Removal of Divalent Cadmium by 8-HQTF-II Terpolymeric Resin

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Abstract:*8-HQTF-II terpolymeric resin was synthesized by condensation of 8-hydroxy quinoline (8-HQ), thiourea and formaldehyde in 1:2:3 mole ratio in the presence of HCl as a catalyst. A synthesized material was authenticated by elemental analysis, FTIR, XRD and ¹H NMR spectroscopy. Cd(II) removal were studied by using 8-HQTF-II via Batch equilibrium method, while Langmuir adsorption isothermand Freundlich adsorption isotherm model were employed for detail adsorption study. The removal efficiency of Cd(II) was found to be increase with adsorbent doses from 1 to 6 gm and at 6 gm maximum efficacy was found. The result shows the maximum removal of Cd(II) can be done nearly 95%.*

Keywords:*adsorption isotherm, batch equilibrium, Cd(II)removal, Terpolymer (8-HQTF-II) resin.*

1. Introduction

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. Cadmium is rare and uniformly distributed element in the earth crust with an average concentration of 0.15 to 0.20 mg/kg. It occurs in the form of inorganic compounds and complexes with chelating agent [1]. Cadmium is one of the most toxic environmental and industrial pollutant because it can damage almostall-important organs[2]. It is a human carcinogen[3]. Even small quantity of Cd assimilation by the body can cause severe high blood pressure, heart disease and can lead to death[4].The acute over exposure to Cd fumes can cause pulmonary diseases while chronic exposure causes renal tube damage and prostate cancer[5].In recent past metal ionseparation is carried by many common and popular methods such as Chemical reduction [6], Nano-filtration [7], bio-accumulation [8] and ion exchange [9], from aqueous effluents. These routes are indeed not cost-effective and difficult to implement in developing/undeveloped countries. Bio-sorption also gained significant attention due to its technical feasibility and economically viability as well as it is cost friendly [10-12]. Terpolymers have potential application in verities of different fields adsorption study is one of the major aspect. Also terpolymers gains attention on account of their wide ranging ion exchange properties [13]. The terpolymers of hydroxyl benzoic acid, urea/thiourea and formaldehyde/trioxane have been widely investigated because of their numerous applications [14-15]. Copolymers have also been synthesized by condensation of a mixture of phenol or hydroxybenzoic acid, various amine and formaldehyde [16-17]. However literature survey revealed that the application of terpolymers made of 8-hydroxy quinline, thiourea and formaldehyde is very scanty in adsorption technique. Therefore, we have carried out synthesis and characterization of this terpolymer and its application is thoroughly studied in the light of surface phenomenon.

Terpolymeric resin as adsorbent reported in this article is effective for cadmium removal from waste water and thus can be productively used for the control of cadmium pollution.

2. Materials and Methods

2.1 Chemicals

Analytical grade chemicals were purchased from Sigma Aldrich and used without further purification. Double distilled water is used for the preparation of solution.

2.2 Synthesis of Terpolymer

A mixture of 8-hydroxy quinoline, thiourea and formaldehyde in 1:2:3 ratio is mixed in 500 mL round bottom flask fitted with water condenser and heated in an electrically operated oil bath at $120 \pm 2^{0}C$ for 6 hours with occasional shaking 2M HCl is used as catalyst. The reaction scheme is shown in fig. 1. Dimmer stat is used to maintain the temperature of the oil bath all through the course. 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 hydroxy quinoline-formaldehyde copolymer which supposes to be present with the terpolymer. The product so obtained needs further purification for that purpose re-precipitation technique is used. Drop wise addition of ice cold 1:1 (v/v) conc. HCl / distilled water with constant stirring is used in the terpolymer which was dissolved in 8% NaOH solution, filtered and precipitated. The yield of the terpolymer resin was found to be 81%. To remove the chloride the precipitated resin product was filtered off washed with hot water and then it is dried and powdered. The purified polymer sample was dried in vacuum at room temperature. Although detail literature survey reveals that some alternative and supportive reaction scheme is also possible in this context [18-19].

Fig. 1. Synthesis of 8-HQTF-II Terpolymeric Resin
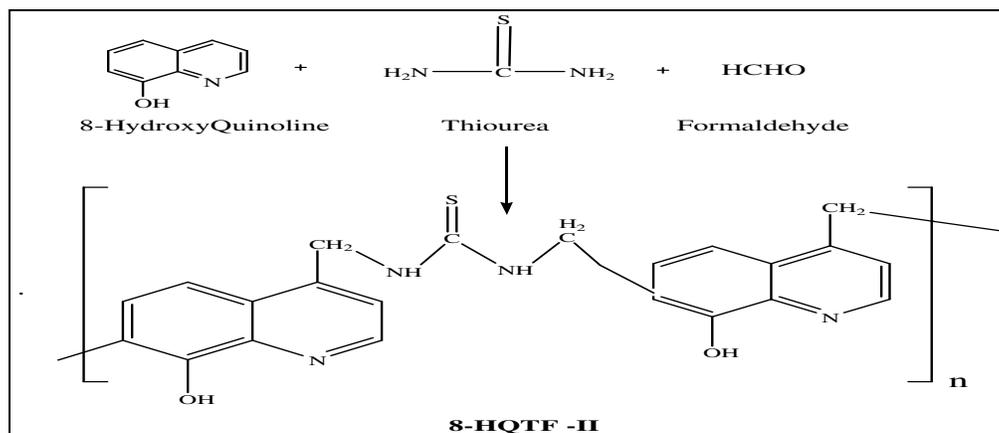
2.3 Preparation of Cd (II) solution
The stock solution of Cd (II) is prepared by dissolving 0.2854g of cadmium sulphate $[3CdSO_4.8H_2O]$ in 1000 mL of distilled water. This stock solution is further used to prepare solution of different concentration solution upon dilution ranging from

concentrations 10-100 mgL^{-1}. Dilute range solution of 0.5N HCl and 0.5N NaOH is used to tune the pH of the solution.

2.4 Batch adsorption Experiment

Batch equilibrium process were conducted with 6 gm of 8-HQTF-II on addition with varying concentration of Cd(II) solution. Different parameters such as effect of adsorbent doses, pH, agitation time, initial concentration of Cd(II) solution also changed to study the adsorption isotherm study. At around 200 rpm the equilibrium mixture is shaken in Rotary shaker, filtered through Whatmman no.42 filter paper and filtrate was analyzed for Cd(II) concentration using UV-Visible Spectrophotometer. The adsorption percent (%) is calculated using the equation (1).

$$\text{Adsorption } \% = \frac{C_0 - C_{eq}}{C_0} \times 100\% \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

where C_0 is the initial concentration of Cd(II) in solution and C_{eq} is the equilibration concentration of Cd(II) in supernatant after centrifugation. Langmuir model was used to judge the obtained result. The model gives the values of linear regression coefficient (R^2) and isotherm constant.

3. Results and Discussion
3.1 FTIR and CHN analysis of 8-HQTF
FTIR spectrum of 8-HQTF-II terpolymeric resin is presented in Fig. 2 Appearance of band at region 3300 cm^{-1} is due to the stretching vibration of phenolic hydroxyl (–OH) group. A peak at 1515 cm^{-1} may be ascribed to N-H bending of secondary amide group [20]. The medium band at 959 cm^{-1} reflects the tetra substitution in the benzene ring which is attributed to (C-H) bending vibration [21]. The methylene bridge associated with 8-hydroxy quinoline can be identified by the peak at 3000 cm^{-1} [22]. The peaks appeared at 1440 and 1167 cm^{-1} are due to methylene bridges coupled with aromatic ring. The peak at 1006 cm^{-1} indicates the presence of C-N stretching. Peak in the range of 1266 cm^{-1} is attributed to C=S stretching vibrations [23].

Fig. 2. FTIR Spectrum of 8-HQTF-II   **Fig. 3.** X-Ray Diffraction pattern of 8-HQTF-II
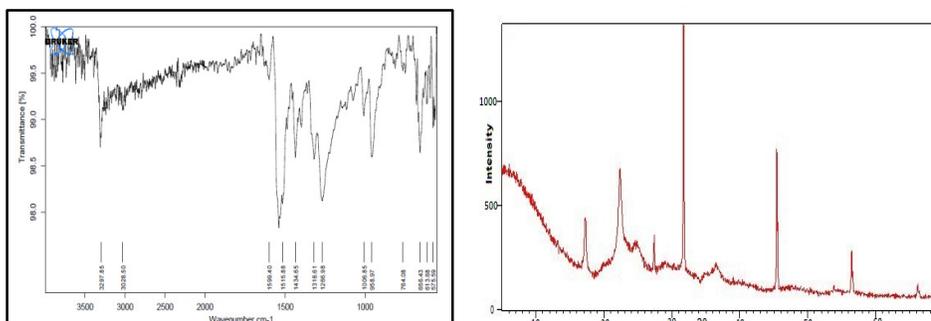
The terpolymer resin was subject to microanalysis for C, H, and N on Perkin Elmer 2400 series II CHNS/O analyzer. All the spectral analysis is carried out at sophisticated analytical instrumental facility (SAIF) Punjab University, Chandigarh, India. The molecular weight of the compound is found to 402g/mole. The result of the analysis is listed in Table 1.

Table1. Element analysis data

| Name of terpolymeric resin	Carbon (%)	Nitrogen (%)	Oxygen (%)	Hydrogen (%)	Empirical formula	Molecular wt.
8-HQTF-II	58.77(Cal.)	17.14(Cal.)	6.53(Cal.)	4.49(Cal.)	$C_{22}N_4H_{18}O_2S$	402
	57.93	17.04	6.39	4.30		

3.2 XRD analysis of 8-HQTF-II

The X-ray diffraction pattern of 8-HQTF-II has shown in Fig. 3 In this spectrum a high intense sharp peak at $2\theta = 32^0$ and 45^0 has shown crystalline nature of the synthesized terpolymer. The spectrum also contains low intense and sharp peaksat $2\theta = 23^0$, 27^0 and 57^0 indicate crystalline nature. Thus it can be concluded that 8-HQTF-II terpolymeric resin exhibits crystalline nature [24-25].

3.3 Thermo gravimetric analysis of 8-HQTF-II

The thermal analysis is most important and acceptable techniques for the determination of lattice water as well as degradation of organic molecules. The TG curve of synthesized 8-HQTF-II terpolymeric resin and its thermal decomposition behavior was investigated at a heating rate of 10^0C min^{-1}. Fig. 4 shows three derivative steps of degradation at temperature of 61.26, 218.76 and 310^0C. The first derivative degradation peak of 3% weight loss was observed at 61.26 ^0C is due to the loss of lattice water [26-27,19] entrapped in the copolymer, is quite fast step, later on TGA curve is quite stable. The second step start to lose weight of 21%, corresponds to the elimination of –OH groups directly attached to the aromatic nuclei is fast degradation step. Whereas, the gradual degradation was observed in the third step from 350^0C onwards was observed due to degradation of organic moiety, corresponds to 55% weight loss which may be due to the elimination of $-CH_2$ bridges and the aromatic nucleus [28-30].

Fig. 4. TG Curve of 8-HQTF-II   **Fig. 5.**^{1}HNMR spectrum of 8-HQTF-II
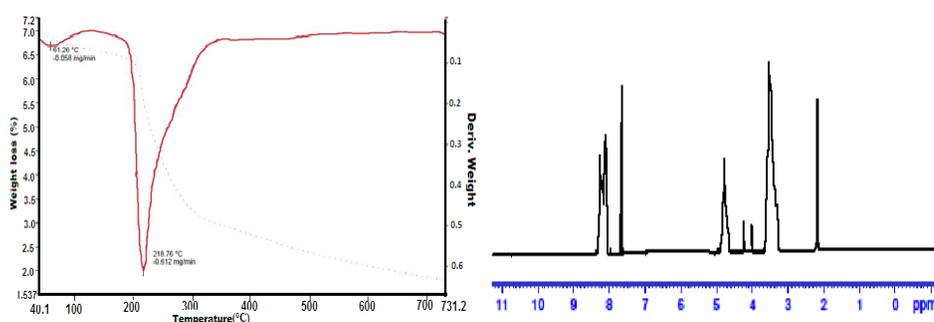
### 3.4 ^{1}HNMR- studies of 8-HQTF-II

^{1}HNMR spectrum of 8-HQTF-II is depicted in Fig. 5 it reveals that the signal at 3.6-4.6(δ) ppm due to methylene proton of the Ar-CH-N linkage. The signal at 8.3 ppm is assigned to the OH group of 8-hydroxyquinoline ring. The signal at 2.2(δ) ppm can be ascribed to–

NH-bridge [19]. The multiple signals observed in the range 7.8(δ) ppm indicate the presence of aromatic protons.

3.5 Effect of pH on adsorption

pH is one the most important factor for the adsorption isotherm study.It controls many other parameters in adsorption study. In Fig. 6 (a) the change of pH on Cd(II) adsorption using 8-HQTF-II as an adsorbent is given in the pH range from 1 to10. From fig. 6 (a), it can be concluded that at pH 6.0 the adsorbate i.e 8-HQTF-II removes 84% of Cd(II).It goes on decreasing slowly with the decreases on further increases in pH.

Fig. 6. (a) Effect of pH on Cd(II) adsorption (b) Effect of Contact time on Cd(II) adsorption
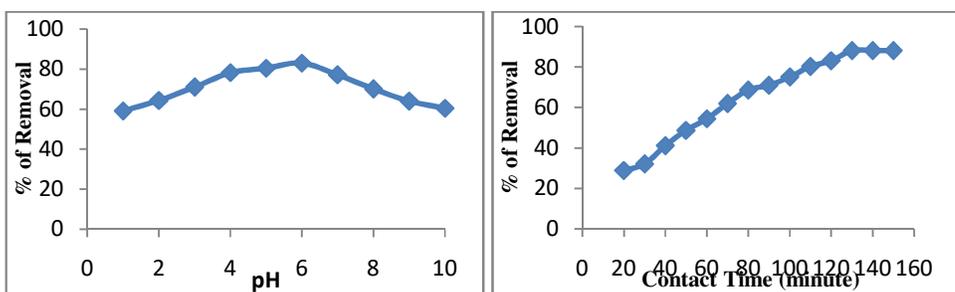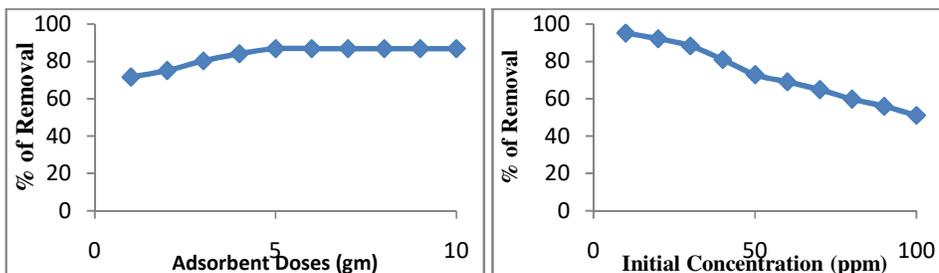

3.6 Effect of contact time on adsorption

Fig. 6 (b) depicts the variation of contact time as a function of Adsorption experiment. It can be seen that Cd(II) removal efficiency of 8-HQTF-II increased from 30% to 89 % when contact time was increased up to 130 min. Thus optimum contact time of 8-HQTF-II for Cd(II) removal was found to be 130 minutes. During the initial stage of adsorption, a large number of vacant surface site are available for adsorption in the adsorbent. After a lapse of the time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the metal ions on the solid surface and the bulk solution phase. Thus, the driving force for the mass transfer between the bulk liquid phase and solid phase decrease with passage of time. This causes the slower down of adsorption process.

3.7 Effect of adsorbent amount

In Fig. 7 (a) Effect of adsorbent dose on removal of metal ion was studied by varying the amount of 8-HQTF-II from 1 to 10 gm/lit, keeping other parameters optimum. It can be observed that on increasing the adsorbent doses from 1 to 6 gm/lit, the percent removal gradually increases for the metal ion. The optimum removal for Cd(II) ion was found to be 87% .The increased adsorption of metal ions with increase adsorbent doses can be attributed to increased surface area and availability of more adsorption sites.

Fig.7. (a) Effect of adsorbent doses on Cd(II) adsorption (b) Effect of initial concentration on Cd(II) adsorption

**3.8 Effect of Initial metal ion concentration.**   The
percentage of adsorption was studied by varying metal ion concentration from 10 to 100
mg/lit keeping other parameters such as pH of solution, adsorbent dose and contact time
optimum. The resultshave been shown in Fig.7 (b). From the figure, it can be observed
that percent removal of Cd(II) found to decrease from 95% to 51%. The decreased in
adsorption efficiency can be justified by the fact that 8-HQTF-II have limited number of
active sites which get saturated beyond certain concentration. This means that at fixed 8-
HQTF-II dose, the number of active adsorption site to accommodate the metal ions
remained unchanged while with higher adsorbate concentration number metal ion to be
accommodated increased. But the actual amount of metal ions adsorbed per unit mass of
adsorbent increased with increase of metal ion concentration in the solution for the
adsorbent. It means that the adsorption is highly dependent on initial concentration of
metal ion.

3.9 Adsorption isotherm

- **Freundlich isotherm**

The Freundlich equation suggests multilayer adsorption. Sorption energy expontially
decreaseson saturation of sorption sites of the adsorbent.Therefore, the parameters 'k_f'
and 'n' were estimated from the intercept and slope of the plots between $\log Q_e$ against
$\log C_e$. Freundlich isotherms have been shown in Fig.8(a). The k_f values of the
adsorbent to remove Cd(II) was found to be 2.930which indicate dominance of
adsorption capacity. The Freundlich exponents 'n' was 2.87 for Cd(II) which reflect
favorable adsorption. The values of R^2 was found to 0.9682 for Cd(II) and which shows
well-fitting of the Freundlich isotherm. The findings indicate that probably the sorption
of metal ion on 8-HQTF-II has multilayer coverage.

Fig. 8(a) Freundlich isotherm of Cd(II) Fig. 8(b) Langmuir isotherm Cd(II) on 8-HQTF-II
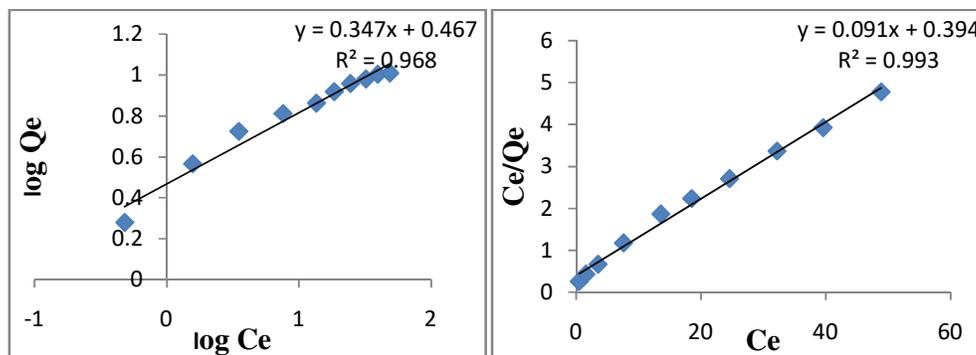
- **Langmuir isotherm**

   The Langmuir sorption isotherm suggests that when the adsorbate occupies the
sites, further sorption cannot take place at thatsites. It is presumed that all adsorption
sites of the adsorbent are energetically equivalent and there is no interaction between
the molecules adsorbed on the neighboring sites.The equilibrium data for Cd(II)
adsorption on 8-HQTF-II were well fitted to Langmuir equation. The linear plots of $\frac{C_e}{Q_e}$
versus C_e have been shown in Fig.8(b). Langmuir monolayer adsorption capacity 'Q_m'
gives an idea about the amount of the adsorbate required to occupy all the available
sites per unit mass of the adsorbent sample. The Langmuir monolayer adsorption
capacities of Cd(II) was found to be 10.91mg/g and corresponding 'b' values was
found to be 0.232 . These lower values of 'b' indicate the affinity between solute and
sorbent site which rules out the possibility of chemisorption. The R^2 values was found

to be 0.9931 for Cd(II) which indicates the best fitting of Langmuir isotherm. One of the features of the Langmuir equation can be defined in terms of dimensionless constant known as separation factor (R_L)which was found to be 0.125 for Cd(II). The R_L values at different initial concentration of metal are in between 0 to 1 are indicative of favorable adsorption on 8-HQTF-II.

4. Conclusion

The terpolymer 8-HQTF-II can be employed for the elimination of Cd(II) from the industrial waste-water. The overall adsorption study shows that at pH 6 and contact time 130 min maximum Cd(II) removal (95%) is noticed. The percentage removal decrease with increase in initial Cd(II) concentration. At 6 gm/L of optimum adsorption dose maximum removal efficacy has been noticed. The monolayer adsorption of Cd(II) onto 8-HQTF-II is raveled due to best fitted data with Langmuir isotherm model.

Acknowledgements

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