

# Purification of wastewater 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 wastewater 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.

**Keywords:** 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 these 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 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 these 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 adsorbent 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<sub>2</sub> 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 CuBr<sub>2</sub>/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  $\lambda = 350\text{--}550$  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:

$$q = (C_0 - C_e) * V / W \quad (1)$$

Where  $q$  (mg/g) is the MB dye adsorbed by SPGMA polymer,  $C_0$  and  $C_e$  (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:

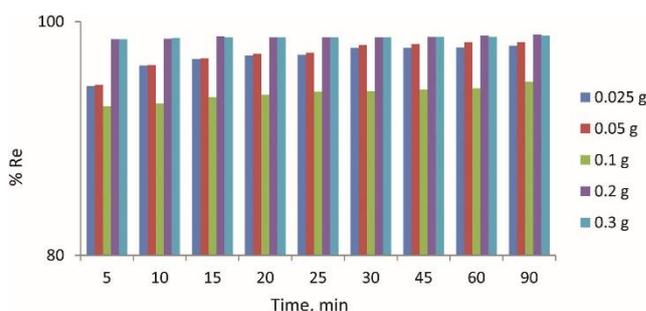
$$\%Re = (C_0 - C_e) / C_0 * 100 \quad (2)$$

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

## 3. Results and discussion

### 3.1. Effect of sorbent dose adsorption

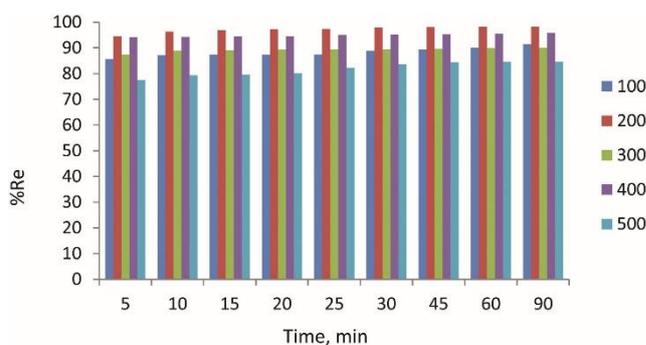
Figure 1 illustrates the adsorption removal from 20 ppm dye concentration. The percentage removal of dye was slightly increased with increasing SPGMA polymer dose from 0.025 g to 0.3 g along the total period of the experiment (90 min) to reach 98% for 0.2 and 0.3 g of sorbent material. This result concludes 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

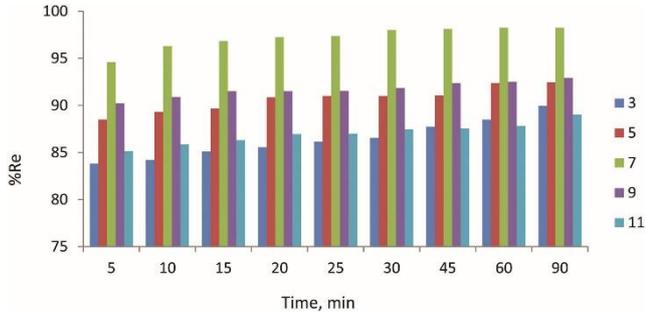
Figure 2 shows the adsorption removal by changing the stirring speed from (100–500 rpm) at different time intervals from 5 to 90 min. The figure concludes that the stroke speed affect slightly as the percentage removal decreased by increasing stirring speed, and the highest percentage removal of dye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



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

### 3.3. Effect of pH change

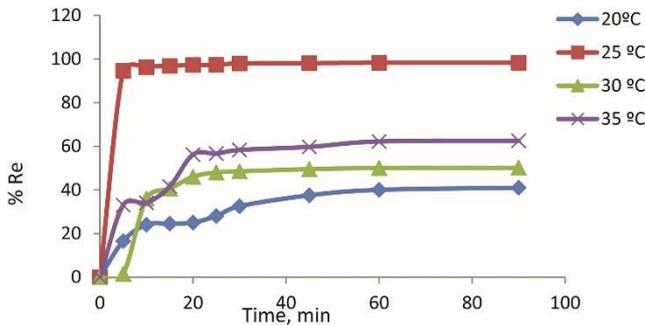
Figure 3 shows adsorption capacity of MB dye by increasing pH value from 3 to 11. The percentage removal of dye increase with increasing pH value to reach maximum value at pH = 7 which record about 98 % dye removal, then decrease to reach the lowest value at pH = 11, so for future studies, the optimum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



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

**3.4. Effect of temperature variation**

As illustrated in Figure 4, the decolonization of MB dye was tested for wide range of temperature from 20 to 35 °C. The results cleared that by increasing the temperature of solution the percentage dye removal increased. To reach the maximum value at 25 °C. While by increasing time for each temperature, it does not have great effect. The temperature effect on adsorption process concludes in two major effects. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent 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: 0.05 g; 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):

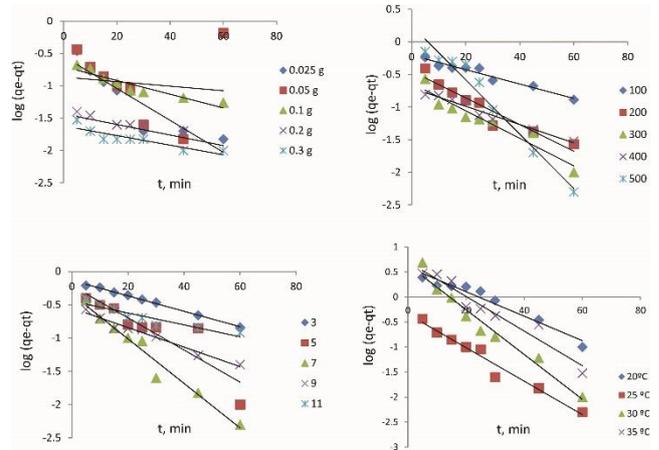
$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

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

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{4}$$

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 Figure 5). The pseudo-first-order model at different parameters studied are summarized in Table 1.



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

While equation (5) expressed pseudo-second-order kinetics (Ho and McKay, 2000; Weber and Morris, 1963):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

As  $k_2$  is the dye adsorption rate constant,  $q_e$  is the amount of MB dye adsorbed at equilibrium (mg/g) and  $q_t$  is the amount of MB dye adsorbed at different time intervals  $t$  (mg/g). Separating the variables in Eq. (7) gives:

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 dt \tag{6}$$

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

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{7}$$

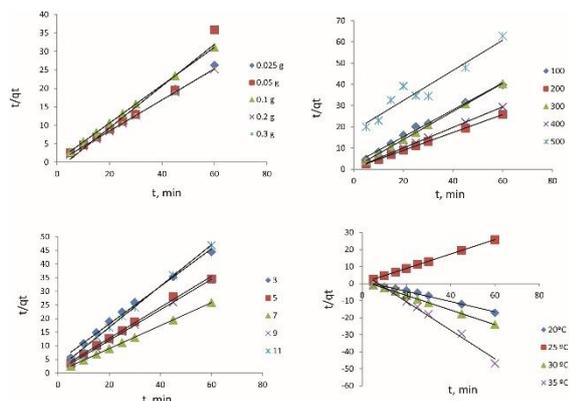
by rearranging Eq. (7) the equation gives the following one:

$$qt = \frac{t}{\left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right)} \tag{8}$$

Which has a linear form of equation (9):

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

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 (Figure 6).



**Figure 6.** Pseudo-second-order kinetics for adsorption of MB onto SPGMA polymer at different parameters

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

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

Dye system	$q_{e,exp}$ , mg/g	Pseudo first order model			Pseudo second order model		
		$K_1$ , min <sup>-1</sup>	$q_{e1}$ , mg/g	$R^2$	$K_2$ , g/mg.min	$q_{e2}$ , mg/g	$R^2$
1 Sorbent dosage							
n = 200 rpm, C <sub>0</sub> = 20 mg/l							
w = 0.025 g	0.41	0.0567	0.283	0.847	13.35	5.378	1
w = 0.05 g	0.35	0.0081	0.1366	0.814	-1.57	3.133	0.949
w = 0.1 g	1.03	0.0244	0.8968	0.879	10.36	3.807	1
w = 0.2 g	0.22	0.0189	0.0368	0.603	122.39	5.666	1
w = 0.3 g	0.24	0.0170	0.0239	0.781	234	5.626	1
2-rpm							
W = 0.05g, pH = 7, C <sub>0</sub> = 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, C <sub>0</sub> = 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-Temperature							
W = 0.05 g, rpm = 200, C <sub>0</sub> = 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 min<sup>0.5</sup>) (Ho and McKay, 1998):

$$q = k_i t^{0.5} + c \quad (10)$$

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 indicates some degree of boundary layer control and this further shows 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 <sup>1/2</sup> )	C	R <sup>2</sup>
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

## 6. 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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