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Carcinogenic Cr(VI) Abetment Applicability of 8-HQPHF-II Terpolymer

[1]RAHANGDALE P.K.; [2]MESHRAM U.P.; [3]SHENDE S.S.; *[4]VILAYATKAR N.D.

[1]Bhawabhuti Mahavidyala, Amgoan-441902, India pkrahangdale@yahoo.co.in
[2]N.K.S.Model College Kamja (GH)- 442203,India _umeshmeshram@rediffmail.com
[3]N.P.W.College, Lakhani- 441804, India sudhakarshende31@gmail.com
[4]S.S.Jaiswal College, Arjuni/Morgoan-441701, India vilayatkar.nitin@gmail.com

Corresponding author, email:vilayatkar.nitin@gmail.com,Contact: +91 9028631242

Abstract

Recently surface water and groundwater gets commonly contaminated with toxic heavy metals. Amongst these heavy metals hexavalent chromium Cr(VI) is more toxic because it is carcinogenic and mutagenic. For this reason, the removal of Cr(IV) from polluted water has received an extensive concern and has become a hot topic in environmental research. The aim of the present investigation is to synthesize an efficient adsorptive material (8-HQPHF-II terpolymer) and to evaluate its practical efficacy towards removal of hexavalent chromium. Its synthesis was done by polycondensation of 8-HydroxyQuinoline, Phenylhadrazine and Formaldehyde in 2:1:3 molar ratio followed by its applicability studies in environmental pollution control with respect to Cr(VI) removal. The characterization and the structural elucidation of the newly prepared terpolymer was carried out using the modern techniques such as elemental analysis, TGA, FTIR, XRD and ^{1}H-NMR spectral studies. The Cr(VI) removal property of the terpolymer was determined by batch equilibrium method. The effects of various parameters like pH, contact time and adoption doses have also been studied and their optimum values are found to be pH 4, 110 min and 5 gm respectively. The adsorption data were found to fit well with the Langmuir and Freundlich isotherm models. At optimum condition nearly 90% abatement of Cr(VI) has been noted using 8-HQPHF-II.Thus the 8-HQPHF-II under study has been proved be as an efficient/successful adsorbent material for removal of Cr(VI) from contaminated water.

Keywords: *Hexavalent chromium, Carcinogenic, Batch method, environmental applications.*

Introduction

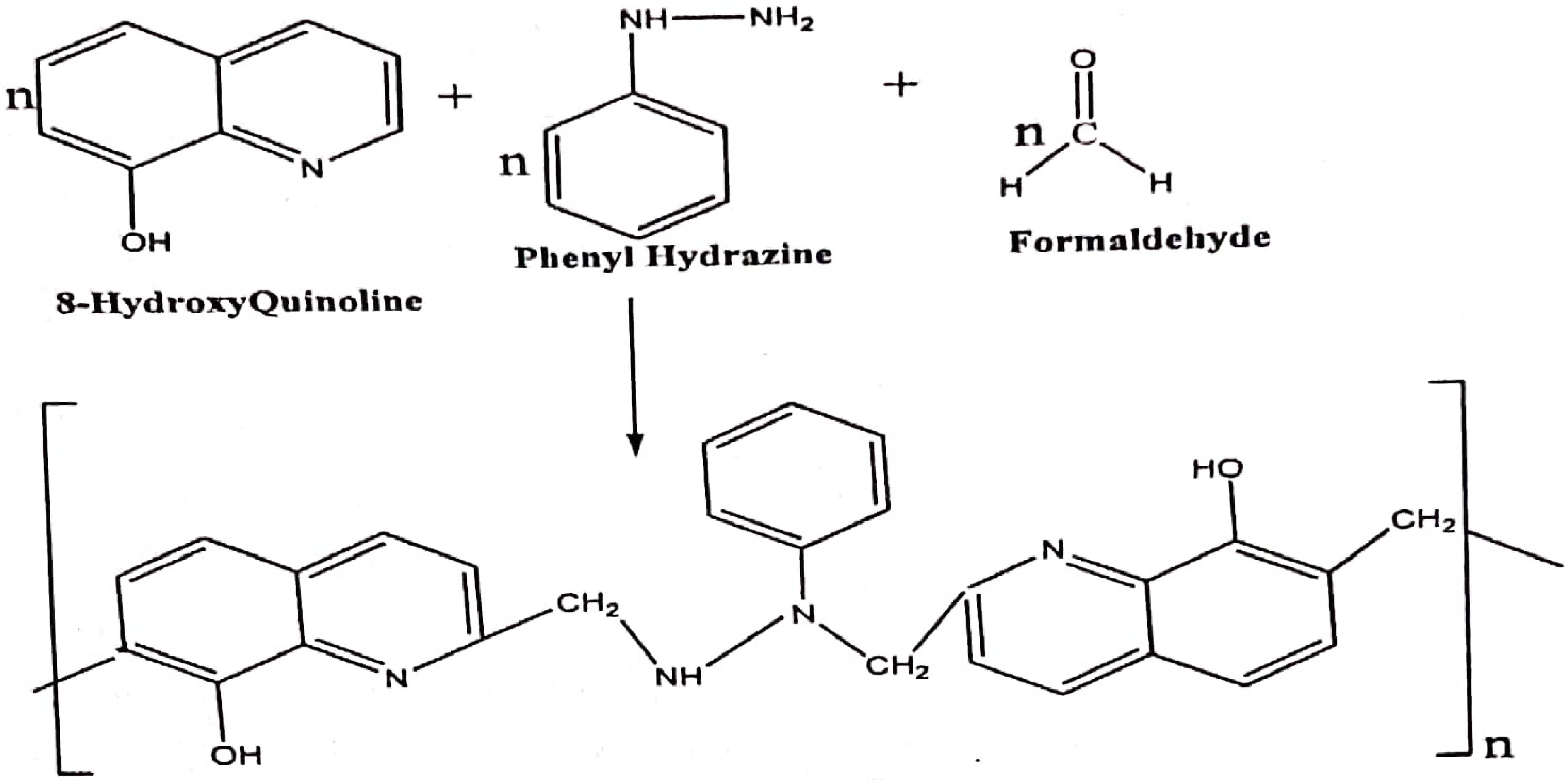
The compounds containing chromium(Cr) are among the most common toxic pollutants in water [1]. Chromium concentration increase in surface water/ground water is a result of its several applications such as in metallurgy, organic chemical synthesis, leather tanning and wood preserving industries [2] etc. In the natural environment, chromium exists mainly in two oxidation states i.e. Cr(VI) and Cr(III); out of these the Cr(VI) is more toxic than Cr(III). Cr(VI) can enter human bodies via ingestion, inhalation or even directly from skin and moves to organs such as liver, kidneys and lungs which cause toxic effect involving genotoxicity, carcinogenicity, mutagenicity and teratogenicity [3,4]. Cr(VI) compounds have been classified as a class I carcinogen for humans by IARC and listed as one of the priority contaminants [5]. Therefore, effective techniques need to be developed for remediation of Cr(VI)-contaminated surface/groundwater. In the present investigation synthesis of terpolymer (8-HQPHF-II) has been attempted by use of starting materials like 8-HydroxyQuinoline, Phenylhadrazine and Formaldehyde(2:1:3) in presence of 2M HCl. Characterization and structure confirmation of the prepared terpolymer was done with the help of various modern techniques such as elemental analysis, TGA, FTIR, XRD and ^{1}H-NMR. The Cr(VI) adsorption using 8-HQPHF-II was investigated including the supportive studies like effect of pH, contact time, adsorbent dosage and initial metal ion concentration by use of batch experiments. The maximum removal of Cr(VI) was obtained to be 90%. Thus 8-HQPHF-II can be successfully used as an efficient adsorbent material for removal of Cr(VI) from aqueous solution and can have a variety of potential environmental applications.

Materials and Methods

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

Synthesis of terpolymer

In RB flask reaction mixture i.e. 8-Hydroxyquinoline, Phenylhadrazine and Formaldehyde(2:1:3 molar ratio) was taken and followed by addition of appropriate amount of 2M HCl which acted as catalyst during the chemical reaction. The RB flask was heated in an electrically operated oil bath at 122 ± 3^{0}C for 6 hrs with occasional shaking. The temperature of the oil bath was controlled with the help of dimmer stat. The solid mass obtained was removed as soon as the reaction period was over. It was repeatedly washed with hot water to remove unreacted monomers. The resinous product was dried in air and powdered. The powder was washed many times with petroleum ether in order to remove Hydroxyquinoline -formaldehyde copolymer which may be present with the desired product. The product so obtained was further purified by re-precipitation technique. The terpolymer was dissolved in 2N NaOH solution, filtered and re-precipitated 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 terpolymer 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 is given in figure 1.



8-HQPHF-II

Fig.1 Reaction scheme and structure of 8-HQPHF-II Terpolymer

Preparation of Cr(VI) solution

The stock solution(100ppm) was prepared by dissolving 0.289 gm of $K_2Cr_2O_7$ in 1 liter double distilled water. Appropriate volume of the stock solution was suitably diluted with double distilled water to obtain the desired concentration for batch experiments. 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 hexavalent Chromium solution and effect of adsorbent doses. The systems were agitated on rotary shaker at 250 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 Freundlich isotherm and Langmuir model were judged. Linear regression coefficient and isotherm constant values were determined from these models.

Characterization of 8-HQPHF-II

FTIR Studies of 8-HQPHF-II

Fig.2. represents the FTIR spectrum of 8-HQPHF-II terpolymer. The band at 3500cm^{-1} attributed the presences of stretching vibrations of phenolic hydroxyl (–OH) group in the terpolymer. The methylene bridge associated with 8-HydroxyQuinoline can be identified by the peak at 2840cm^{-1}[6,7]. A sharp peak appearing at 1592cm^{-1} may be due to C=N stretching vibration[12].The tetra substitution in the benzene ring is established by presence of medium band at 855cm^{-1} which is attributed to (C-H) bending vibration [8]. The peak appeared at 1296cm^{-1} proves the presence of methylene bridge coupled with aromatic ring[9]. The peak at 1387cm^{-1} indicate –C=C- stretching in aromatic nucleus. A signal at 1494 cm^{-1} may be ascribed to N-H bending of secondary amido group[10].

^{1}HNMR- Studies of 8-HQPHF-II

^{1}HNMR spectrum of 8-HQPHFterpolymeric resin has been presented in**Fig.3**. Terpolymer exhibits unsymmetrical pattern of signal in the region 6.8-8.0(δ) ppm which is characteristic of aromatic protons (Ar—H)[6]. The signal at 2.5(δ) ppm is attributed to –NH-bridge. The signal at 9.1(δ) ppm indicates the presence of phenolic group (Ar---OH). The Ar-CH_2 protons are assigned from peak at 5.1(δ) ppm. The much downfield chemical shift for phenolic –OH indicates that the hydroxy group is involved in the intermolecular hydrogen bonding[11,12].

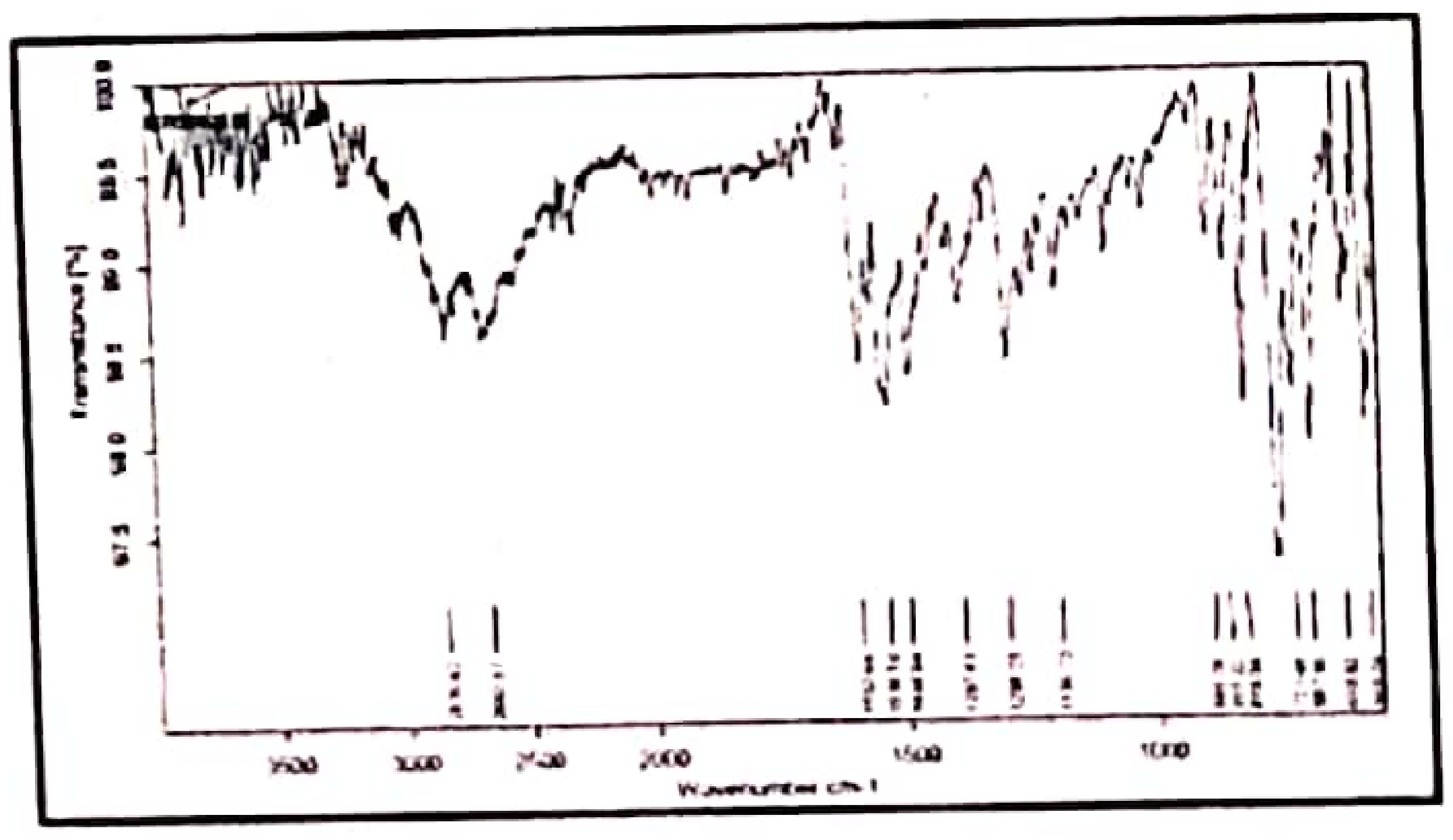


Fig.2 FTIR spectrum of 8-HQPHF-II

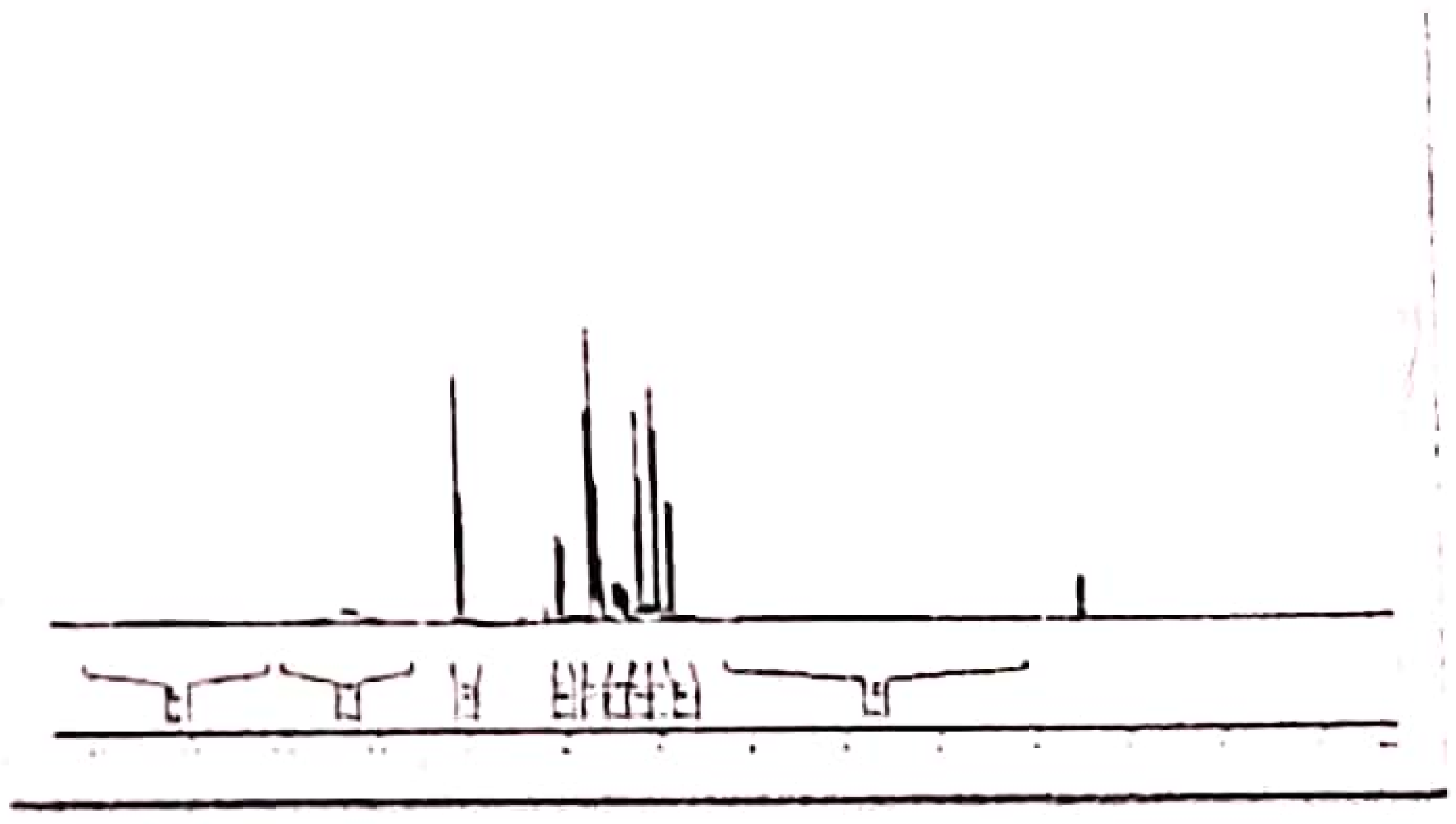


Fig. 3 ^{1}HNMR spectrum of 8-HQPHF-II

XRD Studies of 8-HQPHF-II

Fig. 4 represents the X-ray diffract graph of 8-HQPHF-II. This terpolymer exhibit all sharp peaks at around 2θ = 11^0,15^0,19^0, 22^0, 25^0,27^0 and 29^0 indicate crystalline nature of the polymeric material, but above 29° it is found that the peak become broad that which is indicative of amorphous nature of terpolymer[13,14]. Thus it can be concluded that polymer shows semi-crystalline nature which is a good symptom for adsorption properties.

TGA studies of 8-HQPHF-II

Fig.5 shows TGA curve of 8-HQPHF-II. The first derivative peak can be observed at 70^{0}C-150^{0}C with a weight loss of 4% which may be due to the loss of water molecules entrapped in the copolymer. The weight loss rate is very low at this stage. The second and third peak respectively at 198^{0}C with 40% and 360^{0}C with 90% of weight loss may be due to the elimination of –OH groups attached to the aromatic nucleus. The final decomposition stage can be observed in the range at 480-730^{0}C with 97% weight loss can be considered due to decomposition of the remaining imide moieties of copolymer resin [15,16].

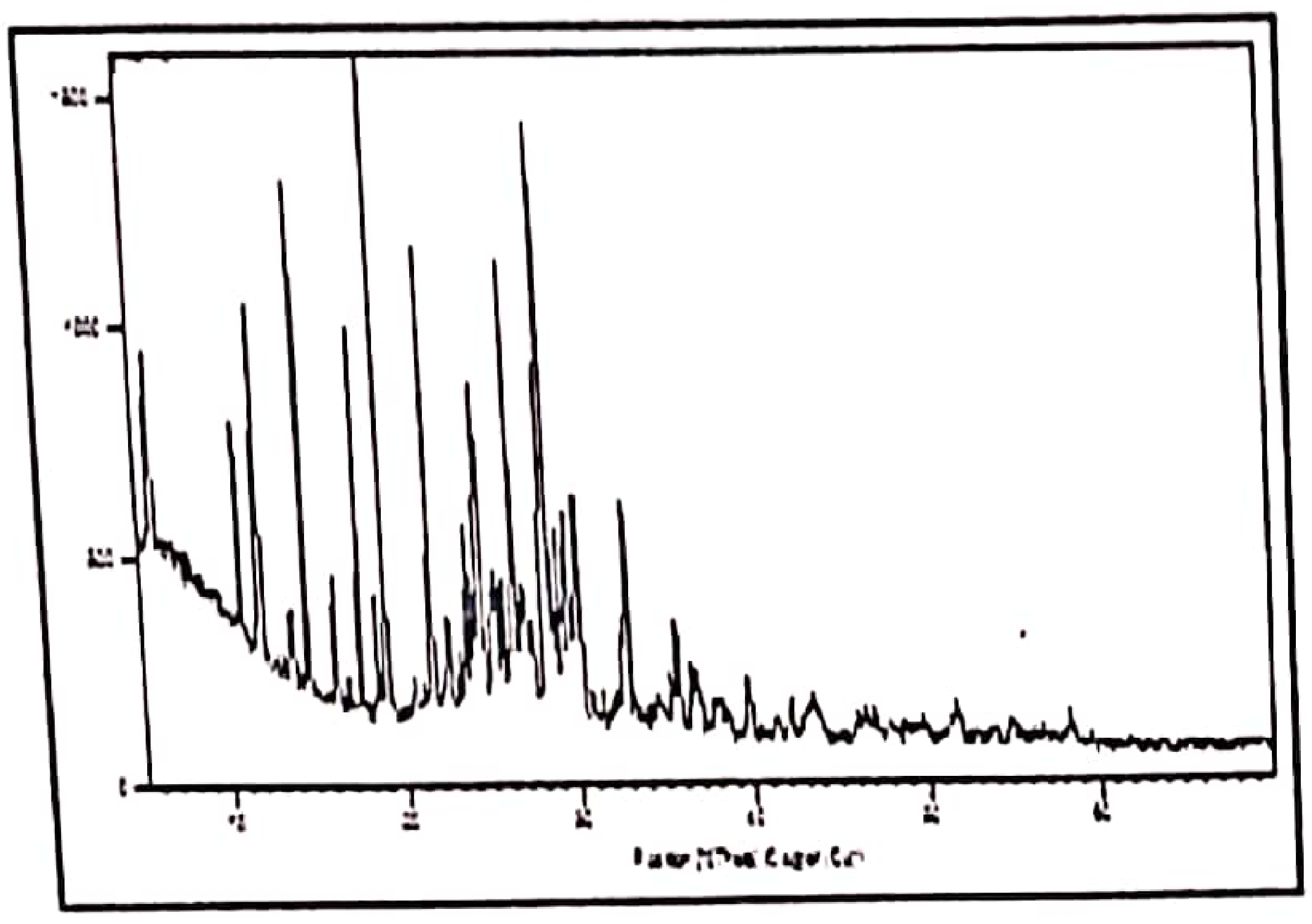


Fig.4 XRD of 8-HQPHF-II

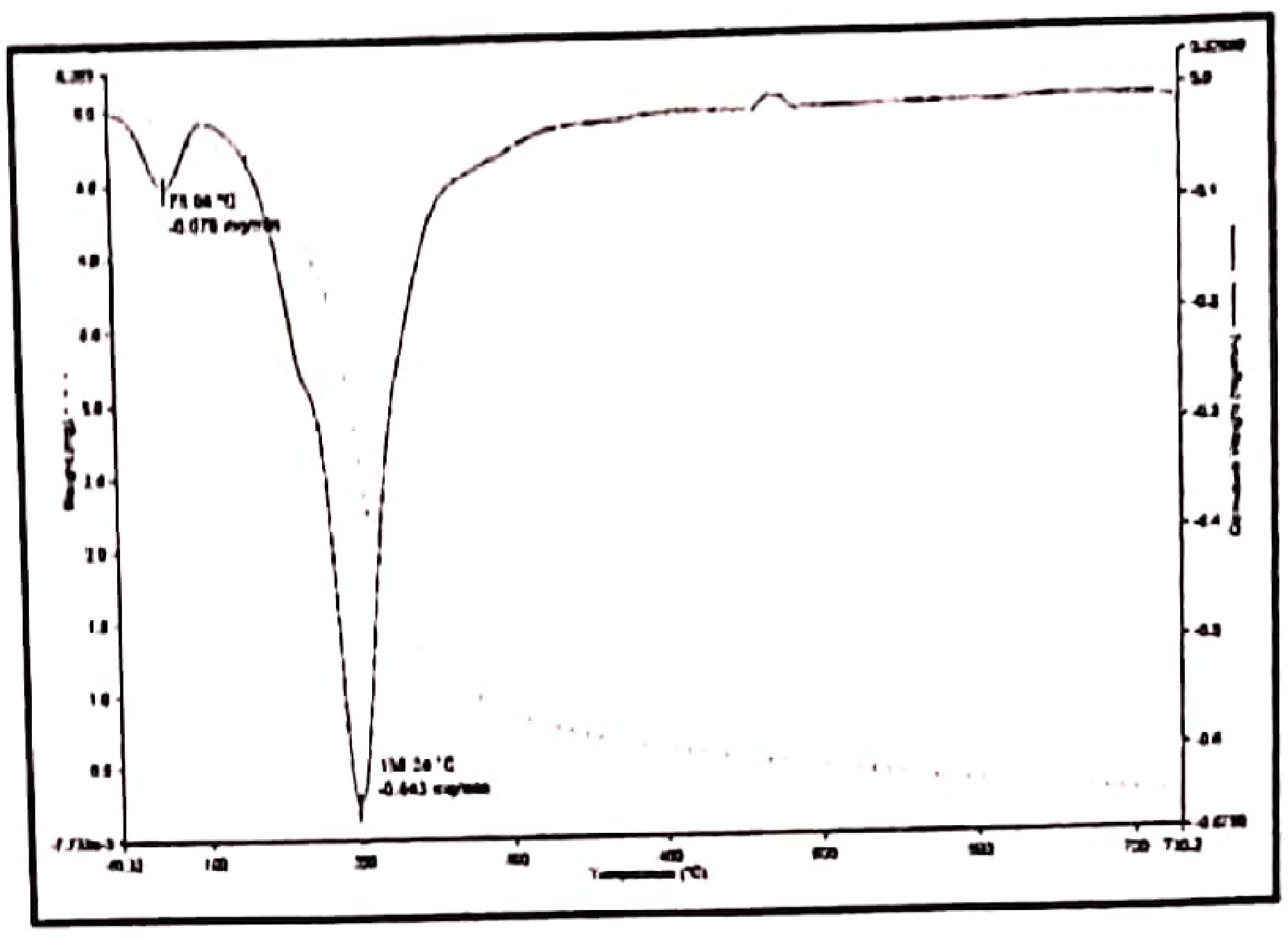


Fig.5 TGA Curve of 8-HQPHF-II

Results and Discussion

Effect of pH on adsorption

Effect of pH on **Cr(VI)** adsorption using 8-HQPHF as an adsorbent has been studied in the pH range 1 to10 and presented in **Fig.6.** It is seen that solution pH plays a very important role in the adsorption of Cr(VI). The percentage removal increases steadily from 64 to 90% when pH is increased from 1 to 4 in **Cr(VI)** adsorption and slowly decreases on further increases in pH.

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 stage, then gradually increases and remains almost constant (near about 91%), after optimum time period of 110 min.

Effect of adsorbent doses

The effect of adsorbent (8-HQPHF-II) 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 5 gm/lit for the 8-HQPHF adsorbent.

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 5 gm/lit of adsorbent dose. The results have 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.

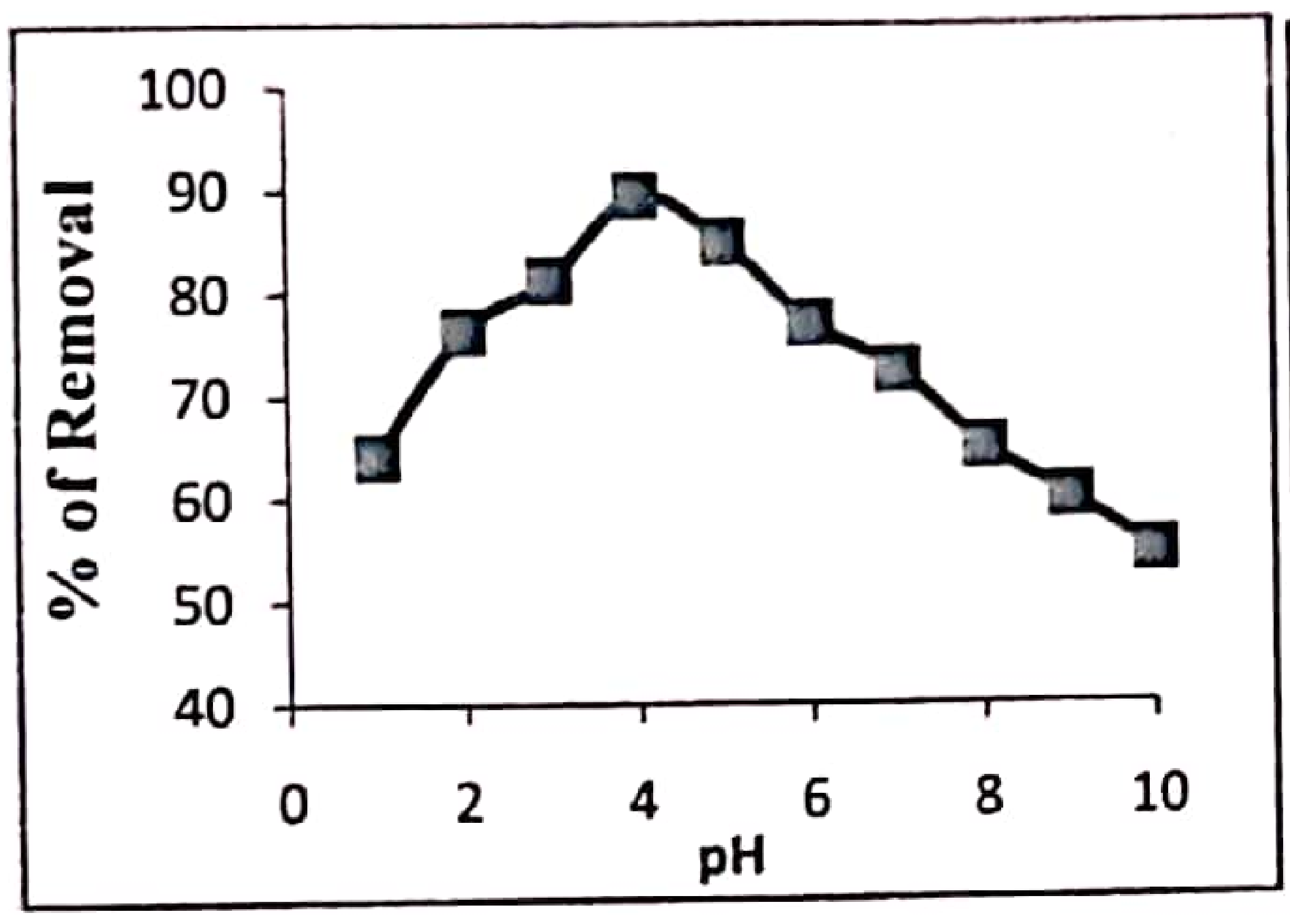


Fig.6 Effect of pH on Cr(VI) removal

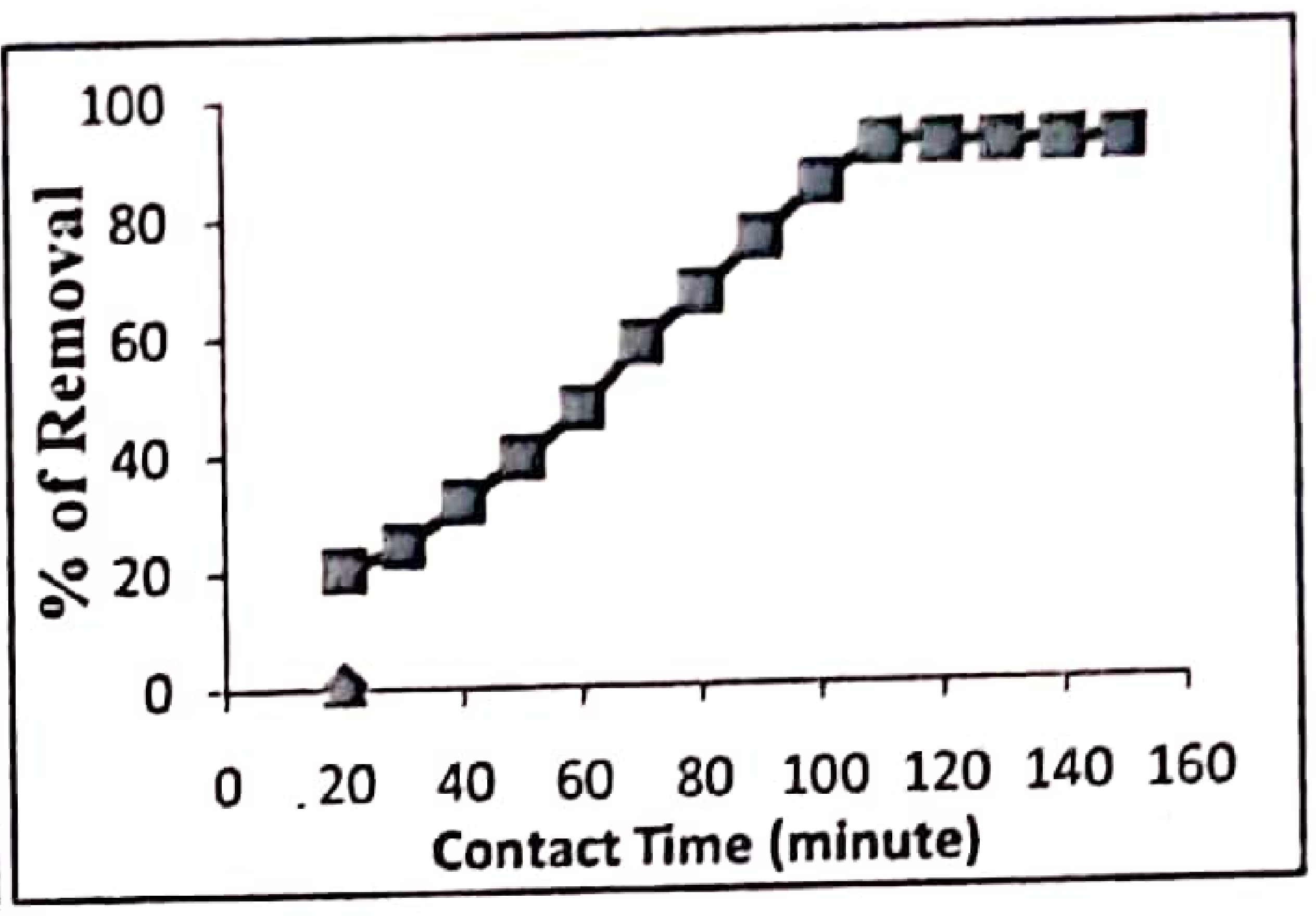


Fig.7 Effect of Contact time on Cr(VI)removal

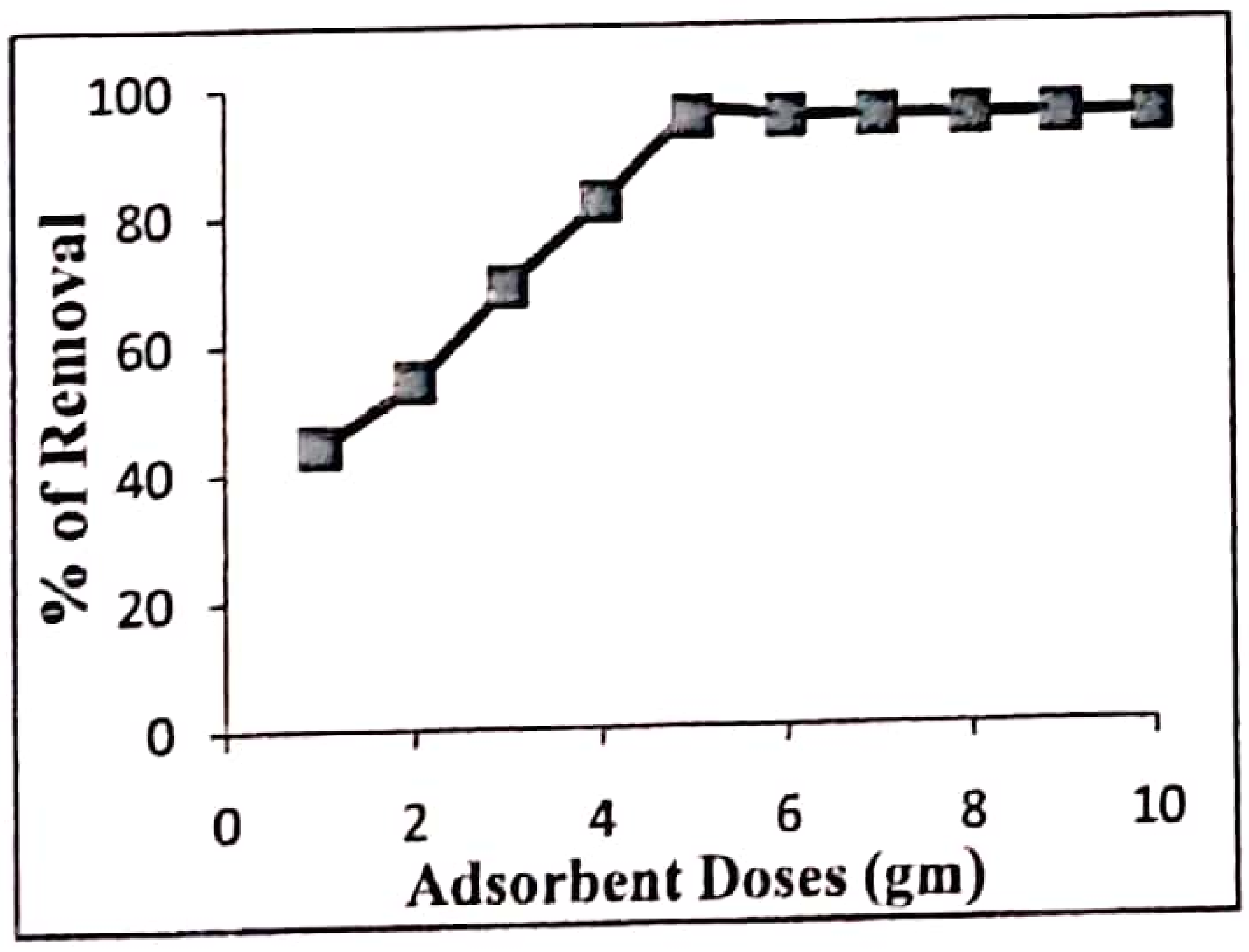


Fig.8 Effect of adsorbent doses on Cr(VI)removal

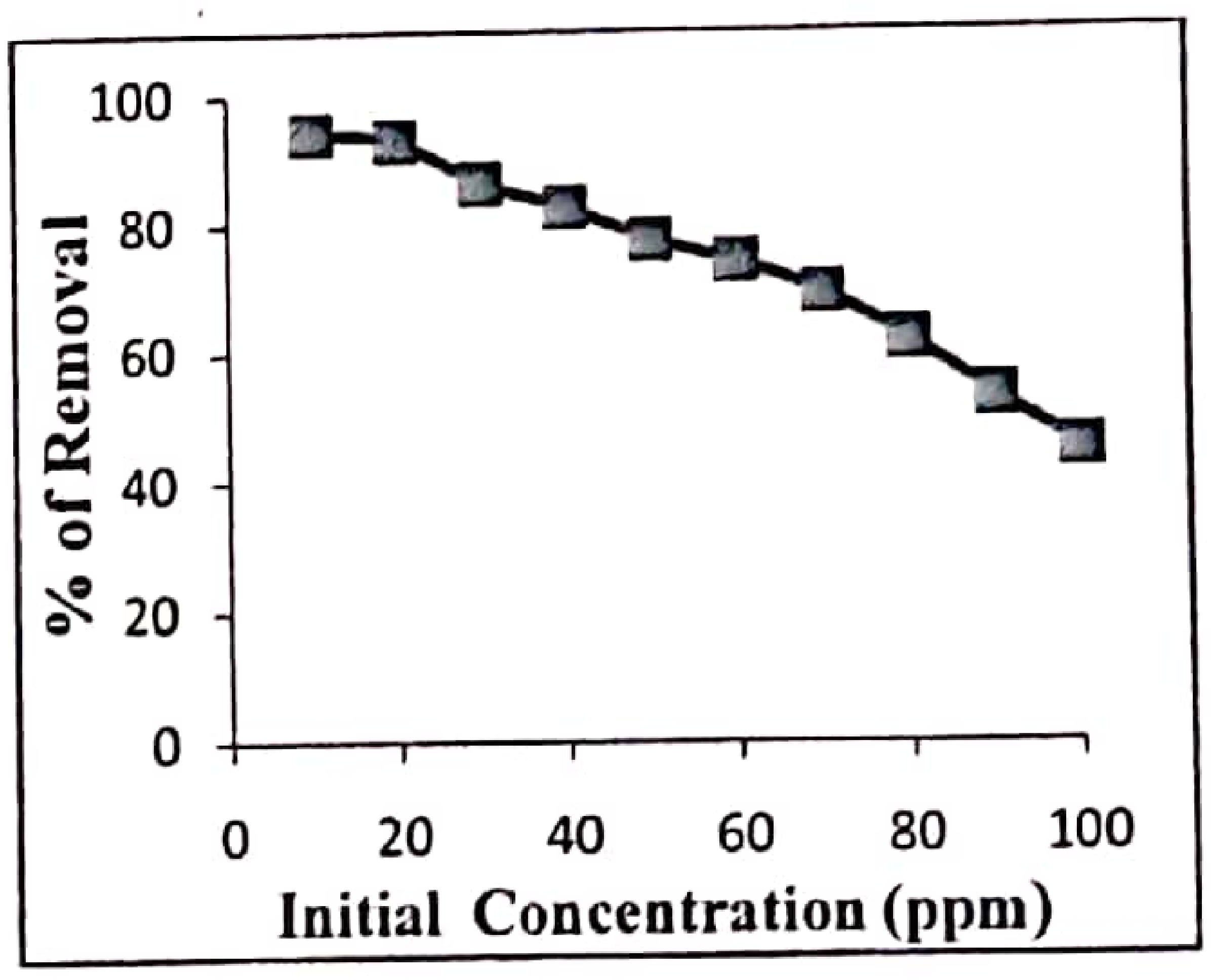


Fig. 9 Effect of initial concentration on Cr(VI) removal

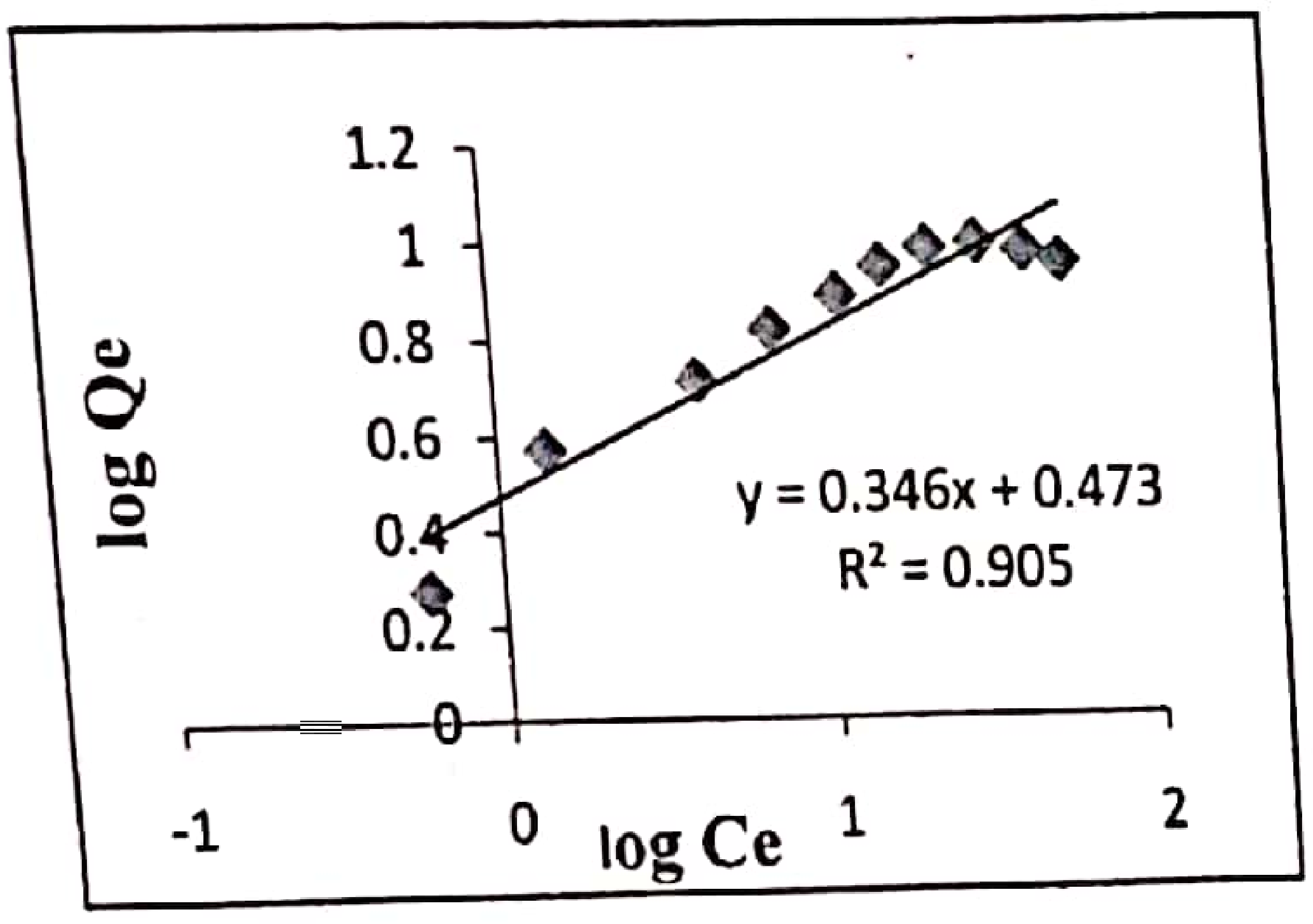
Adsorption Isotherm

Freundlich adsorption isotherm

The plot of log Q_e versus log C_e for Cr(VI) is presented in **Fig. 10** which shows a linear curve and hence the adsorption process obeys Freundlich adsorption isotherm. Freundlich constants 'n' and 'k_f' for Cr(VI)were found to be 2.34 and 2.975 mg/g respectively. The square of the correlation coefficient (R^2) value was found to be 0.9024 for Cr(VI) which shows well-fitting of the Freundlich isotherm. The 'n' values are in between 1 to 10 which indicate the favorable adsorption of Cr(VI)on 8-HQPHF-II.

Langmuir Isotherm

The results obtained from Langmuir model for the removal of Cr(VI) by 8-HQPHF-II has been represented in **Fig.11**. The value of square of the correlation coefficient (R^2) found to be 0.9827 for Cr(VI), which show the best fitting of equilibrium data. The value of 'Q_m' for Cr(VI) was found to be 9.87 mg/g while value of 'b' was 0.426. The lower values of b (less than one) implies an excellent affinity between solute and sorbent sites. To confirm the adsorbtivity of the adsorption process, the equilibrium parameter also called separation factor (R_L) for Cr(VI)was determined and found to be 0.072.



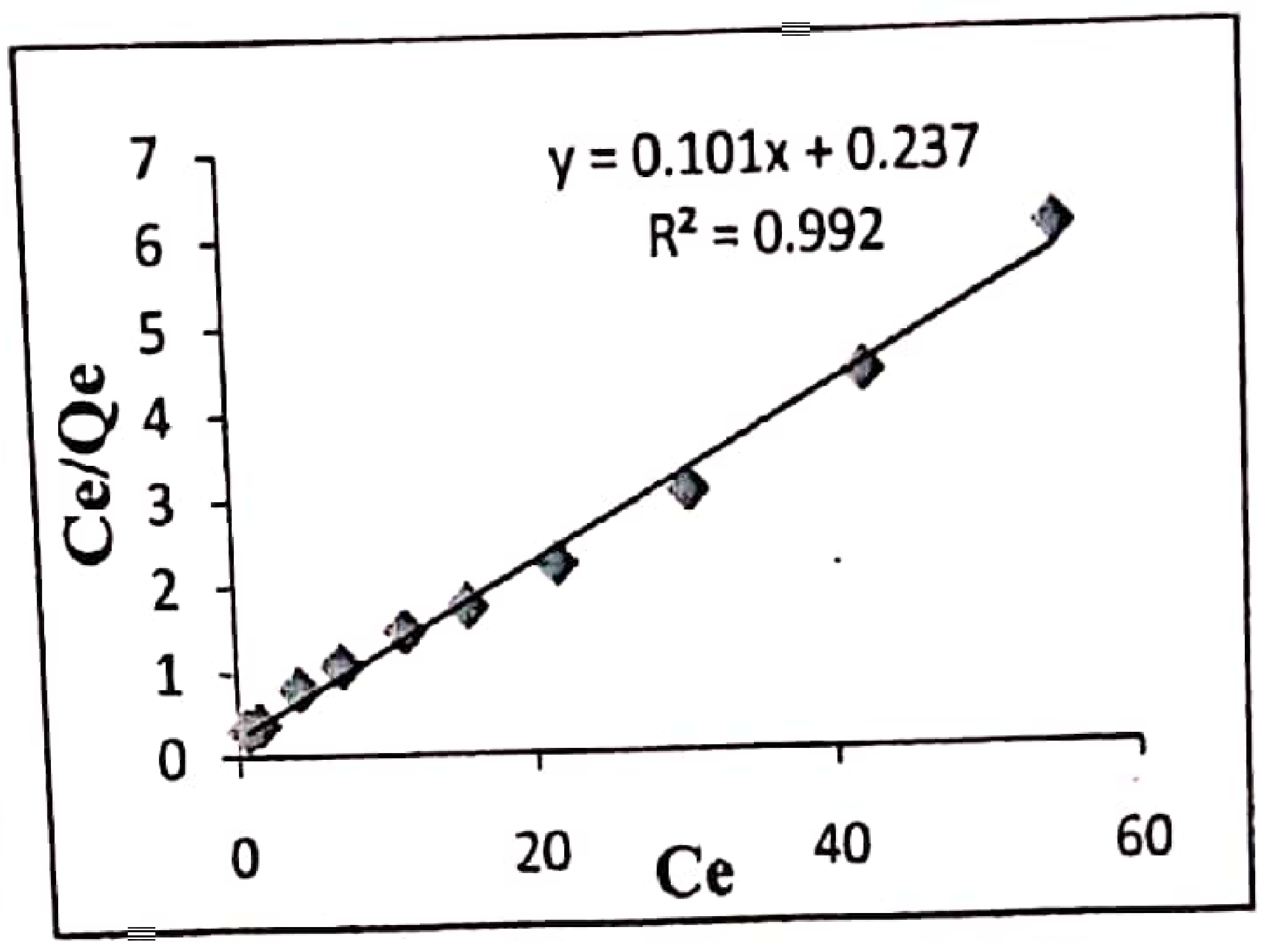


Fig. 10 Freundlich isotherm for the adsorption of Cr(VI)**Fig.11** Langmuir isotherm for the Adsorption ofCr(VI)

Conclusion

Utility of 8-HQPHF-II for the removal of Cr(VI) from the contaminated water is investigated. 8-HQPHF is found to be better adsorbent for removal of Cr(VI).The maximum percentage (90%) for removal of Cr(VI) is noticed at pH 4 with contact time 110 min. The percentage removal decreases with increase in initial Cr(VI) concentration. At 5 gm/lit of optimum adsorption dose maximum removal efficacy has been noticed. The adsorption data are best fitted with Freundlich and Langmuir isotherm model which confirms better adsorption of Cr(VI) onto 8- HQPHF-II. Thus the terpolymer reported in this research article can be successfully used for abetment of toxic/carcinogenic Cr(VI) from contaminated water and thus applicable in pollution control/environmental conservation.

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Authored by:

SHENDE S. S.

From

N.P.W.College, Lakhani- 441804, India

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