Polymethacrylic acid functionalised with dihydroxy benzene as an adsorbent for the removal of Malachite Green dye

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Abstract: The present work reports the investigation performed by comparing the adsorption abilities of modified/grafted polymethacrylic acid (PMAA) functionalized with dihydroxy benzene like catechol (CAT) and catechol-hydroquinone (CAT-HQ) by an oxidative decarboxylation method using potassium dichromate as an oxidant to absorb Malachite green (MG) dye from aqueous solution through batch experiments. The percentage of substitution of monomers with PMAA was found to be 94.5% and 95.7% for PMAA/CAT and PMAA/CAT-HQ respectively. The FTIR and SEM studies were determined to reveal the modification of PMAA. In order to efficiently extract malachite green from the aqueous solution, the effects of different parameters like contact time, pH, dye concentration and adsorbent dosage were systematically studied. The change on the surface morphology of the polymers after the adsorption of dye was analysed using FT-IR spectra and SEM images and found to have considerable changes after the adsorption of the chosen dye. The test of adsorption studies has shown that the Langmuir isotherm model is better than the Freundlich model. The monolayer adsorption capacity of PMAA/CAT and PMAA/CAT-HQ were found to be 97mg/g and 102 mg/g at 31˚C.

Keywords: Polymethacrylic acid, Catechol, Hydroquinone, Malachite Green, Adsorption Isotherm.

1. Introduction
The introduction of waste products into the environment is a significant problem. Dyes have been commonly used in many industries, such as textiles, paper, leather dying, cosmetics, pharmaceutical, food etc. The key contributor to water contamination is the effluent from these factories and there are more than 100000 commercially available dyes with more than 7×10⁵ tonnes of dyes produced each year. It was found that 2% of dyes were discharged from the production unit, while 10 percent were discharged from textiles and other industries[1-3]. Discharging of highly coloured effluent in surface water bodies can hinder the penetration of light, photosynthesis, and food chain in the aquatic.
ecosystem and also affect the aesthetic merits of the environment. In addition, some dyes have been reported as either toxic or mutagenic and carcinogenic for aquatic organisms and human beings [4,5]. Malachite Green (MG) is an important cationic dye belonging to the triphenylmethane family and is used for coloring wool, silk, cotton, and leather products in large quantities. It is an alternative antifungal agent in the fish farming industry, agriculture, and animal husbandry. It raises the risk of cancer and has an impact on the nervous system, reproductive system, brain, kidney, and liver, as it has a mutagenic and carcinogenic[5]. Therefore, being pumped into water streams, the water contaminated with MG dye must be treated carefully. Most of the dyes are stable to photodegradation and biodegradation [6,7]. The conventional water treatment is now the challengeable one and many methods like coagulation and flocculation[8], membrane separation[9], oxidation or ozonation[10,11], electrocoagulation[12], and adsorption[13] are used for elimination of dyes from waste water. Adsorption is an extraordinarily good, affordable, efficient technique among these techniques for extracting dyes from industrial effluents[14].

Polymeric adsorbents are superior to other solid adsorbents due to their greater surface area. The polymers functionalized with redox units like pyridinium, catechol, hydroquinone and mercaptly have been used for the adsorption of metal due to their high chelating capability. It is possible to obtain polymers with the desired functional groups either by preparing new monomers with functional groups interacting with the target cations, followed by polymerization (or) by modifying the existing polymer to the desired functional group by appropriate chemical reaction[15].

In the present investigation, an attempt was made to modify the PMAA with dihydroxy benzenes like catechol and catechol-hydroquinone. The modified PMAA such as PMAA/CAT and PMAA/CAT-HQ were characterized and used to remove Malachite green, a cationic dye from an aqueous solution and their adsorption capacities and efficiencies were compared. To examine the optimum adsorption capacity, the effective parameters such as contact time, pH, dye concentration and adsorbent dose were studied. The surface morphology of PMAA/CAT, PMAA/CAT-HQ, PMAA/CAT-MG and PMAA/CAT-HQ-MG were examined using FT-IR and SEM analysis. The adsorption process was applied to Langmuir and Freundlich models to understand the adsorption mechanism.

2. Experiment

2.1 Materials and Methods

Methacrylic acid (M.Wt = 86.09g, Molecular Formula = C₄H₆O₂), AIBN (2methylpropionimide) (M.Wt = 161.24g, M.Formula = C₈H₁₂N₄), Malachite Green chloride (M.wt = 364.91, M.formula = C₂₃H₂₅ClN₂), Catechol, Hydroquinone (M.wt = 110.11g, M.Formula = C₆H₆O₂) were purchased from Sigma-Aldrich. Conc. Hydrochloric acid, Sodium hydroxide, Potassium dichromate (K₂Cr₂O₇) and Silver nitrate (AgNO₃) were purchased from Merck Ltd., Mumbai. All the chemicals were used as received without further purification.

The UV-Vis spectra were recorded using a Perkin-Elmer Lamba spectrophotometer. Infrared spectra were taken with an ABB-MB-3000 FT-IR. The polymer samples for the infrared analysis were employed in the form of pellets with KBr medium. X-ray diffraction analyses were carried out using Bruker AXS D8 Advance diffractometer (radiation Cu Kα, λ=0.154nm, 35kV, 35mA) at the scan rate of 3°/min. SEM images of the polymers were taken using the JSM -6390LV model operating at an accelerating voltage of 20kV. The viscometric measurements were performed in 0.02M HCl at 30°C using Cannon Ubbelohde suspended viscometer with a pore size of 0.5mm. The viscosity average molecular weight (Mv) was calculated using Mark–Houwink–Sakurada equation[16].

2.2 Synthesis and chemical modification of polymethacrylic acid

Polymethacrylic acid (PMAA) was synthesized using AIBN as a radical initiator through radical polymerization and was chemically modified using K₂Cr₂O₇ as an oxidant [18]. To modify PMAA with catechol and hydroquinone, the standard procedure [17] with slight modification was adopted and their mechanism is given in scheme 1 and scheme 2. The percentage of substitution of the modified PMAA with dihydroxy benzene was calculated using the following standard equation [19].
Where, $n_{VHQ}$ - Number of moles of hydroquinone and catechol (in the form of vinyl hydroquinone and vinyl catechol) present in PMAA/CAT and PMAA/CAT-HQ estimated from the UV calibration curve, $n_{MAA}$ - Number of moles of methacrylic acid present in modified PMAA, $m$ - Sample weight of modified PMAA used in the UV measurement, $M_{MAA}$ and $M_{VHQ}$ are the molecular weights of methacrylic acid and vinyl hydroquinone (vinyl catechol).

2.3 Batch adsorption studies

The stock solution was prepared by dissolving 1g of MG in 1 liter de-ionized water and equilibrium adsorption studies were carried out with different concentrations of MG dye like 25mg/L, 50mg/L, 75mg/L, 100mg/L, 125mg/L, and 150mg/L. The adsorption studies were carried out with 0.1g of synthesized polymers using 100mL of MG dye solutions at pH 7 maintained at the temperature of 31°C and the absorbance was measured using UV spectrophotometer at 617nm. The amount of MG dye adsorbed on the polymers was obtained using the equation, $q_e = (C_o - C_e)V/W$ where $C_o$= initial concentration (mg/L), $C_e$=residual concentration at equilibrium (mg/L), $V$=Volume of solution (L) and $W$=Weight of the polymer (g). The effect of pH, dye concentrations, adsorbent dose, and contact time was studied at 31°C.

2.4 Adsorption Isotherm

An adsorption isotherm is used to characterize the interaction of adsorbate with adsorbents. The isotherm provides a relationship between the concentration of adsorbate in solution and the amount of adsorbate adsorbed on the solid phase when both phase are in equilibrium[20]. Freundlich and Langmuir models were employed to explain the MG dye and modified PMAA interaction and to determine the adsorption capacity of the adsorbent.

2.4.1 Freundlich Isotherm. The Freundlich model is an empirical equation and is used for the heterogeneous framework in which an exponentially distributed active sites provide an empirical relationship between adsorption capacity and equilibrium constant. The mathematical representation of this model is explained using the equation[21]:

$$\log Q_e = \frac{1}{n} \log C + \log K_f$$

where $K_f$ = Freundlich constants related to adsorption capacity(L/g), $1/n$ = adsorption intensity of adsorbent (g/L), The magnitude of $1/n$, fulfils the condition of $0 < 1/n < 1$ for favourable adsorption.

2.4.2 Langmuir Isotherm. The Langmuir isotherm model assumes that dye removal occurs by monolayer sorption on a homogeneous surface and predicts a relationship between $(C_e/Q_e)$ and $C_e$. The Langmuir adsorption isotherm of grafted PMAA was studied using the following equation[22]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}} C_e + \frac{1}{Q_{max}} K_l$$

$C_e$ = equilibrium dye concentration (mg/L), $Q_e$ = amount of dye adsorbed (mg/g) at equilibrium, $Q_{max}$= monolayer sorption capacity (mg/g) and $K_l$ = Langmuir constant(L/mg). The essential character of
the Langmuir adsorption isotherm is also expressed in terms of separation factor [23] \( R_L \) which is given as:

\[
R_L = \frac{1}{C_0 K_L + 1}
\]

\( C_0 \) is the initial dye concentration (mg/L)

The value of \( R_L \) indicates:
- If \( R_L > 1 \) Unfavourable adsorption isotherm,
- \( R_L = 1 \), Linear adsorption isotherm
- \( 0 < R_L < 1 \), Favourable adsorption Isotherm
- \( R_L = 0 \), Irreversible.

3. Results and Discussion

3.1 Percentage of substitution and Molecular Weight of modified PMAA

The grafting percentage of dihydroxy benzene moieties grafted to Poly Methacrylic acid using \( K_2Cr_2O_7 \) as an oxidant was carried at different time intervals varying from 1 hour to 8 hours and the temperature was maintained at 80°C. It is evident from Figure 1 that the percentage of grafting increases with an increase in reaction time and optimized at 6th hour with a maximum percentage of 91 and 95.7% for PMAA/CAT and PMAA/CAT-HQ. The intrinsic viscosity was found to be 0.60 dL g\(^{-1}\) with the molecular weight of 8.2x10\(^5\)gmol\(^{-1}\) for PMAA. The modified PMAA synthesized are found to have an intrinsic viscosity of 1.92dLg\(^{-1}\) with molecular weight 8.51x10\(^5\)gmol\(^{-1}\) for PMAA/CAT and 2.29 dLg\(^{-1}\) with a molecular weight of 12.03x10\(^6\)g mol\(^{-1}\) for PMAA/CAT-HQ, which has confirmed from Figure 2.

![Figure 1. Substitution Percentage of PMAA/CAT and PMAA/CAT-HQ at different time interval](image-url)
3.2 Characterization of chemically modified PMAA

3.2.1 UV-Visible spectra. The success of chemical modification of PMAA with CAT and HQ was certified by UV-visible spectroscopy, which is shown in the figure 3. The UV-visible spectra of PMAA absorbance maximum at 218nm are shifted to a longer wavelength at 323nm and 367nm for PMAA/CAT and PMAA/CAT-HQ [24] and this reveals that the success of modification of PMAA with catechol and catechol-hydroquinone.

3.2.2 XRD Studies. The XRD spectra of PMAA and chemically grafted PMAA are shown in figure 4 and the average crystalline size was calculated from Scherrer’s formula [26]. The XRD pattern of PMAA acid shows a broad diffraction peaks at 2θ =15.45° and 31.22° with d spacing values of 5.72 Å and 2.86 Å indicating its semi crystalline nature. The crystalline size of PMAA was found to be 0.51nm and 0.48nm [26]. The XRD pattern of PMAA/CAT and PMAA/CAT-HQ shows the absence of a significant peak, hence both the grafted polymers were found to be amorphous and this could be
revealed that the distortion in semi crystalline structure of PMAA matrices results from the grafting of dihydroxy benzene moieties [27].

3.2.3 DSC of PMAA and grafted PMAA. The DSC studies of the PMAA and grafted PMAA are given in figures 5a-c. It is clear from the figure 5a that the different phase temperatures were observed for PMAA at 87°C, 132°C, and 231°C Which is related to glass transition temperature (Tg), Crystalline temperature (Tc), and melting temperature (Tm) [28]. The DSC curve of chemically grafted PMAA using K2Cr2O7 as an oxidant is shown in figure 5a and 5b.

The Tg of PMAA/CAT was found to be 103°C, and for PMAA/CAT-HQ, the Tg was observed to be 95°C. The introduction of the dihydroxy benzene moieties into the backbone of PMAA leads to a decrease in the crystalline nature of the polymer by increasing the randomness. The thermal stability of unmodified PMAA is lower and upon grafting of dihydroxy benzene moieties, the thermal stability was found to increase due to change in the tacticity and end group the PMAA[29]. The crystalline temperature of PMAA/CAT and PMAA/CAT-HQ did not exhibit any crystalline temperature and this may be due to the amorphous nature of PMAA/CAT and PMAA/CAT-HQ which is evident from the
x-ray studies. The $T_m$ of PMAA/CAT and PMAA/CAT-HQ were found to be 267°C, and 258°C. The high melting temperature for the modified PMAA confirms the presence of strong interactions between the polymeric backbone and the aromatic moieties of the dihydroxy benzene [30].

3.3 Adsorption Studies

3.3.1 Effect of contact time. The effect of contact time on the removal of MG using modified PMAA like PMAA/CAT, PMAA/CAT-HQ was studied at different contact time like 10min, 20min, 30min, 40min, 50min, 60min, 70min, 80min, and 90 minutes for the fixed dye concentration of 25mg/L, adsorbent dose of 0.25g/L, pH of 6 and at the temperature 31°C and the results are given in the figure 6 and their comparative results are shown in table 1. The A.E of PMAA/CAT was observed to be 17% at the end of 10minutes, and at the end of 20min, 30min, 40min, and 50min, the A.E was gradually increased to 23%, 31%, 36%, and 40% respectively and further increase in time from 60min to 90min the A.E was found to remain constant with 47% and for PMAA/CAT-HQ, the A.E was found to increase gradually from 30% to 50% with increased in time from 10min to 60min and further increase in time, A.E was found to remain constant and this reveals that the effective contact is found to be 60minutes and fixed for further studies.

![Figure 6. Adsorption Efficiency of PMAA/CAT and PMAA/CAT-HQ on to MG dye adsorption at different time intervals](image-url)
3.3.2 Effect of pH on the adsorption of Malachite Green Dye

The effect of pH on the adsorption of the MG dye was examined at different pH like 2, 3, 4, 5, 6, 7, 8, 9, and 10 keeping the other parameters like dye concentration, adsorbent dose, and contact time constant and the results are given in figure 7. The A.E of PMAA/CAT at different pH ranging from 2 to 10 was found to be 22%, 30%, 35%, 40%, 47%, 50%, 50%, 50% and 50% and for PMAA/CAT HQ the A.E was found to 38%, 46%, 51%, 57%, 60%, 65%, 65%, 65% and 65%. The A.E of PMAA/CAT and PMAA/CAT-HQ was maximum at pH 7 and beyond the pH 7, the A.E was found to remain constant and this confirms that the optimum pH is 7 and this pH is fixed for further studies. The increasing trend in A.E of modified PMAA from pH 2-7 is due to an increase in the electrostatic interaction of negatively charged carboxyl and phenolic groups of modified PMAA with the cationic MG dye molecules [31]. The electrostatic interaction between the dye and modified PMAA illustrated in scheme1 and 2 for PMAA/CAT and PMAA/CAT-HQ.

![Figure 7. Adsorption Efficiency of PMAA/CAT and PMAA/CAT-HQ at different pH](image-url)
3.3.3. Effect of modified PMAA dosage on Malachite Green Dye adsorption

The effect of adsorbent dosage on the removal of MG dye was studied at different adsorbent doses like 0.25g/L, 0.5g/L, 1.0g/L and 1.5g/L keeping the other parameters like pH, contact time, and the dye concentration constant. The results are summarised in figure 8 and table.2. The A.E of PMAA/CAT was found to increase from 50% to 95% and the A.C decreased from 50mg/g to 23.8mg/g with an increase of PMAA/CAT dose from 0.5g/L to 1.0g/L and further increase in PMAA dose shows an insignificant change in A.E of PMAA/CAT and further decrease in A.C value with 15.8mg/g. The A.E and A.C of PMAA/CAT-HQ were found to exhibit the same trend as that of PMAA/CAT studied, thus the A.E of PMAA/CAT-HQ was found to increase from 56% to 96% and the A.C was found to decrease from 56mg/g to 24mg/g and a further increase in PMAA dose shows that the A.E value was found to remain the same with the value of 96% and decrease in A.C value of 16.2mg/g. It is evident from the result that (table.2) the A.E of PMAA/CAT and PMAA/CAT-HQ increase with an increase of adsorbent doses from 0.25g/L to 1.0g/L and a further increase in PMAA dose remain the same in A.E and this confirmed that the optimum adsorbent dose of PMAA/CAT and PMAA/CAT-HQ was found to be 1.0g/L. The increasing trend in A.E from 0.25/L to 1.0g/L is due to an increase in the adsorptive surface area and available active sites on the synthesized redox polymers[32].

![Scheme.1](image1)

![Scheme.2](image2)

Figure 8. Adsorption of MG at different PMAA/CAT and PMAA/CAT-HQ doses
Table 2. Comparison of adsorption of MG at different adsorbent doses modified PMAA

| Con (g/L) | PMAA/CAT | PMAA/CAT-HQ |
|-----------|-----------|-------------|
|           | A.E (%)   | A.C (mg/g) | A.E (%) | A.C (mg/g) |
| 0.025     | 50        | 50.0       | 65      | 65.0       |
| 0.050     | 70        | 35.0       | 80      | 40.0       |
| 0.100     | 95        | 23.8       | 97      | 24.3       |
| 0.150     | 95        | 15.8       | 97      | 16.2       |

3.3.4 Effect of concentration of Malachite Green Dye

The influence of MG dye concentration on A.E and A.C of modified PMAA was studied at different MG concentrations like 25mg/L, 50mg/L, 100mg/L, 125mg/L, and 150mg/L using the fixed optimum parameters of pH = 7, modified PMAA dose = 1g/L and the temperature at 31°C are given in figures 9a and 9b and their comparative results are presented in table 3. The A.E of PMAA/CAT at different dye concentrations like 25mg/L, 50mg/L, 100mg/L, 125mg/L, and 150mg/L was found to be 95%, 94%, 89%, 86%, 77% and 70% and the related A.C was observed to be 23.8mg/g, 47.0mg/g, 66.8mg/g, 86.0mg/g, 96.3mg/g and 105.0mg/g. The A.E and A.C of PMAA/CAT-HQ were found to show the same trend as the adsorption of PMAA/CAT exhibited at different MG concentrations studied. The A.E of PMAA/CAT-HQ was found to have a decreasing trend with an increase in MG concentrations ranging from 25mg/L to 150mg/L and the value of A.E was observed to be 97%, 96%, 94%, 89%, 82%, and 75%. The A.C of PMAA/CAT-HQ was found to show the increasing trend with an increase in MG concentration and its values were found to be 24.3mg/g, 48.0mg/g, 70.5mg/g, 89.0mg/g, 102.5mg/g, and 112.5mg/g. The decrease in A.E of PMAA/CAT and PMAA/CAT-HQ at greater MG concentrations is due to the decrease in the number of binding sites of PMAA/CAT and PMAA/CAT-HQ. The increase in A.C of PMAA/CAT and PMAA/CAT-HQ at higher dye concentration is due to an increase in driving force to overcome the mass transfer resistance between dye solution and adsorbent surface [33].

Figure 9. Adsorption efficiency of a) PMAA/CAT and b) PMAA/CAT-HQ at different MG dye concentrations and constant adsorbent dose of 1, pH of 7 maintained at 31°C
Table 3. Table 3 Comparison of adsorption efficiencies and capacities of modified PMAA at different MG dye concentrations, constant adsorbent dose of 1g/L, pH of 7 and temperature maintained at 31°C

| [MG]₀ (mg/L) | PMAA/CAT | PMAA/CAT-HQ |
|--------------|----------|-------------|
|              | A.E (%)  | A.C (mg/g)  | A.E (%)  | A.C (mg/g)  |
| 25           | 95       | 23.8        | 97       | 24.3        |
| 50           | 94       | 47.0        | 96       | 48.0        |
| 75           | 89       | 66.8        | 94       | 70.5        |
| 100          | 86       | 86.0        | 89       | 89.0        |
| 125          | 77       | 96.3        | 82       | 102.5       |
| 150          | 70       | 105.0       | 75       | 112.5       |

3.3.5 FT-IR Studies of Modified PMAA before and after the adsorption of Malachite Green

The FT-IR Spectra of PMAA/CAT and PMAA/CAT-HQ before and after adsorption of MG dye are shown in figures 10a and 10b. The FT-IR spectra of PMAA/CAT and PMAA/CAT-HQ before adsorption of MG dye exhibit a broad band at 3055-3553 cm⁻¹ with a peak band at 3030 cm⁻¹ and 3676-3605 cm⁻¹ with peak band 3347 cm⁻¹ due to -OH stretching frequency[34], the peaks at 2341 cm⁻¹ are due to O-C=O stretching, bands at 1738 cm⁻¹ and 1736 cm⁻¹ indicate the C=O stretching frequency, bands at 1591 cm⁻¹ are due to the C=C aromatic stretching [35]. Peaks at 1441 cm⁻¹ and 1442 cm⁻¹ are due to methyl C-H bending, the peaks at 1219 cm⁻¹ and 1219 cm⁻¹ are due to C-O stretching, and the peak at 740 cm⁻¹ for PMAA/CAT is due to the presence of o-substituted benzene. Peaks at 815 cm⁻¹ and 750 cm⁻¹ for PMAA/CAT-HQ exhibits the presence of ortho and para-substituted benzene [36]. It is also evident from figures 10a and 10b that some of the peaks are shifted, highly intensified, or appeared newly on the FT-IR spectra of modified PMAA after the adsorption of malachite green dye. The OH stretching frequency was shifted to a higher frequency from the band peak 3030 cm⁻¹ to 3452 cm⁻¹ and 3347 cm⁻¹ to 3439 cm⁻¹ for PMAA/CAT-MG and PMAA/CAT-HQ-MG and this shifting may be due to the interaction of -OH group of the polymer molecule and Malachite Green dye[37]. The peaks at 2341 cm⁻¹ for PMAA/CAT and PMAA/CAT-HQ are shifted to 2292 cm⁻¹ and 2297 cm⁻¹ for PMAA/CAT-MG and PMAA/CAT-HQ-MG. The C-O stretching frequency at 1219 cm⁻¹ and 1220 cm⁻¹ are shifted to 1257 cm⁻¹ and 1260 cm⁻¹ after adsorption with malachite green dye which is evident from figures 10a and 10b. The changes in the observed spectral values reveal that there is a possible interaction of functional groups in the modified polymers with MG in the course of the adsorption process.
3.3.6 SEM studies of modified PMAA before and after Adsorption of Malachite Green

The SEM image of PMAA/CAT was observed as a sheet with an uneven surface like morphology (figure 11a) before adsorption was found to change into dense solid like morphology after the adsorption of MG in PMAA/CAT which is given in figure 11b. In the PMAA/CAT-HQ, the surface morphology was found to have stacked sheet like morphology (figure 11c), and after the adsorption of MG, the surface morphology was changed into a rough fracture surface (figure 11d) [38-40] which clearly shows that the malachite green dye is adsorbed on the surface of the modified PMAA.
3.3.7 Langmuir and Freundlich Isotherm of Malachite Green using modified PMAA

The Langmuir isotherms for PMAA/CAT, and PMAA/CAT-HQ were studied and the results are given in Table 4 and their comparative data were fitted to the Langmuir isotherm models which are shown in the figure 12. The Langmuir constant ($K_L$) for PMAA/CAT and PMAA/CAT-HQ were found to be 5.1 and 3.2. The separation factors ($R_L$) of PMAA/CAT were found to be 0.008, 0.004, 0.003, 0.002, 0.0016 and 0.0013 at different MG concentrations like 25mg/L, 50mg/L, 75mg/L, 100mg/L, 125mg/L and 150mg/L, and for PMAA/CAT-HQ the $R_L$ values were found to be 0.012, 0.006, 0.004, 0.003 0.0025 and 0.0021. The correlation coefficient ($R^2$) of the modified PMAA/CAT and PMAA/CAT-HQ were found to be 0.998 and 0.999. The A.C for the PMAA/CAT and PMAA/CAT-HQ were found to be 116.3mg/g and 119.0mg/g. From figure 12 and the table values 4, it is clear that the $R_L$ obeys the condition of $0 < R_L < 1$ and the $R^2$ values are close to unity for PMAA/CAT and PMAA/CAT-HQ and thus strongly favored to Langmuir adsorption isotherm [41].

Figure 12. Langmuir adsorption isotherm of PMAA/CAT and PMAA/CAT-HQ using MG dye
The Freundlich isotherms of PMAA/CAT and PMAA/CAT-HQ were studied and the results are given in table 4, and their comparative data are fitted to the Freundlich model as shown in the figure 13. The intensity factor \((1/n)\) for PMAA/CAT and PMAA/CAT-HQ were found to be 0.40 and 0.36. The \(R^2\) values were found to be 0.935 and 0.926 for the modified PMAA/CAT and PMAA/CAT-HQ and the A.C of the PMAA/CAT and PMAA/CAT-HQ were found to be 26.3mg/g and 32.0mg/g. From table 4, it is evident that the \(1/n\) obeys the condition \(0 < 1/n < 1\), and the observed \(R^2\) values are lesser in Freundlich isotherm compared to the \(R^2\) values obtained in Langmuir adsorption isotherm for PMAA/CAT and PMAA/CAT-HQ and this clearly shows that the adsorption of MG using modified PMAA follows Langmuir adsorption isotherm than the Freundlich isotherm [42].

![Figure 13. Freundlich adsorption isotherm of PMAA/CAT and PMAA/CAT-HQ using MG dye](image)

Table 4. Freundlich and Langmuir adsorption parameters for the adsorption of MG using PMAA/CAT and PMAA/CAT-HQ

| Adsorbent      | Freundlich | Langmuir |
|----------------|------------|----------|
|                | \(K_f\) (mg/g) | \(1/n\) | \(R^2\) | \(Q_{max}\) (mg/g) | \(K_L\) | \(R_L \times 10^{-3}\) | \(R^2\) |
| PMAA/CAT       | 26.3       | 0.40     | 0.935   | 116.3        | 5.1     | 08-1.3               | 0.998   |
| PMAA/CAT-HQ    | 32.0       | 0.36     | 0.926   | 119.0        | 3.2     | 12-2.1               | 0.999   |

4. Conclusion

The PMAA had been chemically modified with catechol and catechol-hydroquinone using \(K_2Cr_2O_7\) as an oxidant. The chemically modified PMAA like PMAA/CAT and PMAA/CAT-HQ were used to remove MG dye from aqueous solution at different conditions like pH, contact time, adsorbent dosage and the dye concentration. The FTIR spectra and SEM image of PMAA/CAT-HQ and PMAA/CAT-HQ-MG revealed that the adsorption of MG takes place on the modified PMAA. The adsorption efficiency and capacity varied depending on the modified polymers. The experimental study showed that the removal capacity of PMAA/CAT-HQ at 25mg/L of MG was found to be 24.3mg/g with the
adsorption efficiency of 97% which is greater than the AE and AC of PMAA/CAT whose adsorption capacity and efficiencies are 23.8mg/g and 95%. The experimental data were investigated using Langmuir and Freundlich isotherm models and they follows Langmuir isotherm model with better regression coefficient values than Freundlich isotherm. In future, these modified PMAAs may use to remove the other cationic dyes and heavy metal ions from the industrial effluents.

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