Purification of waste water from cationic dye using SPGMA polymer: Isotherm and Kinetic study

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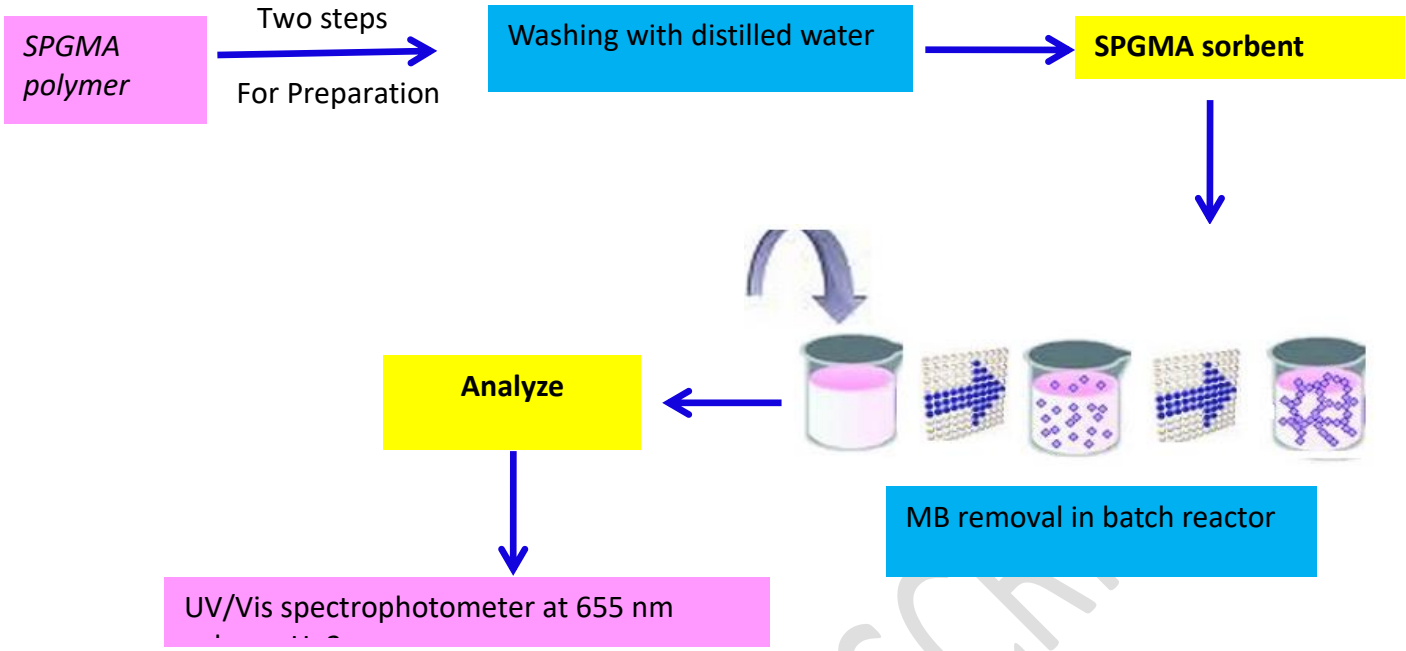


Graphical abstract

ABSTRACT

One of the known methods for dye removing from waste water is using sorbent material for fine removal of dye .The nano- cation exchanger Sulphonated poly glycidyl methacrylate (SPGMA polymer) was used as sorbent material for removing one of the common cationic dyes. SPGMA polymer was prepared and characterized to ensure its surface ability to sorb dye. Percentage removal of Methylene Blue using SPGMA polymer was studied by changing different parameters as sorbent amount, stirring speed, pH and solution temperature. The maximum value for dye removal was about 98%. Adsorption data from experimental work shows that the results fit the pseudo first order model for all parameters studied except for pH study fits pseudo second order. Also sorption mechanism for SPGMA polymer was studied for different dye concentration.

Key words: Methylene Blue, SPGMA, Isotherm, Kinetic, Adsorption.

1. Introduction

One of cationic dyes is Methylene blue (MB) which used in various industries such as cotton, pulp, wool, paper, leather etc., to color their final products. The outlet of these industries containing huge amount of different dyes, discharged this types of dyes into waters drain, cause dangerous to the environment (Gad and El-Sayed, 2009). Acute exposure to MB dye will cause increased heart rate, shock, Heinz body formation, vomiting, cyanosis, jaundicem and quadriplegia (Hameed and Ahmad,2009).

Various methods such as chemical, physical, and biological processes have been used trying to remove of cationic dyes from aquatic media (Barka et al., 2010, Bielska and zymanowski ,2006, MohyEldin et al., 2016, Elahmadi et al., 2009, Karim et al., 2009, Khadhraoui et al., 2009, Lodha and Chaudhari ,2007). However, all of the methods have some limitation and none of the processes described above were successful in removing color from wastewater completely. Dye removal process is the process calling Adsorption. Currently, most effective adsorbent is activated carbon. Which is high cost in production and regeneration this reasons make it uneconomical (Wang et al., 2005). Nowadays, there is an interest in using cheap and potential materials for the adsorption of reactive dyes. Several adsorbents were reported in the literatures such as clay (Tehrani-Bagha et al., 2011) , zeolite (Han et al., 2009) , fly ash (Rastogi et al., 2008), silica gel (Kushwaha et al., 2010) and chitosan (Mahmoodi et al.,2011) for the adsorption of basic dyes from aqueous solution.

In this work decolorize of Methylene blue dyes were studied using prepared polymer (SPGMA). To study the capability of color removal, different parameters that affect the adsorption process (such as time, pH, and dosage of adsorbents, temperature and stirring speed) was studied. The kinetic models and equilibrium studies also carried out to substantiate the relationship with the experimental data for the adsorbent.

2. Materials and methods

2.1. Preparation of methylene blue stock solution

The cationic dye (MB dye) was from "NICE chemicals pvt.ltd company". The stock solution was prepared by dissolving 1.00 g of MB dye in 1000 mL distilled water. Diluting the prepared stock solution with distilled water to make Different concentrations for experiments.

2.2. Preparation of Adsobent material (SPGMA polymer)

Sulphonated poly (glycidyl methacrylate) nano-cation exchanger (SPGMA) were prepared by two steps. First, general procedure for photo ATRP of GMA was as follows. To a 10 mL Schlenk tube containing $CuBr_2$ and TPMA, evacuated and filled with argon. Argon-purged anisole was added under argon atmosphere. Sonicate the mixture in the Schlenk tube for 5 min to form a CuBr2/TPMA complex. Subsequently GMA purged with argon and BPN was added to the Schlenk tube under argon atmosphere. The mixture was degassed by three freeze-pump-thaw cycles and backfilled with argon. Photo polymerization with light of $\lambda > 350$ nm was performed using a medium-pressure mercury lamp in a Spectromat apparatus (Ivoclar AG, Lichtenstein, glass filter λ = 350-550 nm). To prevent heating of the sample during irradiation, the Schlenk tube was placed into a double-layer glass tube. In the outer layer of the finger, water thermo stated to 25°C was circulated. Second, the epoxy groups of PGMA chains were reacted with sodium sulphite (Elkady et al., 2011, Abu-Saied et al., 2013, MohyEldin et al ,2010, MohyEldin et al., 2011, Abu-Saied et al., 2017) , dissolved in alcoholic aqueous solution at 80°C for 2 h. Discharge the excess of sodium sulphite solution after centrifugation at 14,000 rpm for 30 min using ultra speed centrifuge , distilled water used in washing to remove any un-reacted sodium sulphite .The details of the preparation and characterization of SPGMA polymer published before (Abu-Saied et al., 2015)

2.3. Experimental methods and measurements

Batch adsorption technique was used in this work Put 100 mL of different dye concentration on rotary shaker , add different weighted adsorbent to the experimental flasks . Let solution to shake, different samples at different time intervals were taken out from the flasks and separated by

decantation ,then remaining MB dye concentration was analyzed using UV/Vis spectrophotometer at 655 nm (Ultrospec 2000 - Pharmacia Biotech). The effect of various important parameters in adsorption process as adsorbent dose, stirring speed, pH values and temperature was studied.

The equation used in calculating the amount of MB dye adsorbed by SPGMA polymer was:

$$q = (C_0 - Ce) * V/W \quad \textbf{(1)}$$

Where q (mg/g) is the MB dye adsorbed by SPGMA polymer , C_0 and Ce (mg/l) are the initial and equilibrium concentrations of the MB dye, respectively, V (l), the initial volume of MB dye solution, and W (g), the weight of the polymer.

The percentage removal of MB dye from solution was by using the following equation:

$$\%Re = (C_0 - C_e)/C_0 * 100 \quad \textbf{(2)}$$

Where C_0 and Ce (mg/l) are the initial and equilibrium concentrations of the MB dye.

3. Results and discussion:

3.1. Effect of sorbent dose adsorption

Fig (1) illustrates the adsorption removal from 20 ppm dye concentration. The percentage removal of dye was slightly increased with increasing SPGMA polymer dose from 0.025 g to 0.3 g along the total period of the experiment (90 min) to reach 98% for 0.2 and 0.3 g of sorbent material .This result concludes that more surface area was made due to increase of adsorbent mass .Therefore, the total number of active sites increases which increase the percentage removal of dye (Al-Qodah, 2000)

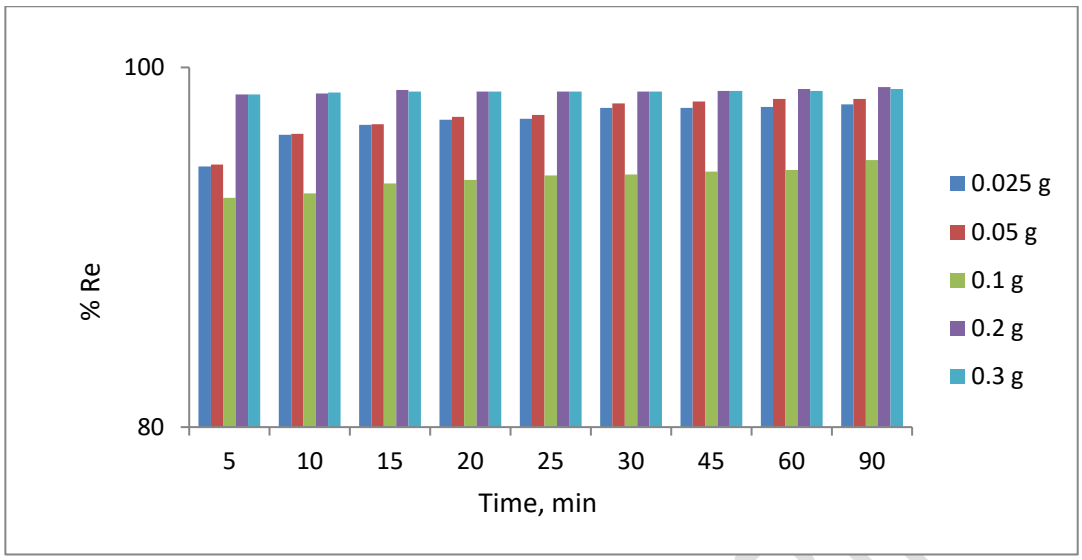


Figure 1. Effect of sorbent dose on adsorption of MB by SPGMA polymer (dye concentration: 20 mg/l; stirring speed 200 rpm; contact time: 90 min).

3.2. Effect of changing the stirring speed

Fig (2) shows the adsorption removal by changing the stirring speed from (100-500 rpm) at different time intervals from 5 to 90 min . The figure concludes that the stroke speed affect slightly as the percentage removal decreased by incrasing stirring speed, and the highest percentage removal of dye was at 200 rpm.

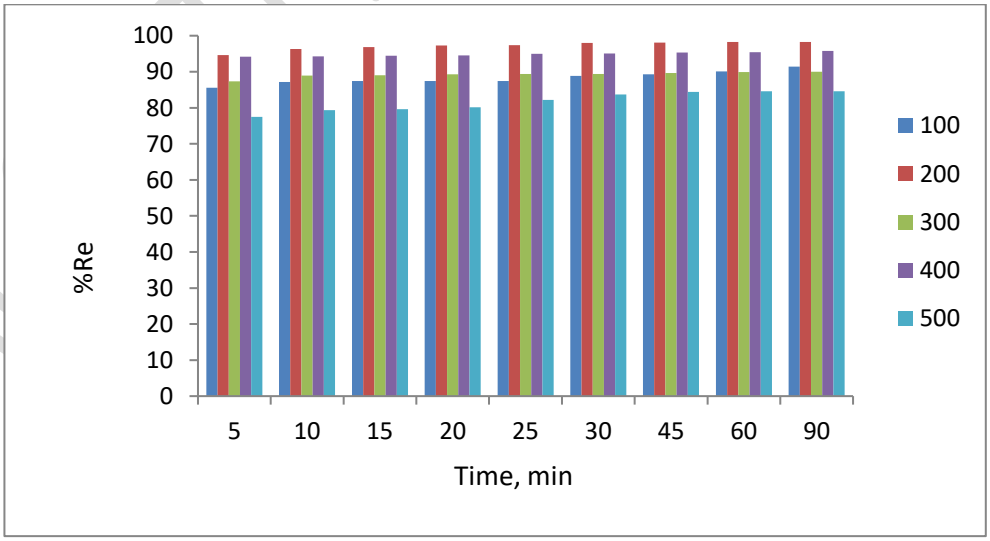
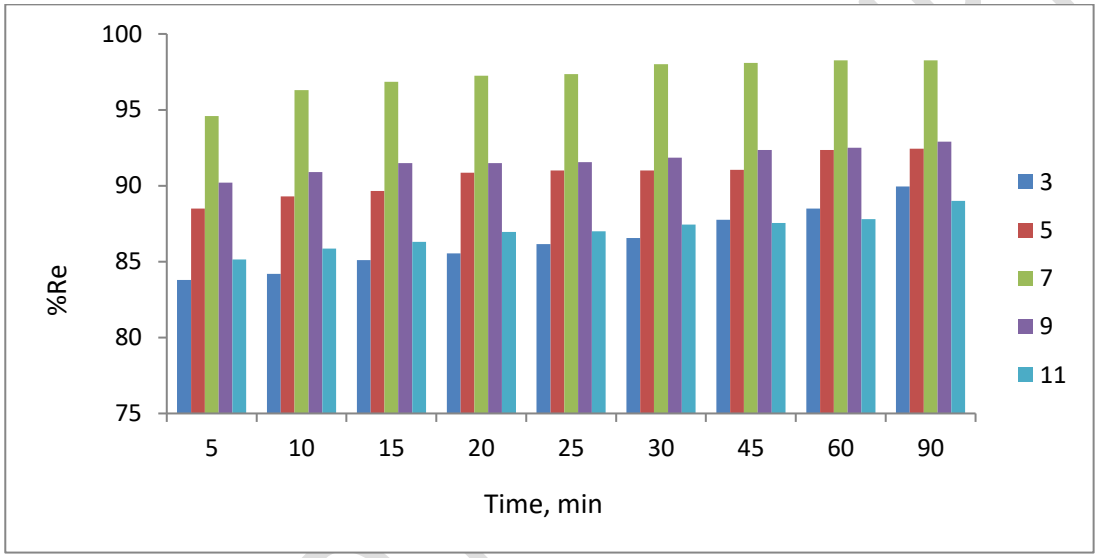


Figure 2. Effect of stirring speed on adsorption of MB by SPGMA polymer (dye concentration: 20 mg/l; sorbent dose: 0.05g ; contact time: 90 min).

144 *3.3. Effect of pH change*

145 Fig (3) shows adsorption capacity of MB dye by increasing pH value from 3 to 11. The percentage
146 removal of dye increase with increasing pH value to reach maximum value at pH= 7 which record
147 about 98 % dye removal, then decrease to reach the lowest value at pH= 11, so for future studies,
148 the optimum pH adopted at pH 7. Also the increasing time from 5 to 90 min for all pH values do
149 not affect the removal percentage.



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151 **Figure 3 .** Effect of pH on adsorption of MB by SPGMA polymer
152 (dye concentration: 20 mg/; stirring speed:200 ; sorbent dose: 0.05g ; contact time: 90 min).
153

154 *3.4. Effect of temperature variation*

155 As illustrated in Fig (4) , the decolonization of MB dye was tested for wide range of temperature
156 from 20 to 35 ^{o}C. The results cleared that by increasing the temperature of solution the percentage
157 dye removal increased. To reach the maximum value at 25^{o}C. While by increasing time for each
158 temperature, it does not have great effect. The temperature effect on adsorbtion process concludes
159 in two major effects. Increasing the temperature is known to increase the rate of diffusion of the
160 adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent
161 particles due to the decrease in the solution viscosity (Lagergren,1898)

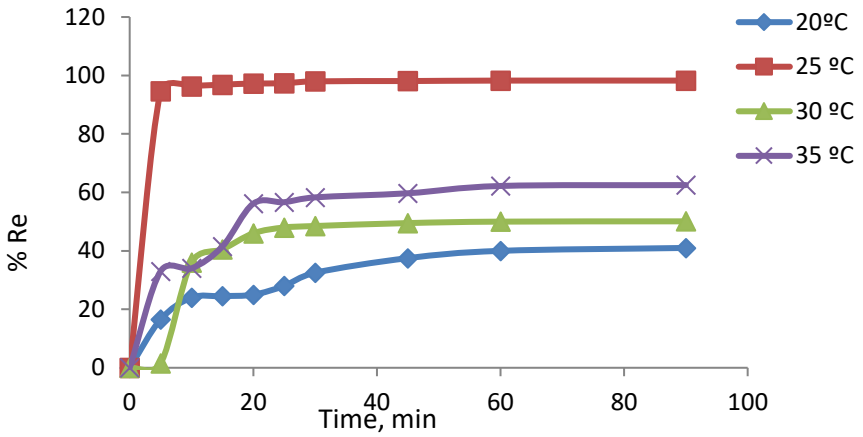


Figure 4 . Effect of Temperature on adsorption of MB by SPGMA polymer (dye concentration: 20 mg/l; sorbent dose: 0.05g ;; stirring speed: 200; pH:7; contact time: 90 min).

4. Adsorption kinetics study:

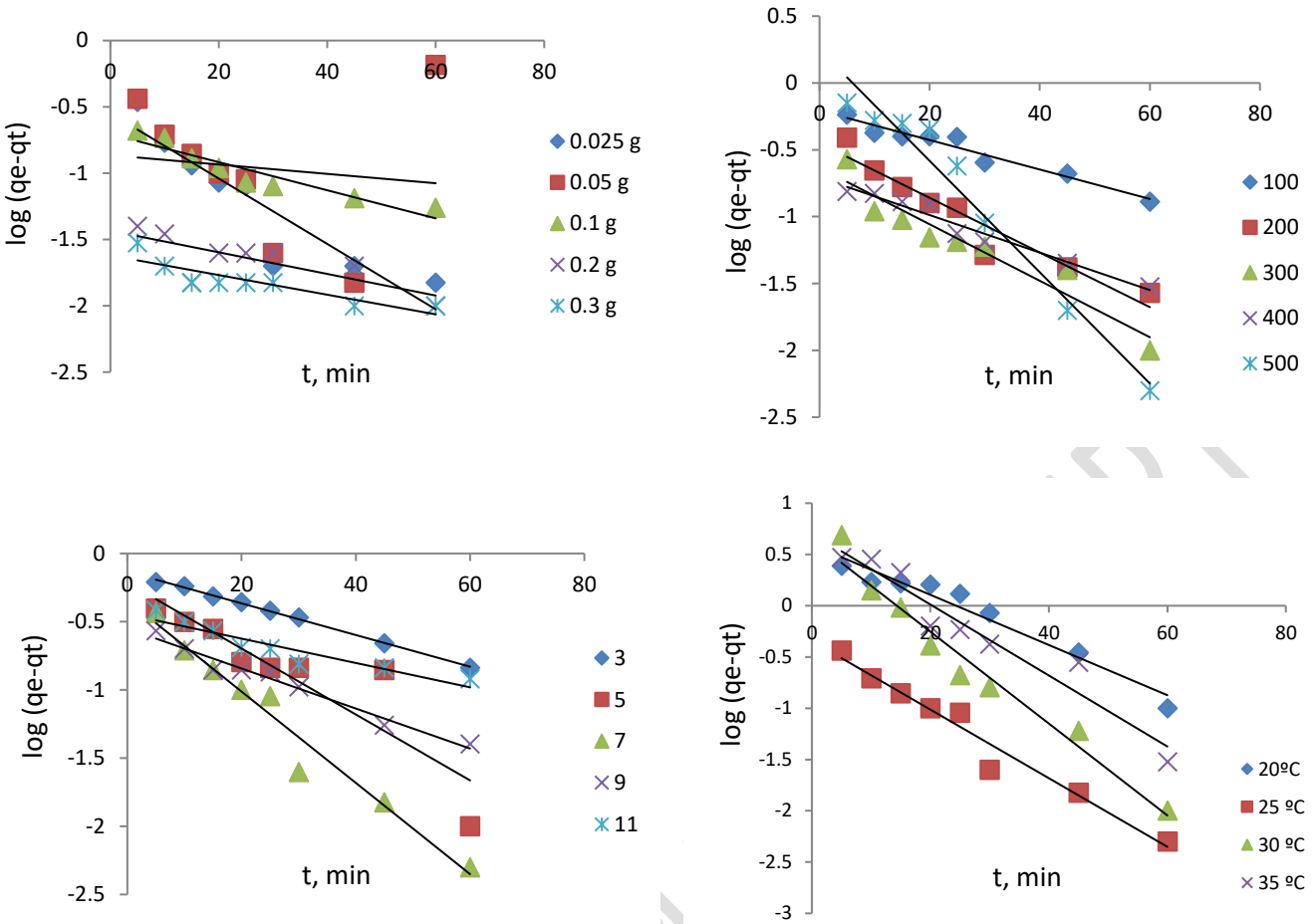
The pseudo-first-order kinetic equation of Lagergren method for adsorption analysis (Ho and McKay, 1998) :

$$\frac{dqt}{dt} = k1\,(qe - qt) \qquad (3)$$

By integrating equation (3) for boundary conditions as t=0 to $t = t$ and q_t=0 to $q_t = q_t$,

$$log(qe - qt) = log\, qe - \frac{k1}{2.303}\, t \qquad (4)$$

Where the equilibrium rate constant is k_1 (1/min), q_e is the MB dye adsorbed on the surface at equilibrium (mg/g), q_t is the MB dye adsorbed at different times (mg/g). The adsorption rate constant (k_1) for MB sorption by SPGMA polymer powder was determined from the figure which illustrates log ($q_e - q_t$) against time t (as in Fig. 5). The pseudo-first-order model at different parameters studied are summarized in Table (1)



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178 **Figure 5.** Pseudo-first-order kinetics for adsorption of MB onto SPGMA polymer at different

179 parameters.

180 While equation (5) expressed pseudo-second-order kinetics (Ho and McKay,2000, Weber and

181 Morris,1963):

182 $$\frac{dqt}{dt} = k2\,(qe - qt)^2 \qquad (5)$$

183 As k_2 is the dye adsorption rate constant, q_e is the amount of MB dye adsorbed at equilibrium

184 (mg/g) and *qt* is the amount of MB dye adsorbed at different time intervals *t* (mg/g). Separating the

185 variables in Eq. (7) gives:

186 $$\frac{dqt}{(qe-qt)2} = k2\,dt \qquad (6)$$

187 By Integrating equation (6) for the boundary conditions t=0 to $t = t$ and q_t=0 to $q_t = q_t$:

$$\frac{1}{qe-qt} = \frac{1}{qe} + k2t \qquad (7)$$

by rearranging Eq. (7) the equation give the following one :

$$qt = \frac{t}{\left(\frac{1}{k2qe2}\right)+\left(\frac{t}{qe}\right)} \qquad (8)$$

Which has a linear form of equation (9) :

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{1}{qe}\,t \qquad (9)$$

As the equilibrium adsorption capacity (q_e), and second order constants k_2 (g/mg min) can be determined experimentally from the slope and intercept of t/q_t versus t figure *as in* (Fig.6.).

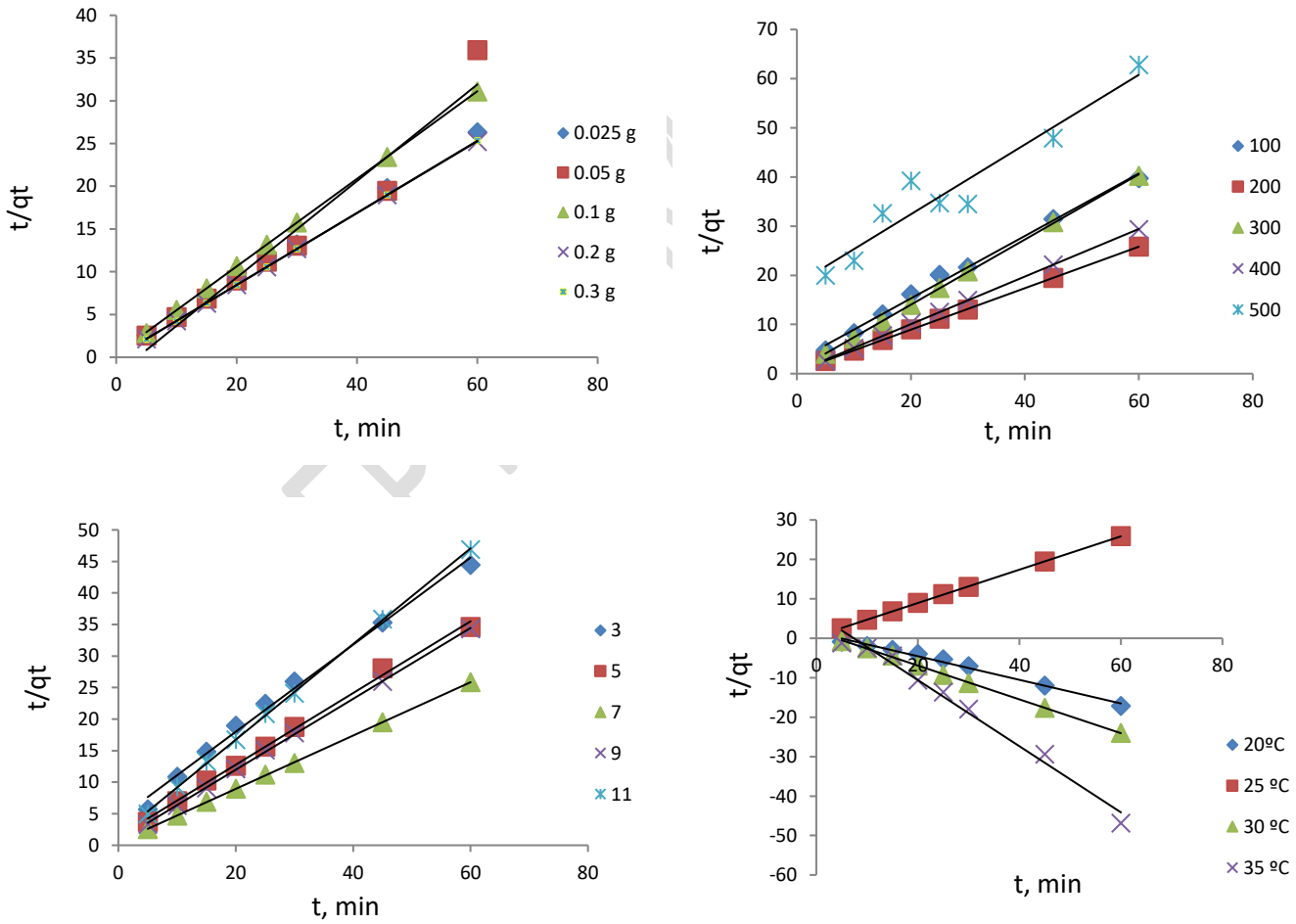

Figure6. Pseudo-second-order kinetics for adsorption of MB onto SPGMA polymer at different parameters

198 Table (1) present he coefficients of the pseudo-first- and second-order adsorption kinetic models.
199 According to values of R^2 for the pseudo-first-order model and the q values ($q_{e,cal}$) calculated for
200 sorbent dose, stirring speed and temperature it seems fitted to it . While, the pseudo-second-order
201 model better represented the adsorption kinetics and this suggests for pH study. The overall rate of
202 MB dye adsorption process appeared to be controlled by chemical process.

203 **Table (1)** Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and
204 calculated and experimental q_e values obtained at different initial MB concentrations for different parameters
205 studied

Dye system		Pseudo first order model			Pseudo second order model		
	$q_{e,exp}$ mg/g	**K_1** min^{-1}	**q_{e1}** mg/g	**R^2**	**K_2** g/mg.min	**q_{e2}** mg/g	**R^2**
1 Sorbent dosage							
n= 200 rpm C_0=20 mg/l							
w= 0.025g	0.41	0.0567	0.283	0.847	13.35	5.378	1
w= 0.05g	0.35	0.0081	0.1366	0.814	-1.57	3.133	0.949
w= 0.1g	1.03	0.0244	0.8968	0.879	10.36	3.807	1
w= 0.2g	0.22	0.0189	0.0368	0.603	122.39	5.666	1
w= 0.3g	0.24	0.0170	0.0239	0.781	234	5.626	1
2- rpm							
W= 0.05g pH=7							
C0=20 mg/l							
rpm= 100	1.72	0.0253	1.222	0.949	0.155	1.5745	0.9939
rpm= 200	0.35	0.0469	0.3549	0.922	0.354	2.3702	0.9999
rpm= 300	2	0.0486	1.832	0.911	0.579	1.5087	0.9998
rpm= 400	0.85	0.0322	0.696	0.962	0.612	2.066	0.9998
rpm=500	3.08	0.0958	2.779	0.965	0.029	1.4098	0.9196
3- pH							
W= 0.05g rpm=200							
C0=20 mg/l							
pH=3	2.01	0.0267	0.735	0.9973	0.1138	1.449	0.9927
pH=5	1.51	0.0557	0.611	0.8035	0.2314	1.759	0.9968
pH=7	0.35	0.0772	0.453	0.9665	0.366	0.366	0.999
pH=9	1.42	0.0338	0.282	0.9698	0.424	1.779	0.9996
pH=11	2.2	0.0205	0.358	0.8839	0.365	1.3989	0.9996
4-Tempreture							
W=0.05g rpm=200							
C0=20 mg/l							
T=20	4.8	0.0564	3.628	0.9524	0.062	3.339	0.9896
T=25	0.35	0.0772	0.453	0.9665	0.366	2.365	0.999
T=30	9.98	0.1032	8.392	0.9665	0.11	2.332	0.9994
T=35	7.5	0.0797	5.062	0.936	0.113	1.192	0.9834

5. Mechanism of Sorption Process:

In a solid–liquid adsorption process: the transfer of adsorbate is controlled either by boundary layer diffusion (called external mass transfer) or by intraparticle diffusion (called mass transfer through the pores), or by both processes. Generally accepted the adsorption dynamics consists of three consecutive steps: The first is the transport of adsorbate molecules from the bulk solution to the external surface of the adsorbent by diffusion through the liquid boundary layer, second is the diffusion from the external surface and into the pores of the adsorbent, finally, Adsorption on the active sites on the internal surface of the adsorbent pores.

The overall rate of adsorption is controlled by film or intraparticle diffusion, or by combination of both. The rate controlling step in systems characterized by dilute concentrations of adsorbate, poor mixing, and small particle size adsorbent is the boundary layer diffusion. Also, it has been cleared in many studies that boundary layer diffusion is dominant during the initial adsorbate uptake, then gradually adsorption rate becomes controlled by intraparticle diffusion after the adsorbent's external surface is loaded with the adsorbate.

Equation (10) present intraparticle diffusion parameter, k_i(mg/g min0.5) (Ho and McKay,1998):

$$q = k_i\, t^{0.5} + c \qquad \textbf{(10)}$$

as q is the MB dye adsorbed (mg/g) at time t, while k_i is intraparticle diffusion constant (mg/g min), and c is the intercept. It can be calculated from the slope of the linear plot of q_t versus $t^{1/2}$. The slope of the curve of different initial concentrations shows the k_{id} values as shown in Table (2). Theoretically, the graph of k_i versus $t^{0.5}$ should separate at least to four linear regions that represent boundary layer diffusion, followed by intraparticle diffusion in macro, meso, and micro pores. These four regions are followed by a horizontal line representing the system at equilibrium. *Also,* the figure of dye uptake, illustrate q_t versus square root of time ($t^{1/2}$) should be linear if intraparticle diffusion is involved in dye adsorption process and if these lines pass through the origin point, intraparticle diffusion is the rate controlling step. If the lines do not pass through the origin point , this is indicate of some degree of boundary layer control and this further show that the intraparticle

diffusion is not the only rate-limiting step. The boundary layer thickness can be indicated by the intercept value as the intercept increase, the greater the boundary layer effect.

Table (2). Intraparticle diffusion constants for different initial MB concentrations

Initial concentration (mg/L)	k_{id} (mg/g $min^{1/2}$)	C	R^2
5	0.0483	1.8282	0.9303
10	0.0195	1.8679	0.8432
15	0.0291	1.8025	0.8335
20	0.0272	1.7375	0.9127
25	0.1687	0.3519	0.8149

Conclusions:

The present results in this study show that the SPGMA polymer has high ability to adsorb methylene blue dye from wastewater with removal percentage about 98% and more. Different parameters are studied and Adsorption kinetics was studied .comparing q calculated and q experimental shows that the results follows pseudo first order for sorbent dose, rpm and temperature while fitted pseudo second order for pH. Also the results clear that the overall MB dye adsorption rate controlled by chemical process. This research concludes the ability of SPGMA polymer in removal of cationic dye with high removal efficiency.

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