Removal of Arsenic by adsorption by Terpolymeric Resin

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ABSTRACT
8-HQTF-III terpolymeric resin has been prepared by condensation of 8-HydroxyQuinoline(8-HQ) Thiourea (T) and Formaldehyde (F) in 3:1:4 molar ratio using 2M HCl as a catalyst and was proved to be a good adsorbent for removal of As(III). The newly prepared terpolymer was characterization and its structural elucidation was confirmed by TGA, XRD, FTIR and ^{1}H-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 8-HQTF-III doses have also been studied and reported. The adsorption data were found to fit well with the Langmuir and Freundlich model. The percent removal of As(III) was found to be increase with adsorbent doses from 1 to 6 gm. and maximum efficacy was found at 5gm. At optimum condition nearly 80% abatement of As(III) has been noted using 8-HQTF-III. The results revealed that the terpolymeric resin as adsorbent reported in this article is effective for removal of As(III) from wastewater and thus can be successfully used for control of Arsenic pollution.
Keywords: Arsenic pollution, wastewater treatment, Langmuir isotherm,

I. INTRODUCTION

Water is one of the most essential requirements for living being to survive because all physiochemical processes of body require aqueous medium this is due to Moreover, 70–80% of the mass of most living bodies consists of water and various mineral and organic salts.[1].The problem of water pollution arises due to the disposal of heavy metals from industries from the last few decades. Different industrial discharge effluents which containing toxic metals can cause severe contamination of ground water and surface water. The presence of arsenic in water is due to natural weathering process, geochemical reactions, biological activity, combustion of fossil fuels, volcanic eruptions, gold mining, leaching of man-made arsenic compounds, smelting of metals ores, desiccants, wood preservatives, agricultural pesticides and many other anthropogenic activities [2-4]. Arsenic in inorganic forms affects more than 200 million population worldwide, and its long-term exposure causes serious illness, dysfunction of the nervous system, skin cancer, lung cancer, kidney failure, liver diseases, urinary bladder cancer, cardiovascular and peripheral disease[5].Heightened awareness of arsenic toxicity and regulatory changes has prompted considerable research efforts toward developing methods for arsenic removal from drinking water [6]. The removal of methylene blue from wastewater were reported by using numerous methods such as liquid-liquid extraction, reverse osmosis, advanced oxidation process, electro coagulation, electrochemical oxidation, ozonation, and membrane filtration. However, adsorption method gives some advantages due to its simple design, high efficiency and low costs with unhazardous by products [7,8].Therefore it is necessary to remove As(III) from environment, in order to prevent the deleterious impact of As(III) on ecosystem and public health.. The necessity to reduce the amount of heavy metal ions pollution in wastewater streams has led to an increasing interest in terpolymers [9-12]. The aim of this research work is therefore to terpolymeric resin and to carry out the adsorption studies of arsenic.

II. MATERIALS AND METHODS

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

2.1 Synthesis of terpolymer

A mixture 8-HydroxyQuinoline(8HQ), Thiourea(T) and Formaldehyde(F) in 3:1:4 molar ratio in the presence of 200ml 2M HCl as a catalyst was taken in 500 ml round bottom flask fitted with

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water condenser and heated in an electrically operated oil bath at 120 ± 2^0C for 6 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 hydroxyquinoline - 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 is given in figure 1,
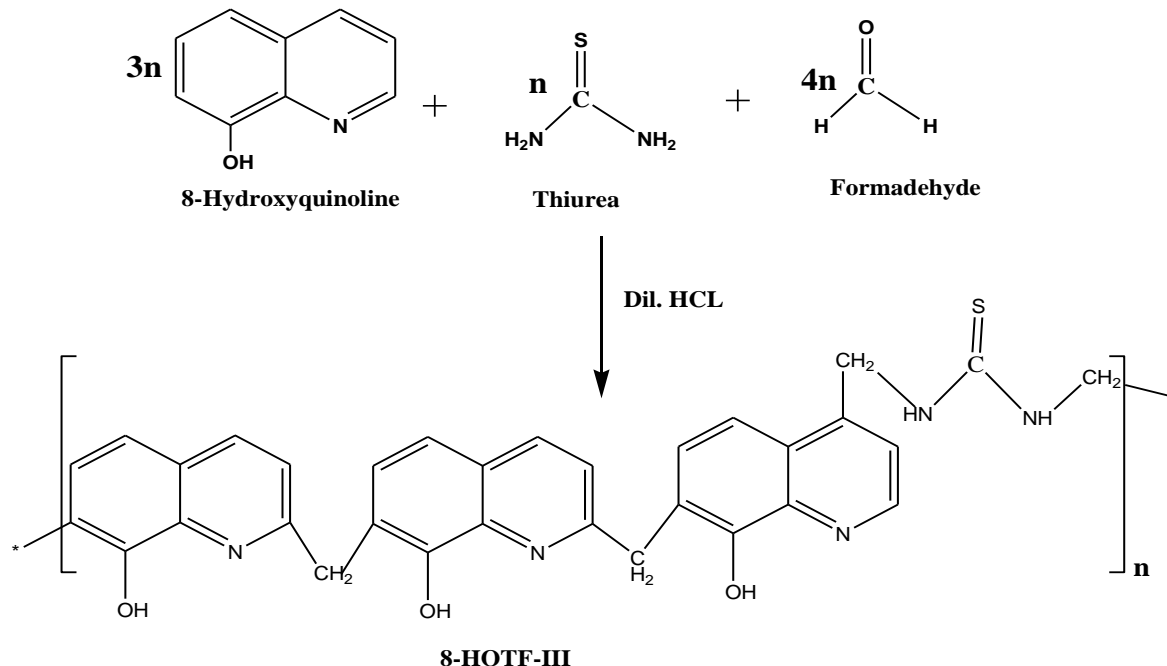

8-HQTF-III
Fig.1 Reaction scheme and structure of 8-HQTF-III

2.2 Preparation of As (III) solution
Arsenic (III) stock solution (100 ppm) was prepared by dissolving 420 mg of sodium arsenate in 1 L of deionized water. The pH of the solution was adjusted to 7.0 (±0.1), using 0.1 M nitric acid and 0.1 M NaOH. The solution was shaken well and then stored in dark. Further dilutions were made using this solution.

2.3 Batch Experiment
Batch equilibrium studies were conducted with different parameters such as pH, agitation time, initial concentration As(III) 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 As(III) concentration using

UV-Visible Spectrophotometer. From experimental data, the applicability of Freundlich isotherm and Langmuir model were judged. Linear regression coefficient (R_2) and isotherm constant values were determined from these models.

III.   CHARACTERIZATION
3.1 FTIR spectrum of 8-HQTF-III
FTIR spectrum of 8-HQTF-III terpolymeric resin is presented in **Fig 2.** The methylene bridge associated with 8-HydroxyQuinoline can be identified by the peak at $3000 cm^{-1}$[13]. Appearance of band at region $3300 cm^{-1}$ is due to the stretching vibration of phenolic hydroxyl (–OH) group. The peaks appeared at 1440 and $1167 cm^{-1}$ are due to methylene

bridges coupled with aromatic ring[14,15]. The peak at 1006cm^{-1} is due to C-N stretching. A sharp peak at appearing a 1266 cm^{-1}may be attributed to C=S stretching vibrations.A peak at 1515cm^{-1} may be ascribed to N-H bending of secondary amide group[14].The tetra substitution in the benzene ring is established by presence of medium band at 959cm^{-1} which is attributed to (C-H) bending vibration [16].

3.2 XRD analysis of 8-HQTF-III

The X-ray diffractographof 8-HQTF-III has shown in**Fig. 3.** In this spectrum a high intense sharp peak at 2θ= 32^{0}and 45^{0} show crystalline nature of terpolymer. The spectrum also contains low intense and sharp peaksat 2θ= 23^{0},27^{0}and 57^{0} again indicate crystalline nature. Thus it can be concluded that 8-HQTF-III terpolymer resin exhibits crystalline nature.

3.3[1]HNMR-studies of 8-HQTF-III

^{1}HNMR spectrum of 8-HQTF is depicted in **Fig. 4**. The NMR spectrum reveals that the signal at 3.6-4.6(δ) ppm due to methylene proton of the Ar-CH-N linkage The signal at 2.5(δ) ppm can be attributed to –NH-bridge. The multiple signals observed in the range 7.9-9.1 (δ) ppm indicate the presence of aromatic protons.The signal at 5.3(δ) ppm indicate presence of phenolic group (Ar--OH).

3.4Thermogravimetric analysis of 8-HQTF-III

Fig. 5 shows TG curve of 8-HQTF-III. There are derivative peaks observed at temperature 61.26, 218.76 and 310^{0}C. The first derivative peak at temperature 61.26^{0}Cwith a weight loss of 3% which may be due to the removal of water molecule incorporated in the copolymer. The weight loss is very low. The second derivative peak can be observed at 218^{0}C with 21% of weight loss. This weight loss seems to be due to the elimination of –OH groups directly attached to the aromatic nuclei. In the third stage, the decomposition starts at 350°C with 55% weight loss which may be due to the elimination of –CH$_2$ bridges and the aromatic nucleus [17].
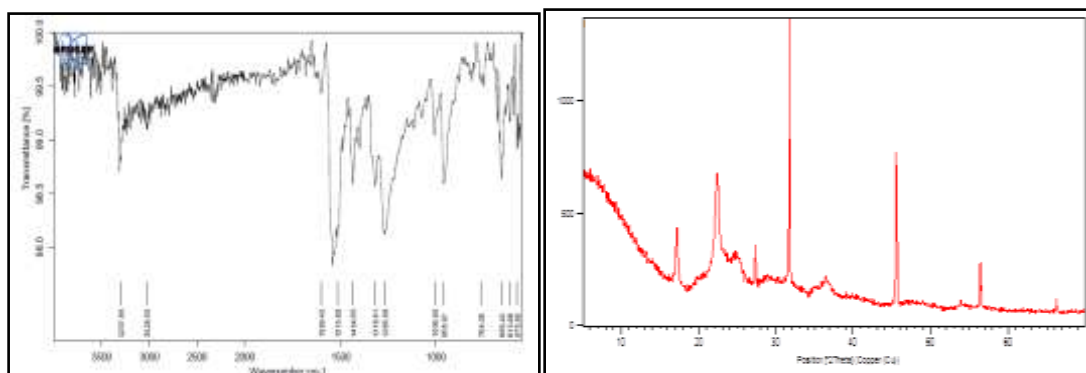

Fig. 2 FTIR Spectrum of 8-HQTF-IIIFig.3 X-Ray Diffraction pattern of 8-HQTF-III
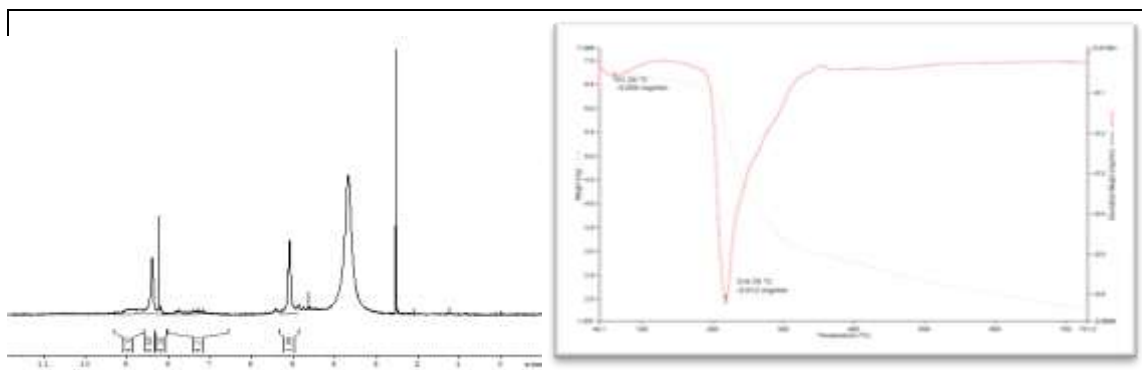

Fig. 4[1]H NMR spectrum of 8-HQTF-IIIFig. 5 TGA Curve of8-HQTF-III

IV.   RESULTS AND DISCUSSION

4.1   Effect of pH on adsorption

Effectof pH on As(III) adsorption using 8-HQTF-III 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 As(III). The percentage removal increases steadily from 36 to 78 % when pH is increased from 1 to 6 and slowly decreases on further increases in pH.

4.2   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 As(III) binding with adsorbent was greater in the initial stages then gradually increases and remains almost constant near about 79%, after optimum period of 110 min.

4.3   Effect of adsorbent doses

The effect of adsorbent (8-HQTF-III) doses on percent removal of As(III) in the range 1 to 10gm is represented in Fig.8. The initial As(III) 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-HQTF-III adsorbent.

4.4 Effect of the Initial concentration of As(III) solution.

The Experimental studies were carried with varying initial concentration of As(III) ranging from10 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 As(III) removal decreases with increasing concentration of adsorbate.

4.5Adsorption Isotherm
4.5.1 Freundlich Adsorption Isotherm

The Freundlich equation is employed for the adsorption of As(III) on the 8-HQTF-III and equilibrium data well fitted in the linear plots of $\log Q_e$ versus $\log C_e$ which have been shown in Fig.10. The values of 'k_f'for As(III) was found to 2.830 mg/g. The value of n which gives idea about intensity of adsorption was found to be 2.84 for As(III) and Thesquare of the correlation coefficient (R^2) values was found to be 0.9572 for As(III) which implies the best fitting of Freundlich isotherm.

4.5.2 Langmuir Isotherm

The isotherm data have been linearized using Langmuir equation and is plotted between Ce/qe versus Ce which have been shown in Fig.11. The Langmuir constant qm, which is measure of the monolayer adsorption capacity of 8-HQTF-III is obtained as 10.05 The Langmuir constant b which denotes adsorption energy is found to be 0.265. The high value (0.9942) of regression correlation coefficient (R^2) indicates good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of As(III) onto 8-HQTF-III. The dimensional parameter, R_L, which is measure of adsorption favorability is found to be 0.128 ($0 < R_L < 1$) which confirms the favorable adsorption process for As(III) on 8-HQTF-III adsorbent.
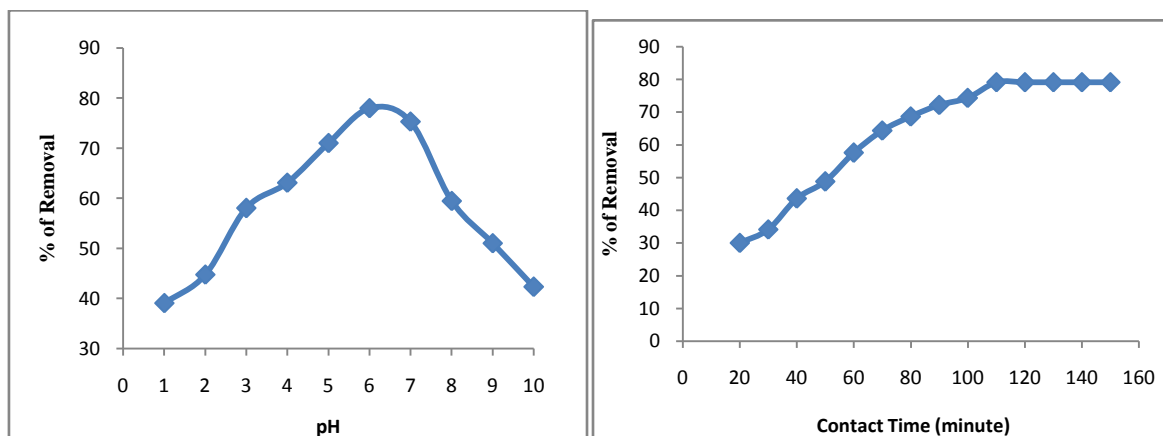

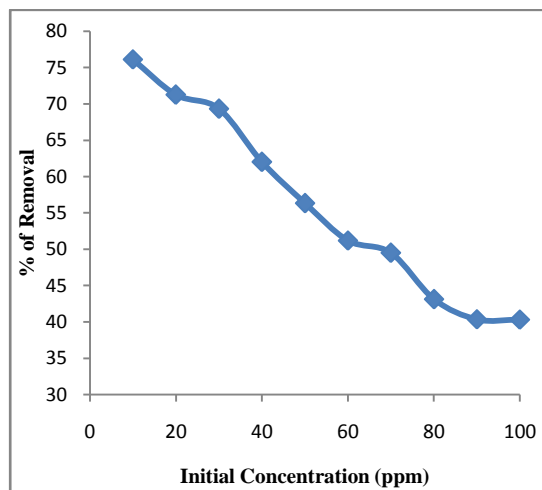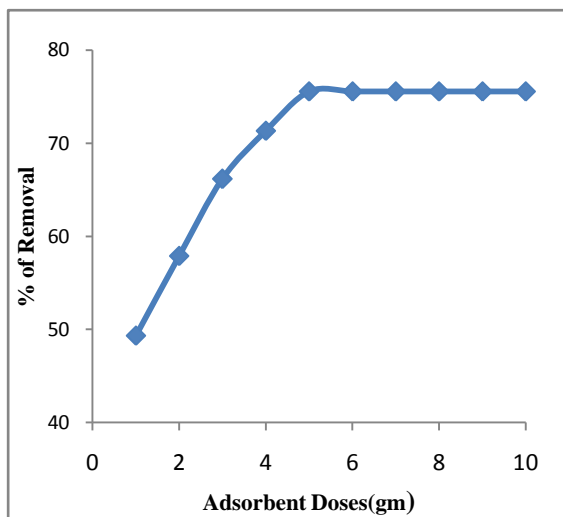**Fig.6.   Effect of pH on As(III) by 8-HQTF-IIIFig.7Effect of Contact time on As(III) by 8-HQTF-III**

Fig. 8. Effect of initial concentration on As(III) by 8-HQTF-III Fig. 9Effect of initial concentration on As(III) by 8-HQTF-III
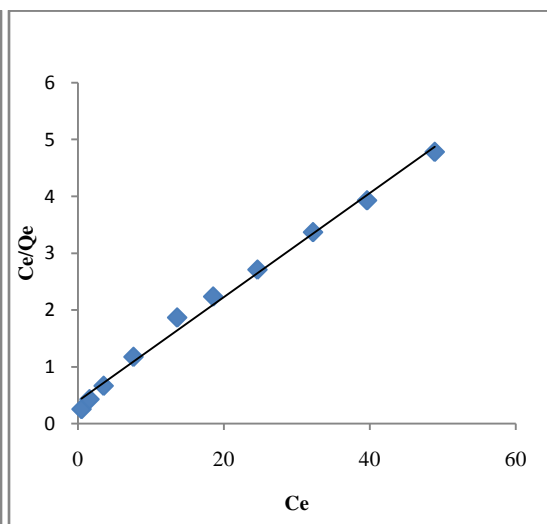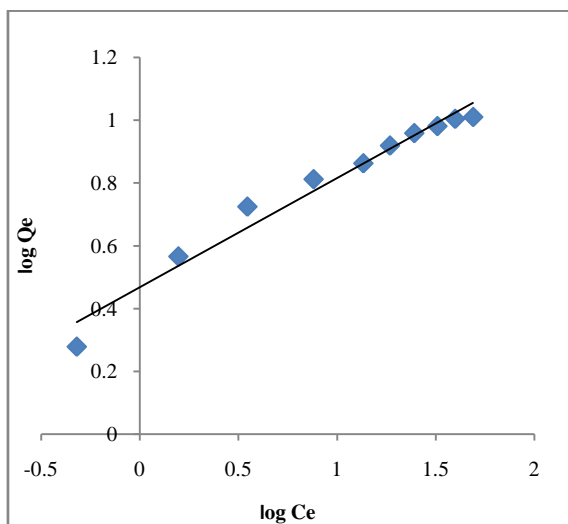

Fig.10 Freundlich isotherm for the adsorption of As(III)Fig. 11 Langmuir isotherm for the adsorption of As(III)

V.   CONCLUSION

Utilization of **8-HQTF-III** for the removal of As(III) from the industrial waste-water is investigated. 4-HAMF is found to be better adsorbent for removal of As(III). The maximum percentage(79%) for removal of As(III) is noticed at pH 6 with contact time 110 min. The percentage removal decrease with increase in initial As(III) 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 the monolayer adsorption of As(III) onto **8-HQTF-III**. Thus the terpolymer reported in this research article can be successfully used for abetment of toxic divalent cadmium from contaminated water and thus applicable in pollution control.

VI.   ACKNOWLEDGMENT

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