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Removal of Methylene Blue using Terpoylmeric Resin by Adsorption from Wastewater

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ABSTRACT
The effort to remove methylene blue in waste water had been conducted using adsorption process. 8-HQPHF-III terpolymeric resin has been prepared by condensation of 8-Hydroxy Quinoline (8-HQ), Phenyl Hydrazine (PH) 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 Methylene Blue(MB). The newly prepared terpolymer was characterization and its structural elucidation was confirmed by TGA, XRD, FTIR and [1]H-NMR spectral studies. The Dye 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-HQPHF-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 MB was found to be increase with adsorbent doses from 1 to 4 gm. and maximum efficacy was found at 4gm. At optimum condition nearly 80% abatement of MB has been noted using 8-HQPHF-III. The results revealed that the terpolymeric resin as adsorbent reported in this article is effective for removal of MB from wastewater and thus can be successfully used for control of Methylene Blue pollution.

Keywords: *Methylene blue, wastewater treatment, pollution.*

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I. Introduction

In water sources occurrence of synthetic dyes gives hazardous effects to aquatic organism and human health when discharge directly to environment. More than 10,000 dyes have been widely used in textile, paper, rubber, plastics, leather and cosmetic, pharmaceutical, and food industries [1].The dyes consist of poisonous and complex components with slow degradation rate. Furthermore, the presence of dyes components affects the undesirable color change in water system. The unfavorable impact is not only from esthetics point of view but also from the decline of sun light penetration, thus reducing photosynthetic activity [2, 3]. As dyes are designed to resist breakdown with time, exposure to sunlight, soap and oxidizing agent cannot be easily removed by conventional wastewater treatment processes due to their complex structure and synthetic origins [4]. MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans [5]. 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 [3, 6]. The use of terpolymers in all spheres of life has been abundantly increased in recent years because of novelty and versatility. They occupy the pivotal position in the field of polymer science. The progress in this field has been extremely rapid, as they are generally useful in packaging, adhesives and coatings in electrical sensors, ion-exchangers, organometallic semiconductors, activators, catalyst and thermally stable materials [7-10]. The present work reports the synthesis and characterization of a terpolymer resin (8-HQPHF-III) from 8-HydroxyQuinoline, PhenylHadrazine and Formaldehyde for application on methylene blue removal from wastewater.

II. Materials and Methods

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

Synthesis of terpolymer -A mixture 8-Hydroxy Quinoline (8-HQ), Phenyl Hydrazine (PH) 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 water condenser and heated in an electrically operated oil bath at 110 ± 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.

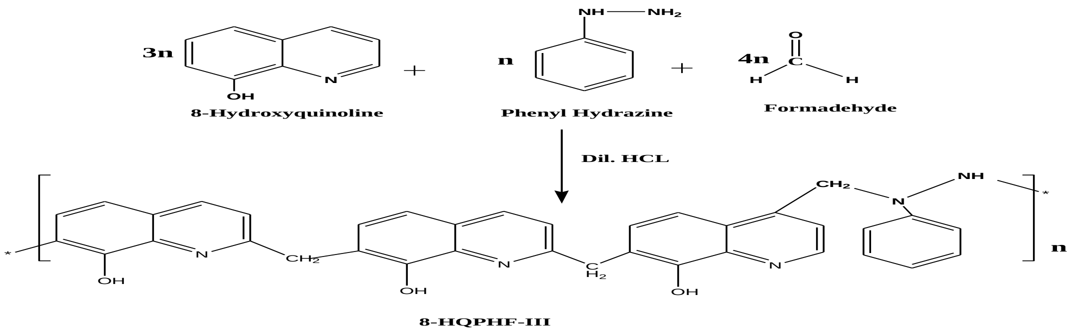


Fig. 1 Reaction scheme and structure of 8-HQPHF-III Terpolymeric Resin

Preparation of Metylene Blue solution -A stock solution of methylene blue of concentration 500 ppm (500 mg/L) was prepared by dissolving (0.5000)g of methylene blue in a 1000 mL volumetric flask, agitated by using a magnetic stirrer for a period of time and completed with distilled water up to the mark. 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.

Batch Experiment **-**Batch equilibrium studies were conducted with different parameters such as pH, agitation time, initial concentration MB 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 MB 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 of 8-HQPHF-III

A. FTIR Studies of 8-HQPHF-III

Fig.2. represents the FTIR spectrum of 8-HQPHF-III terpolymeric resin. A peak at 1494 cm^{-1} may be ascribed to N-H bending of secondary amido group[11]. The broad band at 3400cm^{-1} indicates presences of stretching vibrations of phenolic hydroxyl (–OH) group. The peak appears at 1296cm^{-1} proves the presence of methylene bridge coupled with aromatic ring[11-12]. A sharp peak appearing at 1592cm^{-1} may be due to C=N stretching vibration[13].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 [14]. The peak at 1387cm^{-1} indicate – C=C- stretching in aromatic nucleus. The methylene bridge associated with 8-HydroxyQuinoline can be identified by the peak at 2840cm^{-1}.

B. XRD Studies of 8-HQPHF-III

Fig. 3 represents the X-ray diffractograph of 8-HQPHF-III. This terpolymer exhibit very sharp peak indicates crystalline nature of synthesized material. All sharp peaks at around 2θ = 110, 150, 190, 220, 250, 270 and 290 indicate highly crystalline nature of the polymeric material.

C. ^{1}HNMR- Studies of 8-HQPHF-III

^{1}HNMR spectrum of 8-HQPHF-III terpolymeric resin has presented in Fig.4. The signals at 9.1(δ) ppm indicate presence of phenolic group (Ar--OH).The signal at 2.5(δ) ppm is attributed to –NH-bridge. The much downfield chemical shift for phenolic –OH indicates that the -OH group is involved in the intermolecular hydrogen bonding of –OH group [15]. ^{1}HNMR spectrum of 8-HQPHF-III terpolymer resin exhibits unsymmetrical pattern of signal in the region 6.8-8.0(δ) ppm which is characteristic of aromatic protons (Ar—H). The Ar-CH_2 protons are assigned from peak at 5.1(δ) ppm.

D. TGA studies of 8-HQPHF-III

Fig.5 shows TG curve of 8-HQPHF-III. The first derivative peak temperature can be observed at 76^{0}C-150^{0}C with a weight loss of 3% which may be due to the loss of water molecule entrap in the copolymer. The weight loss rate is very low at this stage. The second and third peak at 198^{0}C with 45% and 360^{0}C with 87% of weight loss may be due to the elimination of –OH groups attached to the aromatic nucleus. The final decomposition stage observed in the range at 480-730^{0}Cwith 96% weight loss can be considered due to decomposition of the remaining imide moieties of copolymer resin [16].

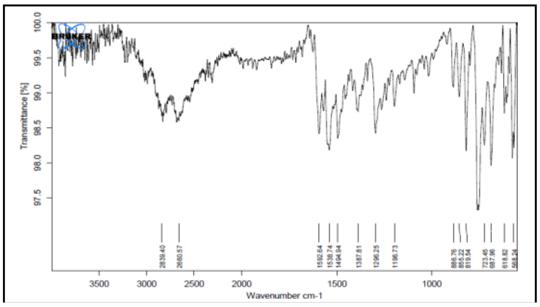


Fig. 2 FTIR Spectrum of 8-HQPHF-III

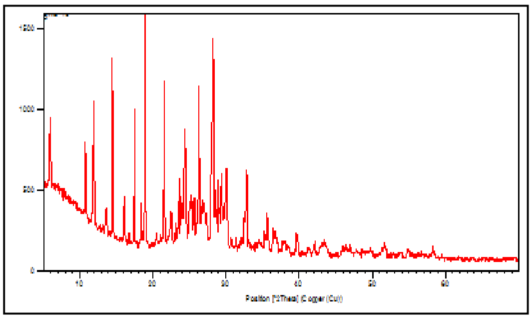


Fig. 3 X-Ray Diffraction pattern of 8-HQPHF-III

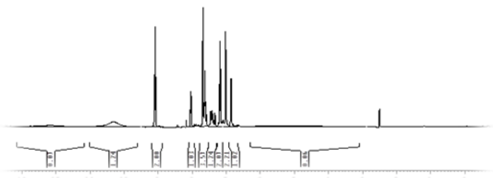


Fig. 4 ^{1}H NMR spectrum of 8-HQPHF-III

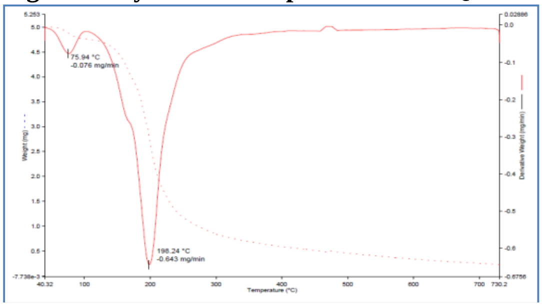


Fig.5 TGA Curve of 8-HQPHF-III

IV. Result and Discussion

Effect of pH on adsorption

Effect of pH on MB adsorption using 8-HQPHF-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 MB. The most favorable adsorption was seen at basic pH 5–9 with 80 % removal of MG dye. So for further study pH 7–8 was maintained.

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 MB binding with adsorbent was greater in the initial stages then gradually increases and remains almost constant near about 77%, after optimum period of 100 min.

Effect of adsorbent doses

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

Effect of the Initial concentration of MB solution.

The Experimental studies were carried with varying initial concentration of MB ranging from 10 to 100 ppm using 4 gm/lit. of adsorbent dose. The results have shown in Fig.9. The results demonstrate that at a fixed adsorbent dose the percentage of MB removal decreases with increasing concentration of adsorbate.

Adsorption Isotherm

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.10. The Langmuir constant qm, which is measure of the monolayer adsorption capacity of 8-HQPHF-III is obtained as 10.55 The Langmuir constant b which denotes adsorption energy is found to be 0.235. The high value (0.9938) of regression correlation coefficient (R^2) indicates good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of MB onto 8-HQPHF-III. The dimensional parameter, R_L, which is measure of adsorption favorability is found to be 0.137 ($0< R_L< 1$) which confirms the favorable adsorption process for MB on 8-HQPHF-III adsorbent.

Freundlich Adsorption Isotherm

The Freundlich equation is employed for the adsorption of MB on the 8-HQPHF-III and equilibrium data well fitted in the linear plots of $\log Q_e$ versus $\log C_e$ which have been shown in Fig.11. The values of 'k_f'for MB was found to 2.951 mg/g. The value of n which gives idea about intensity of adsorption was found to be 2.13 for MB and. The square of the correlation coefficient (R^2) values was found to be 0.9511 for MB which implies the best fitting of Freundlich isotherm.

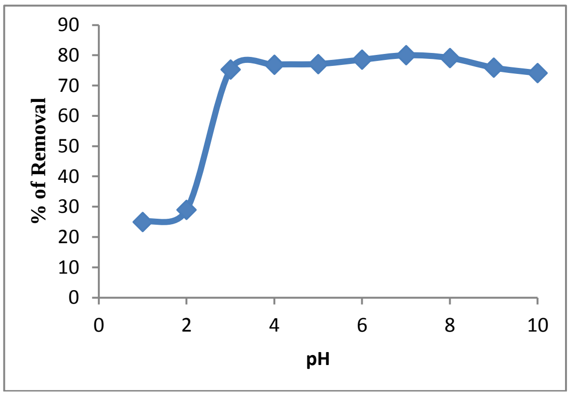


Fig.6. Effect of pH on MB by 8-HQPHF-III

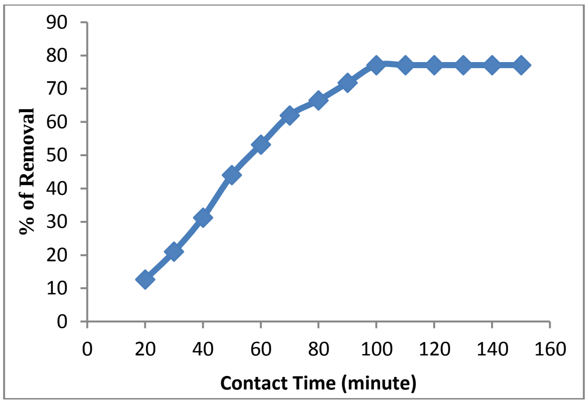


Fig.7 Effect of Contact time on MB by 8-HQPHF-III

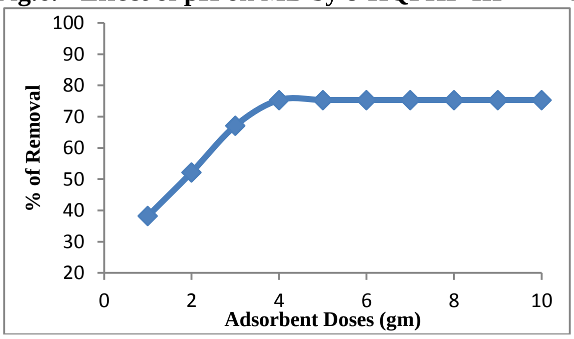


Fig.8 Effect of adsorbent doses on MB by 8-HQPHF-III

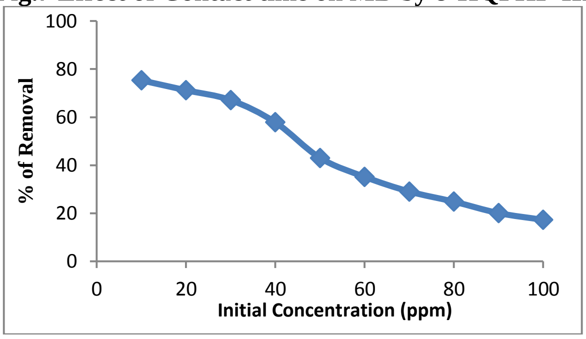
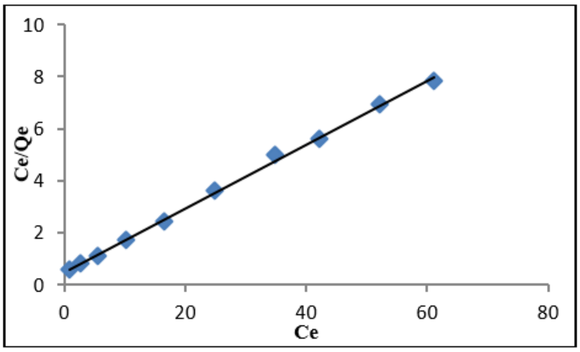


Fig.9 Effect of initial concentration on MB by 8-HQPHF-III



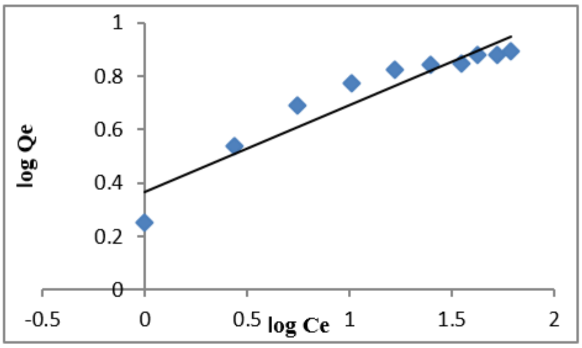


Fig.10 Langmuir isotherm for MB on 8-HQPHF-III Fig.11 Freundlich isotherm for MB on 8-HQPHF-III

V. Conclusion

Utilization of 8-HQPHF-III for the removal of MB from the industrial waste-water is investigated. 8-HQPHF-III is found to be better adsorbent for removal of MB. The maximum percentage(80%) for removal of MB is noticed at pH 7 with contact time 100 min. The percentage removal decrease with increase in initial MB concentration. At 4 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 MB onto 8-HQPHF-III. Thus the terpolymer reported in this research article can be successfully used for abetment of Methylene Blue dye from contaminated water and thus applicable in pollution control.

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