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Adsorption of Methylene Blue Dye Using Polymethacrylic Acid Functionalized with Dihydroxy Benzene

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Abstract

Poly Methacrylic Acid was synthesized by radical polymerization and functionalized with dihroxy benzenes like catechol and catechol-hydroquinone by an oxidative decarboxylation using potassium dichromate as an oxidant. The percentage of substitution was found to be 91% and 95.7% for the synthesized PMAA/CAT and PMAA/CAT-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. From the study, the adsorption capacity of PMAA/CAT and PMAA/CAT-HQ were found to be13.3mg/g and14.7mg/g with the adsorption efficiencies of 95% and 98% at pH 7 studied for 50 minutes with the initial dye concentration of 15mg/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 analysis and found to have considerable changes after the adsorption of the methylene blue. Adsorption isotherms like Langmuir and Freundlich models were carried out 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.

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1.INTRODUCTION

The introduction of waste products into the environment is a significant problem. Dyes have been commonly used in many branches of industry, such as textile, paper, leather dying cosmetics, pharmaceutical and food, effluents from those industries are the main contributor to water pollution. There are more than 1,00,000 commercially available dyes 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 industries [1-3]. Discharging of highly coloured 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 organisms and human being[4-6]. Methylene blue (MB) with complex aromatic molecular structure is the widely used organic substance for dying 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 wastewater[7]. Most of the dyes are stable to photodegradation and biodegradation [8-10]. Thus, coloured wastewater poses a challenge to the conventional wastewater treatment techniques. There are several methods such as coagulation and flocculation[11], membrane separation[12], oxidation or Ozonation[13, 14], electrocoagulation[15] and adsorption[16] have been employed for removing dyes. Among these techniques, adsorption is the excellent, cheap, effective and potential technique for removing dyes from industrial effluents [17].

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 an organometallic 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 ability [18-20] 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 reaction [21].

In the present study, an attempt was made to modify the poly methacrylic acid with dihydroxy benzenes like catechol and catechol-hydroquinone. The modified poly methacrylic acid such as PMAA/CAT and PMAA/CAT-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, dye concentration, pH, and adsorbent dose were studied. The surface morphology of PMAA/CAT, PMAA/CAT-HQ, PMAA/CAT-MB and PMAA/CAT-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 for Pseudo first order and pseudo-second-order equation to determine its reaction mechanism.

2. MATERIALS AND METODS

2.1. Materials

Methacrylic acid (M.wt = 86.09g, M.Formula = $C_4H_6O_2$), AIBN (2methylpropionimide) (M.Wt = 161.24g, M.Formula = $C_8H_{12}N_4$), Methylene Blue (M.wt = 319g, M.formula = $C_{16}H_{18}ClN_3S$), Catechol, Hydroquinone (M.wt = 110.11g, M.Formula = $C_6H_6O_2$) were purchased from Sigma-Aldrich. Corp. Hydrochloric acid, Sodium hydroxide, Potassium dichromate ($K_2Cr_2O_7$) and Silver nitrate ($AgNO_3$) 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 initiator and it was chemically modified using potassium dichromate as an oxidant. The standard procedure[22] with slight modification was adopted to carry out the synthesis chemically modified PMAA with catechol and catechol- 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 equation [23].

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

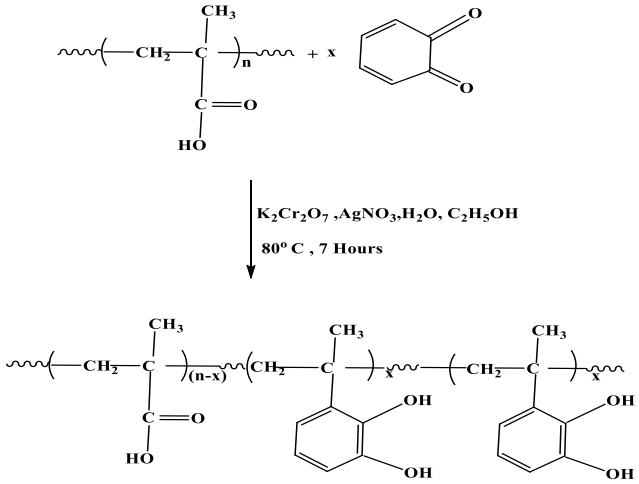
$$n_{MAA} = \frac{m - n_{HQ}M_{VHQ}}{M_{MAA}}$$

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

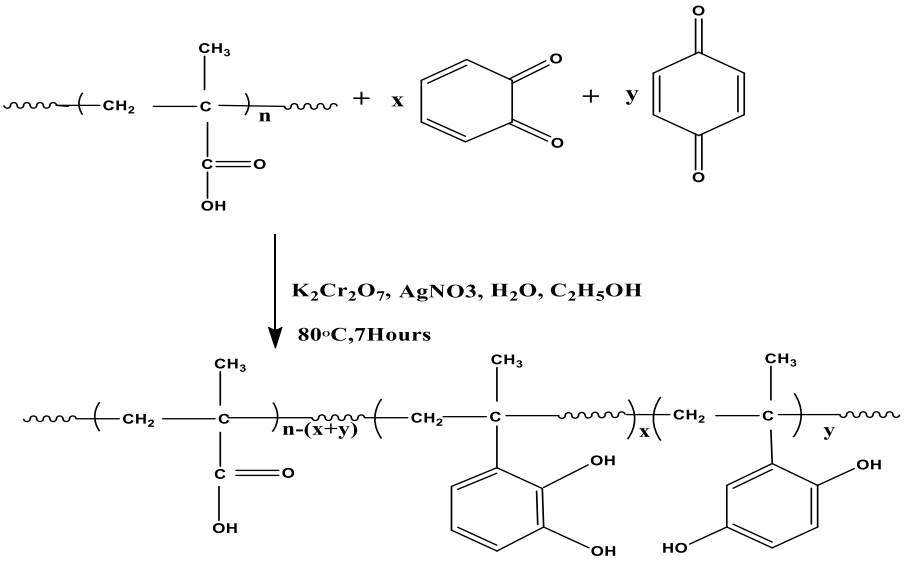
n_{MAA} = Number of moles of methacrylic acid present in PMAA-HQ

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).



Scheme 1: The mechanism for the chemical modification of PMAA with catechol



Scheme 2: The mechanism for the chemical modification of PMAA with catechol-hydroquinone

2.3. Batch adsorption studies

Equilibrium adsorption studies were carried out with different concentrations of MB dye like 5mg/L, 7.5mg/L, 10mg/L, 12.5mg/L, 15 mg/L, 17.5 mg/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 was allowed up to 70 minutes and the test solution was removed from the shaker and centrifuged. The solution bearing unabsorbed MB concentration was measured using UV specrophotomer at 668nm.

The concentration of MB adsorbed on the synthesised polymer was attained 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 contact time and dye concentration were also studied on the adsorption of MB with 0.1g of adsorbent, different initial dye concentrations like 5mg/L, 7.5mg/L, 10 mg/L, 12.5 mg/L, 15 mg/L and 17.5 mg/L at constant pH of 7 maintained at the temperature 31˚C.

In order to examine 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 contact time, dye concentration and adsorbent dosage 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 , 0.075 g/L , 0.1g/L , 0.125 g/L , 0.150 g/L and the other parameters like contact time, pH and dye concentration were kept constant.

3. RESULTS AND DISCUSSION

3.1. Effect of substitution percentage

The oxidative decarboxylation conditions of minisci[24]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 which behaves like nucleophile and reacts with benzoquinone[24, 25].The degree of substitution of carboxylic acid group by catechol or catechol-hydroquinone 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/Catechol-hydroquinone for different reaction time like 1,2,3,4,5,6 and 7 hrs were measured, and the results are given in terms of substitution percentage in figure.1 and table1. From the comparative results given in table and 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%, 90.5%, 90.6%, 90.8% and 91% for one to six hours for PMAA/CAT. The percentage of substitution for PMAA/CAT-HQ was found to be 56.8%, 59.2%, 71.5%, 84.2%, 95.5%, and 95.7% for one to sixth hour. The highest percentage of substitution found to be 91% and 95.7% for PMAA/CAT and PMAA/CAT-HQ at the optimum time sixth hour. [26]

Figure 1: The Percentage of substitution of PMAA/CAT and PMAA/CAT-HQ at different time intervals

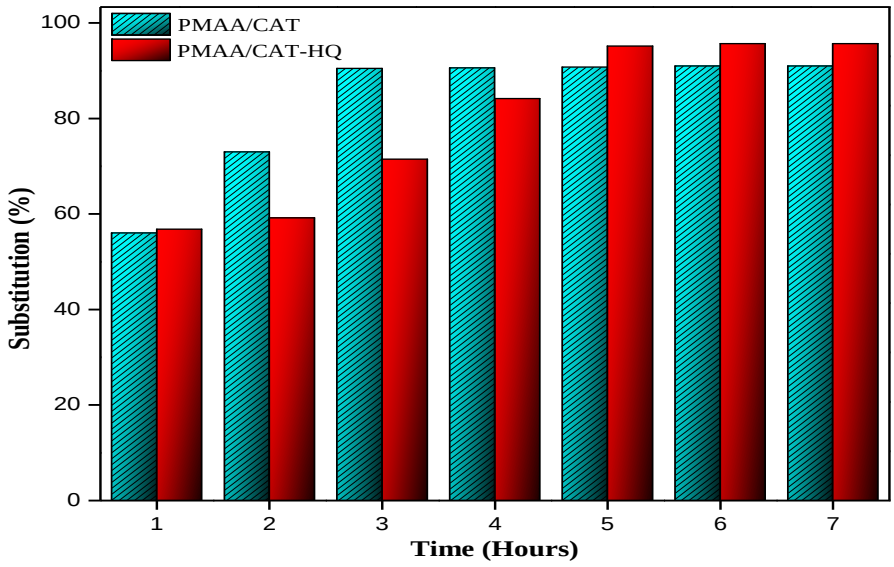


Table: 1 Percentage of substitution of dihydroxy benzene with PMAA

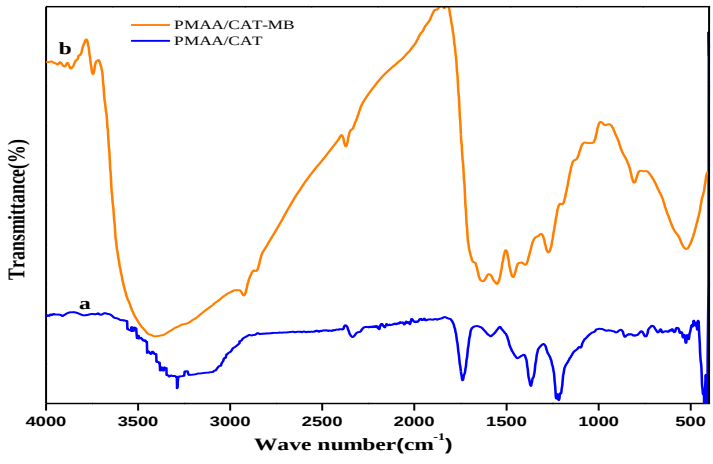
Time (Hours)	Substitution (%)	
	PMAA/CAT	PMAA/CAT-HQ
1	56.0	56.80
2	73.0	59.20
3	90.5	71.50
4	90.6	84.20
5	90.8	95.50
6	91.0	95.70
7	91.1	95.70

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

The FTIR spectral characterization was used to determine functional groups present in the compounds. FTIR spectra of PMAA/CAT and PMAA/CAT-MB, PMAA/CAT-HQ and PMAA/ CAT-HQ-MB before and after adsorption of MG dye are given in figures 2 and 3. The peak values and the corresponding stretching frequency of PMAA/CAT, PMAA/CAT-HQ, PMAA/CAT-MB and PMAA/CAT-HQ-MB are summarised in table 2. The IR spectrum of PMAA/CAT (Figure 2) exhibits a band from 3055-3553 cm^{-1}, indicates the O-H stretching[24], and there is a peak at 1739 cm^{-1} indicating C=O stretching[25], peak at 1591 cm^{-1} shows C=C aromatic stretching[26], peak at 1441 cm^{-1} shows methyl C-H bending, peak at 1368 cm^{-1} is due to C-C aromatic stretching and peak at 740 cm^{-1} is due to the presence o-substituted benzene. The IR spectrum of PMAA/CAT-HQ (Figure.3) exhibits a band at 3037-3547 cm^{-1} indicating O-H stretching, and there is a peak at 1591 cm^{-1} showing aromatic C=C stretching, peak at 1442 cm^{-1} indicating methylene C-H bending, peak at 1370 cm^{-1} showing C-C aromatic stretching, 1227 cm^{-1} indicates C-O stretching, peak at 815 cm^{-1} is due to p-substituted benzene and peak at 750 cm^{-1} is due to o-substituted benzene[27].

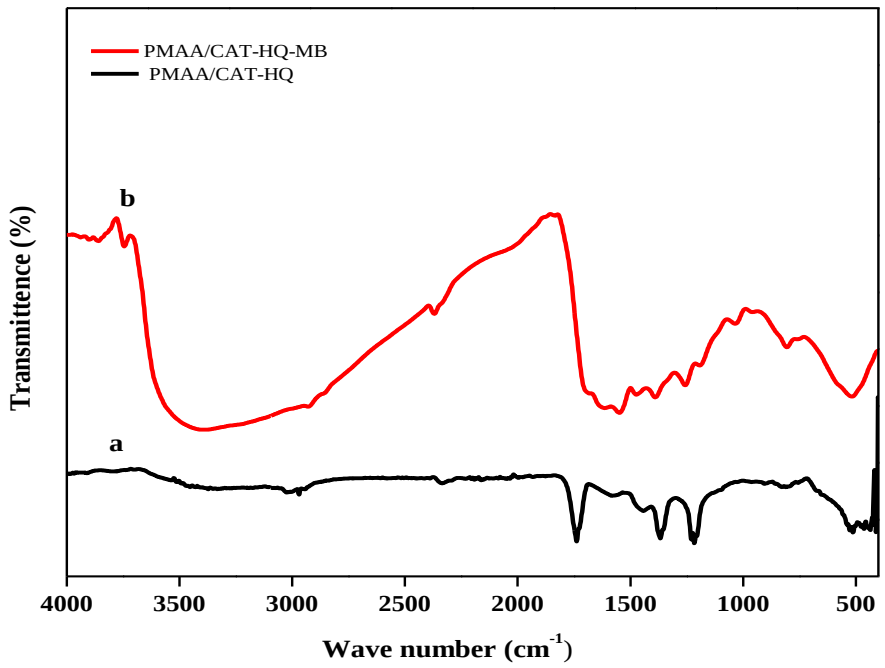
It is evident from the figures 2 and 3 that the some of the peaks are shifted or highly intense or appeared newly or disappeared from the IR spectrum for modified PMAA after the adsorption of methylene blue. The FTIR spectrum of PMAA/CAT-MB is found to exhibits a new peaks at 1628 cm^{-1} indicating C=N stretching[28], a band from 3412 cm^{-1} is due to O-H stretching[29], a peak for methyl C-H bending exhibits at 1464 cm^{-1}, a peak at 1267 cm^{-1} indicating C-O stretching[30]. The IR spectrum of PMAA/CAT-HQ-MB exhibits a new peak at 2372cm^{-1} indicating N-H stretching, a band from 3710 -2400 cm^{-1} is due to O-H stretching, a peak at 1463 cm^{-1} is due to C-H methyl bending[31] and a peak at 1273 cm^{-1} is due to C-O stretching[32] are found to shift to higher frequency. The changes in the spectral values observed reveals that there is a possible interaction of functional groups in the modified polymers with MB in the course of adsorption process.

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



a-PMAA/CAT b-PMAA/CAT-MB

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



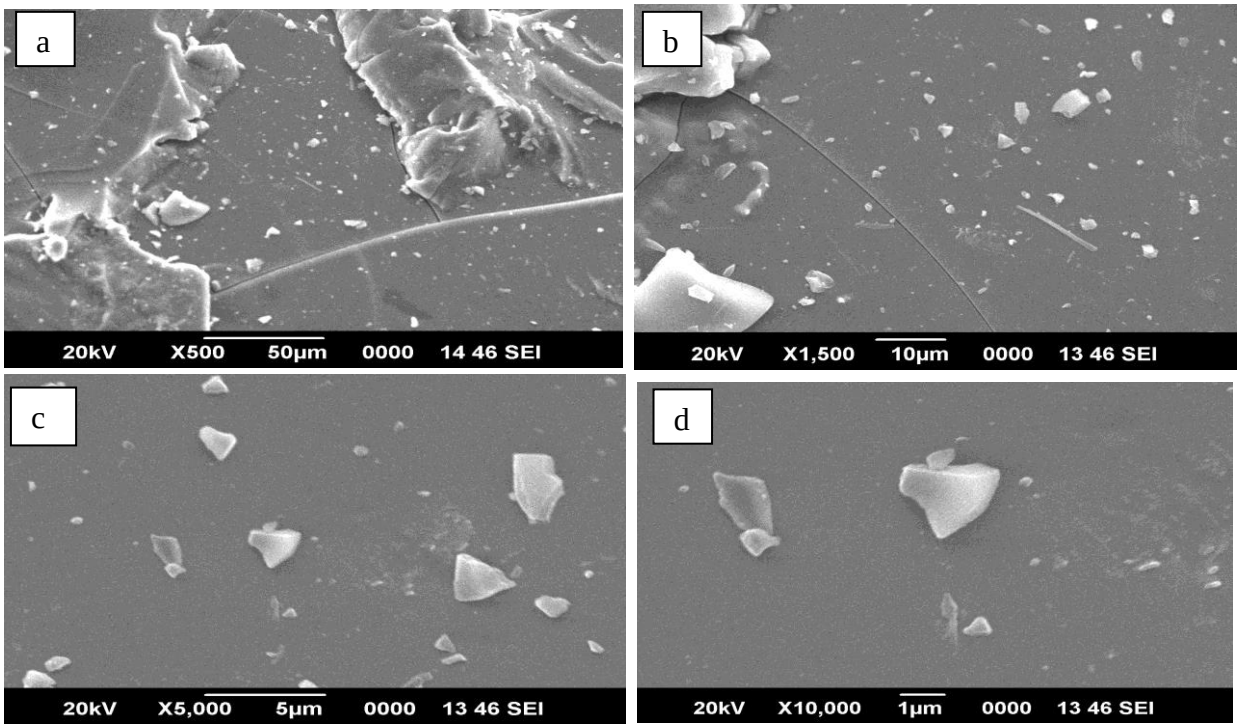
a-PMAA/CAT-HQ b-PMAA/CAT-HQ-MB

Table: 2 FTIR Spectra for modified PMAA before and after adsorption of MB

Band position(cm^{-1})				Assignment
PMAA/CAT	PMAA/CAT-HQ	PMAA/CAT-MB	PMAA/CAT-HQ-MB	
3055-3553	3037-3547	3412	3710-2400	O-H stretching
-	-	-	2372	N-H stretching
1739	1736	-	-	C=O stretching
-	-	1628	1627	C=N stretching
1591	1591	-	1552	C=C aromatic stretching
1441	1442	1464	1463	Methyl C-H bending
1368	1370	1393	1398	C-C aromatic stretching
1219	1219	1267	1273	C-O stretching
-	815	-	806	p-substituted benzene
740	750	816	757	o-substituted benzene

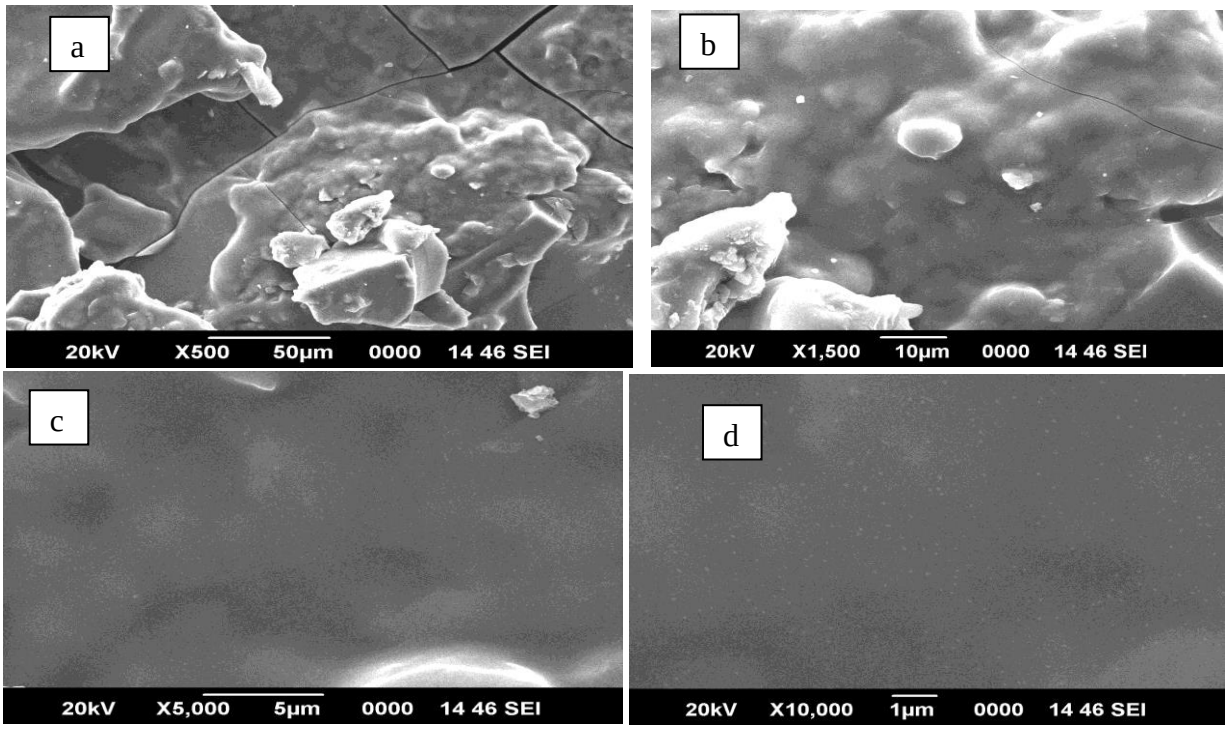
The SEM images of Modified PMAA with catechol and catechol - hydroquinone before and after the adsorption of MB dye at different magnifications are given in figures 4,5 6 and 7. The PMAA/CAT exhibit sheet with uneven surface like arrangement and PMAA/CAT-HQ shows stacked sheet like morphology[33] before adsorption as it is evident from the SEM figures 4 and 5. After the adsorption of Methylene blue dye, the SEM image was found to change in to fracture surface like morphology[34] in PMAA/CAT-MB and sponge fracture[35] like morphology in PMAA/CAT-HQ-MB and this confirms that the adsorbate are adsorbed on the surface of the synthesized redox polymers.

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



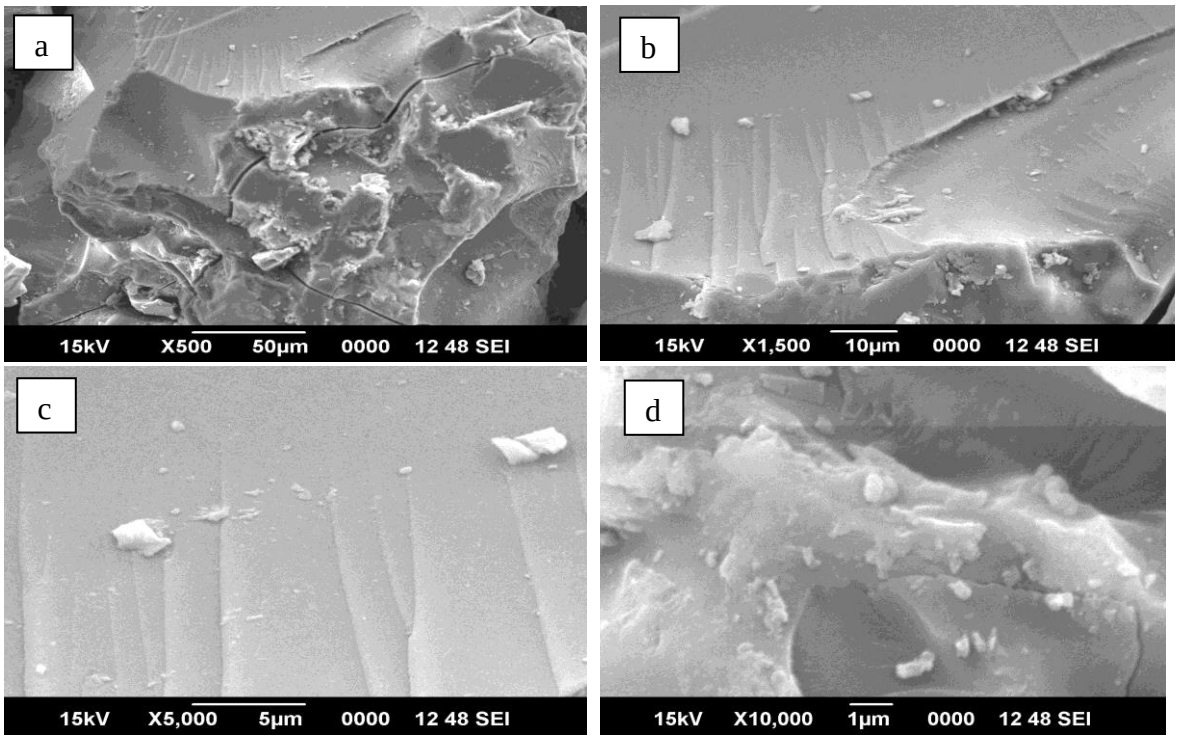
a-500x b-1500x c-5000x d-10000x

Figure 5: SEM images of PMAA/CAT-HQ at different magnifications before adsorption of MB



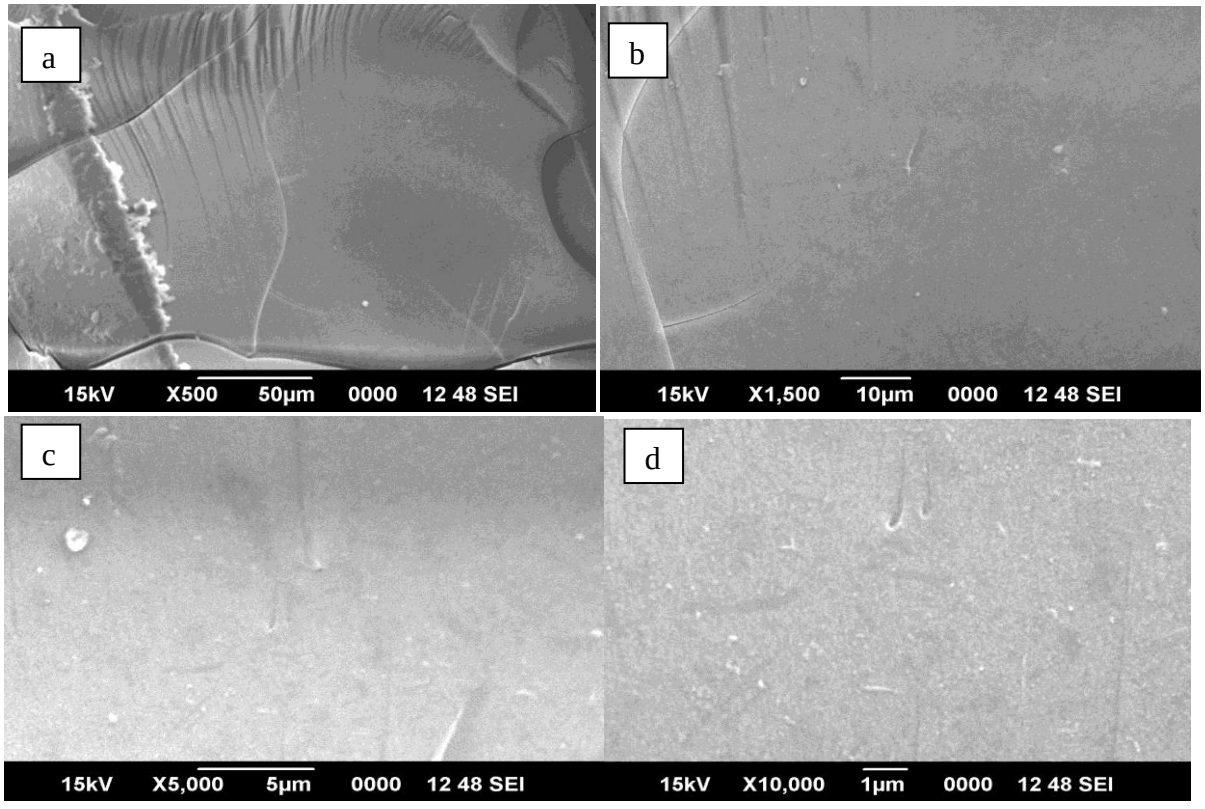
a-500x b-1500x c-5000x d-10000x

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



a-500x b-1500x c-5000x d-10000x

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



a-500x b-1500x c-5000x d-10000x

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, 20min, 30min, 40min, 50min, 60min and 70minutes with the fixed dye concentration of 15mg/L, adsorbent dose 0.1g/L, pH of 7 and at the temperature 31˚C and the values are given in table.3 and their comparative results are shown in figures 8 and 9. At the initial time of 10 min, the adsorption efficiency of PMAA/CAT for 15mg/L was found to be 28 %. The adsorption of MB dye was found to increase with increase in time up to 50 minutes with the adsorption efficiency of 89 % and 98 % for PMAA/CAT and PMAA/CAT-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 catechol- hydroquinone.

Figure 8: Adsorption of MB using PMAA/CAT at different dye concentrations

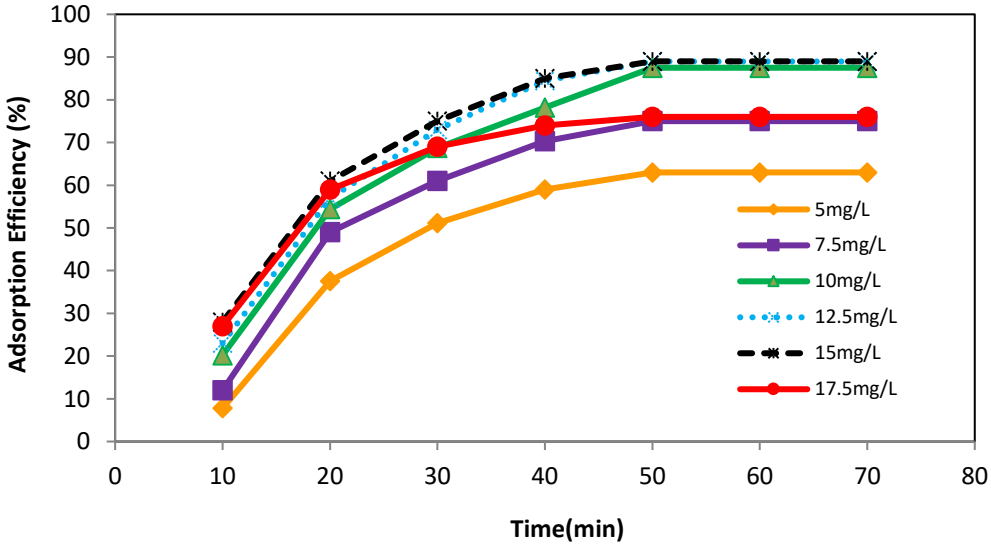
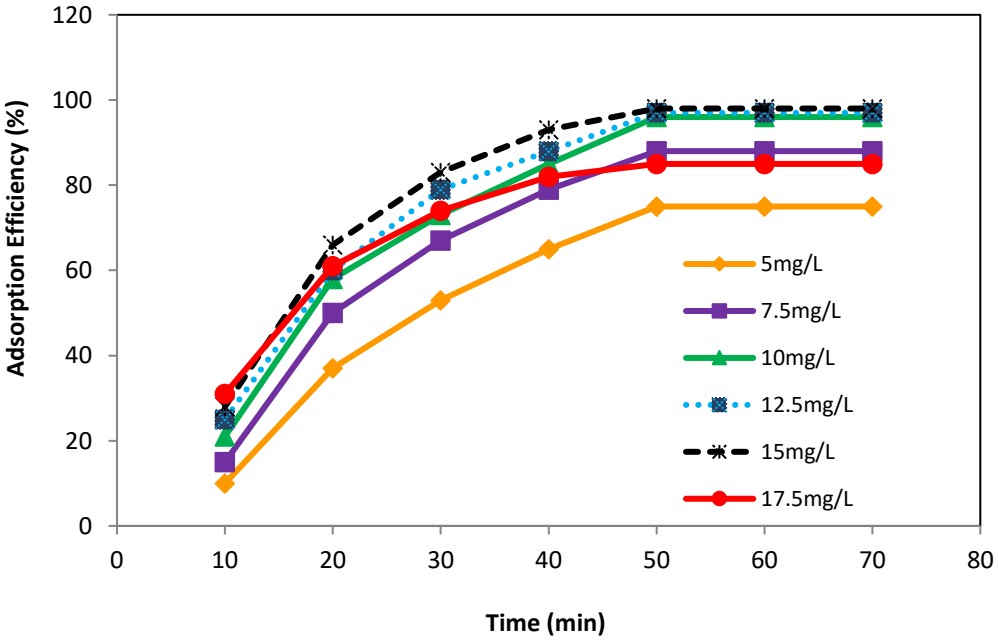


Figure9: Adsorption of MB using PMAA/CAT-HQ at different dye concentrations



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/CAT-HQ. The experiments were carried out at different dye concentrations like 5 mg/L, 7.5 mg/L, 10 mg/L, 12.5 mg/L, 15 mg/L and 17.5 mg/L, and at constant pH of 7, adsorbent dose 0.1g/L, and at the fixed time of 50 min and the results are given in figures 8 and 9 and the comparative values are given in table 3. From the figure and table values, it is seen that the adsorption efficiency increases with increase in the dye concentration[36] and reached the optimum value at 15mg/L with efficiency of 89% for PMAA/CAT at the time intervals of 50 mins. The adsorption efficiency at different dye concentration was found to be 63%, 75%, 87.5%, 88% , and 89% and the adsorption capacity was found to be 3.15 mg/L, 5.62 mg/L, 8.75 mg/L , 11.0 mg/L and 13.35 mg/L for PMAA/CAT [37]. Further increase of dye concentration to 17.5 mg/L, the adsorption efficiency and capacity was found to decrease[38] and this confirms the optimum dye concentration as 15mg/L. The adsorption efficiency at different dye concentration was found to be 75%, 88%, 96%, 97%, and 98% and the adsorption capacity was found to be 3.75 mg/L, 6.6 mg/L ,9.60 mg/L, 12.13 mg/L and 14.70 mg/L for PMAA/CAT-HQ. The efficiency of adsorption was found to decrease for PMAA/CAT and PMAA/CAT-HQ specifically at the concentration of 17.5mg/L and this may be due to decrease in the number of active sites on the adsorbent and this can be explained, the number of active sites would have been greater initially which would become saturated above a certain dye concentration.[38]

Table 3: The Adsorption Efficiency and Capacity of synthesised polymers at different MB dye concentrations and time intervals

$[MB]_o$ (mg/L)	Time (min)	PMAA/CAT		PMAA/CAT-HQ	
		A.E (%)	A.C (mg/g)	A.E (%)	A.C (mg/g)
5.0	10	7.80	0.39	10	0.50
	20	37.6	1.88	37	1.85
	30	51.1	2.55	53	2.65
	40	59.0	2.95	65	3.25
	50	63.0	3.15	75	3.75
	60	63.0	3.15	75	3.75
	70	63.0	3.15	75	3.75
7.5	10	12.0	0.90	15	1.13
	20	49.0	3.70	50	3.75
	30	61.0	4.60	67	5.03
	40	70.3	5.27	79	5.93
	50	75.0	5.62	88	6.60
	60	75.0	5.62	88	6.60
	70	75.0	5.62	88	6.60
10.0	10	20.0	02.00	21	2.10
	20	54.4	05.44	58	5.80
	30	68.7	06.87	73	7.30
	40	78.2	78.20	85	8.50
	50	87.5	87.50	96	9.60
	60	87.5	87.50	96	9.60
	70	87.5	87.50	96	9.60
12.5	10	23.0	02.90	25	03.13
	20	57.0	07.13	60	07.50
	30	73.0	09.20	79	09.88
	40	84.5	10.57	88	11.00
	50	88.0	11.00	97	12.13
	60	88.0	11.00	97	12.13
	70	88.0	11.00	97	12.13

	10	28.0	04.20	28	04.20
	20	61.0	09.15	66	09.90
	30	75.0	11.25	83	12.45
15.0	40	85.0	12.75	93	13.95
	50	89.0	13.35	98	14.70
	60	89.0	13.35	98	14.70
	70	89.0	13.35	98	14.70
	10	27.0	04.72	31	05.43
	20	59.0	10.32	61	10.68
	30	69.1	12.10	78	13.65
17.5	40	74.0	12.95	83	14.53
	50	76.0	13.30	85	14.87
	60	76.0	13.30	85	14.87
	70	76.0	13.30	85	14.87

A.E- Adsorption Efficiency, A.C-Adsorption Capacity

Table 4: Adsorption Efficiencies and capacities of PMAA/CAT and PMAA/CAT-HQ at different adsorbent concentration

Conc (g/L)	PMAA/CAT		PMAA/CAT-HQ	
	A.E (%)	A.C (mg/g)	A.E (%)	A.C (mg/g)
0.025	54	8.1	60	9.00
0.050	65	9.8	70	10.5
0.075	75	11.3	84	12.6
0.100	89	13.3	98	14.7
0.125	89	13.3	98	14.7
0.150	89	13.3	98	14.7

A.E- Adsorption Efficiency, A.C-Adsorption Capacity

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, 0.075 g/L, 0.1g/L, 0.125 g/L, 0.150 g/L keeping the other parameters like pH, contact time and the dye concentration. The results are summarised in figure 10 and table 4. 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 dye[39], 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 89% and 13.3mg/g and the adsorption efficiency and capacity was found to be 98 % and 14.7 mg/g for PMAA/CAT-HQ. 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 sites on the synthesized redox polymers. [40]

Figure 10: A.E and A.C of PMAA/CAT and PMAA/CAT-HQ

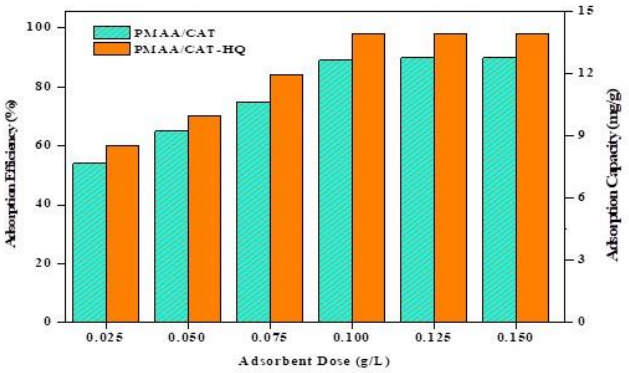


Table 4: Adsorption Efficiencies and capacities of PMAA/CAT and PMAA/CAT-HQ at different adsorbent concentration

Conc (g/L)	PMAA/CAT		PMAA/CAT-HQ	
	A.E (%)	A.C (mg/g)	A.E (%)	A.C (mg/g)
0.025	54	8.1	60	9.00
0.050	65	9.8	70	10.5
0.075	75	11.3	84	12.6
0.100	89	13.3	98	14.7
0.125	89	13.3	98	14.7
0.150	89	13.3	98	14.7

A.E-Adsorption Efficiency, A.C-Adsorption Capacity

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, adsorbent dose and contact time constant and the comparative values are given in figure 11 table.5. 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 which confirms that the effective optimum pH as 7 .

The MB dye removal was high at the pH 7 with the adsorption efficiency of 89% and 98% for PMAA/CAT and PMAA/CAT-HQ with the adsorption capacities of 13.35 mg/L and 14.7 mg/L. The presence of ionisable groups such as carboxyl and phenolic groups on the polymeric structure can affect the percentage of removal of dye and the adsorption capacities of the polymers[41]. 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 molecules[42]. At pH 7, the adsorption efficiency is increased as the electrostatic interaction between dye molecule and polymer is increased which is illustrated in scheme 3 and 4, this confirms that the favourable adsorption is at higher pH and not favoured at lower pH[43,44].

Figure 11: A.E and A.C of PMAA/CAT and PMAA/CAT-HQ at different pH

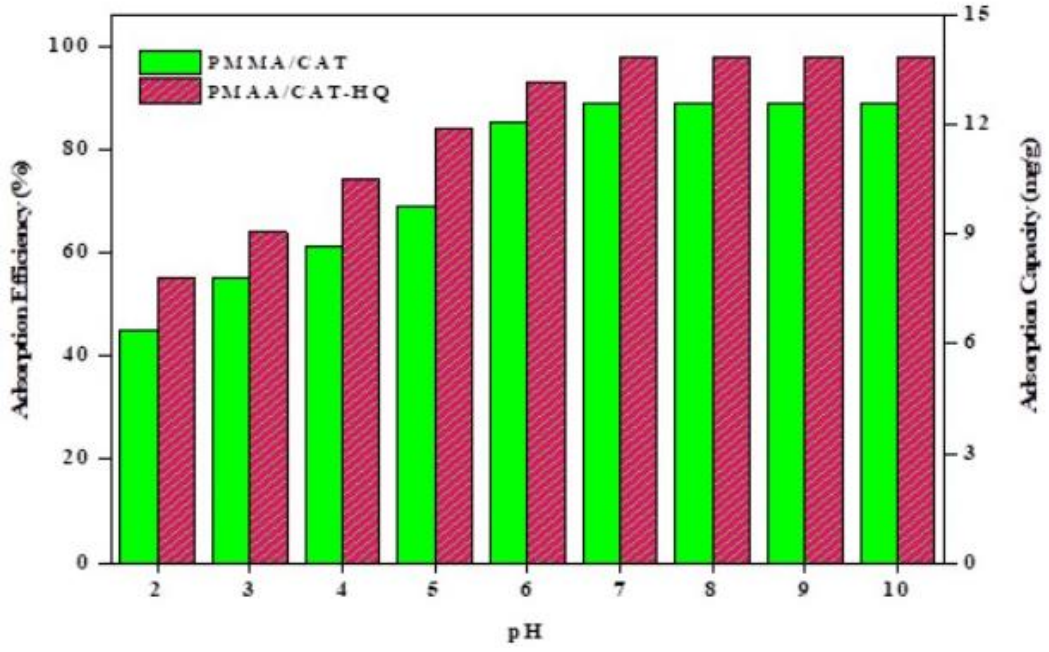
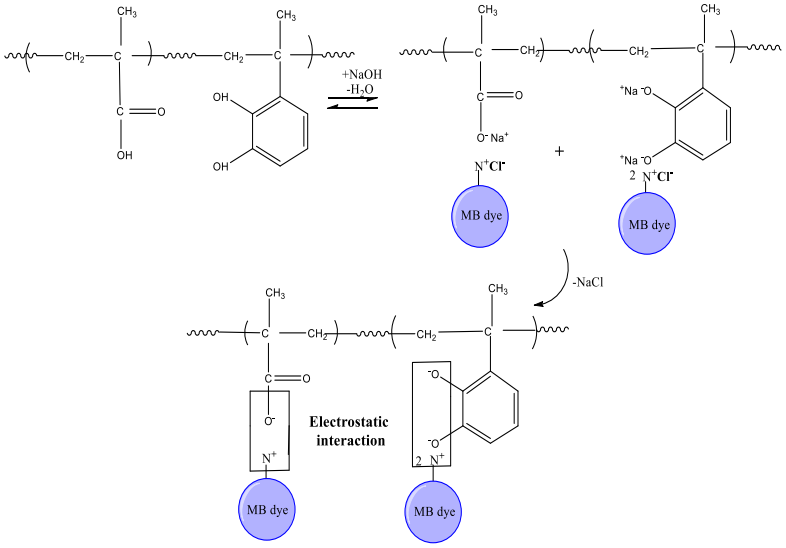


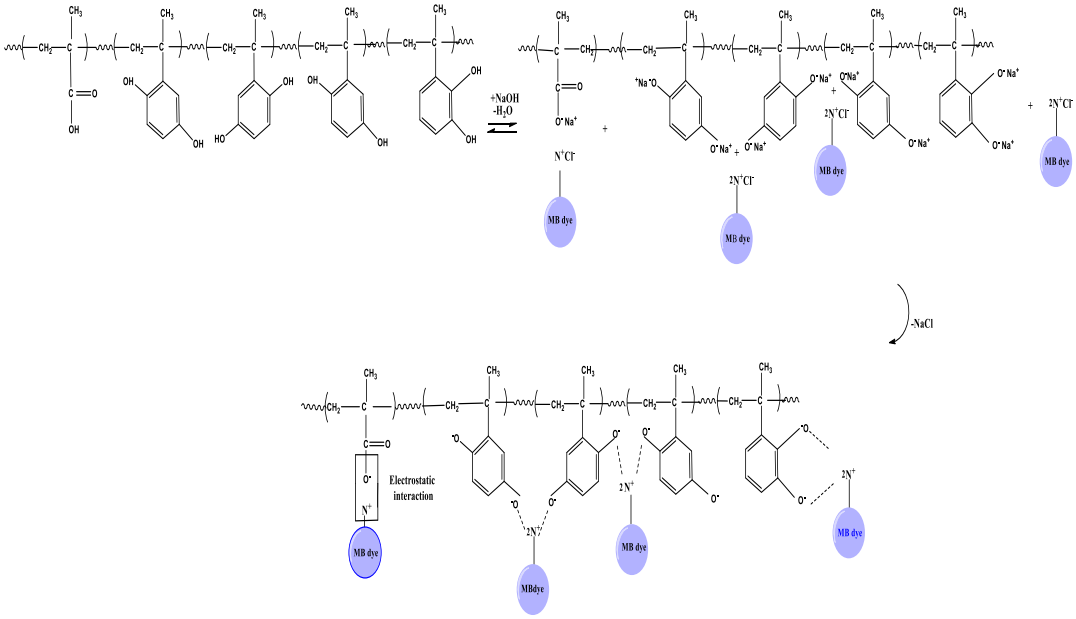
Table 5: Adsorption Efficiencies and Capacities of PMAA/CAT and PMAA/CAT-HQ at different pH

pH	PMAA/CAT		PMAA/CAT-HQ	
	A.E (%)	A.C (mg/g)	A.E (%)	A.C (mg/g)
2	45	06.75	55	08.25
3	55	08.25	64	09.60
4	61	09.15	74	11.10
5	69	10.35	84	12.60
6	85	12.75	93	14.00
7	89	13.35	98	14.70
8	89	13.35	98	14.70
9	89	13.35	98	14.70
10	89	13.35	98	14.70

A.E-Adsorption Efficiency, A.C-Adsorption Capacity



Scheme 3 Electrostatic interaction between MB and PMAA /CAT



Scheme 4 Electrostatic interaction between MB and PMAA /CAT-HQ

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 of dye 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 interms 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 $LogQ_e = 1/n \log C_e + \log K_f$ 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 from 5-15mg/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 and Langmuir model which are shown in figures 12,13 14 and 15 and the corresponding correlation coefficients and the isotherm constants were calculated and are presented in table.6. The monolayer and multilayer adsorption capacities for PMAA/CAT were found to be 3.20mg/g and 2.40mg/g and the mono and multilayer capacities were found to 3.06mg/g and 5.07 mg/g for PMAA/CAT-HQ as shown in table.

The correlation coefficient is a measure of degree of relationship present between the linearly related variables. The correlation coefficient values for Langmuir[47] are closer to unity with the values of R^2=0.940 for PMAA/CAT and R^2=0.962 for PMAA/CAT-HQ than the correlation coefficient for Freundlich[48] with R^2=0.930 and 0.944 for PMAA/CAT and PMAA/CAT-HQ as shown in the table 6. From the result it is evident that the adsorption of MB on PMAA/CAT and PMAA/CAT-HQ follows the Langmuir isotherm model[49].

Figure 12: Freundlich isotherm model for the adsorption of MB using PMAA/CAT

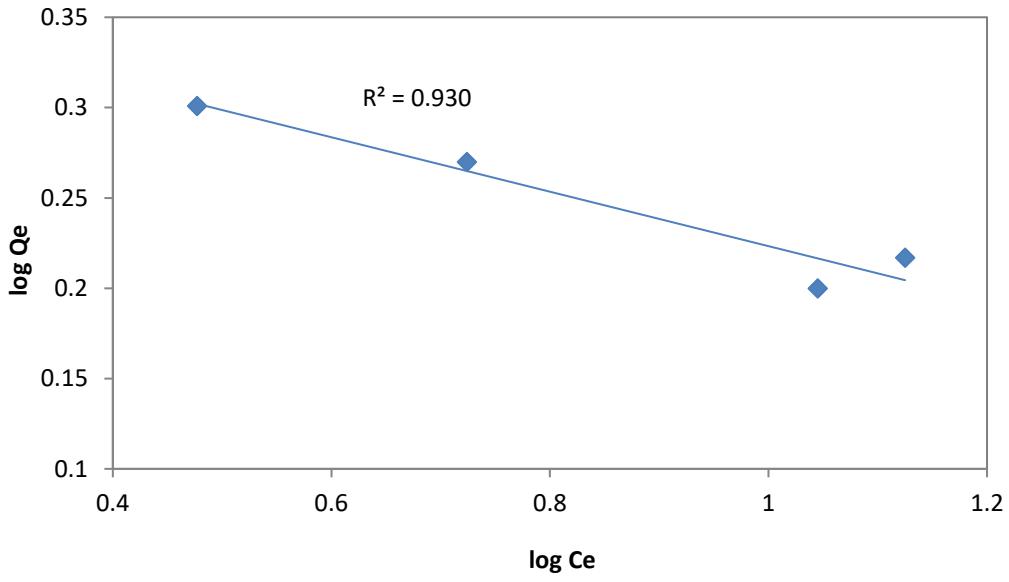


Figure 13: Langmuir isotherm model for the adsorption of MB using PMAA/CAT

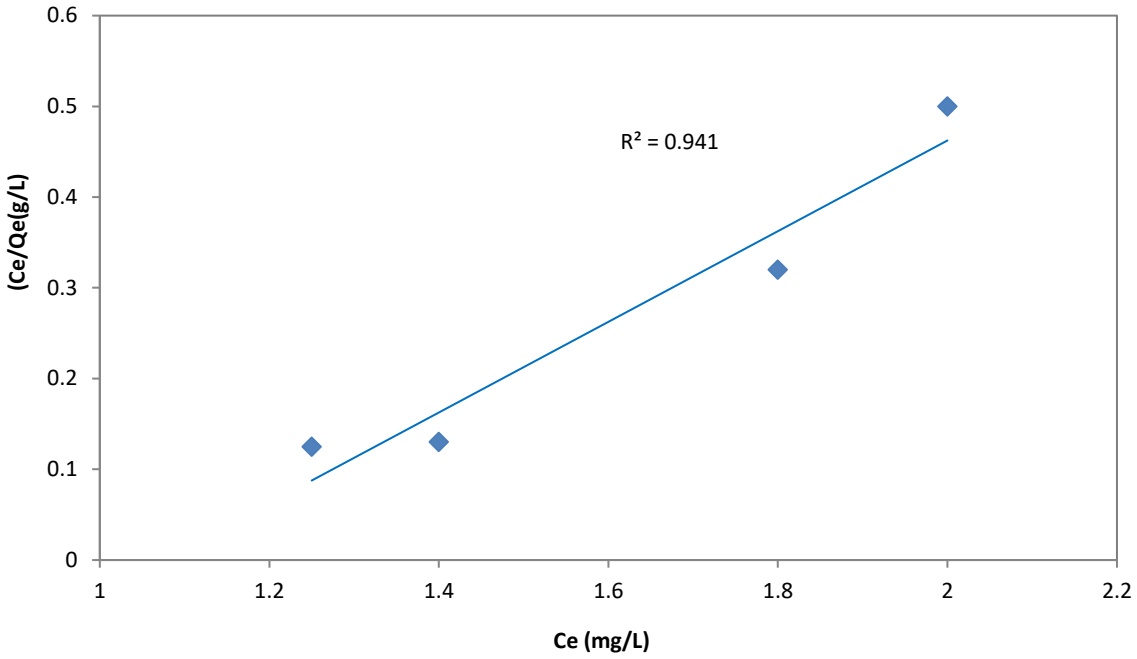


Figure 14: Freundlich isotherm model for the adsorption of MB using PMAA/CAT-HQ

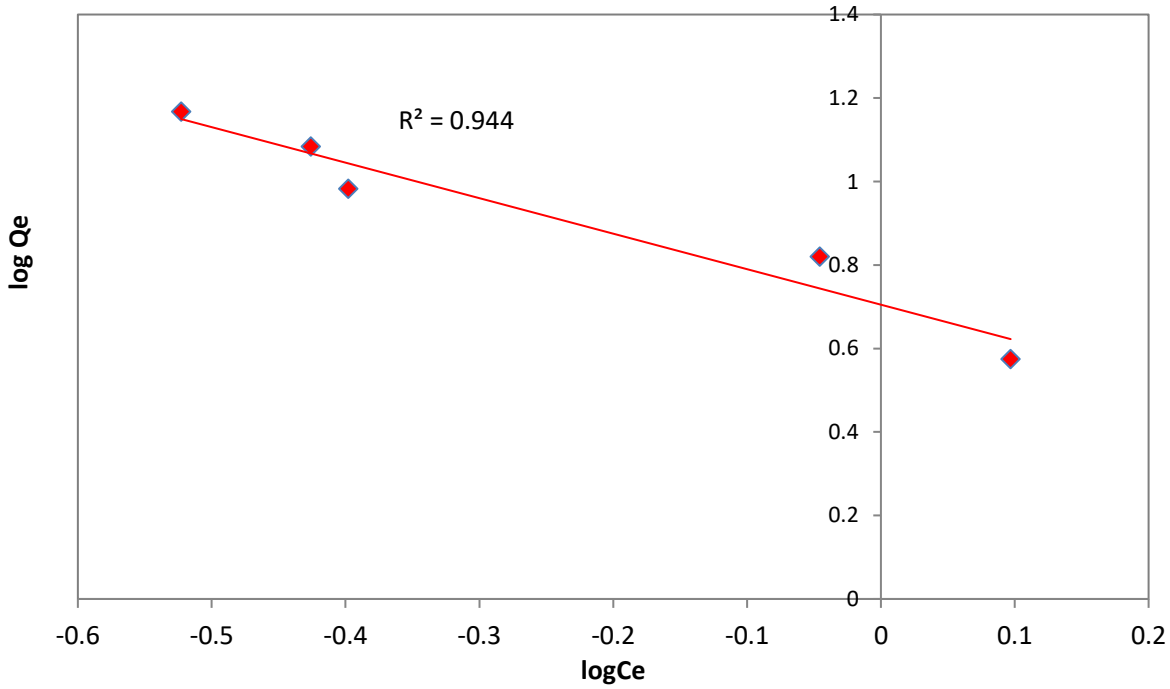


Figure 15: Langmuir isotherm model for the adsorption of MB using PMAA/CAT-HQ

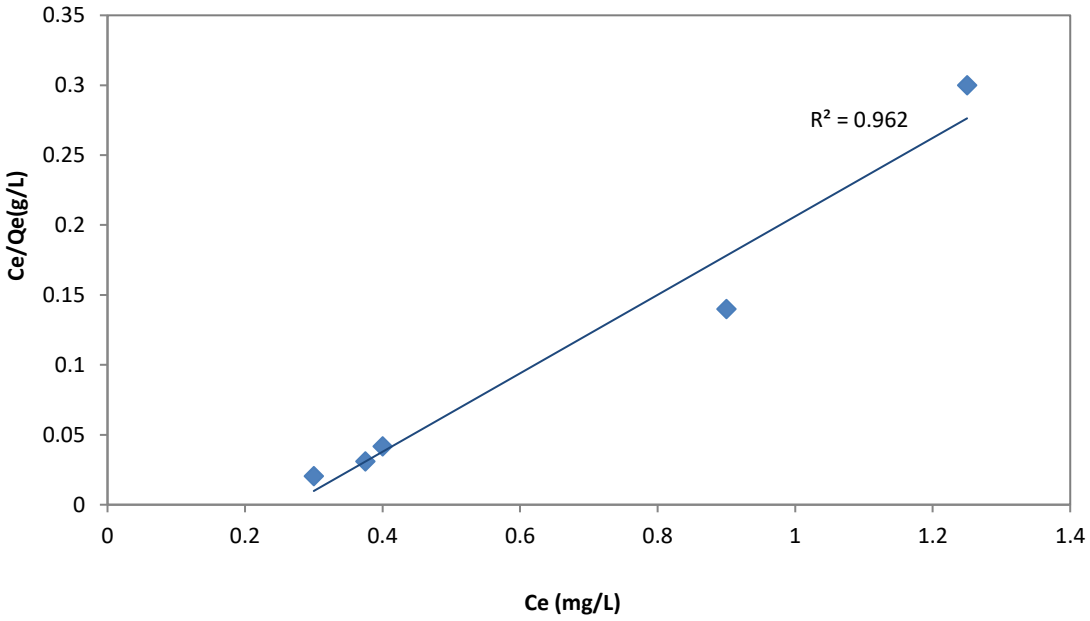


Table 6: Comparison of Freundlich and Langmuir Adsorption parameters for the adsorption of MB using PMAA/CAT and PMAA/CAT-HQ

Adsorbent	Freundlich			Langmuir			
	K_f (mg/g)	n	R^2	Q_{max} (mg/g)	K_L	R_L	R^2
PMAA/CAT	2.40	1.54	0.930	3.20	0.58	0.08	0.940
PMAA/CAT-HQ	5.07	1.17	0.944	3.60	3.73	0.02	0.962

3.5. Study of Adsorption kinetics

Adsorption kinetics studies were carried out to understand the rate of adsorption of methylene blue dye on PMAA/CAT and PMAA/CAT-HQ using pseudo-first and pseudo second-order reactions.

Pseudo first order kinetic equation was proposed by Langergen and Svenska[50], which is expressed as Log (Qe-Qt) = log Qe-(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 Qe 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 process[51,52].

The pseudo-second-order reaction was proposed by Ho and Mckay[53] and it is represented by the linear equation t/Qt = 1/$k_2Q^2_e$+1/Q_e t Where k_2 ($gm.g^{-1}.min^{-1}$) is the second order rate constant. The pseudo second order kinetics is based on the assumption that the rate limiting step involves in chemisorption's process through a force 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 biosorption[54].

Figure 16: Plots of pseudo first order model for the removal of MB using PMAA/CAT at different dye concentrations

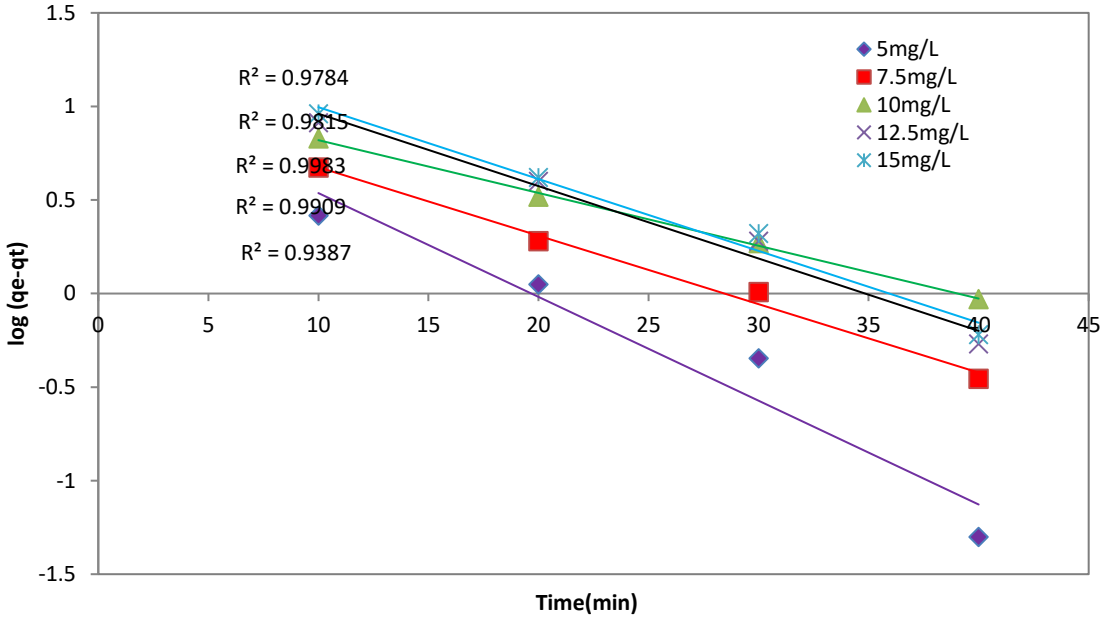


Figure 17: Plots of pseudo second order model for the removal of MB using PMAA/CAT at different dye concentrations

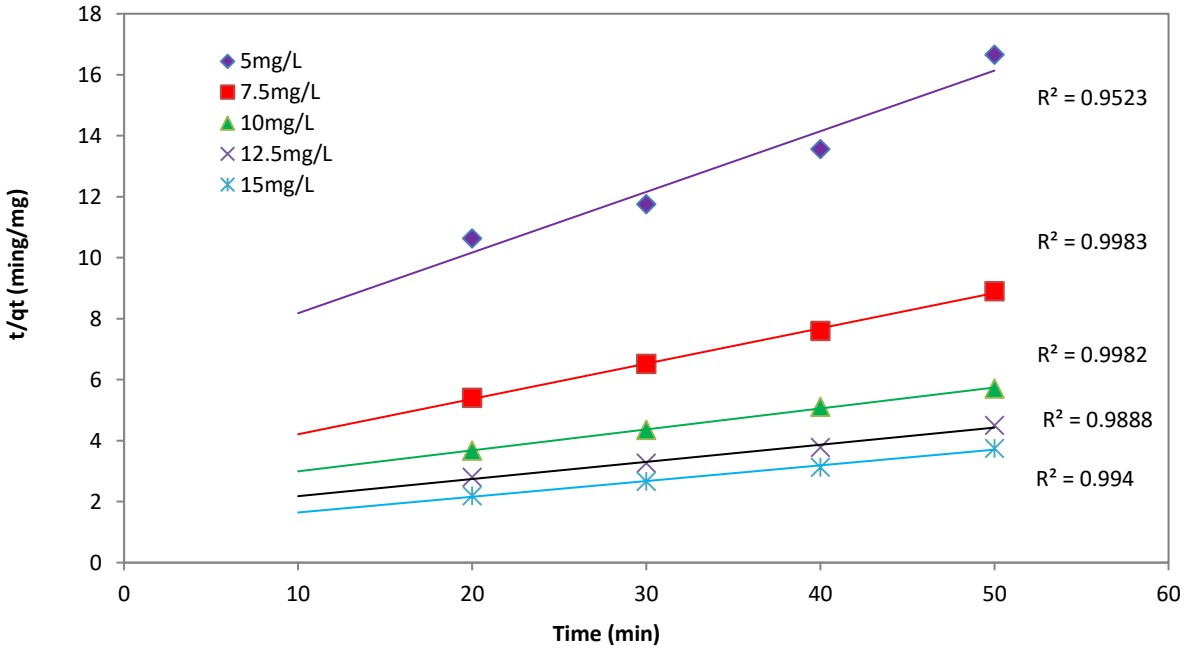


Figure 18: Plots of pseudo first order model for the removal of MB using PMAA/CAT-HQ at different dye concentrations

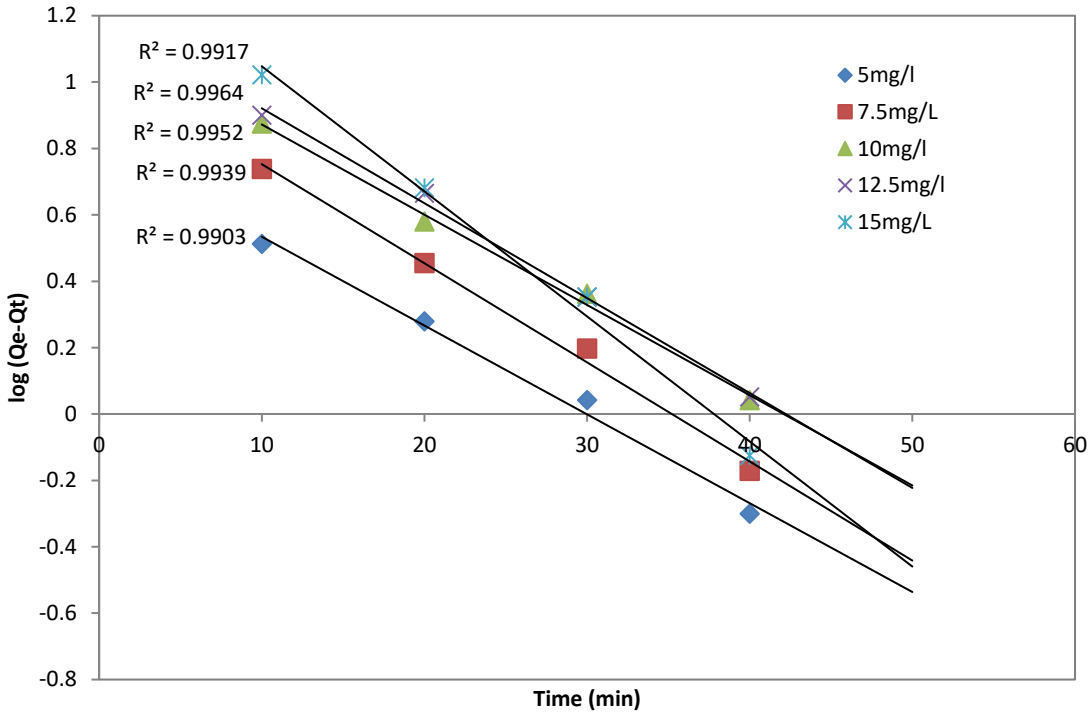


Figure 19: Plots of pseudo second order model for the removal of MB using PMAA/CAT-HQ at different dye concentrations

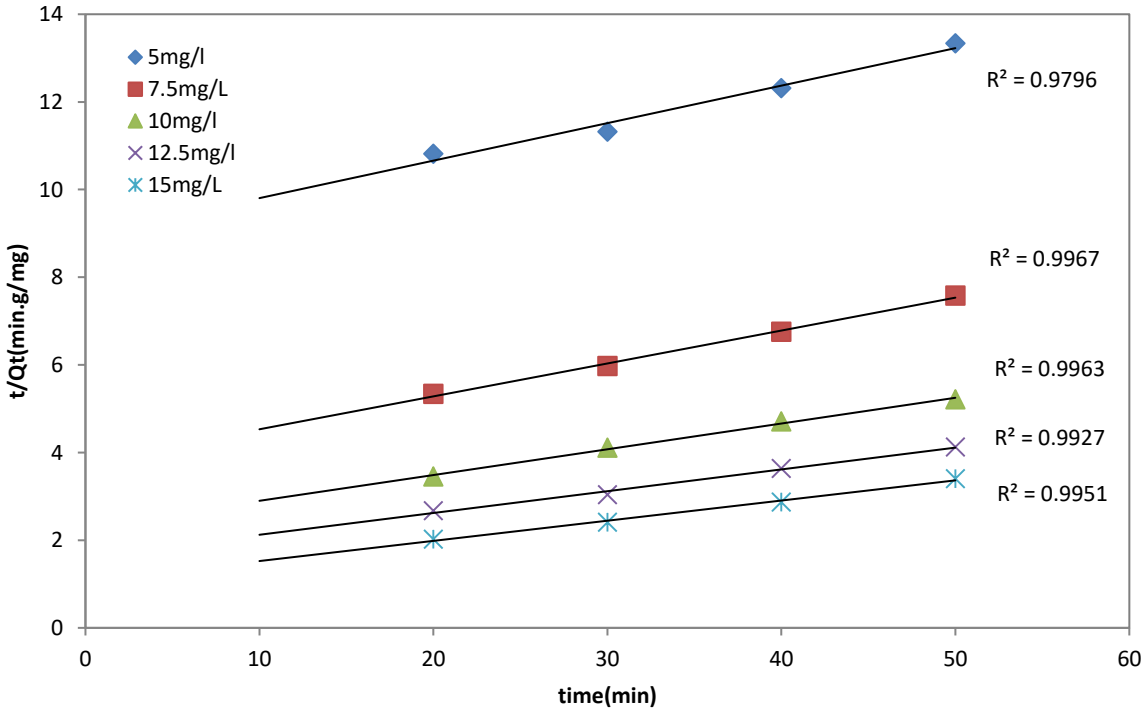


Table 7: Pseudo first and second order kinetic parameters for PMAA/CAT at different dye concentration

$[MB]_o$ (mg/L)	Pseudo first order			Pseudo second order		
	Q_{e1} (mg/g)	$k_1 \times 10^{-2}$ (min^{-1})	R^2	Q_{e2} (mg/g)	$k_2 \times 10^{-3}$ (g/mg/min)	R^2
5.0	12.33	12.3	0.938	5.05	6.30	0.952
7.5	11.01	08.3	0.990	8.69	4.33	0.998
10.0	12.60	06.4	0.998	14.70	2.01	0.998
12.5	22.28	08.7	0.978	17.85	1.90	0.988
15.0	24.00	08.7	0.981	19.60	2.30	0.994

$[MB]_o$ – Malachite green dye concentration

Table 8: Pseudo first and pseudo second order kinetic parameters for the adsorption of PMAA/CAT-HQ at different dye concentration

$[MB]_o$ (mg/L)	Pseudo first order			Pseudo second order		
	Q_{e1} (mg/g)	$k_1 \times 10^{-2}$ (min^{-1})	R^2	Q_{e2} (mg/g)	$k_2 \times 10^{-3}$ (g/mg/min)	R^2
5.0	06.34	6.17	0.990	11.70	0.82	0.980
7.5	11.25	6.88	0.994	13.31	1.50	0.997
10.0	27.73	6.26	0.995	17.00	1.50	0.996
12.5	16.10	6.70	0.996	20.12	1.52	0.995
15.0	26.56	8.68	0.992	21.70	2.12	0.995

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 5-15 mg/L on PMAA/CAT and PMAA/CAT-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/Qt versus t for the adsorption of MB at different concentration on PMAA/CAT and PMAA/CAT-HQ are given in figures 16,17 and 18,19 and their comparable results given in the tables 7 and 8. It is evident from the table 7 that the adsorption capacities, Qe_1 and Qe_2 increases with increase of dye concentration. The Qe_1, k_1 and R^2 values for PMAA/CAT at 15mg /L of MB dye concentration were found to be 24mg/g, 8.7x 10^{-2} $min^{-1}$and 0.981. The Qe_2, k_2 and R^2 values were found to be 19.06 mg/g 2.30x10^{-3}min.mg^{-1}. g^{-1}. This indicates that the adsorption of MB at different concentrations studied on PMAA/CAT shows better correlation coefficient values for pseudo second order kinetics model than pseudo first order model. The experimental qe values determined for Qe_2 are better than the qe values determined for Qe1. In addition, the rate constant (k_2) for pseudo second order reaction decreases on increasing the concentration of dye from 5mg/L to 12.5mg/L and this may be due to slowing down the reaction speed with increase in dye concentration and this controls the rate of adsorption[55]. The comparison of pseudo first and second order reaction for PMAA/CAT-HQ shows that the adsorption of MB at lower concentration like 5mg/L follows pseudo first order kinetics whereas the higher concentration follows second order kinetics which is evident from the table 8. In addition, the adsorption capacity values calculated for Pseudo first order (Qe_1) reaction was not in correlation with experimental values whereas, the adsorption capacity values calculated for pseudo second order (Qe_2) follows the experimental adsorption capacity values for all the concentration of MB dye studied for the PMAA/CAT-HQ[56].

4. CONCLUSION

In the present research work, PMAA had been modified with dihydroxy benzenes like catechol and catechol-hydroquinone using potassium dichromate as an oxidant. The modified PMAA such as PMAA/CAT and PMAA/CAT-HQ were used to as an adsorbent to remove methylene blue from aqueous solution at different conditions like pH, contact time, adsorbent dosage and the dye concentration. The FTIR spectra

and SEM images of PMAA/CAT, PMAA/CAT-HQ, PMAA/CAT-MB and PMAA/CAT-HQ-MB revealed that the adsorption of MB takes place on the modified PMAA and the adsorption varied depending on the pH, dye and adsorbent concentration. The adsorption efficiency and capacity varied depending on the polymers. The experimental study showed that the removal capacity of PMAA/CAT-HQ was found to be 14.7 mg/g with the adsorption efficiency of 98% which is greater than PMAA/CAT whose adsorption capacity and efficiencies are 13.3mg/g and 89%. 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 adsorption kinetics of MB using PMAA/CAT and PMAA/CAT-HQ was studied for pseudo first order and pseudo-second-order kinetics. The result showed that adsorption kinetics favoured to pseudo-second-order model with greater correlation coefficient values than the pseudo first order kinetics.

REFERENCES

[1] K. Ravikumar, B. Deebika, K. Balu, Decolourization of aqueous dye solutions by a novel adsorbent: application of statistical designs and surface plots for the optimization and regression analysis, J. Hazard. Mater. 122 (2005) 75–83.

[2] J.W. Lee, S.P. Choi, R. Thiruvenkatachari, W.G. Shim, H. Moon, Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes, Dyes Pigm. 69 (2006) 196–203.

[3] J.R. Easton, P. Cooper, Colour in Dye house Effluent, the Society of Dyers and Colorists, Alden, Oxford, 1995 pp. 9–21.

[4] P.K. Dutta, An overview of textile pollution and its remedy, Indian J. Environ. Prot.14 (1994) 443–446.

[5] K.C. Chen, J.Y. Wu, C.C. Huang, Y.M. Liang, S.C.J. Hwang, Decolorization of azo dye
using PVA-immobilized microorganisms, J. Biotechnol. 101 (2003) 241–252.

[6] R. Gong, Y. Ding, M. Li, C. Yang, H. Liu, Y. Sun, Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution, Dyes Pigm.64 (2005) 187-192.

[7] D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl.Clay Sci. 20 (2002) 295–300.

[8] W.T. Tsai, C.Y. Chang, M.C. Lin, S.F. Chien, H.F. Sun, M.F. Hsieh, Adsorption of acid
dye onto activated carbons prepared from agricultural waste bagasse by ZnCl2 activation, Chemosphere 45 (2001) 51–58.

[9] J. Yener, T. Kopac, G. Dogu, T. Dogu, Adsorption of Basic Yellow 28 from aqueous solutions with clinoptilolite and amberlite, J. Colloid Interface Sci. 294 (2006) 255–264.

[10] S. Wang, Y. Boyjoo, A. Choueib, A comparative study of dye removal using fly ash treated by different methods, Chemosphere 60 (2005) 1401–1407.

[11] J. Panswed, S. Wongchaisuwan, Mechanism of dye wastewater color removal by magnesium carbonate-hydrated basic, Water Sci. Technol. 18 (1986) 139–144.

[12] G. Ciardelli, L. Corsi, M. Marucci, Membrane separation for wastewater reuse in the textile industry, Resour. Conserv. Recycl. 31 (2000) 189–197.

[13] K. Swaminathan, S. Sandhya, A. Carmalin Sophia, K. Pachhade, Y.V. Subrahmanyam, Decolorization and degradation of H-acid and other dyes using ferrous-hydrogen peroxide system, Chemosphere 50 (2003) 619–625.

[14] M. Muthukumar, N. Selvakumar, Studies on the effect of inorganic salts on decolouration of acid dye effluents by ozonation, Dyes Pigm. 62 (2004) 221–228.

[15] A. Alinsafi, M. Khemis, M.N. Pons, J.P. Leclerc, A. Yaacoubi, A. Benhammou, A. Nejmeddine, Electro-coagulation of reactive textile dyes and textile wastewater, Chem. Eng. Process. 44 (2005) 461–470.

[16] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses, Chemosphere 61 (2005) 492–501.

[17] M. Mitchell, W.R. Ernst, G.R. Lightsey, Bull. Adsorption of textile dyes by activated carbon produced from agricultural, municipal and industrial-wastes, Environ. Contam. Toxicol. 19 (1978) 307–311.

[18] Saad Moulay, Polymers with dihydroxy/ dialkoxy benzene moieties, C.R. Chimie12(2009)577–601.

[19] SaadMoulay, Razika Mehdaoui, Poly (methacrylic acid) bound dihydroxy benzene units: redox polymers, J.Appl. Polym. Sci. 100 (2006) 954–961.

[20] Pickup, PeteraG ,Conjugatedmetallopolymers. Redoxpolymerswith interacting metal based redoxsites, J.Mater.Chem.9(1999)1641–1653.

[21] S.S.Kalaivani, T.Vidhyadevi, A.Murugesan, K.V.Thiruvengadaravi, D.Anuradha, S.Sivanesan, L.Ravikumar, Theuse of new modified poly(acrylamide) chelating resin with pendent benzo thiazole groups containing donor atoms in there moval of heavy metalions from aqueous solutions, WaterResour.Ind.5(2014)21–35.

[22]S.Moulay, R.Mehdaoui, Hydroquinone/catechol bearing polyacrylic acid: redox polymer, React.Funct.Poly.61(2004) 265–275.

[23] Saad Moulay,Razika Mehdaoui, Poly (methacrylicacid)-bound dihydroxy benzene units :redoxpolymers, J.Appl.Polym.Sci. 100(2006)954–961.

[24] Bertini, F.; Caronna, T.; Galli, R.; Minisci, F.; Porta, O. Chim Ind1972, 54, 425.

[25] Minisci, F. Top Curr Chem 1976, 62, 1.

[26] V.Vetriselvi, R.Jaya Santhi, Redox polymer as an adsorbent for the removal of chromium(VI) and lead(II) from the tannery effluents,Water Resources and Industry.10(2015) 39-52.

[27] Lulu Fan, Chuannan Luo, Xiangjun Li, Fuguang Lu, Huamin Qiu, Min Sun, Fabrication of novel magnetic chitosan grafted with graphene oxide to enhance adsorption properties for methyl blue, J. Hazardous Materials 215– 216 (2012) 272– 279.

[28] Yeoh Ying Ling, Faiz Bukhari Mohd Suah, Extraction of malachite green from waste water by using polymer inclusion membrane, Journal of Environmental Chemical Engineering 5 (2017) 785–794.

[29] Sara. Dawood, Tushar Kanti Sen, Chi Phan, Adsorption removal of Methylene Blue (MB) dye from aqueous solution by biochar prepared from Eucalyptus sheathiana bark: kinetic, equilibrium, mechanism, thermodynamic and process design, Desalination and Water Treatment 57 (2016) 28964–28980.

[30] Li Zhou, Jiachang Huang, Benzhao He, Faai Zhang, Huabin Li, Peach gum for efficient removal of methylene blue and methyl violetdyes from aqueous solution, Carbohydrate Polymers 101 (2014) 574– 581.

[31] Yun Xing and Guifang Wang, Poly (methacrylic acid)-modified sugarcane bagasse for enhanced adsorption of cationic dye, Environmental Technology Vol. 30, No. 6, May 2009, 611–619.

[32]. Zhang, Hua, et al. “Simultaneous Detection of Hydroquinone and Catechol on Electrochemical-Activated Glassy Carbon Electrode by Simple Anodic and Cathodic Polarization.” Journal of Solid-State Electrochemistry, 21 (2016) 735–745.

[33].Purkait, Taniya, et al. “Large Area Few-Layer Graphene with Scalable Preparation from Waste Biomass for High-Performance Supercapacitor.” Scientific Reports, vol. 7, no. 1, 2017

[34]. Le, Minh-Tai, and Shyh-Chour Huang. “Thermal and Mechanical Behavior of Hybrid Polymer Nanocomposite Reinforced with Graphene Nanoplatelets.” Materials, 8 (2015) 5526–5536.

[35]. Seidel, Juliana Matos, and Sônia Maria Malmonge. “Synthesis of PolyHEMA Hydrogels for Using as Biomaterials. Bulk and Solution Radical-Initiated Polymerization Techniques.” Materials Research, 3 (2000) 79–83.

[36] Mahmut Ozacar , I. Ayhan Sengil, Adsorption of metal complex dyes from aqueous solutions by pine sawdust, Bio resource Technology 96 (2005) 791–795.

[37] Taha M. Elmorsi1, Equilibrium Isotherms and Kinetic Studies of Removal of Methylene Blue Dye by Adsorption onto Miswak Leaves as a Natural Adsorbent, Journal of Environmental Protection, 2011, 2, 817-827.

[38] Solairaj Dhananasekaran , Rameshthangam Palanivel , Srinivasan Pappu , Adsorption of Methylene Blue, Bromo phenol Blue , and Coomassie Brilliant Blue by a-chitin nano particles, J. Advanced Research (2016) 7, 113–124.

[39] Mehdi Shirzad-Siboni, Alireza Khataee , Sang W. Joo Kinetics and equilibrium studies of removal of an azo dye from aqueous solution by adsorption onto scallop, J.Industrial and Engineering Chemistry 20 (2014) 610-615.

[40] R.L.Uma, V.C.Srivastava,I.D.Mall and D.H.Lataye,Rice Husk Ash as an Effective Adsorbent; Evaluation of Adsorptive Characteristics for Indigo Carmine dye.Journal of Environmental Management,90 (2009) 710-720.

[41] Gamze Guclu , Sibel Keles, Removal of Basic Dyes from Aqueous Solutions Using Starch-Graft-Acrylic Acid Copolymers, Journal of Applied Polymer Science, Vol.106, 2422–2426 (2007).

[42] Yun Xing and Guifang Wang, Poly (methacrylic acid)-modified sugarcane bagasse for enhanced adsorption of cationic dye, Environmental Technology, 30 (2009) 611–619.

[43] Gregorio Crini, Kinetic and equilibrium studies on the removal of cationic dyes from aqueous solution by adsorption onto a cyclodextrin polymer, Dyes and Pigments 77 (2008) 415-426.

[44] Rita Dhodapkar, N.N. Rao, S.P. Pande, S.N. Kaul, Removal of basic dyes from aqueous medium using a novel polymer: Jalshakti, Bioresource Technology 97 (2006) 877–885.

[45] H. Freundlich, Adsorption in solution, Phys. Chem. Soc. 40 (1906) 1361–1368.

[46] I. Langmuir, J. Am. Chem. Soc. 38 (11) (1916) 2221.

[47] Sibel Kılınc Alpat, Ozge O zbayrak, Senol Alpat, Husamettin Akcay, The adsorption kinetics and removal of cationic dye, Toluidine Blue O, from aqueous solution with Turkish zeolite, Journal of Hazardous Materials 151 (2008) 213–220.

[48] P.K. Malik, Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics, Journal of Hazardous Materials B113 (2004) 81–88.

[49] Qiang Huang, Meiying Liu, Junyu Chen, Ke Wang, Dazhuang Xu,Fengjie Deng, Hongye Huang, Xiaoyong Zhang, and Yen Wei, Enhanced removal capability of

kaolin toward methylene blue by mussel-inspired functionalization, J Mater Sci (2016) 51:8116–8130.

[50] S. Lagergren, Zur theorie der sogenannten adsorption geloester stoffe, Kungliga Svenska Vetenskapsakad, Handl. 24 (1898) 1–39.

[51] Y.S. Ho, G. McKay Pseudo-second order model for sorption processes Process Biochemistry 34 (1999) 451–465.

[52] G. McKay, Y.S. Ho, J.C.Y. Ng, Biosorption of copper from waste waters: a review, Separ. Purif. Meth. 28 (1999) 87–125.

[53] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J.70 (1998) 115–124.

[54] Yuh-Shan Ho, Review of second-order models for adsorption systems, Journal of Hazardous Materials B136 (2006) 681–689.

[55] Yesim Sag, Yucel Aktay, Kinetic studies on sorption of Cr(VI) and Cu (II) ions by chitin, chitosan and Rhizopus arrhizus, Biochemical Engineering Journal 12 (2002) 143–153.

[56] P.K. Malik, Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics, Journal of Hazardous Materials B113 (2004) 81–88.