ISSN:1007-1172

PAPER ID: JSJ.U-3031

UGC-CARE Approved (Group - II) Active Journal - 2020

JOURNAL OF SHANGHAI JIAOTONG UNIVERSITY

website: shjtdxxb-e.cn e-mail: editorjsju@gmail.com

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Synthesis, Characterization and Application of 4-HAMF Terpolymeric Resin

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Has been published in

VOLUME 17, ISSUE 4, APRIL - 2021

Dr. Xuhui Feng
Editor-In-Chief

6.2

Scopus

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Synthesis, Characterization and Application of 4-HAMF Terpolymeric Resin

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Abstract

A novel 4-HydroxyAcetophenone-Melamine-Formaldehyde(4-HAMF) terpolymeric resin has been prepared by condensation of 4-HydroxyAcetophenone(4-HA),Melamine(M) and Formaldehyde(F) in 1:1:2 molar ratio using 2M HCl as a catalyst and was proved to be a good adsorbent for removal of Cd(II). The characterization and the structural elucidation of the prepared terpolymer were confirmed by elemental analysis, FTIR, XRD, TGA 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 4-HAMF doses have also been studied and reported. The adsorption data were found to fit well with the Langmuir and Freundlich isotherm models. At optimum condition nearly 94% abatement of Cd(II) has been noted using 4-HAMF. The results revealed that the terpolymeric resin as adsorbent reported in this article is effective for removal of Cd(II)from wastewater and thus can be successfully used for control of Cd pollution.

Keywords -Terpolymeric resin, wastewater treatment, Langmuir isotherm and Freundlich

isotherm.

1. Introduction

Many industrial waste stream may contain heavy metals such as Cd, Cr, Ni, Pb etc including the waste liquids generated by metal finishing or metal processing industries. Cadmium considered as hazardous pollutant due to their toxicity, even at low concentration and non-biodegradability. Increasing level of cadmium in natural water bodies poses serious problem to all living species including humans. It is therefore to reduce concentration of cadmium in effluents/wastewater before it is discharged into the water bodies[1]. 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[2]. Cadmium and its compounds are also used in paints, pigments, plastics, electroplating, equipments, machineries, baking channels and photography[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]. The usual methods for removal Cd(II) from aqueous effluents include chemical reduction, nano filtration, bioaccumulation, ion exchange and adsorption on silica composites/activated carbon materials[6]. However these approaches are not cost-effective and

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ISSN: 1007-1172

difficult to implement in developing/undeveloped countries. Bio-sorption a technically feasible and economical process has gained increased creditability during recent years[7].

Terpolymer resins now a days have wide range applications like adhesives, retardants, binders, dyes, fungiciders, ion–exchangers, biosensors, reversible electrical cell, surface coating material, solar cells and light emitting diodes etc[8]. A new chelating sorbent for metal ion extraction has also been studied[9].The purpose of present study is to explore the adsorption behave of cadmium on newly synthesized terpolymer 4-HAMF at different condition. The present study deals with synthesis and characterization of 4-HAMF by spectral method for first time. One of the important application of functional terpolymer is their capability to recover metal from wastewater.

2. 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 4-HydroxyAcetophenone, Melamine and Formaldehyde(F) in 1:1:2 molar ratio in the presence of 200ml 2M HCl as a catalyst was taken in 500 ml round bottom flask fitted with water condenser and heated in an electrically operated oil bath at 115 ± 2^{0}C 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, while elemental analysis is given in table1.

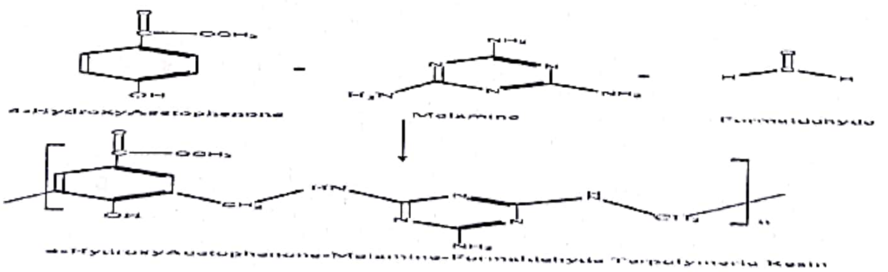


Fig.1 Reaction scheme and structure of 4-HAMF Terpolymeric Resin

Name of terpolymeric resin	Carbon (%)	Nitrogen (%)	Oxygen(%)	Hydrogen (%)	Empirical formula of repeated unit	Molecular formula of repeated unit
4-HAMF	54.54(Cal.)	29.37(Cal.)	11.18(Cal.)	4.89(Cal.)	$C_{13}H_{14}N_6O_2$	286

	54.40	25.80	11.00	4.89		

Table No.1- Elemental analysis of 4-HAMF Terpolymeric resin

2.2 Preparation of Cd (II) solution

A Cd(II) stock solution having 500mgl^{-1} concentration was prepared by dissolving 0.2854g of cadmium sulphate [$3CdSO_4.8H_2O$] in 1000ml of distilled water. This solution was diluted to proper proportions to obtain various standard solutions ranging their concentrations 10-100mgl^{-1}. pH adjustment was done using 0.5N HCl and 0.5N NaOH solution.

2.3 Batch Experiment

Batch equilibrium studies were conducted with different parameters such as pH, agitation time, initial concentration Cd(II) 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 Cd(II) 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.

3. Characterization of 4-HAMF Terpolymeric Resin

3.1 FTIR Studies of 4-HAMF

FTIR spectrum of 4-HAMF terpolymeric resin has shown in Fig. 2. The broad band at 3400cm^{-1} indicates presences of stretching vibration of phenolic hydroxyl (–OH) group. The peak appears at 1168, 1272 and 785cm^{-1}are due to methylene bridges coupled with aromatic ring[10]. The tetra substitution in the benzene ring is established by presence of medium band at 842cm^{-1} which is attributed to (C-H)bending vibration[11]. A peak at 1503cm^{-1} may be ascribed to N-H bending of secondary amide group[12]. A sharp peak at appearing a 1551cm^{-1} may be due to C=N stretching vibration[13]. The peak at 1323cm^{-1} indicates –C=C- stretching in aromatic vibration.

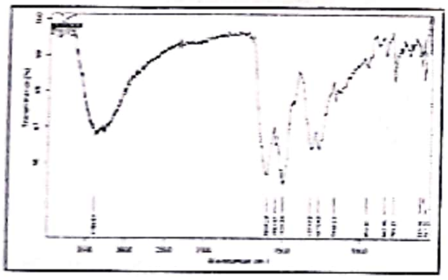


Fig. 2 FTIR Spectrum of 4-HAMF

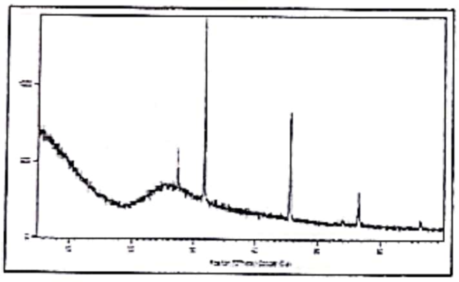


Fig. 3 X-Ray Diffraction pattern of 4-HAMF

3.2 XRD Studies of 4-HAMF

The X-ray diffractograph of 4-HAMF terpolymeric resin has shown in Fig.3. In spectrum a sharp peak obsevered at $2\theta = 32^0$ and 47^0 which show crystaline nature of newly synthesised material. Two low intense and sharp peaks observed around 27^0 and 57^0 confirm that terpolymer is crystaline in nature.

3.3 ^{1}HNMR- Studies of 4-HAMF

[1]HNMR spectrum of 4-HAMF terpolymeric resin is represented in Fig.4. The signals at 3.8 (δ) ppm are assigned as Ar-CO-CH_3 protons. The signal at 2.3(δ) ppm is attributed to –NH-bridge. The Ar-CH_2 protons are assigned at 4.1(δ) ppm. [1]HNMR spectrum of 4-HAMF terpolymer resin show unsymmetrical pattern in the region 6.8-7.8(δ)ppm which is characteristic of aromatic protons (Ar—H). The signal at 2.6(δ) ppm is due to free N-H proton. The signal at 8.2(δ)ppm indicates presence of phenolic group (Ar--OH). The much downfield chemical shift for phenolic(–OH) clearly indicates involment of the -OH group in intermolecular hydrogen bonding[14].

3.4 TGA studies of 4-HAMF

The TGA curve of 4-HAMF has shown in Fig.5. It can be seen from figure that four consecutive weight loss steps have been shown by 4-HAMF. The first derivative peak at 60^0C with a weight loss of 7% which may be due to the removal of water molecule present in the copolymer. The rate of weight loss is noticed to be slow at this stage. The second and third peaks respectively at 210^0C with 20% and 325^0C with 31% of weight loss may be assigned due to the elimination of –OH groups attached to the aromatic nuclei. In the fourth stage, the weight loss is observed in the range 450 to 650^0C with 52% of weight loss which may be due to the elimination of –CH_2 and the aromatic nucleus[15]. Up to 700^0C nearly 65% of weight loss has been noticed.

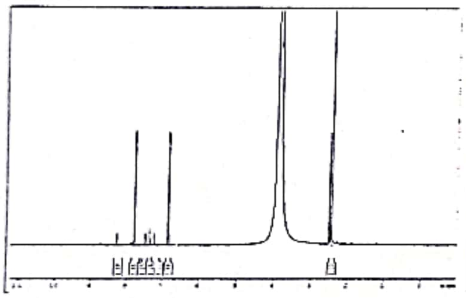


Fig. 4 [1]HNMR spectrum of 4-HAMF

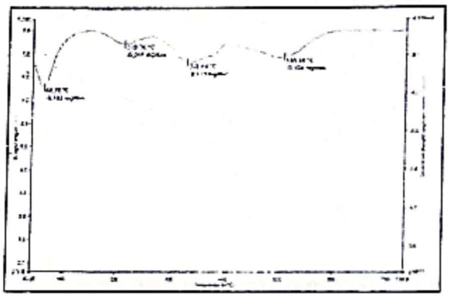
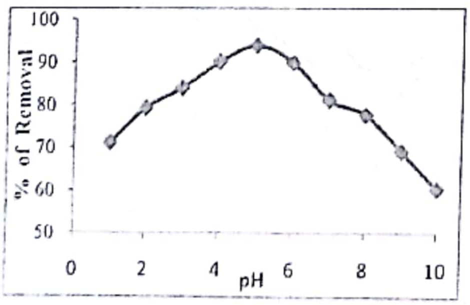


Fig. 5 TGA Curve of4-HAMF

4. Results and Discussion

4.1 Effect of pH on adsorption

Effect of pH on Cd(II) adsorption using 4-HAMF as an adsorbent has been studied in the pH range 1to10 and presented in Fig.6. It is seen that solution pH plays a very important role in the adsorption of Cd(II). The percentage removal increases steadily from 71 to 94% when pH is increased from 1 to 5 in Cd(II) adsorption and slowly decreases on further increases in pH.



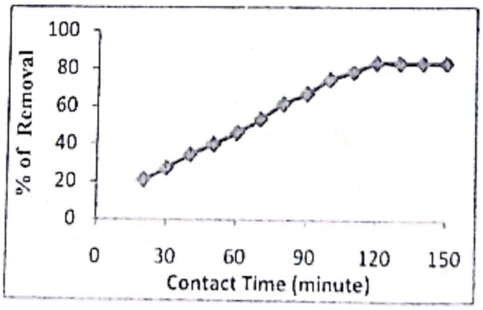
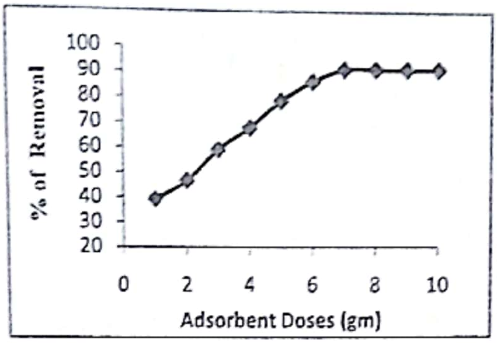


Fig. 6 Effect of pH on Cd(II) by 4-HAMF Fig. 7 Effect of Contact time on Cd(II) removal by 4-HAMF



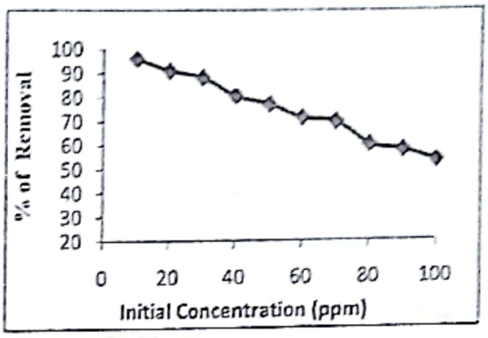
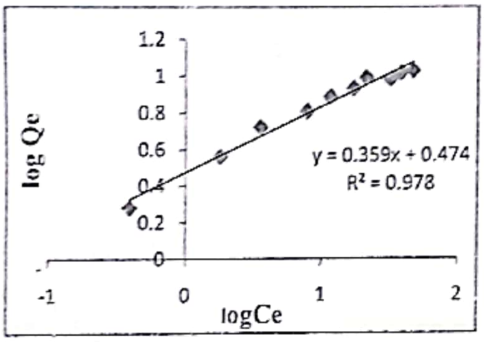


Fig. 8 Effect of adsorbent doses on Cd(II) removal Fig. 9 Effect of initial concⁿ on Cd(II) removal



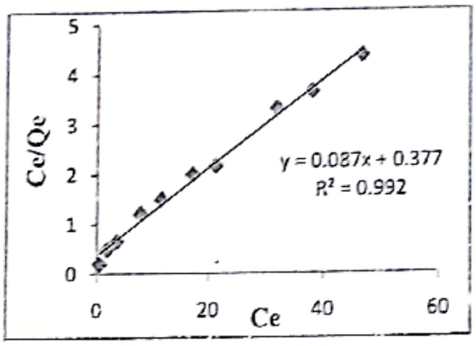


Fig.10 Freundlich isotherm for the adsorption of Cd(II) Fig. 11 Langmuir isotherm for the Adsorption Cd(II)

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 Cd(II) binding with adsorbent was greater in the initial stages then gradually increases and remains almost constant near about 83%, after optimum period of 120 min.

4.3 Effect of adsorbent doses

The effect of adsorbent (4-HAMF) doses on percent removal of Cd(II) in the range 1 to 10gm is represented in Fig.8. The initial Cd(II) 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 7 gm/lit. for the 4-HAMF adsorbent.

4.4 Effect of the Initial concentration of Cd(II) solution

The Experimental studies were carried with varying initial concentration of Cd(II) ranging from 10 to 100 ppm using 7gm/lit.of adsorbent dose. The results have shown in Fig.9. The results demonstrate that at a fixed adsorbent dose the percentage of Cd(II) removal decreases with increasing concentration of adsorbate.

5. Adsorption Isotherm

5.1 Freundlich adsorption isotherm

The plot of $\log Q_e$ versus $\log C_e$ for Cd(II) is presented in Fig.10 which show linear curves and hence the adsorption process obeys Freundlich adsorption isotherms. Freundlich constants 'n' and 'k_f' for Cd(II)) were found to be 2.78 and 3.02 respectively. The square of the correlation coefficient (R^2) values was found to be 0.9785 for Cd(II) which shows well-fitting of the Freundlich isotherm. The 'n' values are in between 1 to 10 which indicate the favorable adsorption of Cd(II) on 4-HAMF.

5.2 Langmuir adsorption Isotherm

The results obtained from Langmuir model for the removal of Cd(II) by 4-HAMF has been represented in Fig.11. The values of square of the correlation coefficient (R^2) was found to be 0.9929 for Cd(II), which show the best fitting of equilibrium data. The values of 'Q_m' for Cd(II) was found to be 11.40 mg/g while values of 'b' was 0.230. The lower values of b(less than one) implies an excellent the affinity between solute and sorbent sites. To confirm the adsorbility of the adsorption process, the equilibrium parameter also called separation factor (R_L) for Cd(II) was calculated which were found to be 0.125.

6. Conclusion

Utilization of 4-HAMF for the removal of Cd(II) from the industrial waste-water is investigated. 4-HAMF is found to be better adsorbent for removal of Cd(II). The maximum percentage(94%) for removal of Cd(II) is noticed at pH 5 with contact time 120 min. The percentage removal decrease with increase in initial Cd(II) concentration. At 7 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 Cd(II) onto 4-HAMF. 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.

7. Acknowledgment

Authors are highly thankful to to the Principal, S.S.Jaiswal college, Arjuni/Moregaon for providing necessary laboratory facilities. Authors are also thankful to Director SAIF Punjab University, Chandigarh and SAIF Cochin University, Kerala for characterization of terpolymer.

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