

Adsorption of Methylene Blue dye using Polymethacrylic acid modified with dihydroxy benzene-Redox polymer

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ABSTRACT

In the present work, Poly Methacrylic Acid was synthesized by radical polymerization and functionalized with catechol and hydroquinone by an oxidative decarboxylation using potassium dichromate as an oxidant. The percentage of substitution was found to be 91% and 94.5% for PMAA/CAT and PMAA/HQ respectively. The modified polymers were used as an adsorbent to remove Methylene Blue dye from aqueous solution. The effect of various parameters, such as contact time, pH, dye concentration, and adsorbent dosage, were systematically examined and fixed the optimum time, pH, dye concentration and the adsorbent dosage for the effective removal of methylene blue from the aqueous solution. The adsorption capacity of PMAA/CAT and PMAA/HQ were found to be 24.3mg/g and 24.5mg/g with the adsorption efficiencies of 97% and 98% at pH 7 studied for 50 minutes with the initial dye concentration of 25mg/L for 0.1g/L of the adsorbents. The changes on the surface of the polymers before and after the adsorption was analysed using FTIR spectra and SEM images and found to have considerable changes after the adsorption of the methylene blue. Equilibrium isotherms like Langmuir and Freundlich models were carried out for modified PMAA and were found to follow Langmuir adsorption isotherm model better than the Freundlich model. The adsorption kinetic study were carried out for pseudo first-order and pseudo-second order and results showed that the adsorption of MB on modified PMAA were controlled by pseudo- second- order kinetics.

Keywords: Polymethacrylic acid, Catechol, Hydroquinone, Methylene Blue, Adsorption Isotherm, Adsorption Kinetics.

1. Introduction

Effluents from industries like textile, paper, leather dyeing, cosmetics, pharmaceutical and food coloring, etc are the main contributors to colored effluent and water pollution. There are more than 1,00,000 commercially available with over 7×10^5 tons of dyes manufactured per year. It was observed that 2% of dyes discharged from manufacturing unit, while 10 percent was discharged from textile and other industries¹⁻³. Discharging of highly colored effluent in surface water bodies can hinder penetration of light, photosynthesis, and food chain in aquatic ecosystem and also affect aesthetic merits of the environment. In addition, some dyes have been reported either toxic or mutagenic and carcinogenic for the aquatic organism and human being⁴⁻⁶. Methylene blue (MB) is the widely used organic substance for dyeing cotton, wood, and silk and it can cause eye burns which may lead to permanent injury to the eyes of human beings and animals. On inhalation, it affects the respiratory system and may cause nausea, vomiting, profuse sweating, mental confusion, and methemoglobinemia. Therefore it is important to remove MB from wastewater⁷. Most of the dyes are stable to photodegradation and biodegradation⁸⁻¹⁰. Thus colored wastewater poses a challenge to the conventional wastewater treatment techniques. There are several methods such as coagulation and flocculation¹¹, membrane separation¹², oxidation or Ozonation^{13, 14}, electrocoagulation¹⁵ and adsorption¹⁶ have been employed for removing dyes. Among these techniques, adsorption is the excellent, cheap, effective and potential technique for removing dyes from industrial effluents¹⁷.

Polymeric adsorbents are superior to other solid adsorbents due to their large surface area and adjustable surface chemistry. Polymers bound with redox units, being either internal parts of the polymer matrices or connected once are distinguished by oxydo-reduction chemistry features. The redox entities are organometallics such as metallocenes and organics such as mercaptyl, catechol, hydroquinone and pyridinium salts. Their functional groups of redox type are a pendant group or an internal part of the polymeric chain. The redox polymers exhibit redox properties, adsorption of metal cations through their chelating ability¹⁸⁻²⁰ of polymers with desired functional groups and it can be obtained either synthesizing new monomers with functional group interacting with the target cations, followed by polymerisation or by converting the groups in the existing polymer in to the desired functional group by suitable chemical reaction²¹.

In the present investigation, an attempt was made to modify the polymethacrylic acid with dihydroxy benzenes like catechol and hydroquinone. The modified polymethacrylic acid such as PMAA/CAT and PMAA/HQ were used to remove Methylene blue, 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/HQ, PMAA/CAT-MB and PMAA/HQ-MB were examined using FTIR and SEM analysis. The adsorption process was applied to Langmuir and Freundlich models to understand the adsorption mechanism. In addition, the adsorption kinetics studies were performed using Pseudo first order and pseudo-second-order equation to determine its reaction mechanism.

2. Materials and methods

2.1. Materials

Methacrylic acid (M.wt = 86.09g, M.Formula = C₄H₆O₂), AIBN (2methylpropionimide) (M.Wt = 161.24g, M.Formula = C₈H₁₂N₄), Methylene Blue (M.wt = 319g, M.formula = C₁₆H₁₈ClN₃S), Catechol, Hydroquinone (M.wt = 110.11g, M.Formula = C₆H₆O₂) were purchased from Sigma-Aldrich. Corp. 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.

2.2. Synthesis of chemically modified PMAA with dihydroxy benzene

Polymethacrylic acid (PMAA) was synthesized via a radical polymerization using AIBN as a radical initiator²² and it was chemically modified using potassium dichromate as an oxidant. The standard procedure²² with slight modification was adopted to carry out the synthesis chemically modified PMAA with catechol and hydroquinone and their mechanisms are given in scheme 1 and scheme 2.

The percentage of substitution of the modified PMAA with dihydroxy benzene was calculated using following standard equation²³.

$$S (\%) = \frac{n_{VHQ}}{n_{MAA} + n_{VHQ}} \times 100$$

$$n_{MAA} = \frac{m - n_{HQ} M_{VHQ}}{M_{MAA}}$$

n_{VHQ} = Number of moles of hydroquinone and catechol (in the form of vinyl hydroquinone and vinyl catechol) present in PMAA-HQ estimated from the UV calibration curve

n_{MAA} = Number of moles of methacrylic acid present in PMAA-HQ

m = Sample weight of PMAA-HQ 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

Equilibrium adsorption studies were carried out with different concentrations of MB dye like 25mg/L, 50mg/L, 75mg/L, 100mg/L, 125mg/L, 150mg/L. At an about 0.1g of synthesised polymer was added to each concentration of MB solution maintained at pH 7 and at 31°C. A series of different concentration of MB solution with 0.1g of adsorbent were placed in shaker at constant speed of 160 rpm. The process over after 80 minutes of adsorption, the test solution was removed from the shaker and centrifuged the mixture and then the solution bearing unadsorbed MB concentration was measured using UV spectrophotometer at 668nm. The concentration of MB adsorbed was obtained using the equation, $q_e = (C_0 - C_e)V/W$ where C_0 = 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 contact time and dye concentration were studied using 25mg/L of MB, 0.025g of adsorbent, and at pH of 6 maintained at the temperature 31°C.

In order to find the effect of pH on the adsorption of MB, the adsorption equilibrium was carried out at different pH like 2, 3, 4, 5, 6, 7, 8, 9 and 10 using 0.1M NaOH and 0.1M HCl solution and the other parameters like adsorbent dosage, dye concentration, contact time were kept constant. In order to find out the influence of adsorbent on MB, the adsorption process was carried out at different concentration of adsorbent like 0.025g/L, 0.05g/L, 0.1g/L, 0.150 g/L and the other parameters like pH, contact time, and dye concentration were kept constant.

3. Results and discussion

3.1. Effect of substitution percentage

The oxidative decarboxylation conditions of minisci²⁴ were applied to the chemical modification of PMAA with dihydroxy benzene. The mechanistic pathway for the modification of PMAA with potassium dichromate/silver nitrate were used to initiate the oxidative decarboxylation resulting in polymeric radical and this behaves like nucleophile and reacts with benzoquinone^{24, 25}. The degree of substitution of carboxylic acid group by hydroquinone or catechol were estimated by UV absorbance of the modified PMAA. The calibration curve of various concentration of Catechol/Hydroquinone solution like 1mg/mL, 2mg/mL,

3mg/mL, 4mg/mL and 5mg/mL at 288nm were drawn. From the calibration curve, the concentrations of Catechol/hydroquinone for different reaction time varying from 1-7 hrs were measured and the results are given in terms of substitution percentage in figure.1. From the comparative figure, it was clear that the percentage of substitution of dihydroxy benzene in polymeric chain of PMAA was found to increase up to six hours and further increase in time, the rate of substitution remained the same and no change was observed in the substitution. The rate of percentage of substitution was found to be 56%, 73%, 82.5%, 88.1%, 90.1% and 91.0% for one to six hours for PMAA/CAT. The percentage of substitution for PMAA/HQ was found to be 60.1%, 71.3%, 82.3%, 93.2%, 93.7% and 94.5% for one to sixth hour. The highest percentage of substitution was found to be 91% and 94.5% for PMAA/CAT and PMAA/HQ at the optimum time sixth hour.²⁶

3.2. IR and SEM studies of modified PMAA before and after the adsorption of Methylene Blue dye

The FT-IR spectra of PMAA/CAT and PMAA/HQ before and after adsorption of MB dye are given in figures 2 a,b and 3 a,b and from the spectra it is evident that the PMAA/CAT shows peaks at 3055-3553 cm^{-1} (O-H stretching)²⁷, 1738 cm^{-1} (C=O stretching)²⁸, 1591 cm^{-1} (aromatic C=C stretching)²⁹, 1441 cm^{-1} (methyl C-H bending), 1393 cm^{-1} (methylene C-H bending), 1220 cm^{-1} (C-O stretching), 796 cm^{-1} (C-H out of plane bending) and 740 cm^{-1} (o-substituted benzene stretching)³⁰ before the adsorption of dye (Figure 2a). After the adsorption of methylene blue dye it was observed that some of the peaks are shifted (or) highly intensified or disappeared and this is evident from the figure 2b. The MB dye loaded on PMAA/CAT shows new peaks at 1628 cm^{-1} (C=N stretching), 1188 cm^{-1} (C-C stretching), 1016 cm^{-1} (C-N stretching)³¹, 531 cm^{-1} (C-S stretching), 3412 cm^{-1} which is due to O-H stretching³², 1464 cm^{-1} is due to methylene C-H bending, 1393 cm^{-1} is due to methyl C-H bending and a peak at 1219 cm^{-1} (C-O stretching) is found to shift at 1267 cm^{-1} after the adsorption of methylene blue dye.

The PMAA/HQ shows peaks at 3000-3660 cm^{-1} (O-H stretching)³³, 3269 cm^{-1} (aromatic C-H stretching), 1591 cm^{-1} (aromatic C=C stretching), 1450 cm^{-1} (methylene C-H bending), 1358 cm^{-1} (methyl C-H bending), 1198 cm^{-1} (C-C stretching), 1098 cm^{-1} (C-O stretching)³⁴ and 806 cm^{-1} (p-substituted benzene stretching). From the above FTIR spectral values it is clear that the adsorbents exhibit number of peaks, indicating the nature of bond functioning in the modified polymer as shown in figures 3a. After the adsorption of the dye in PMAA/HQ (figure.3b) shows new peaks at 1618 cm^{-1} , 1028 cm^{-1} due to C-N stretching, a peak at 524 cm^{-1} is due to C-S stretching and high intense peaks at 1496 cm^{-1} is due to methylene C-H bending and a peak at 1442 cm^{-1} shows the presence of methyl C-H bending³⁵. The changes in the spectral values observed reveals that there is a possible interaction of functional groups of modified polymers with MB in the course of adsorption process.

The SEM images of Modified PMAA with catechol and hydroquinone before and after the adsorption of MB dye at different magnifications are given in figures 4 and 5 and figures 6 and 7. The PMAA/CAT exhibit sheet-like uneven surface morphology and PMAA/HQ shows sheet with slight grooves like morphology before adsorption as it is evident from the SEM figure 4 and 5. After the adsorption of Methylene blue dye, the SEM image was found to change in to fractured surface like morphology in PMAA/CAT-MB and dense solid like morphology in PMAA/HQ-MB and this confirms that the adsorbate are adsorbed on the surface of the synthesized redox polymers.

3.3 BATCH ADSORPTION STUDIES

3.3.1 Effect of time

The effect of contact time on the removal of MB was studied by varying contact time like 10min, 20 min, 30 min, 40 min, 50 min, 60 min and 70 minutes with the fixed dye concentration of 25mg/L, adsorbent dose 0.025g/L, pH of 6 and at the temperature 31°C and the values are given in figure. 8. At the initial time of 10 min, the adsorption efficiencies of PMAA/CAT and PMAA/HQ were found to be 19% and 25%. The adsorption of MB dye was found to increase with increase in time up to 50 minutes with the adsorption efficiency of 50 % and 58% for PMAA/CAT and PMAA/HQ and reached the saturation state and further increase in time, the adsorption efficiency remained the same and this confirms the optimum time for effective adsorption of MB dye was found to be 50 min for the modified PMAA with catechol and hydroquinone and it is used for further studies.

3.3.2 Effect of Dye concentration

The removal efficiency was considerably influenced by the concentration of MB dye in an aqueous solution and it was studied on PMAA/CAT and PMAA/HQ. The experiments were carried out at different dye concentrations like 25mg/L, 50mg/L, 75mg/L, 100mg/L, and 150mg/L, and constant pH of 7, adsorbent dose 0.1g/L, and at the fixed time of 50 min and the results are given in figures 9 and 10 and the comparative values are given in table 1. The adsorption efficiency at different dye concentration was found to be 97%, 94%, 91%, 88%, 81% and 73%, and the adsorption capacity was found to be 24.3mg/L, 47.0mg/L, 68.3mg/L, 88.0mg/L, 101.3mg/L and 109.5mg/L for PMAA/CAT³⁶. From the figure and table values, it is seen that the

adsorption efficiency decreases from 97% to 73% and adsorption capacity increases from 24.3mg/g to 109.5mg/g with increase the dye concentration³⁷ from 25mg/L to 150mg/L for PMAA/CAT, and for PMAA/HQ the adsorption efficiency change was found from 98% to 75% and the capacity was from 24.5mg/g to 112.5mg/g. The decreasing values in adsorption efficiency and increasing value in adsorption efficiency is due to increase in driving force on increasing dye concentration³⁸.

3.3.3. Effect of adsorbent dose

The effect of adsorbent dosage on the removal of MB dye was studied at different adsorbent dose like 0.025g/L, 0.05g/L, 0.1g/L, 0.150 g/L keeping the other parameters like pH-7, contact time 50min, the dye concentration 25mg/L and the results are summarised in figure.11 and table 2. From the figure and table it is evident that the adsorption efficiency and capacity increases up to 0.1g/L and further increase in the adsorbent dosage shows an insignificant change in the removal of MB dye³⁹, and this confirms the optimum adsorbent dose as 0.1g/L. The adsorption efficiency and capacity for PMAA/ CAT at 0.1g/L was found to be 97% and 24.3mg/g and for PMAA/HQ, the adsorption efficiency and capacity was found to be 98% and 24.5 mg/g. Initially the increase in the dye removal efficiency and adsorption capacity with an increase in adsorbent concentration is due to increase in the surface area and available active centers on the synthesized redox polymers⁴⁰.

3.3.4. The effect of pH

The effect of pH on the adsorption of the MB dye was examined at different pH like 2, 3, 4, 5, 6, 7, 8, 9 and 10 keeping the other parameters like dye concentration=25mg/L, adsorbent dose=0.025 and contact time constant and the results are given in table 3 and the comparative results are given in figure.12. From the figure and table it is evident that the adsorption efficiency increased with the increase in the pH from pH 2 to 7 and further increase in the pH, the adsorption efficiency remains the same. For this reason pH 7 was fixed as an optimum pH. The MB dye removal was high at the pH 7 with the adsorption efficiency of 55% and 62% for PMAA/CAT and PMAA/HQ with the adsorption capacities of 13.8mg/L and 15.5mg/L. The presence of ionisable groups such as carboxyl and phenolic groups on the polymer structure can affect the percentage of removal of dye and the adsorption capacities of this polymer⁴¹. At low pH, the carboxyl groups and phenolic groups are present in non-ionized form and no interaction can occur between the phenolic groups and the cationic MB dye molecules⁴². At pH 7, the adsorption efficiency is increased as the electrostatic interaction between dye molecule and polymer is increased as illustrated in scheme 3 and 4, this results in the favourable adsorption at high pH and not favoured at low pH^{43,44}.

3.4. Adsorption isotherm

The adsorption isotherm of MB was studied by Langmuir and Freundlich linear model^{45,46}. The Langmuir model assumes that the removal of dye occurs on a homogeneous surface by monolayer sorption, and predicts a relationship between (C_e/Q_e) and C_e according to equation $C_e/Q_e = (1/Q_{max}) C_e + 1/Q_{max} K_L$ where C_e (mg/L)= equilibrium MB concentration, Q_e (mg/g) is the amount adsorbed at equilibrium, Q_{max} =monolayer sorption capacity and K_L (L/mg) is the Langmuir constant. The essential character of the Langmuir isotherm is also expressed in terms of favourability factor R_L which is given in the equation $(1/CoK_L + 1)$ Where K_L (L/mg) is the Langmuir constant and Co is the initial dye concentration (mg/L).

The value of R_L indicates the followings.

$R_L > 1$ - the isotherm is unfavourable, $R_L = 1$ - linear, $0 < R_L < 1$ - the isotherm is favourable and $R_L = 0$ - irreversible.

The Freundlich model is an empirical equation and is used for the heterogeneous system where active sites are distributed exponentially. This isotherm provides an empirical relationship between the sorption capacity and equilibrium constant of the sorbent. The mathematical representation of this model is explained using the equation $\log Q_e = 1/n \log C_e + \log K_f$ where K_f (mg/g) and n are the Freundlich constants related to adsorption capacity and adsorption intensity of adsorbents, respectively. The magnitude of n gives an indication of the favourability of adsorption.

The Langmuir and Freundlich isotherms were obtained using different dye concentrations varying 25-150mg/L and the concentration of the adsorbent was kept constant as 0.1g/L and at constant contact time of 50 minutes. The resulted adsorption isotherm data were fitted with Freundlich (figure 13, 14) and Langmuir model which are shown in figures 15 and 16 and the corresponding correlation coefficients and the isotherm constants were calculated and are presented in table.4. From the table values and figures it is clear that the correlation coefficient values for Langmuir⁴⁷ are closer to unity with the values of $R^2=0.998$ for PMAA/CAT and $R^2=0.999$ for PMAA/HQ than the correlation coefficient for Freundlich⁴⁸ with $R^2=0.970$ and 0.958 for PMAA/CAT and PMAA/HQ. Therefore the adsorption of MB on PMAA/CAT and PMAA/HQ follows the Langmuir isotherm model⁴⁹. The probability constant value ($R_L=9.3-1.6, 14-2.0$) and the correlation coefficient ($R^2=0.998, 0.999$) strongly supports that PMAA/CAT and PMAA/HQ follows Langmuir isotherm and the

comparative study shows that Langmuir adsorption isotherm is favourable more than for adsorption of MB on PMAA/HQ than PMAA/CAT.

3.5. Study of Adsorption kinetics

In order to understand the rate of adsorption of methylene blue dye on PMAA/CAT and PMAA/HQ, adsorption kinetics were studied for pseudo-first and pseudo second-order reactions.

Pseudo first order kinetic equation was proposed by Langergen and Svenska⁵⁰, which is expressed as $\log(Q_e - Q_t) = \log Q_e - (k_1/2.303) t$ Where Q_e and Q_t (mg/g) are the amounts of MB adsorbed at equilibrium and at time (min) respectively, and k_1 (min⁻¹) is the rate constant of adsorption. Pseudo first order kinetics is differed from first order kinetics in two aspects that (i) the parameter $\log Q_e$ always is not equal to the intercept of the plot $\log(Q_e - Q_t)$ vs. time but it is equal for first order kinetic adsorption process, (ii) it is only to predict the rate at initial stage of the adsorption reaction, but it fails to study the rate of overall adsorption.^{51,52} process.

The pseudo-second-order was proposed by Ho and McKay⁵³ can be represented by the linear equation $t/Q_t = 1/k_2 Q_e^2 + 1/Q_e t$ Where k_2 (mg.g⁻¹.min⁻¹) is the second order rate constant. The pseudo second order kinetics is based on the assumption that the rate limiting step involves in chemisorptions process through a forces of sharing or exchange of electrons between adsorbent and adsorbate. As this model predicts well the rate of the overall adsorption process compared to pseudo first order kinetics, it is a better reliable model to find the rate of overall adsorption process like biosorption⁵⁴.

3.5.1 The study of pseudo first and pseudo second order on MB using modified PMAA

The adsorption of MB at different dye concentration varying from 25-150mg/L on PMAA/CAT and PMAA/HQ were carried out and the experimental data obtained were summarised in table 5 and 6 for Pseudo first order and second order kinetic studies. The pseudo first order plot $\log(Q_e - Q_t)$ versus t and pseudo second order plot t/Q_t versus t for the adsorption of MB at different concentration on PMAA/CAT and PMAA/HQ are given in figure.17,18 and 19, 20 and their comparable results given in the tables 5 and 6 and this indicates that the adsorption of MB at different concentration studied on PMAA/CAT and PMAA/HQ shows better correlation coefficient values for pseudo second order kinetics model than pseudo first order model. In addition, the rate constant (k_2) for pseudo second order reaction decreases on increasing the concentration of dye from 25mg/L to 150mg/L and this may be due to slowing down the reaction speed with increase in dye concentration and this controls the rate of adsorption⁵⁵.

The adsorption capacity values calculated for Pseudo first order (Q_{e1}) reaction was not in correlation with experimental values whereas, the adsorption capacity values calculated for pseudo second order (Q_{e2}) follows the experimental adsorption capacity values for all the concentration of MB dye studied for the synthesized modified PMAA⁵⁶. As it is evident from the table 5 and 6, the adsorption capacity of the synthesised polymers on the adsorption of a maximum initial dye concentration of 150mg/L were found 97mg/g and 101.0mg/g for modified catechol and hydroquinone using pseudo second order model and this confirms that PMAA/HQ has greater adsorption capacity than PMAA/CAT on adsorption of MB.

4. Conclusion

The PMAA had been modified with catechol and hydroquinone using potassium dichromate as an oxidant. The modified PMAA like PMAA/CAT and PMAA/HQ were applied to remove MB 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, PMAA/HQ, PMAA/CAT-MB and PMAA/HQ-MB revealed the adsorption of MB takes place on the modified PMAA. The adsorption efficiency and capacity varied depending on the polymers. The experimental study showed that the removal capacity of PMAA/HQ at 25mg/L MB concentration was found to be 24.5mg/g with the adsorption efficiency of 98% which is greater than PMAA/CAT whose adsorption capacity and efficiencies are 24.3mg/g and 97%. The experimental data were investigated using Langmuir and Freundlich model and they follows Langmuir isotherm model with better regression coefficient values than Freundlich isotherm. The Langmuir isotherm favourability factor R_L was found greater for PMAA/HQ than PMAA/CAT on the adsorption of MB. The adsorption kinetics of MB using PMAA/CAT and PMAA/HQ was studied by pseudo first order and pseudo-second-order model. The result showed that adsorption kinetics favoured to pseudo-second-order model with greater regression coefficient values than the pseudo first order kinetics.

Table 1: The comparative Adsorption efficiency and Capacity of synthesised polymer using MB at different concentrations and time intervals

[MB] ₀ (mg/L)	Time (min)	PMAA/CAT		PMAA/HQ	
		A.E (%)	A.C (mg/g)	A.E (%)	A.C (mg/g)
25	10	63.0	15.8	64.0	16.0
	20	68.0	17.0	69.0	17.3
	30	75.0	18.8	76.0	19.0
	40	87.0	21.8	89.0	22.3
	50	97.0	24.3	98.0	24.5
	60	97.0	24.3	98.0	24.5
	70	97.0	24.3	98.0	24.5
50	10	59.0	29.5	60.0	30.0
	20	64.0	32.0	65.0	32.5
	30	72.0	36.0	72.0	36.0
	40	82.0	41.0	84.0	42.0
	50	94.0	47.0	96.0	48.0
	60	94.0	47.0	96.0	48.0
	70	94.0	47.0	96.0	48.0
75	10	54.0	40.5	55.0	41.3
	20	59.0	44.3	60.0	45.0
	30	65.0	44.8	66.0	49.5
	40	75.0	56.3	76.0	57.0
	50	91.0	68.3	94.0	70.5
	60	91.0	68.3	94.0	70.5
	70	91.0	68.3	94.0	70.5
100	10	50.0	50.0	51.0	51.0
	20	55.0	55.0	56.0	56.0
	30	60.0	60.0	62.0	62.0
	40	70.0	70.0	71.0	71.0
	50	88.0	88.0	90.0	90.0
	60	88.0	88.0	90.0	90.0
	70	88.0	88.0	90.0	90.0
125	10	45.0	056.3	46.0	057.5
	20	49.0	061.3	50.0	062.5
	30	53.0	066.3	56.0	070.0
	40	64.0	080.0	65.0	081.3
	50	81.0	101.3	84.0	105.0
	60	81.0	101.3	84.0	105.0
	70	81.0	101.3	84.0	105.0
150	10	39.0	058.5	40.0	060.0
	20	44.0	066.0	45.0	067.5
	30	48.0	072.0	49.0	073.5
	40	56.0	084.0	58.0	087.0
	50	73.0	109.3	75.0	112.5
	60	73.0	109.3	75.0	112.5
	70	73.0	109.3	75.0	112.5

A.E-Adsorption efficiency, A.C-Adsorption capacity, [MB]₀-Initial dye concentration

Table 2: The comparison of influence of adsorbent dosage of PMAA/CAT and PMAA/HQ on MB dye

Conc (g/L)	PMAA/CAT		PMAA/HQ	
	A.E (%)	A.C (mg/g)	A.E (%)	A.C (mg/g)
0.025	55	13.8	61	15.3
0.050	76	19.0	80	19.8
0.100	97	24.3	98	24.5
0.150	97	24.3	98	24.5

Table- 3: The influence of pH on MB adsorption

pH	PMAA/CAT		PMAA/HQ	
	A.E (%)	A.C (mg/g)	A.E (%)	A.C (mg/g)
2	25	06.25	32	08.00
3	33	08.25	40	10.00
4	40	10.0	46	11.50
5	44	11.00	51	12.80
6	50	12.50	58	14.50
7	55	13.80	62	15.50
8	55	13.80	62	15.50
9	55	13.80	62	15.50
10	55	13.80	62	15.50

A.E-adsorption efficiency, A.C-adsorption capacity.

Table 4: The comparison of Freundlich and Langmuir isotherm parameters for the adsorption of MB using PMAA/CAT and PMAA/HQ

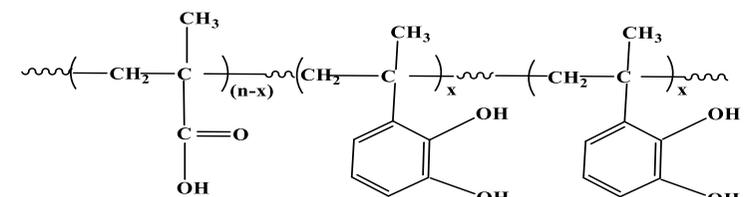
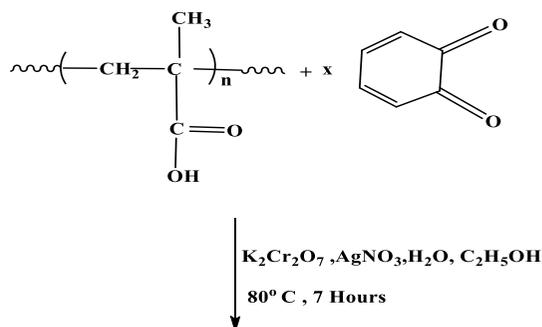
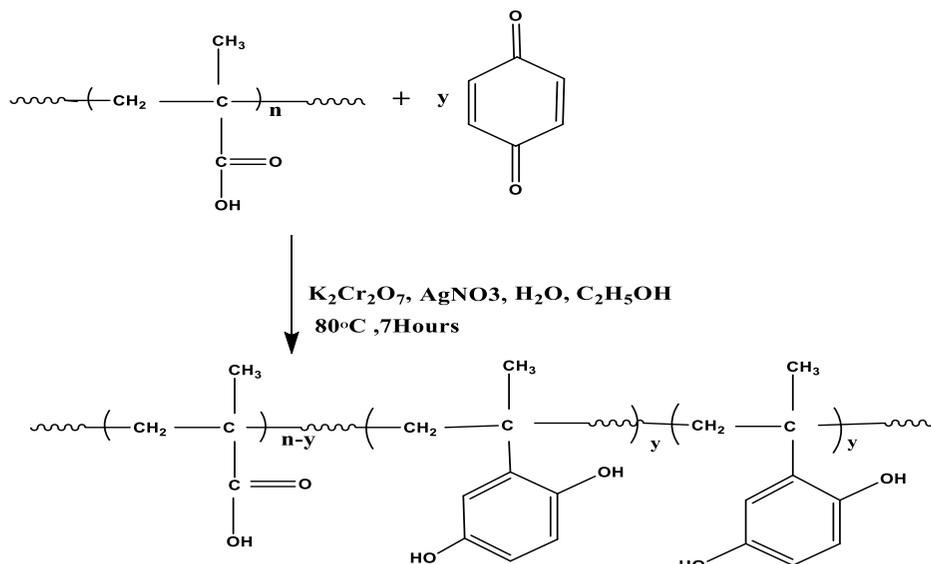
Adsorbent	Freundlich			Langmuir			
	K _f (mg/g)	n	R ²	Q _{max} (mg/g)	K _L	R _L ×10 ⁻³	R ²
PMAA/CAT	29.8	2.50	0.970	120	4.3	9.3-1.6	0.998
PMAA/HQ	35.8	2.77	0.958	121	2.9	14-2.0	0.999

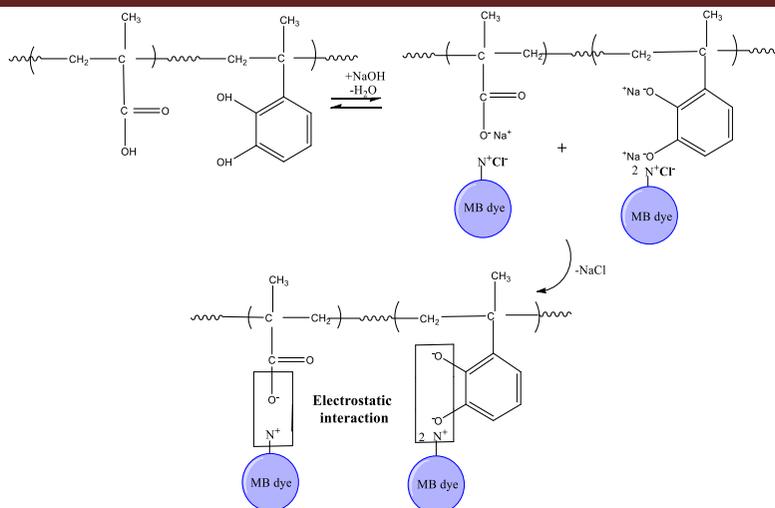
Table 5: Pseudo first and second order parameters for the adsorption of MB on PMAA/CAT at different dye concentration

[MB] ₀ (mg/L)	Pseudo first order			Pseudo second order		
	Q _{e1} (mg/g)	k ₁ ×10 ⁻² (min ⁻¹)	R ²	Q _{e2} (mg/g)	k ₂ ×10 ⁻⁴ (g/mg/min)	R ²
25	14.5	3.40	0.879	24.8	53.7	0.972
50	27.7	3.10	0.923	47.2	27.4	0.978
75	39.2	2.40	0.922	64.0	20.7	0.976
100	51.5	2.20	0.936	78.0	17.1	0.973
125	61.7	2.10	0.870	91.7	13.1	0.956
150	66.6	2.00	0.939	97.0	12.6	0.975

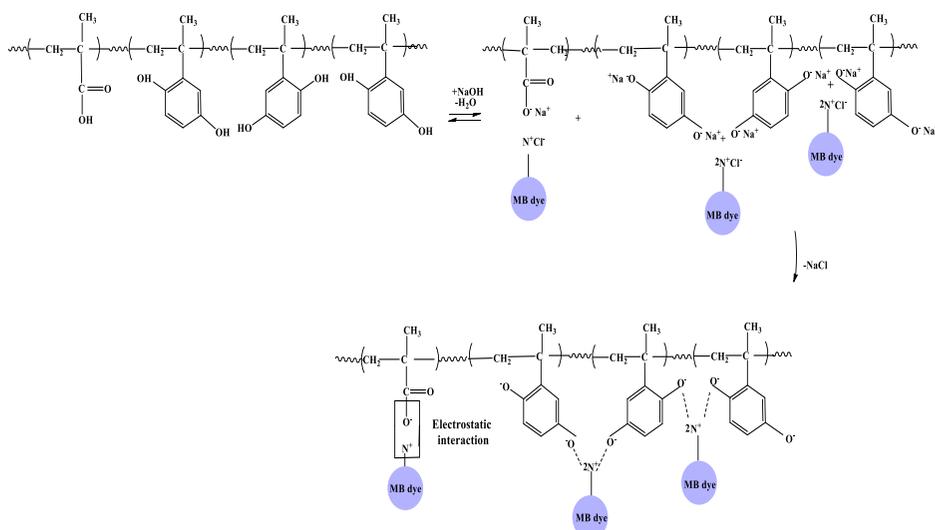
Table 6: Pseudo first and pseudo second order parameters for the adsorption of MB on PMAA/HQ at different dye concentration

[MB] ₀ (mg/L)	Pseudo first order			Pseudo second order		
	Q _{e1} (mg/g)	k ₁ ×10 ⁻² (min ⁻¹)	R ²	Q _{e2} (mg/g)	k ₂ ×10 ⁻⁴ (g/mg/min)	R ²
25	15.3	3.8	0.860	25.4	50.7	0.968
50	29.0	3.1	0.888	48.0	26.2	0.970
75	40.2	2.2	0.927	65.0	20.8	0.976
100	52.2	2.1	0.943	81.3	16.3	0.978
125	63.5	2.0	0.929	94.3	12.8	0.971
150	69.7	1.9	0.922	101.0	11.5	0.968

**Scheme 1. Reaction Scheme of modification of PMAA catechol****Scheme 2. Reaction Scheme of modification of PMAA using hydroquinone**



Scheme 3. Electrostatic interaction between MB dye and PMAA/CAT



Scheme 4. Electrostatic interaction between MB dye and PMAA/HQ

Figure 1: The Percentage of substitution of catechol and hydroquinone in polymeric chain at different time intervals

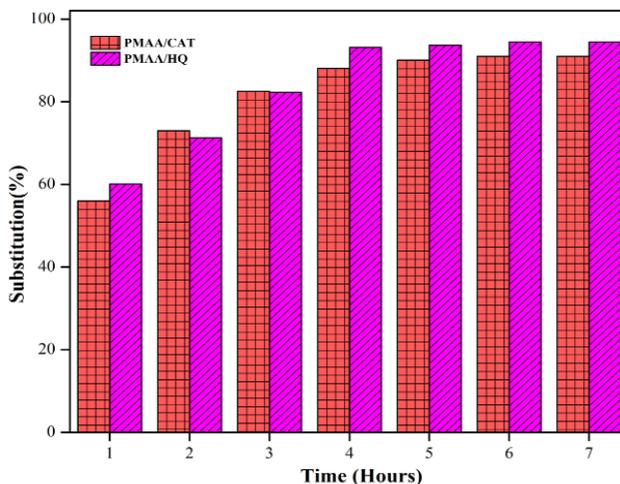
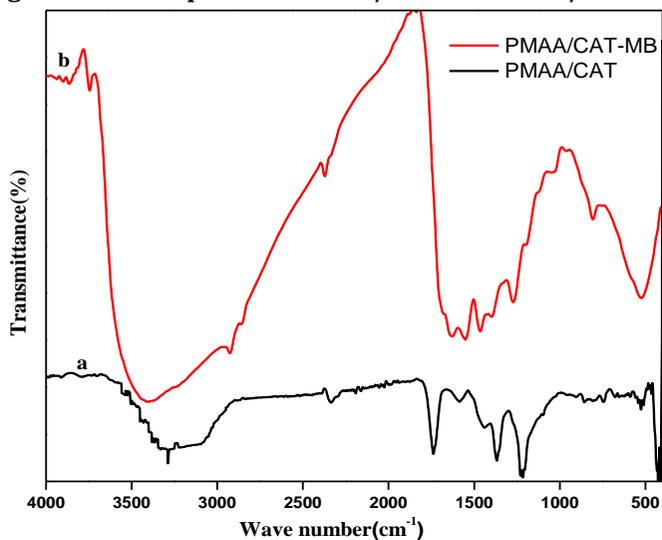


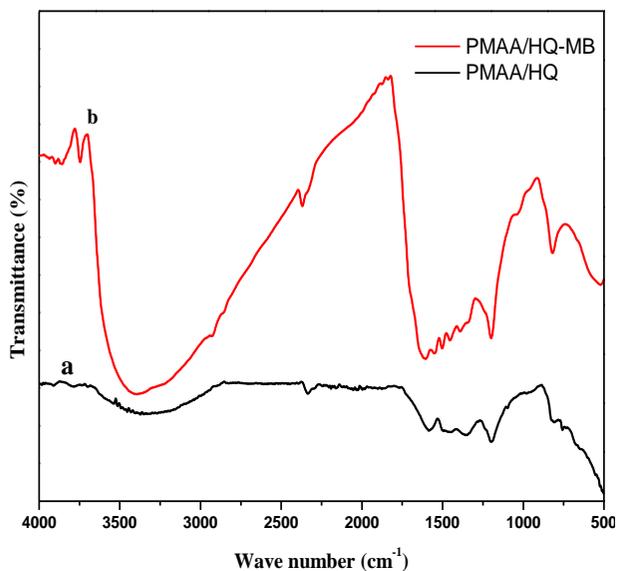
Figure 2: FTIR spectra of PMAA/CAT and PMAA/CAT-MB



a. PMAA/CAT

b. PMAA/CAT-MB

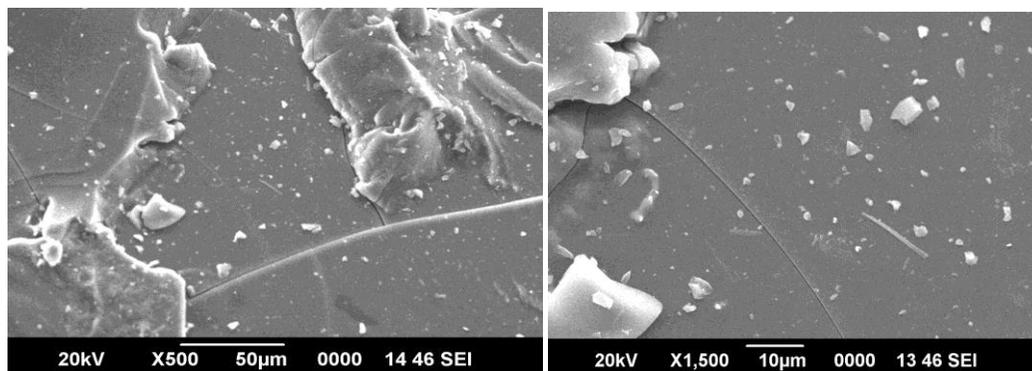
Figure 3: FTIR spectra of PMAA /HQ and PMAA/HQ-MB



a. PMAA/HQ

b. PMAA/HQ-MB

Figure 4: SEM images of PMAA/CAT at different magnifications



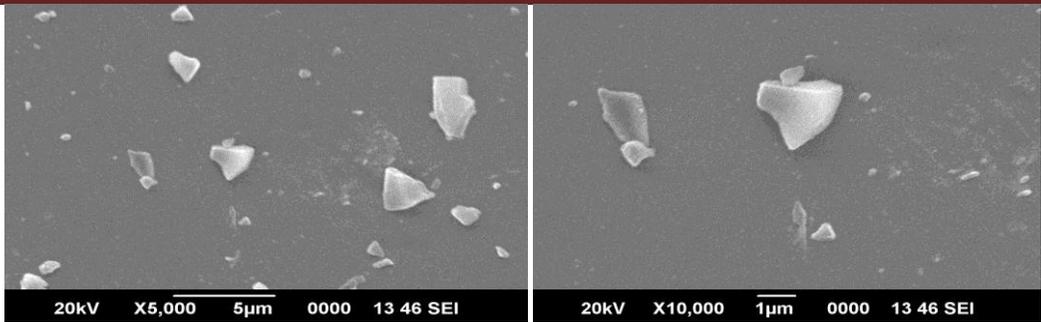


Figure 5: SEM images of PMAA/HQ at different magnifications

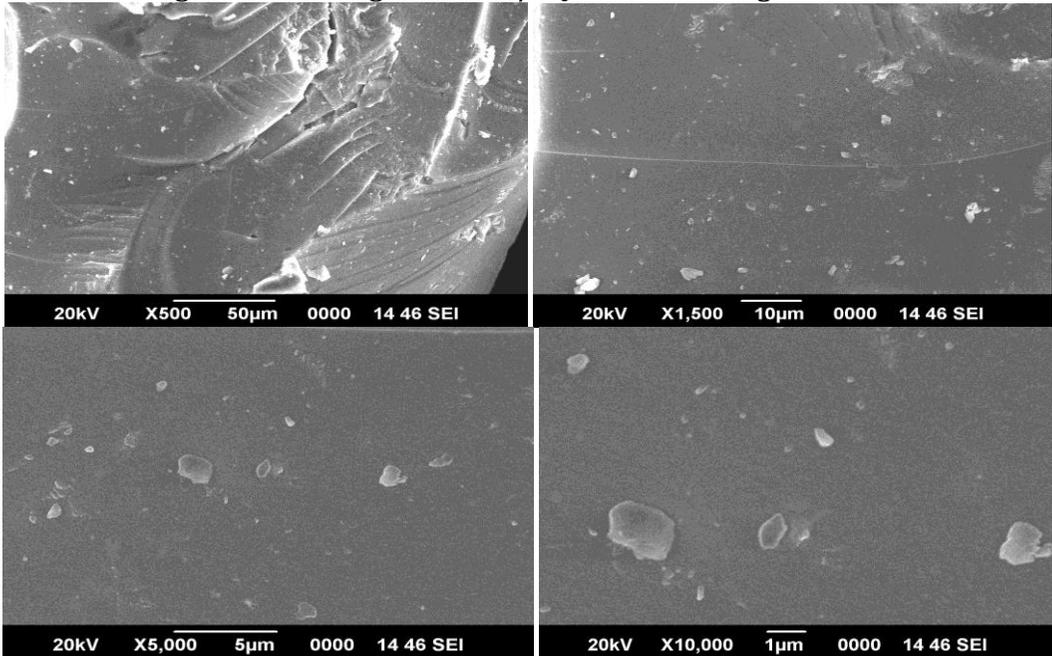


Figure 6: SEM images of PMAA/CAT-MB at different magnifications

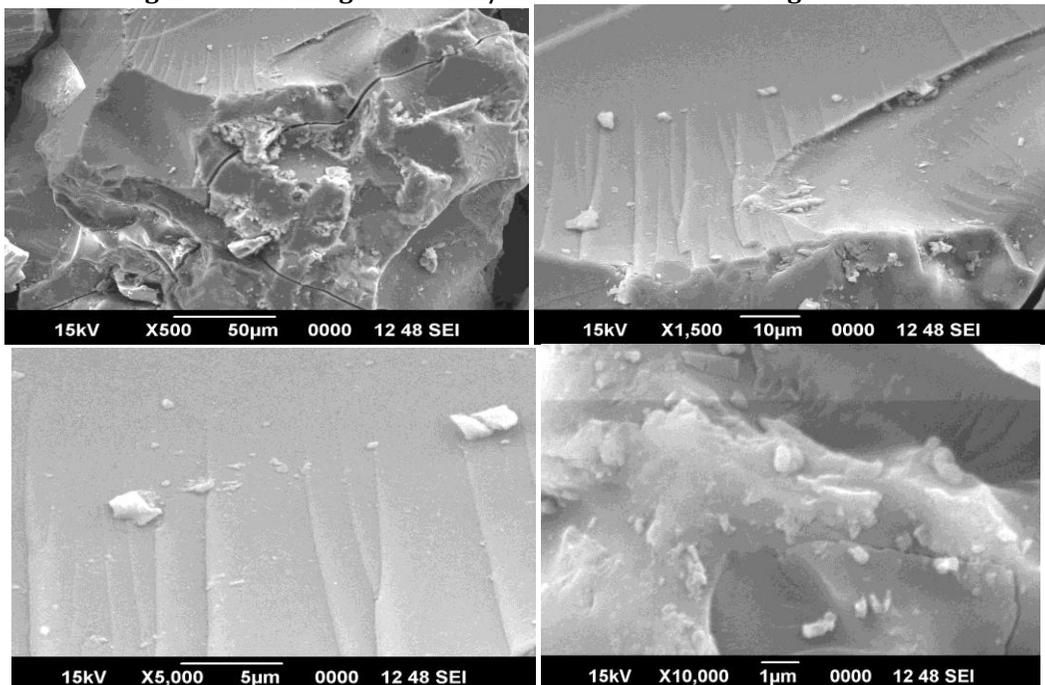


Figure 7: SEM images of PMAA/HQ-MB at different magnifications

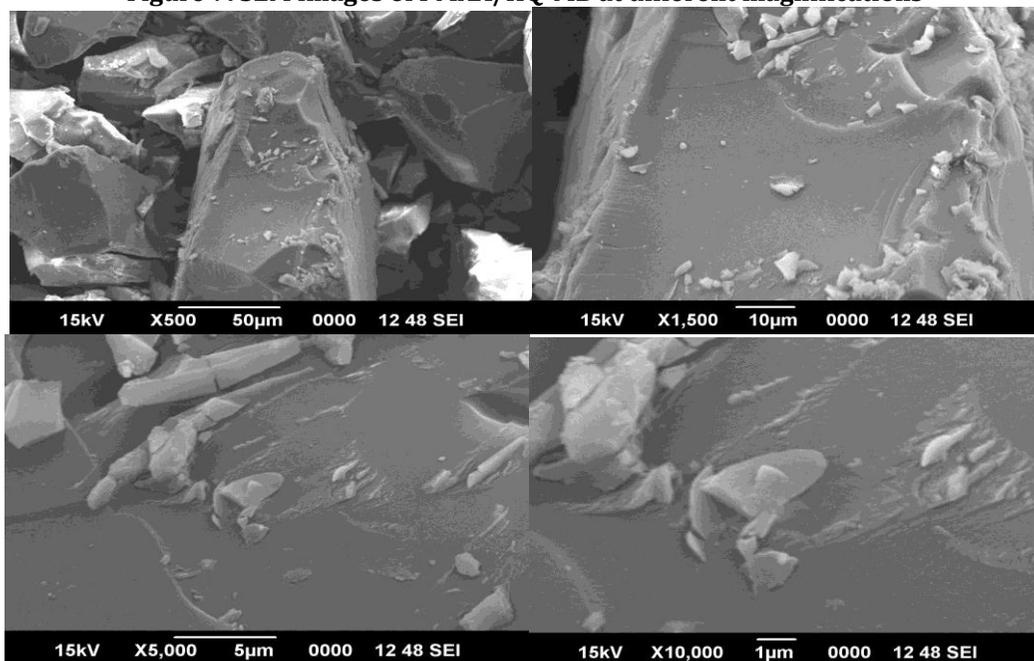


Figure 8: Adsorption of MB on PMAA/CAT and PMAA/HQ at different time intervals

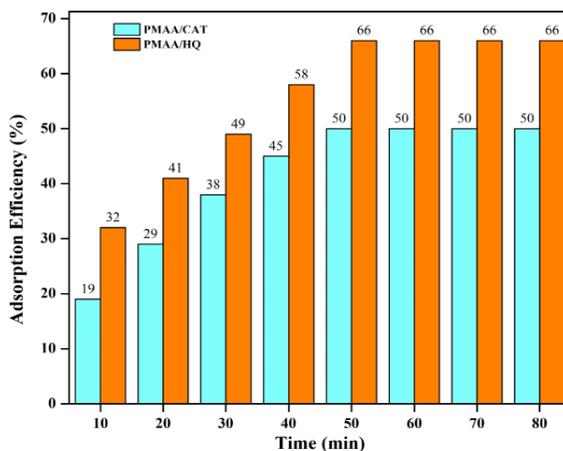


Figure 9: Adsorption of MB on PMAA/CAT at different dye concentrations

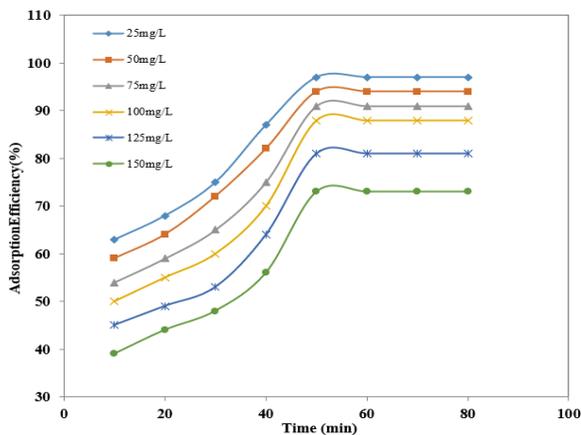


Figure 10: Adsorption of MB on PMAA/HQ at different dye concentrations

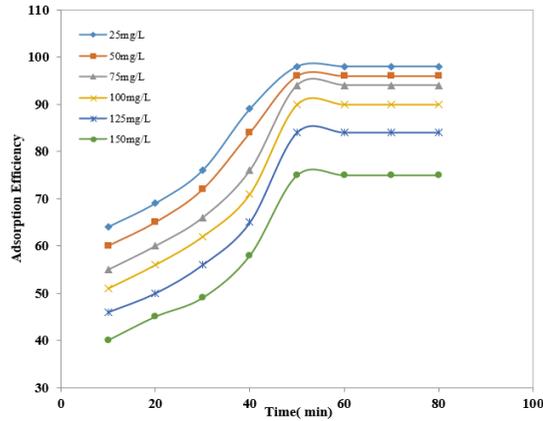


Figure 11: Effect of adsorbent dosage on adsorption of MB at constant pH and dye concentration

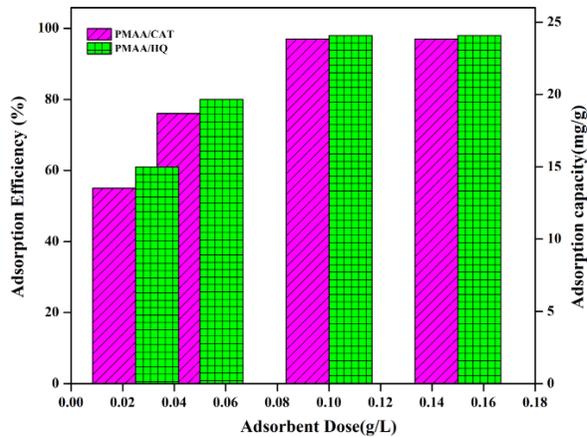


Figure 12: Effect of pH on adsorption of MB for PMAA/CAT and PMAA/HQ at constant dye concentration and adsorbent dose

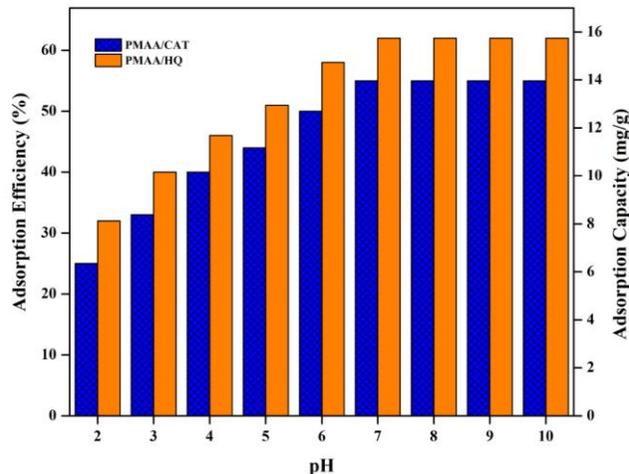


Figure 13: Freundlich model on the adsorption of MB using PMAA/CAT

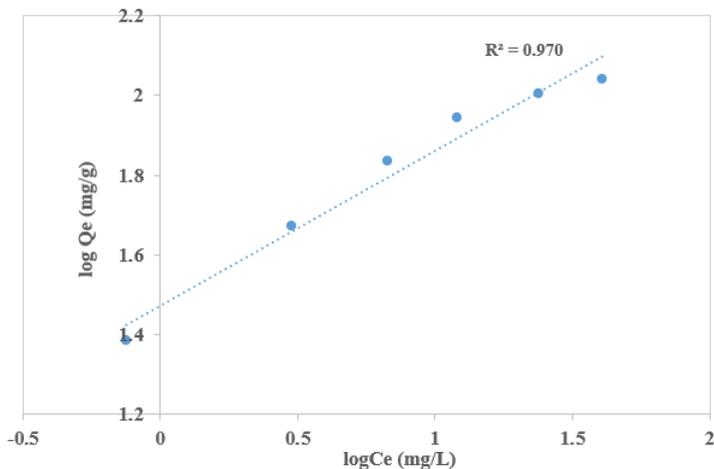


Figure 14: Freundlich model on the adsorption of MB using PMAA/HQ

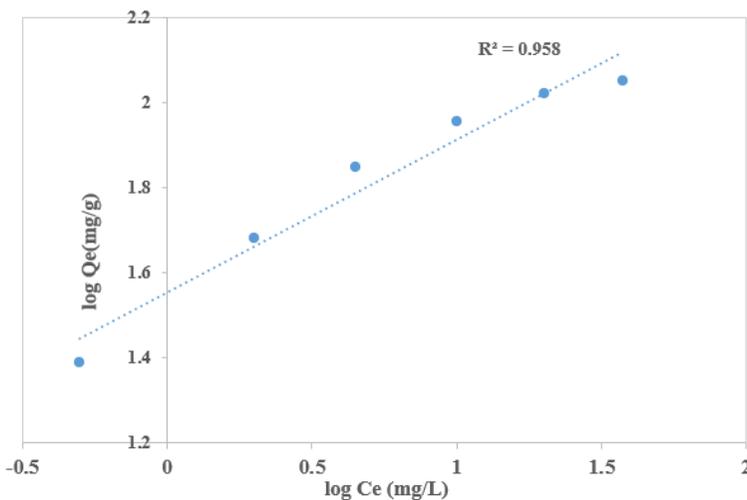


Figure 15: Langmuir model on the adsorption of MB using PMAA/CAT

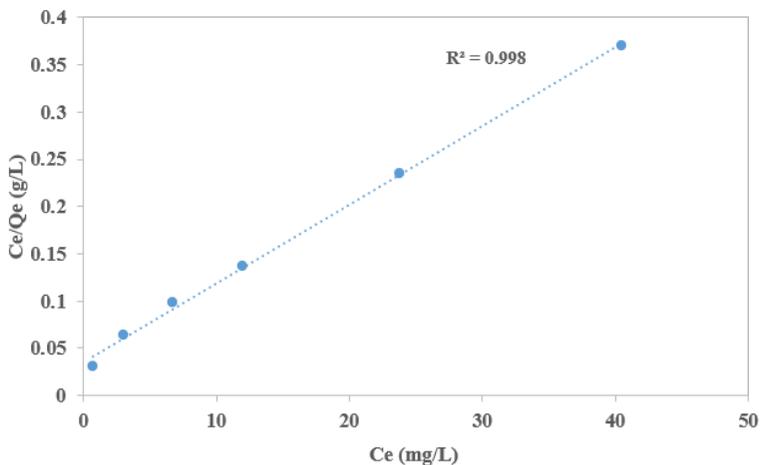


Figure 16: Langmuir model on the adsorption of MB using PMAA/HQ

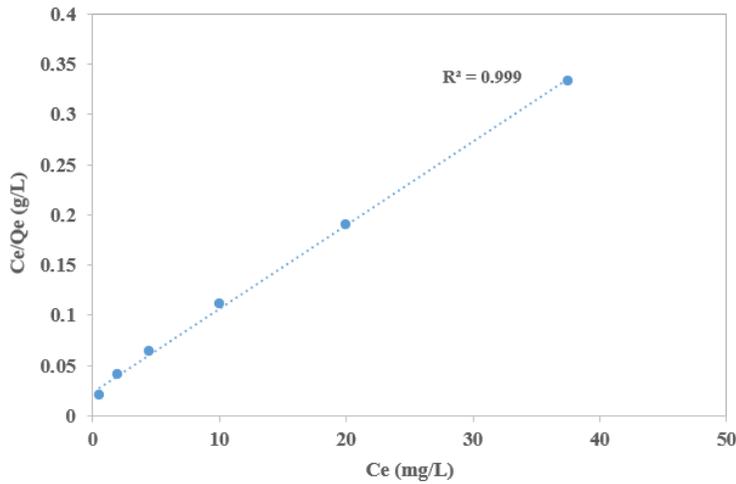


Figure 17: Plots of pseudo first order model for the removal of MB using PMAA/CAT at different dye concentration

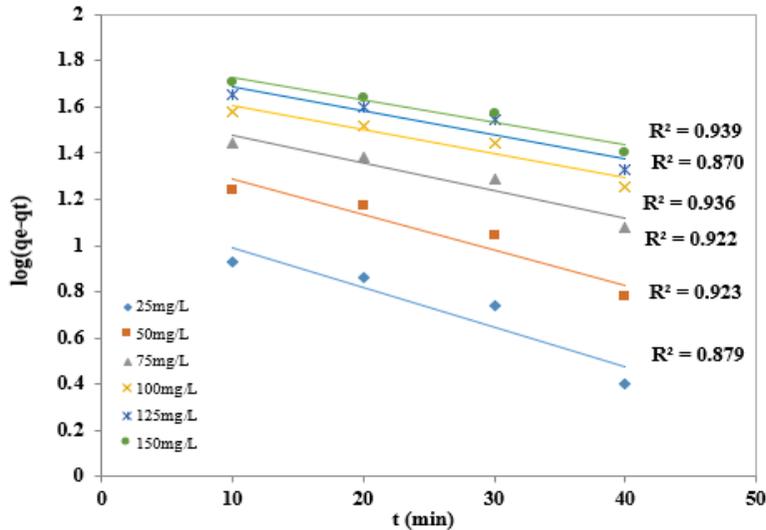


Figure 18: Plots of pseudo second order model for adsorption of MB using PMAA/CAT at different dye concentration

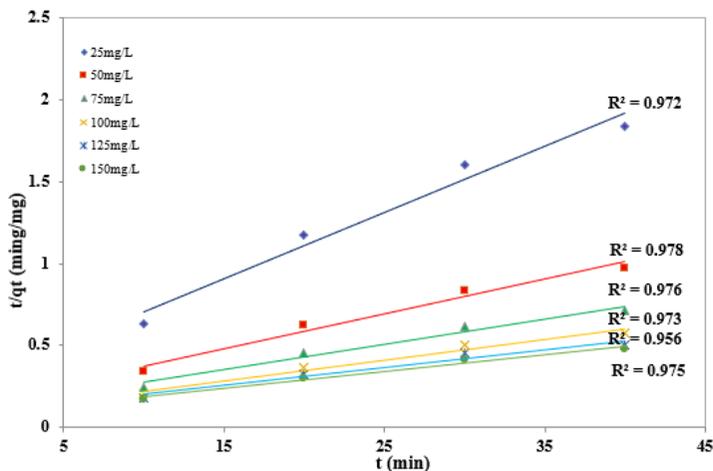


Figure 19: Plots of pseudo first order model for the removal of MB using PMAA/HQ at different dye concentration

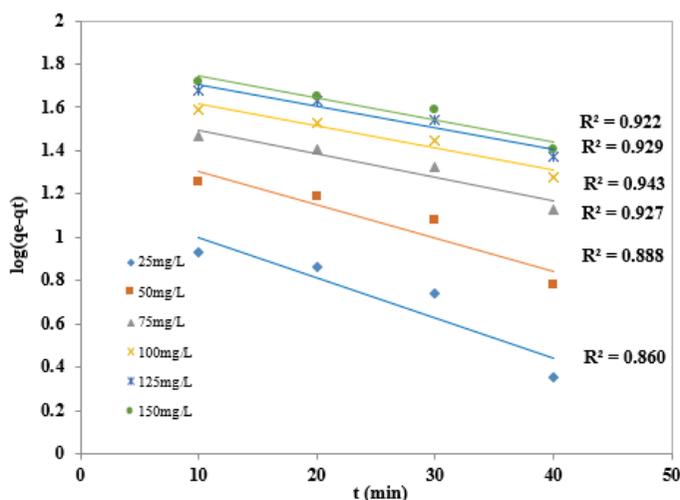
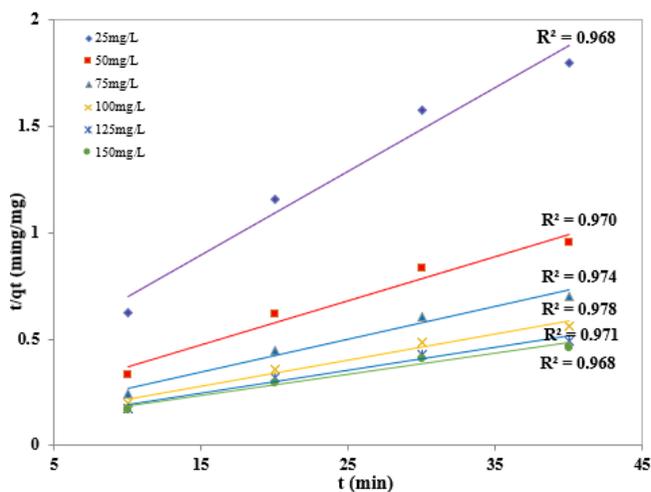


Figure 20: Plots of pseudo second order model for adsorption of MB using PMAA/HQ at different dye concentration



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