

ADSORPTION CHARACTERISTICS OF EXPANDED POLYSTYRENE FOAM AS A FILTRATION MEDIA FOR WATER AND WASTEWATER TREATMENT

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ABSTRACT

Numerous filtration materials were proposed for water and wastewater treatment processes. Expanded Polystyrene (EPS) is a lightweight plastic material having an effective size of 0.63mm, spherical shape and density 30 kg/m³. Series of batch experiments were performed to estimate the removal behavior and the adsorption capacity of the material as a criterion for the material selection. The kinetic models of adsorption process were investigated using Methylene blue dye (MB) by varying the initial dye concentration (1-5 mg/l), adsorbent dose (0.5-3 gm), PH (2-8) and contact time (0.5-6 hours). The analysis of kinetic data was performed using pseudo-first and second-order kinetics. Pseudo-second order kinetic model gave a superior correlation for the experimental data. The results were analyzed using Langmuir and Freundlich isotherm models. Langmuir isotherm equation fitted better and the adsorption of MB onto the surface of Expanded polystyrene is physical in nature and adsorption represents favorable condition. The adsorption capacities of MB improved from 0.012753 to 0.035732 mg/g with increasing the dye concentration from 1 to 5 mg/L. The dosage of EPS was also found to be an important variable influencing the MB adsorption and it decreased with increasing the EPS dosage. The adsorption capacity of EPS increased with increasing the PH of the aqueous solution. Accordingly, Expanded Polystyrene was shown to be an effective alternative for the dyes removal from industrial wastewater. EPS could also act as an effective filtration material that provides washing water saving due to its low density.

Keywords: Expanded polystyrene, adsorption, methylene blue, wastewater treatment

1 INTRODUCTION

Many industries including textiles, cosmetics, leather, plastics, pigments units, and paper containing dyes in their wastewater (Crini, 2006, Elabbas et al., 2016). Water streams, rivers, and lakes can be polluted and colored even with little amounts of colored dyes. Many of these dyes are toxic nature, have many dangerous effects on the human health as cancer (Moussavi and Khosravi, 2011). The blending of colors in water may also change the characteristics of water and cause undesirable effects on the customers (Upadhyay et al., 2017). So the discharges containing these dyes ought to be treated before they are released into the water streams (Choy et al., 1999). In developing countries, water pollution, which arises due to the discharge of unprocessed industrial effluents into the environment is of major concern by research in recent years. Methylene blue (MB) is a cationic dye used in many industries, for example, in chemical industry and pharmaceutical industry. The Methylene blue dye removal can be estimated in batch adsorption experiments under different conditions and the results may be used as criteria for the selection of the most suitable condition. Adsorption is a procedure of attracting and retaining molecules on the surface of a solid, a standout amongst the best advancements generally utilized in worldwide, and a compelling technique for the expulsion of dyes from water. Adsorption is an important treatment process particularly if the adsorbent is economical, accessible, and does not require any extra pretreatment ventures before the

utilization. Some advantages of adsorption process are its relative simplicity, low cost, and possible reuse of the adsorbent (Elabbas et al., 2016, Gupta, 2009). The goal of the present experimental study is to evaluate the capacity of Expanded polystyrene to expel Methylene blue from water by assessing the adsorption limit and adsorption energy parameters under various initial dye concentration, PH, adsorbent portion, and contact time. The equilibrium isotherms were portrayed by different adsorption models and the isotherm constants were resolved.

2 METHODOLOGY

Batch adsorption systems have been used at laboratory scale to assess the ability of Expanded polystyrene foam to adsorb Methylene blue. This trial set-up (group investigation), is normally called a batch experiment and comprises of setting a fixed measure of the material with a mass m (g) in a container containing a volume V (ml) of a prepared MB aqueous at one of a scope of expanding fixations. The samples are mixed at speed v (rpm) for a period t (h) at temperature T ($^{\circ}\text{C}$). The difference between the final and initial MB concentrations in solution at equilibrium (assumed to be reached at time t), C_e and C_o , respectively, is assumed to be sorbed to the material (Reddy et al., 2014).

2.1 Adsorbent

Expanded polystyrene foam is a polymer with thermoplastic properties produced from the petroleum derived movement, styrene. Its chemical formula is (C_8H_8). It is a lightweight plastic material consisting of small spherical shaped particles containing 98% air. It is inert and safe for contact with food products. No physical or chemical treatments were performed prior to batch adsorption experiments. EPS characteristics were summarized in "Table 1".

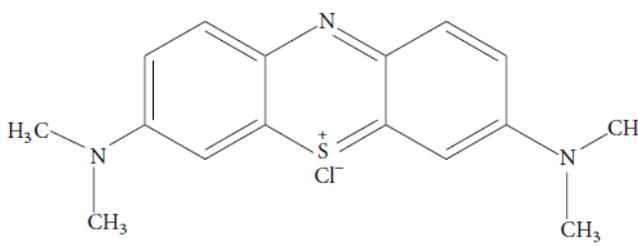
Table 1. Characteristics of Expanded polystyrene beads (EPS)

Characteristics	EPS beads
Shape	spherical
Minimum size	0.6
Maximum size	1.2
Effective size	0.63
Uniformity coefficient	1.43
Porosity	0.3492
Density	30 Kg/m ³

2.2 Adsorbate

The methylene blue dye (MB) was obtained from Sigma- Aldrich, USA. The physical and chemical characteristics of the dye are given in "Table 2" (Aldrich, 2019).

Table 2. chemical characteristics of MB

Properties	Values
Chemical structure	
Chemical formula	C ₁₆ H ₁₈ N ₃ SCl
Wave length	665 nm
Molecular weight	319.86 (g mol ⁻¹)
Type	Cationic dye
Color	Blue
Solubility	Soluble in water

2.3 Adsorption Studies

To prepare a stock solution of methylene blue of concentration 500 ppm (500mg/L), 0.5 g of methylene blue was dissolved in a 1000 mL volumetric flask; further desired concentration of adsorbate was prepared from the stock solution by diluting it. Solutions of hydrochloric acid HCl (0.1 M) and sodium hydroxide NaOH (0.1 M) were also prepared for pH adjustments. The adsorption of MB dye on EPS was investigated by varying one parameter under consideration and keeping other parameters constant, adsorbent dose, contact time, initial dye concentration, and the effect of pH. The batch experiments of the adsorption studies were carried out at room temperature (25 ± 1°C). In each experiment, a pre-weighed amount of EPS was added to 50 mL of dye solution and completely immersed in a 250 mL Pyrex beakers and agitated at 300 rpm using a magnetic stirrer for a given period of time. 6 mL samples were taken using a syringe then analyzed. The dye concentration of the solution was determined at wavelength of maximum absorption (λ_{max}) 665 nm, by UV-visible-1600 spectrophotometer. The amount adsorbed of MB by a unit mass of the adsorbent (EPS) at equilibrium (Q_e) and the percentage of adsorption (%R) were calculated according to "equation (1), (2)":

$$Q_e = \frac{C_o - C_t}{m} \times V \quad (1)$$

$$\%R = \frac{C_o - C_t}{C_o} \times 100 \quad (2)$$

where C_e is the concentration of adsorbate at equilibrium; C_t is the concentration of adsorbate at time t ; C_o is the initial concentration; m is the mass of the adsorbent; and V is the volume of the adsorbate.

2.4 Adsorption Kinetic Studies

Contact time is one of fundamental importance parameters to determine the efficaciously use of EPS as an adsorbent. The effects of contact time on adsorption of methylene blue onto EPS were studied out by adding 2 g of EPS to 50 mL of different initial MB concentrations (1, 2, 3, 4 and 5 mg/L) pH from 7.5 to 8, and shaken at 300 rpm. Samples (6 mL) were removed every 30 min for 2 hours. Thereafter, samples were removed every 1 hour until equilibrium. The adsorption capacities

increase until it reaches a maximum value after which there is no increment in adsorption capacity of the adsorbent.

2.5 Effect of initial dye concentration, adsorption isotherms, adsorbent dose, and pH solution

The effect of initial MB dye concentration were carried out by adding 2 g of EPS to 50 mL of different initial MB concentrations (1,2,3,4 and 5 mg/L) at a constant pH of 8. The results were applied to adsorption equations.

The influence of EPS dosage on the adsorption approach was investigated by adding different amounts (0.5, 1, 2,2.5 and 3 g) of EPS into five 250 mL beakers each containing 50 mL of fixed initial MB dye concentration (3 mg/L) and agitated at 300 rpm utilizing a stirrer for 6 hours.

The impact of pH solution on the adsorption process were conducted by adding 2 g of EPS into four 250 mL beakers each containing 50 mL of fixed initial MB dye concentration (3 mg/L) and agitated at 300 rpm using a stirrer for 6 h. The range of solution pH was adjusted between 2 and 8. The pH was adjusted by adding NaOH (0.1 M) or HCl (0.1 M) solutions.

3 RESULTS AND DISCUSSION

3.1 Adsorption Kinetic Studies

The adsorption capacity of MB by EPS for five initial concentrations can be detected from “Fig. 1”, which shows that the amount of adsorbed MB expanded with expanding initial MB concentration. The amount of MB adsorbed increased from 0.012753 to 0.035732 mg/g with increasing the MB concentration from 1 to 5 mg/L. The adsorption of MB was rapid until 3 hours and then the adsorption was gradual and finally attained saturation at equilibrium (5-6 hours). This may return to the easily accumulation of the MB on the EPS particals at the beginging due to their different charges, and over the time, the attached MB repulse the same charged MB to minimize their accumulation on the EPS, which decrease the accumulation rate and consequencely the adsorption rate.

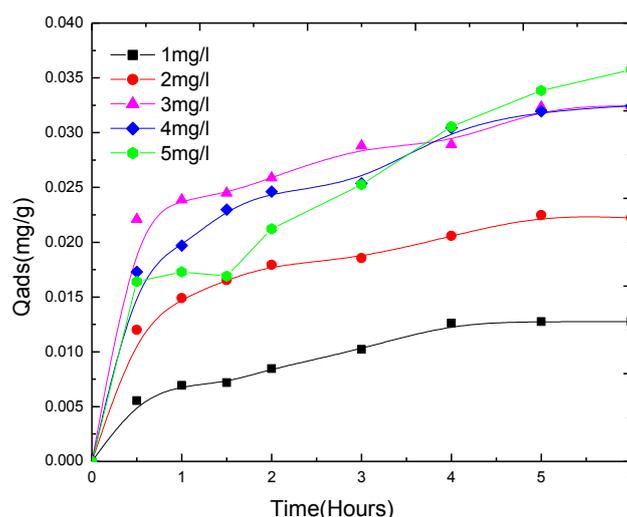


Figure 1. The adsorption capacity of MB by EPS for different initial concentrations.

“Fig. 2” shows the influence of the initial MB concentration on the removal percentage. The amount of MB adsorbed decreased with the increasing initial MB concentration. The removal percentage of adsorbed MB onto EPS decreased from 51% to 28.586% as the initial concentration

was increased from 1 to 5 mg/L. The interpretation may be that at higher MB concentrations the adsorption sites on EPS become saturated (Özer et al., 2007). As the MB concentration is higher, the ratio of MB to EPS is greater, and therefore the percentage of MB removed is lower.

Pseudo-first and second-order kinetics (Equations. (3) and (4)) were used to analyze the adsorption kinetics for different initial concentrations of MB onto EPS. The pseudo-first-order model with linear form was reported by Lagergren (Lagergren, 1898). k_1 represent the pseudo-first-order adsorption rate constant (s^{-1}), and Q and Q_e are the different amounts of MB adsorbed per gram of adsorbent at time t and at equilibrium, respectively. The pseudo-first-order adsorption rate constant (k_1) is determined by the slope of the plot of $\ln(Q_e - Q)$ versus t “Fig. 3”.

$$\ln(Q_e - Q) = \ln Q_e - k_1 t \tag{3}$$

Ho’s Pseudo-second-order kinetics (Ho and McKay, 1999), based on the adsorption equilibrium, is shown linearized as :

$$\frac{t}{Q} = \frac{1}{K_2 \times Q_e^2} + \frac{1}{Q_e} \times t \tag{4}$$

where K_2 ($h \text{ g/mg}$) is the pseudo-second-order constant, Q is the adsorbed amount at time t and Q_e (mg/g) is the adsorbed amount at equilibrium. The values of k_2 and Q_e can be determined experimentally from the slope and intercept of a plot of t/Q versus t “Fig. 4”.

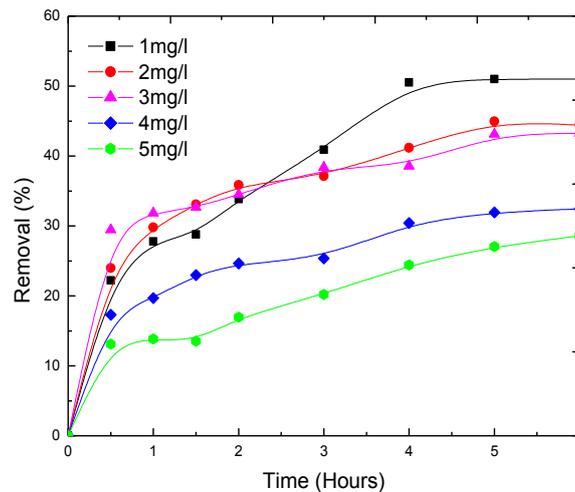


Figure 2. The influence of the initial MB concentration on the percentage removal of MB.

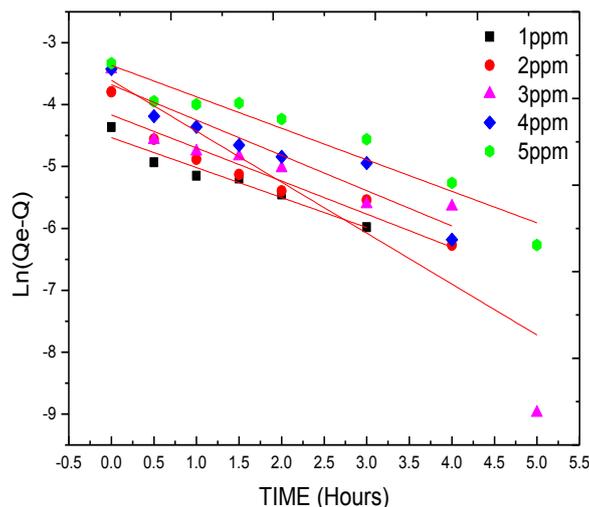


Figure 3. Pseudo-first-order kinetics of adsorption of MB onto EPS for different MB initial concentrations.

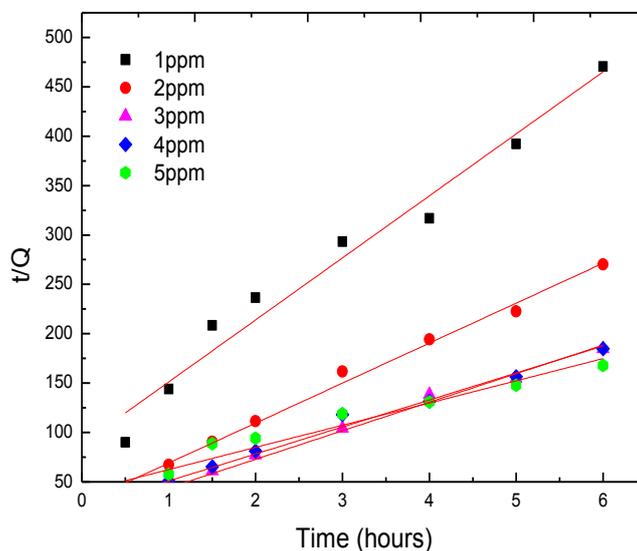


Figure 4. Pseudo-second-order kinetics for adsorption of MB onto EPS for different MB initial concentrations.

“Table 2” listed the results of rate constant studies for different kinetic models. The adsorption system will follow a specific kinetic model if the correlation coefficient R^2 value is closer to 1 and theoretical calculated values $Q_e(\text{cal})$ is close to that of the experimental value (Farooq et al., 2010). The relationship coefficients of the kinetic model of pseudo-second order were very high and the theoretical $Q_e(\text{cal})$ values were much closed to the experimental values $Q_e(\text{exp})$ given in “Table 3”. It can be noticed that as the initial concentration of MB increases, $Q_e(\text{exp})$ values also increase, this is due to, the considerable challenge for the vacant locales at high concentration which prompts the higher adsorption rates (Theydan and Ahmed, 2012). From these results, it can be concluded that the pseudo-second order kinetic model compared to the pseudo-first order model, provided a superiour correlation for the adsorption of MB onto EPS.

Table 3. Adsorption kinetic parameters for MB adsorption.

Pseudo-first-order kinetic parameters				
Co mg/l	Q _e (exp) mg/g	Q _e (cal) mg/g	K ₁ 1/h	R ²
1	0.012753	0.01075	0.48443	0.93199
2	0.022475	0.015513	0.53448	0.9061
3	0.032449	0.027138	0.8234	0.75409
4	0.032449	0.025247	0.57045	0.89118
5	0.035732	0.034597	0.50934	0.9162
Pseudo-second-order kinetic parameters				
Co mg/l	Q _e (exp) mg/g	Q _e (cal) mg/g	K ₂ h/gm/mg	R ²
1	0.012753	0.015922	44.63662	0.96809
2	0.022475	0.024702	57.402	0.99264
3	0.032449	0.034605	55.42133	0.99087
4	0.032449	0.036577	31.729	0.98527
5	0.035732	0.044461	12.67477	0.9241

3.2 Adsorption isotherm of MB onto EPS

Adsorption Isotherm Models: Adsorption isotherm describes how adsorbates interact with adsorbents at equilibrium at constant temperature. So, the correlation of the equilibrium data by either empirical or theoretical equations is necessary to practical operation (Poots et al., 1976). The Langmuir and Freundlich isotherms are the most well-known isotherms used for describing the adsorption systems at equilibrium.

- *The Langmuir Adsorption Isotherm.* The Langmuir isotherm presumes that adsorption occurs at homogeneous sites within the adsorbent Surface and adsorption only takes place on a single monolayer. Saturation happens when the adsorbate molecules occupy the sites where no more molecules can be adsorbed at that site (Langmuir, 1918). Equation (5) represents the linear form of Langmuir equation.

$$\frac{C_e}{Q_e} = \frac{1}{K_L \times Q} + \frac{C_e}{Q} \quad (5)$$

Where Q_e is the amount of MB adsorbed on EPS at equilibrium, C_e is the equilibrium MB concentration in the solution, Q is the maximum adsorption capacity and K_L is the adsorption equilibrium constant.

A plot of C_e/ Q_e versus C_e indicates a straight line of slope 1/Q and an intercept of 1/K_LQ.

- *The Freundlich adsorption Isotherm.* The empirical equation of Freundlich isotherm assumes the heterogeneous system (Freundlich, 1907). And there is interaction between adsorbate molecules adsorbed that gives multilayer surface coverage. The description of the used Freundlich isotherm equation can be expressed as:

$$Q_e = K_f \cdot C_e^{1/n} \quad (6)$$

where Q_e is the quantity of solute adsorbed at equilibrium, mg of adsorbate per g of adsorbent, C_e is the adsorbate concentration at equilibrium, where K_f is the maximum multilayer adsorption

capacity and n is the adsorption intensity (Hussein et al., 2004). Equation (7) expresses the linear form of the Freundlich isotherm.

$$\log Q_e = \log K_f + 1/n \cdot \log C_e \tag{7}$$

A plot of $\log Q_e$ against $\log C_e$ indicates a straight line of slope $1/n$ and an intercept $\log K_f$.

Accordingly, the equilibrium data obtained from the experiments were evaluated to the fitness with the Langmuir (Eq. (5)) and Freundlich (Eq. (7)), models. “Fig. 5” and “Fig. 6” show that the data of methylene blue adsorption isotherm fitted both Langmuir and Freundlich isotherms, respectively. The best fitted model was determined based on the estimation of coefficient R^2 . The data from the isotherm evaluation is summarized in “Table 4”.

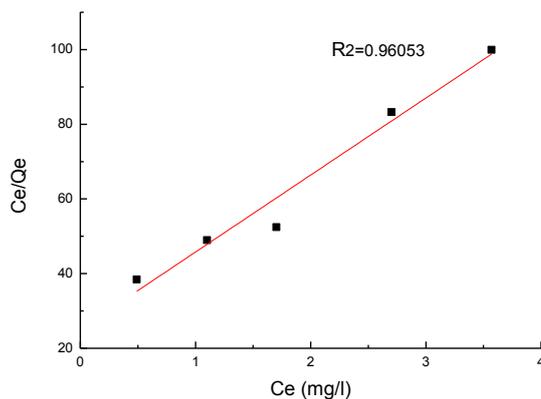


Figure 5. Langmuir isotherm for the adsorption of MB onto EPS.

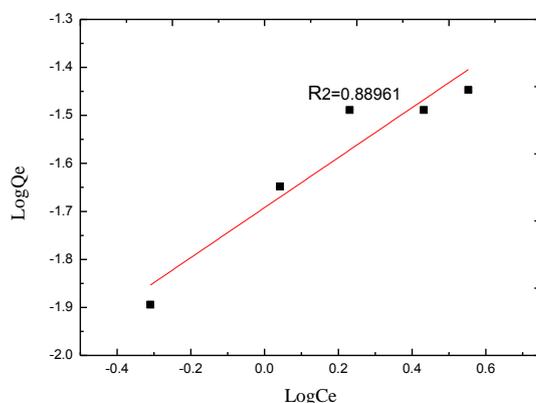


Figure 6. Freundlich isotherm for the adsorption of MB onto EPS.

Table 4. Langmuir and Freundlich isotherm parameters for MB adsorption.

Isotherm constant	Value
R^2 (Langmuir)	0.96053
Q (mg/g)	0.048487
K_L (L/mg)	0.819886
R^2 (Freundlich)	0.88961
n	1.92097
K_f (L/mg)	0.02032

Comparing R^2 values of Langmuir and Freundlich isotherm, Langmuir isotherm equation fitted better so a monolayer adsorption proceeds over a surface containing a finite number of adsorption sites. The Langmuir isotherm can express whether the adsorption is favorable or unfavorable by means of R_L , which is a dimensionless constant referred to as separation factor. R_L was estimated by equation (8) according to previous studies (Mckay et al., 1987, Hall et al., 1966).

$$R_L = \frac{1}{1 + K_L.C_0} \tag{8}$$

where R_L is a dimensionless constant separation factor, C_0 the initial concentration of MB (mg/l) and K_L is the Langmuir isotherm constant (L/g). R_L indicates the type of the isotherm according to “Table 5”.

Table 5. Values of separation factor R_L (El Qada et al., 2006) .

R_L	type of the isotherm
$0 < R_L < 1$	Favorable
$R_L > 1$	Unfavorable
$R_L = 0$	Irreversible
$R_L = 1$	Linear

R_L values were found to be 0.5495, 0.3788, 0.289, 0.2337 and 0.1961 for MB concentrations 1,2,3,4,5 respectively. confirming that all the system shows favorable adsorption of the MB dye onto EPS.

The heterogeneity factor n can be used to indicate the adsorption type whether its linear ($n = 1$), chemical process ($n < 1$), or a physical process ($n > 1$). From the experimental data, “Table 3” shows that value of the heterogeneity factor is greater than 1. So it can be concluded that adsorption of MB onto the surface of EPS is physical in nature and adsorption represents favorable adsorption condition (Namasivayam et al., 1994, Mahmoud et al., 2012). This is in great assent with the findings of R_L values.

3.3 The influence of initial dye concentration

From “Fig. 7”, As the concentration of MB increases, the adsorption uptake capacities increase. This may return to the higher availability of MB molecules with increasing the concentration of MB in the solution, which increase the attachment capability of MB on EPS.

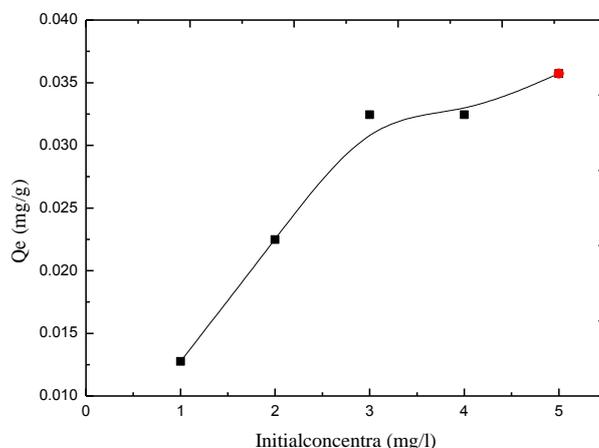


Figure 7. Amount adsorbed at equilibrium versus initial concentration.

3.4 The influence of adsorbent dose

The quantity of adsorbent contributes an important role in the adsorption of MB from the aqueous solution. "Fig. 8" shows the monitoring of the adsorption capacity Q_e versus dose of EPS at initial concentration of 3 mg/l. It can be observed from the plot that quantity of MB adsorbed is varied with varying adsorbent mass and it decreased with increasing adsorbent mass. This may be assigned to the fact that the total surface area available for the adsorption of MB decreases as the amount in grams of adsorbent is increased, that may return to the overlapping or aggregation of adsorption sites (Das and Mondal, 2011).

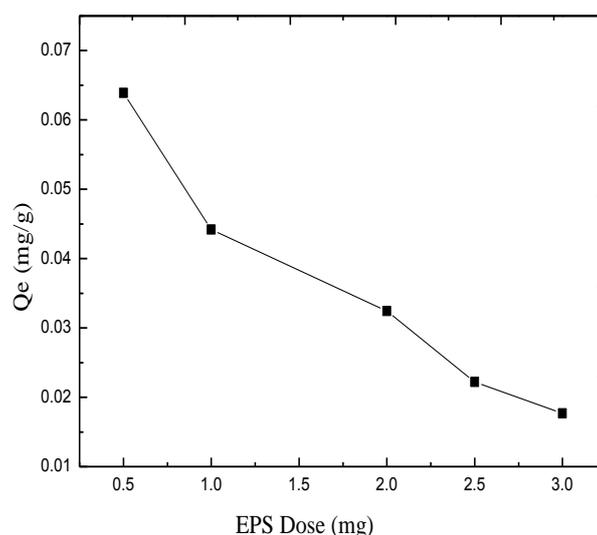


Figure 8. Adsorbed amount at equilibrium versus EPS dose.

3.5 The effect of pH

The influence of pH on the adsorption of MB onto EPS at an initial concentration of 3 mg/l and dose of 2 gm EPS in a PH range of 2 to 8 is illustrated in "Fig. 9", which show that as the PH of the solution increases the adsorption capacity increases. The lower adsorption capacity at a low pH may be because the cationic dyes are in competition with the H^+ ions presented in high concentration in the solution, while at a higher solution pH, there is a decrease in the H^+ ions and increase in OH^- . (Vadivelan and Kumar, 2005, Lai and Chen, 2001). This insure that adsorption of cationic dye may be enhanced at higher pH (Chen and Lin, 2001). The maximum adsorption of the MB dye was detected at pH 8.

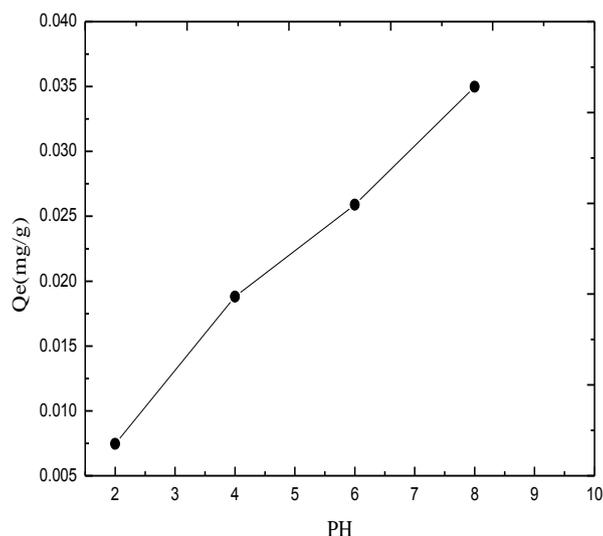


Figure 9. Adsorbed amount at equilibrium versus solution PH.

4 CONCLUSIONS

This study introduced the expanded polystyrene foam (EPS) as an adsorbent for dye removal. The adsorption performance of the EPS foam has been examined in the Methylene blue dye synthetic aqueous solutions with a batch system. The adsorption of MB on EPS was found to be dependent on initial solution concentration, adsorbent dose, contact time, and pH. The adsorption capacity was found to increase with increasing the initial dye concentration and contact time. It also was found to decrease with increase of adsorbent dose. The best removal was obtained at pH of 8. The adsorption kinetic was well described by the pseudo-second-order model. The results of adsorption were best introduced by the Langmuir isotherm, demonstrating a homogenous monolayer adsorption on the EPS surface. Expanded Polystyrene can be an effective adsorbent for the removal of Methylene blue from water. The use of the material could encourage the recycling of expanded polystyrene as it widely used in packaging of equipments. Further studies should focus on improving the properties of expanded polystyrene to increase its adsorption capacity.

ABBREVIATIONS

- Co Initial MB concentration
- Ce Equilibrium MB concentration
- Ct Concentration of adsorbate at time t
- EPS Expanded Polystyrene
- k1 The pseudo-first-order adsorption rate constant
- K2 The pseudo-second-order constant
- Kf The maximum multilayer adsorption capacity
- KL The adsorption equilibrium constant
- MB Methylene blue dye
- m Mass (g)
- n The adsorption intensity
- Qe The quantity adsorbed by a unit mass of an adsorbent at equilibrium
- Q Amount of MB adsorbed per gram of adsorbent at time t
- Qe(cal) Theoretical calculated values
- Qe(exp) Experimental values
- %R Adsorption percentage
- R2 Correlation coefficient
- RL Separation factor
- T Temperature ($^{\circ}\text{C}$)

t time
V Volume (ml)
v Speed v (rpm)

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