde in the molar ratio of 1:1:2 in the presence of 2M HCl as a catalyst.
- RPHF-I terpolymer has been characterized by CHN estimation, FTIR, NMR and XRD studies.
- Most probable structure has been proposed and reported in the paper.
- RPHF-I terpolymer is proved to be an excellent sorbent for Cr (VI).
- The newly synthesized RPHF-I Terpolymer sorbent can be used to remove toxic Cr (VI) from industrial/mining effluents *i.e.* contaminated water. Thus, the water can be purified and used for potable purpose after treatment using this material.
- The optimum parameters for efficient application of the RPHF-I terpolymer material under present investigation are: adsorbent dose 6.0 g, pH5.5 and contact time140 min.

Future scope

Studies can be extended for testing applicability of this material for removal of other toxic heavy metals from contaminated water and fabrication of suitable columns for water purification using this new RPHF-I terpolymer adsorbent.

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