Heavy Metal Abetment Efficacy of New Terpolymer RPHF-II Derived From Resorcinol, phenyl hydrazine and Formaldehyde

SUDHIRKUMAR MASKEY[1],
Yashwantrao Chawhan College,
Lakhandur-441803, India

PRATIBH BURHATE[2],
Shri Shivaji Science College,
Nagpur-440012, India

PRALHAD RAHANGDALE[3]
Bhawabhuti Mahavidyalaya, A
mgaon-441902, India

ABSTRACT

All human being need fresh water for carrying out physiological, sociological, cultural and other activities. Unfortunately multifarious activity of human being for development and welfare lead to generation and release of objectionable material into the freshwater system which causes water pollution. Thus many areas of surface water and groundwater are now contaminated with heavy metals. Cr(VI) is highly soluble and reactive and considered to be acute toxic, carcinogenic and mutagenic to living organisms and hence more hazardous than other heavy metals. In the present work, a new terpolymer, RPHF-II was synthesized using resorcinol (R), phenyl hydrazine (PH) and formaldehyde (F). This copolymer was characterized using modern techniques like ^{1}H-NMR, FTIR, XRD and SEM. The Cr(VI) adsorption was investigated using new terpolymer RPHF-II. Effect of pH, contact time, adsorbent dosage and initial Cr(VI) ion concentration was studied using batch experiments. The maximum removal of Cr(VI) was obtained to be 91 % and optimal removal was favored at pH 5. The removal of Cr (VI) by terpolymer was found to be increasing with increase in contact time as well as with adsorption dose with stationary phase achieved at 150 min and 5.5 gm/lit respectively. The new terpolymer RPHF-II can be successfully used as an efficient material for removal of Cr(VI) from aqueous environments such as domestic and industrial effluents and can have a variety of potential environmental applications.

Keyword: Heavy metals removal, objectionable material, Terpolymers, batch experiments Adsorption.

Introduction

The pollution of water resources due to the indiscriminate disposal of heavy metal has been causing world wise concern for the last few decades. It is well known that some metals can have toxic or harmful effects on many forms of the life.[1] Metals which are significantly toxic to human beings and ecological environment ,includes chromium, copper, lead, mercury cadmium, nickel iron etc.[2]Heavy metals are a general collective term applying to the group of metals and metalloids with an atomic density greater than 6 g cm-3.[3] Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders, therefore they must be removed before discharge.[4] Cr(VI) is highly soluble and reactive and considered to be acute toxic, carcinogenic and mutagenic to living organisms and hence more hazardous than other heavy metals.[5-6]

In animal studies, chromium was found to accumulate 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, and tissue chromium levels decline with age. Recent study shows that Cr (VI) compounds have been shown to cause lung cancer in humans when inhaled. The report on Carcinogens lists Cr (VI) Compounds as known human carcinogens.[7-8]

This study is an attempt to synthesize and characterize new terpolymer with heavy metal adsorbent properties for their removal from environment, specifically Cr (VI), from contaminated water.[9-10]In the present investigation, terpolymer RPHF-II was synthesized by using resorcinol (R), phenyl hydrazine (PH) and Formaldehyde (F) in 2:1:3 molar ratios of the reacting monomer. This copolymer has been characterized using modern techniques like ^{1}H-NMR, FTIR and XRD. The maximum removal of Cr (VI) was obtained to be 91% and optimal removal was favored at pH 5. The removal of Cr (VI) by terpolymer was found to be increasing with increase in contact time as well as with adsorption dose with stationary phase achieved at 150 min and 5.5 gm/lit respectively. The new terpolymer RPHF-II can be successfully used as an efficient material for removal of Cr(VI) from aqueous environments such as domestic and industrial effluents and can have a variety of potential environmental applications.

Material And Method

Chemicals

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

Synthesis Of (RPHF-II) Terpolymer

The terpolymer (RPHF -I) was synthesized by condensing Resorcinol, phenyl hydrazine with formaldehyde in molar ratio (2:1:3) in the presence Hydrochloric acid (2M) used as catalyst. The reaction mixture was taken in 500ml round bottom flask with water condenser and heated in an electrically operated oil bath at 122 ± 2^{0}C for 5hr. with occasional shaking. The temperature of the oil bath was controlled with the help of dimmer stat. The solid mass obtained is removed immediately as reaction process was over. The separated terpolymer product (RPHF-II) was later purified. The solid terpolymer product was repeatedly washed with hot DI 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 resin product was filtered off, washed with hot water until it was free from chloride ions, dried and powdered. The purified polymer sample was dried in vacuum at room temperature. The finely ground resin 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 91%. The reaction taking place and proposed structure of (RPHF-II) is shown as below Figure:-1

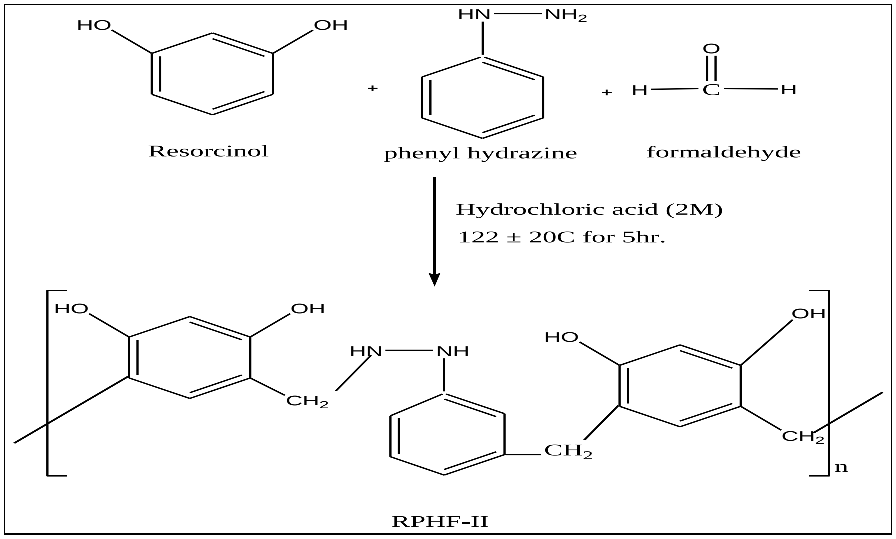


Fig1-Reaction and Suggested Structure of RPHF-II Terpolymer

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 filtrate was analyzed for Cr(VI) concentration using UV-Visible Spectrophotometer. From experimental data, the applicability of Langmuir model was judged. Linear regression coefficient (R^2) and isotherm constant values were determined from the model.

Characterization of Terpolymer

Characterization of terpolymer was carried out by techniques like Fourier Transform Infra-Red (FTIR), Nuclear Magnetic Resonance (^{1}H-NMR) and X-Ray Diffraction (XRD) analysis and the concerned spectra/image have been presented. The elemental analysis, FTIR, ^{1}H-NMR, and XRD was carried out at Sophisticated Analytical Instrumental Facility (SAIF) Punjab University, Chandigarh and SAIF Cochin

Results And Discussions

The FTIR spectrum of RPHF-II terpolymer is depicted in Fig.1 and the spectral data are present. A broad absorption band appeared in the region 3536.51-3033.64cm-1 may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intermolecular hydrogen bonded polymeric association.[11] The Methylene bridge associated with resorcinol can be identified by the peak at 2918 and 2856.78 cm-1.[12] The peaks appeared at 1499 and 1198.9 cm^{-1} is due to CH_2 bridge coupled with aromatic ring.[13-14] A peak appeared at 1358.01cm-1 can be assigned to in plane bending vibration of phenolic –OH in plane bending.[15] A sharp strong peak at 1598.57 cm-1 may be ascribed to N-H bending of secondary amide group.[16]1,2,3,5 tetra substituted aromatic ring may be identified by the peaks at 1278.17 ,953.73 and834.95 cm-1.[17] A strong peak appeared at 1079.26 and 1030.21cm-1 may be due to C-N stretching of Ar-NH_2 .[18]

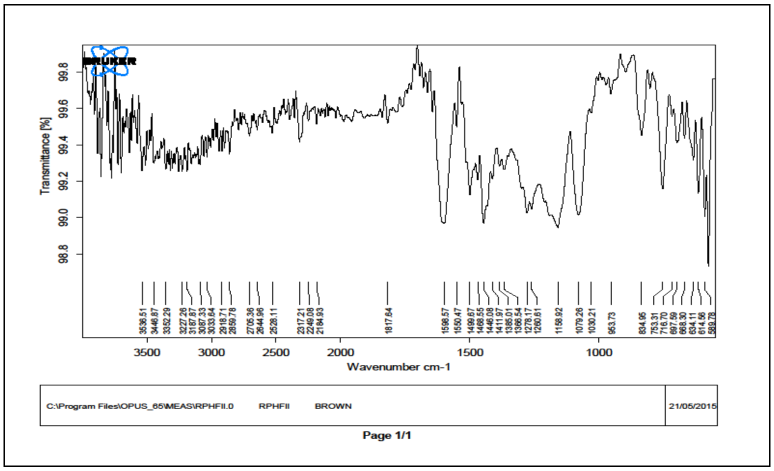


Fig 2:- FTIR Spectra of RPHF-II Terpolymer

The [1]H NMR spectrum of RPHF-II copolymer resin is depicted in Figure 3. The chemical shift (δ) ppm observed is assigned on the basis of the literature.[19-20] The signals in the region at 6.4-7.1 (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–CH2 bridge. A singlet observed in the region 3.5 (δ) ppm is due to Methylene proton of Ar–CH2–N moiety. A signal observed at 4.2 (δ) ppm is due to proton of amines Ar-NH moity. A singlet observed in the region 1.3 (δ) ppm may be attributed to the protons in –NH linkage. The signal at 8.2(δ) ppm is assigned due to phenolic –OH group involved intramolecular hydrogen bonding.

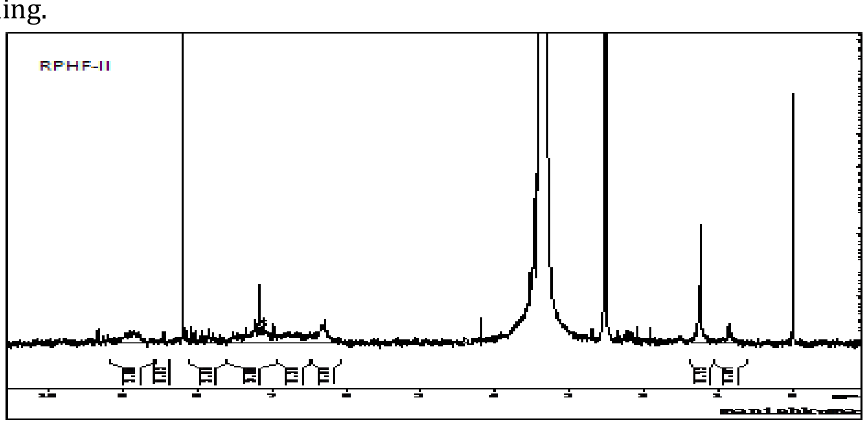


Fig 3:- [1]H-NMRSpectra of RPHF-II Terpolymer

The figure 4 depicts the XRD pattern of the RPHF-II terpolymer , a broad diffused peak and absence of well defined peak clearly pointed out the amorphous nature[21]

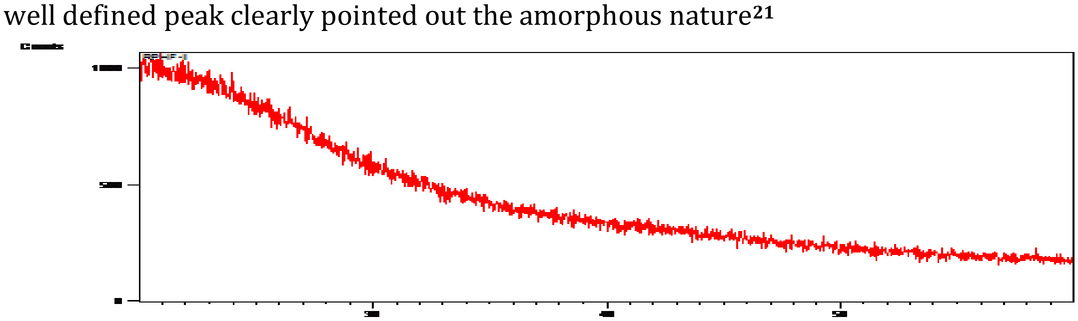


Fig 4:- XRD Spectra of RPHF-II Terpolymer

Fig.5 The scanning electron microscopy (SEM) of RPHF-II indicates that it has clear pore structure developed. There is no cellulosic structure form on the surface but there are very small and many cavities over the surface of the RPHF-II. Due to this cavity like structure of the surface of the material possessed high surface area and high adsorptive properties. Adsorption of any heavy metal depends upon the pore size of the terpolymer So RPHF-II has high tendency to absorb any heavy metals on his surface and has excellent adsorbent.[22]

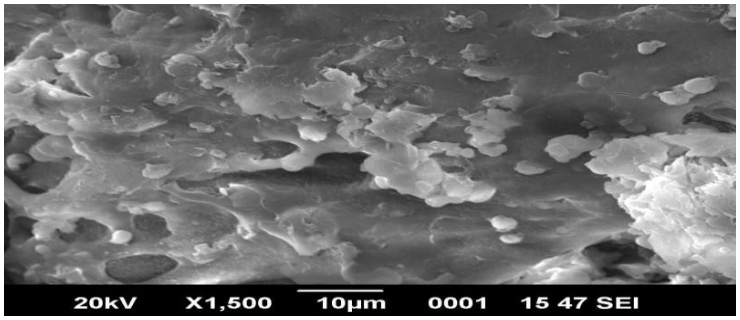
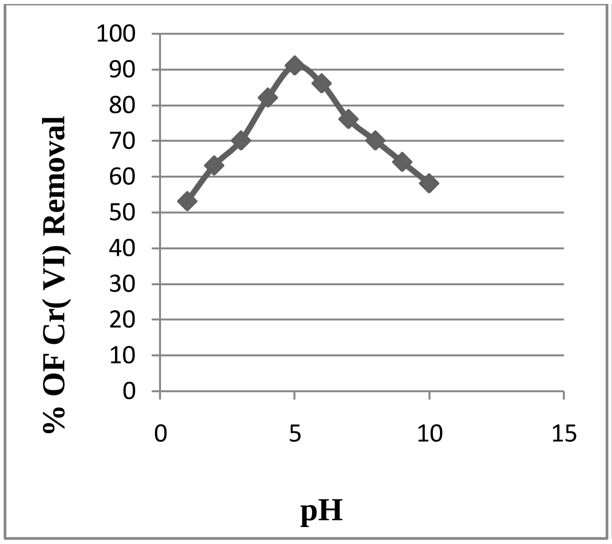


Fig.5. The scanning electron microscopy (SEM) of RPHF-II

Removal of Cr (VI) By RPHF-II Terpolymer

Effect of pH:
pH is an important parameter for adsorption of metal ions from the aqueous solution because it affects the solubility of the metal ions. Adsorbent has been studied in the pH range 1 to10. The effect of pH on the removal of Cr(VI) using RPHF-II was studied (Fig.6). The maximum chromium removal efficiency (91%) was noticed at pH 5.

Effect of Contact Time:
Efficient uptake of Cr(VI) ion with effect of contact time by RPHF-II was studied and result are shown in(fig.7). Indicate that the Cr(VI) removal ability of RPHF-II increased with increasing in contact time before equilibrium is reached. Other parameters such as dose of RPHF-II, pH of solution and initial concentration was kept optimum. The percentage removal of Cr(VI) was studied within time range 10 to 200 min. After 150 minute negligible effect has been noticed on adsorption of Cr(VI). Thus 150 minute is the optimum time for these batch experiments.



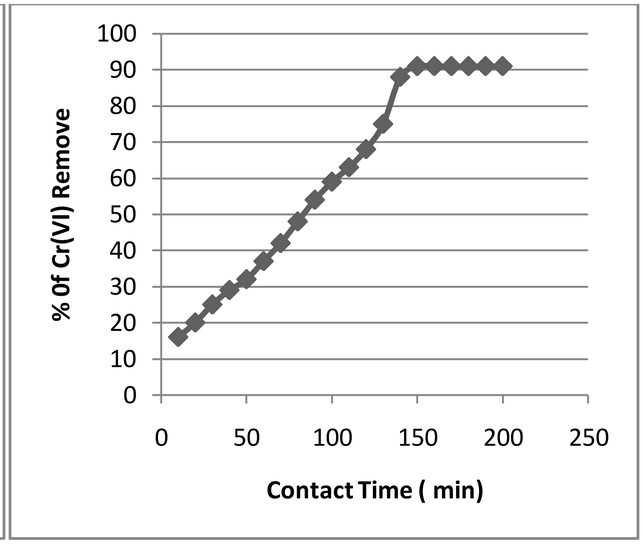


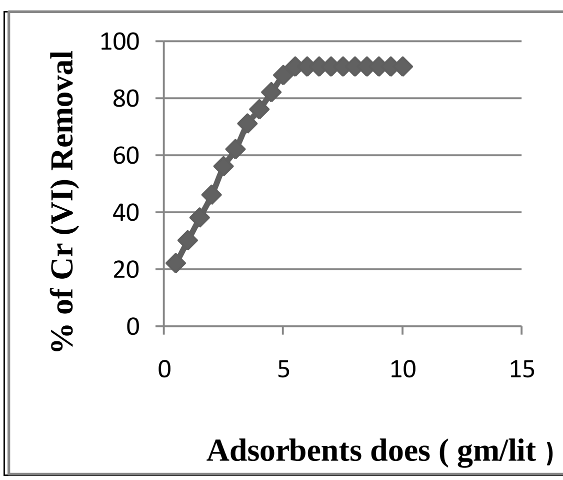
Fig.6. Effect of pH on Cr(VI) adsorption **Fig.7.Effect of Contact time on Cr (VI)adsorption**

Effect of Adsorbent Dosage

The effect of dosage on the removal of Cr(VI) was studied by varying the amount of RPHF-II from 1 to 10 g/l while keeping other parameters (pH , contact time and initial concentration) constant as shown in (fig.8.) From the figure, The initial Cr(VI) concentration taken was 35 ppm. The percentage of Cr(VI) removal was found to increase from 22 to 91. The increase in Cr(VI) removal with increase in RPHF-II doses is due to the increase in surface area and adsorption sites available for adsorption. However after certain dose it becomes constant and it is treated as an optimum adsorbent dose, which is found to be 5.5 gm/lit. for the RPHF-II adsorbent.

Effect of Initial Metal Ion Concentration

The effect of initial metal ion concentration on the percentage removal of Cr(VI) by RPHF-II as shown in (fig.9.) In the present study adsorption experiments were performed to study the effect of initial Cr(VI) concentration by varying it from 10-100ppm solution while maintaining the Adsorbent dose 5.5gm/lit



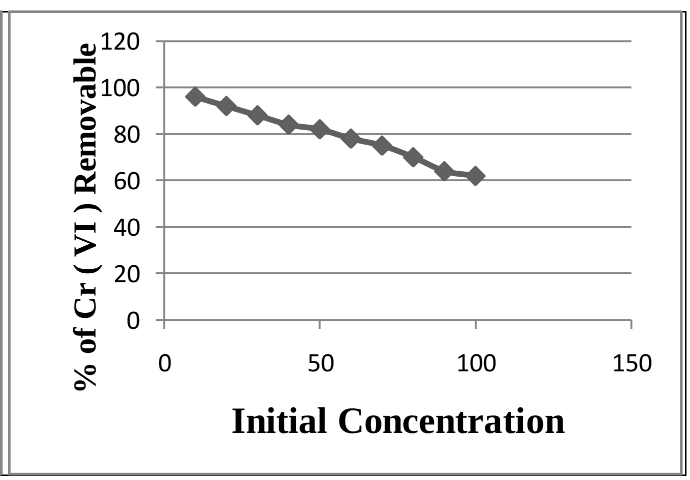


Fig.8. Effect of Adsorbent Does on Cr(VI) adsorption **Fig.9.Effect of initial ion concentration on Cr(VI) adsorption**

Adsorption Isotherm

The isotherm data have been linearized using the Langmuir equation and is plotted between Ce/Qe versus Ce. The Langmuir constant qm, which is measure of the monolayer adsorption capacity of RPHF-II is obtained as 12.82. The Langmuir constant 'b' which denotes adsorption energy, is found to be 2.19.The high value (0.996) 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 the RPHF-II. The dimensional parameter, RL, which is a measure of adsorption favorability is found to be 0.0106(0< RL < 1) which confirms the favorable adsorption process for Cr(VI) on RPHF-II adsorbent.

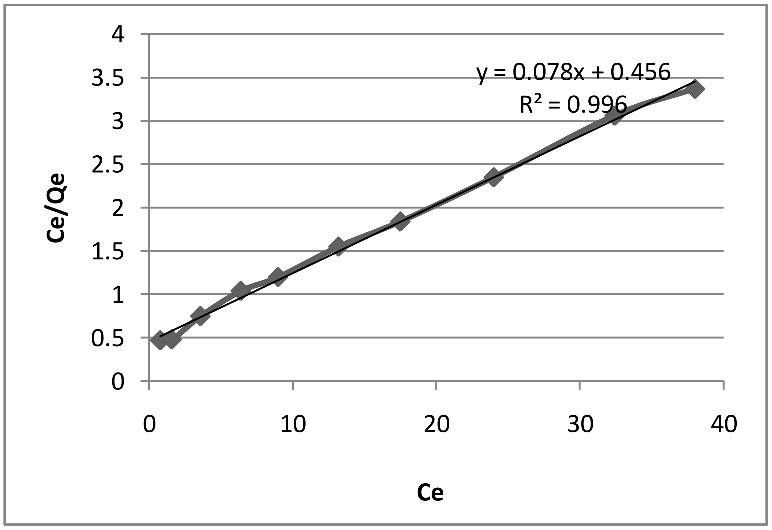


Fig.10. Langmuir isotherms for the adsorption of Cr(VI) on RPHF-II

Conclusion

RPHF-II terpolymer is successfully synthesized with a good yield based on condensation reaction of resorcinol and phenyl hydrazine with Formaldehyde in the molar ratio of 3:1:2 in the presence of HCl as a catalyst. RPHF-II terpolymer is characterized by FTIR, NMR, XRD and SEM studies. Removal of poisonous Crominium from aqueous solution is possible using RPHF-II terpolymer which effectively removes more than 91 % of Cr(IV) at 308 K. The optimum parameters for efficient application of the RPHF-II terpolymer material under present investigation was at adsorbent dose, pH and contact time 5.5 g, 5 pH and 150 min respectively. The adsorption data satisfactorily explained by Langmuir isotherms. Sorption of Cr(IV) follows pseudo second order kinetics. The values of RL factor ranging from 0 to 1 indicate the favorable adsorption situation. Thus the newly generated RPHF-II has been proved to be an excellent adsorbent which can employed for removal of Cr(IV) from polluted water

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