Jurnal
Teknologi

Full Paper

ADSORPTION OF METHYLENE BLUE ON ALGINATE-GRAFTED-POLY (METHYL METHACRYLATE)

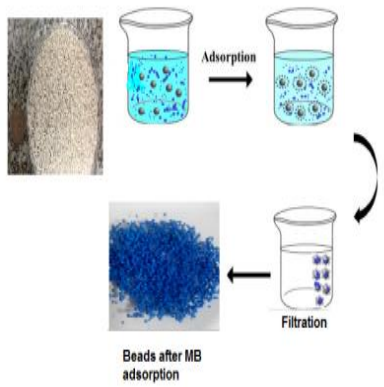
Article history
Received
10 February 2015
Received in revised form
28 May 2015
Accepted
4 June 2015

Ahmed Salisu[a], Mohd Marsin Sanagi[a,b*], Khairil Juhanni Abd Karim[a], Neda Pourmand[a], Wan Aini Wan Ibrahim[a]

[a]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
[b]Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

*Corresponding author
marsin@kimia.fs.utm.my

Graphical abstract



Abstract

In this study, the removal of methylene blue (MB) dye using alginate-graft-poly (methyl methacrylate) beads was investigated. The effects of adsorption parameters namely initial pH and initial dye concentration were studied. The removal efficiency of the beads has been found to be dependent on initial dye concentration and initial pH. The experimental equilibrium data was fitted successfully to Langmuir isotherm model with the maximum monolayer coverage of 5.25 mg g^{-1} and adsorption kinetics data has been well fitted by a pseudo-second-order kinetic model. The alginate based beads could be used as low-cost and eco-friendly adsorbent for removal of trace amount of methylene blue from aqueous solution.

Keywords: Low-cost, sodium alginate, methyl methacrylate, methylene blue, trace

Abstrak

Dalam kajian ini, penyingkiran pewarna metilena biru (MB) menggunakan manik alginate-cangkuk-poli(metilmetakrilat) telah diselidiki. Kesan parameter penjerapan iaitu pH awal dan kepekatan awal pewarna telah dikaji. Kecekapan penyingkiran manik tersebut didapati bergantung kepada kepekatan awal dan pH awal. Data keseimbangan eksperimen didapati bertepatan dengan model isoterma Langmuir dengan liputan satu lapisan maksimum 5.25 mg g^{-1} dan data kinetic penjerapan bersesuaian dengan model kinetic tertib kedua. Manik berasaskan alginat tersebut boleh digunakan sebaai bahan penjerap kos rendah dan mesra-alam sekitar bagi penyingkiran metilena biru surih dari larutan akueus.

Kata kunci: Kos rendah, natrium alginate, metil metacrilat, metilena biru, surih

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1.0 INTRODUCTION

The presence of dyes in industrial effluents is a major concern due to their harmful effects to both aquatic organisms and humans. Dyes wastewaters are discharge into the environment by various sources but the major one being textile industries. Various conventional treatment processes are available for the removal of dyes from wastewater such as photocatalytic degradation, biological degradation, chemical oxidation, membrane separation, coagulation and adsorption. Among these techniques adsorption is the most efficient because of low cost,

east of operation and design, flexibility and insensitive to toxic pollutants [1-2]. The feasibility of using non-conventional low-cost adsorbents for the removal of pollutants from aqueous media has been reviewed [3-5]. Polysaccharides such as chitin, chitosan and alginate are known to have affinity to remove many pollutants. One of the important characteristics of alginate is the ability to form hydrogels [6]. An aqueous solution of alginate is capable of chelating with divalent metal ions such as Ba^{2+}, Ca^{2+} forming strong gel material. Calcium alginate beads have been reported to be effective material for removal of heavy metal ions in aqueous solutions [7-9]. Calcium alginate immobilized microbial cultures was studied to remove dyes [10]. Alginate beads have been studied on the removal of basic black dye [11]. Kaushal and Tiwari (2010) reported the removal of Rhodamine-B (a basic dye) from aqueous solution by adsorption onto crosslinked alginate beads [12]. Alginate (Figure 1) is a polysaccharide material largely obtained from seaweed species of brown algae [13]. It is a potential material for the removal of basic dyes due various ligands such as hydroxyl and carboxyl functional groups on the backbone. In this study, alginate grafted poly (methyl methacrylate) beads was prepared by conventional radical polymerization using benzoyl peroxide (BPO) as initiator and the graft copolymer formed was further crosslinked using $CaCl_2$ solution as a crosslinking agent and adsorption of methylene blue was investigated by using batch adsorption method. Because cationic dyes like methylene blue (Figure 2) are more toxic and difficult to decolorize than anionic dyes [14]. Therefore, an increased interest has been focused on removing such dyes from wastewater. The PKa value of methylene blue is 3.8.

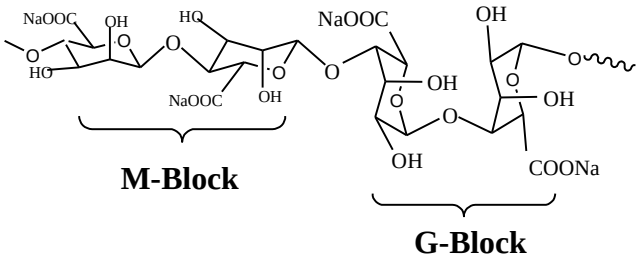


Figure 1 Molecular structure of sodium alginate

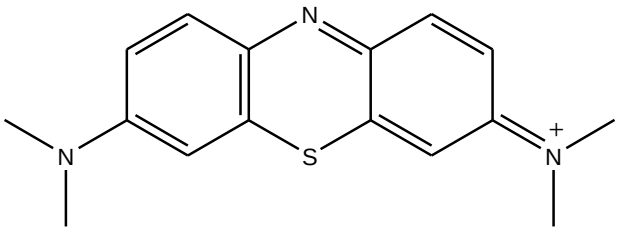


Figure 2 Chemical structure of methylene blue

Table 1 Langmuir and Freundlich isotherm model constants and coefficient of determinations for adsorption of MB onto Alg-g-PMMA

Langmuir model					Freundlich model		
q_eExp (mg/g)	q_eCal (mg/g)	b (L/mg)	R_L	R^2	K_F (mg/g)	n	R^2
4.67	5.25	2.70	0.07	0.999	4.02	1.83	0.951

2.0 EXPERIMENTAL

2.1 Materials and Reagents

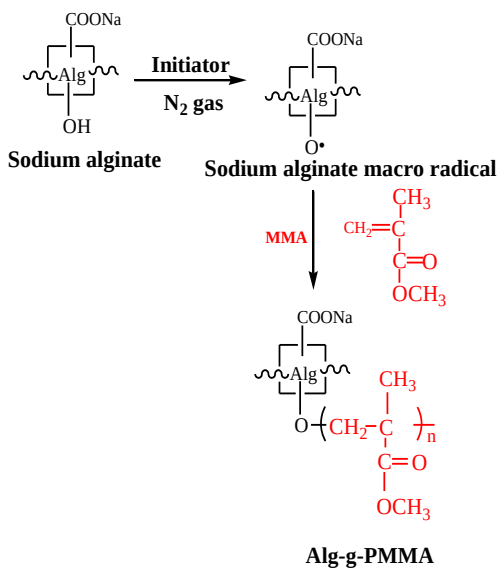
Sodium alginate, methyl methacrylate (MMA), benzoyl peroxide (BPO) and methylene blue (MB) were purchased from Sigma-Aldrich (USA), MMA monomer was distilled under reduced pressure prior to use. BPO was further purified by dissolving in chloroform and precipitated in excess methanol. Methanol and acetone were purchased from QRëc (Selangor, Malaysia). All other chemical reagents were analytical grade and used as received.

2.1.1 Graft Copolymerization

The grafting reactions were carried out under nitrogen atmosphere in a 250 mL three-necked flask equipped with a reflux condenser and a magnetic bar stirrer and a gas inlet system, immersed in a constant temperature oil bath. For each experiment, sodium alginate solution was prepared by slow addition of weighed amount of sodium alginate into the reaction flask containing distilled water (100 mL). After sodium alginate was completely dissolved, the required amount of BPO dissolved in 2 mL of acetone was added slowly to the reaction flask. The mixture was stirred for 20 min., and the required amount of MMA monomer was added. Graft copolymerization was carried out using different amounts of sodium alginate, methyl methacrylate, BPO, reaction time (1-5 h) and reaction temperature (60-90 °C). The nitrogen atmosphere and stirring were maintained throughout the experiments. After the reaction time was over, the slurry was poured into methanol. The precipitate was filtered, washed with acetone, dried in a vacuum oven at 60 °C until a constant weight

and kept in a desiccator. The products obtained were extracted for 24 h using acetone by Soxhlet extraction to remove the poly(methyl methacrylate) homopolymer. Finally alginate-grafted-poly(methyl methacrylate) (Alg-g-PMMA) was dried under vacuum at 60 °C to a constant weight. The steps of the graft copolymer formation is shown scheme 1.

The graft copolymer was characterized by Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The maximum grafting percentage (212%) was achieved using 1% w/v of sodium alginate, 7.99 × 10^{-1} M of methyl methacrylate, 4.13 × 10^{-3} M of benzoyl peroxide, reaction temperature of 80°C and reaction time of 2 hours.



Scheme 1 Reaction scheme for the preparation of Alg-g-PMMA

2.1.2 Beads Preparation

In the preparation of the beads, 2 g of the graft copolymer (Alg-g-PMMA) was crushed into smaller particles and then mixed with 100 mL of distilled water. The mixture was then stirred using a mechanical stirrer at 1500 rpm, which formed colloidal solution. The resultant colloidal solution was added dropwise into a $CaCl_2$ solution (0.1 mol L^{-1}) using a syringe with needle (1.2 × 38 mm) and the solution immediately formed solid gel beads. The beads were allowed to cure in the mother liquor overnight and thereafter filtered and washed thrice with distilled water (250 mL). The beads were then dried in a vacuum oven at 60 °C.

2.1.3 Batch Adsorption Experiment

Stock solution of methylene blue (1000 mg L^{-1}) was prepared by dissolving accurately weighed quantity of methylene blue in deionized water and subsequently diluted with deionized water to the required concentration. Adsorption experiments were carried out using conical flask (50 mL). A known amount of the Alg-g-PMMA beads was mixed with 10 mL of methylene blue solution whose concentration and pH were determined. After the flasks were shaken for the desired time at room temperature (298 ± 2 K), the suspension were centrifuged, filtered and the residual dye concentration in the supernatant was measured at the maximum wavelength corresponding to the maximum absorption for the dye solution (663.92 nm), using ultraviolet-visible spectrophotometer (LAMDA 35, Perkin Elmer, USA). Calibration curve was plotted between absorbance and concentration of the dye solution to obtained absorbance-concentration profile. The pH of the solution was adjusted by adding either HCl (0.1M) or NaOH (0.1M).

2.1.4 Adsorption Isotherm Studies

Adsorption isotherm studies were carried out with a fixed initial adsorbent dose at different dye concentration. Dye solution (10 mL) with the initial concentrations of 2 mg L^{-1} to 10 mg L^{-1} and adjusted to pH 7 at room temperature (298 ± 2) K were stirred in 50 mL conical flasks. The supernatants were then analyzed to measure the concentrations of the dye. The isotherm models Langmuir and Freundlich were used to describe the adsorption of the dye on the adsorbents. The equilibrium adsorption capacity of the adsorbent was calculated as:

$$q_e \text{ (mg/g)} = \left(\frac{C_o - C_e}{M \text{ (g)}}\right) \times \text{Volume (L)} \quad (1)$$

where C_o and C_e are initial and the equilibrium concentrations of dye solution, respectively (mg L^{-1}). M is the mass of the adsorbent (g) and V is the volume of solution (L).

3.0 RESULTS AND DISCUSSION

3.1 FTIR Analysis

The FTIR spectrum of sodium alginate (Figure 3a) showed a broad absorption band at 3426 cm^{-1} was attributed to O-H stretching vibration. The peaks at 1600, 1407 and 1023 cm^{-1} were due to asymmetric and symmetric stretching of (COO^-) and C-O stretching, respectively. Additional peaks at 2994 and 1730 cm^{-1} in the spectrum of the grafted sodium alginate (Figure 3b) were due to stretching of C-H and C=O of ester, respectively, which confirmed the grafting reaction.

3.2 Scanning Electron Microscopy Analysis

SEM images of sodium alginate (NaAlg) before and after grafting are shown in Figure 4. By comparing

the surface morphology of the grafted NaAlg (Figure 4b) with ungrafted (Figure 4a), we observed that the morphology of NaAlg was greatly changed by the grafted poly(methyl methacrylate) chains, and this is another proof of grafting. The availability of pores and internal surface is clearly displayed in the SEM image of graft copolymer which may enhance adsorption rate of the dye in the solution.

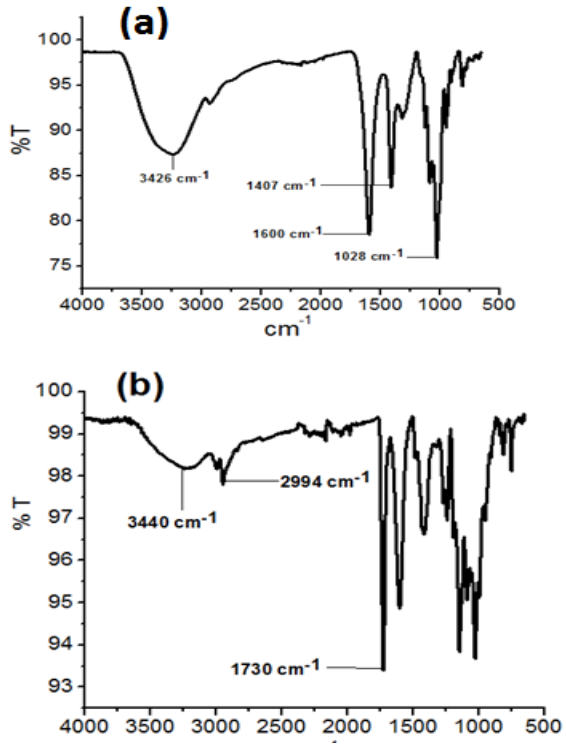


Figure 3 FTIR spectra of (a) sodium alginate (b) Alg-g-PMMA graft copolymer

3.3 Effect of Initial pH

The pH of the dye solution is an important factor in the adsorption processes especially on the adsorption capacity. It influences not only the surface charge, and the degree of ionization of the functional groups of the adsorbent, but also the dye chemistry. The effect of the initial pH on the dye removal percentage is shown in Figure 5. The pH of the solution was varied from 2 to 9, the amount of adsorbent (0.1 g), dye concentration (6 mg L^{-1}) and contact time (1 h). The results indicated that the removal percentage of methylene blue increased with increasing pH up to7, and then decreased. The effect of pH on the adsorption performance can be explained by interaction between the adsorbent active sites and the adsorbate. Alginate possesses various functional groups such as hydroxyl and carboxyl groups together with long chains of PMMA grafted onto it. In addition, alginate has pKa value in the range of 3.4 to 4.5. At pH 7, electrostatic attractions exist between the negatively charged surfaces of the adsorbent, due to the functional groups and positively charged cationic dye molecule. At lower pH, the number of positively charged sites on the adsorbent increased due to increase in proton ions concentration in the system which does not favor the uptake of the dye due to electrostatic repulsion.

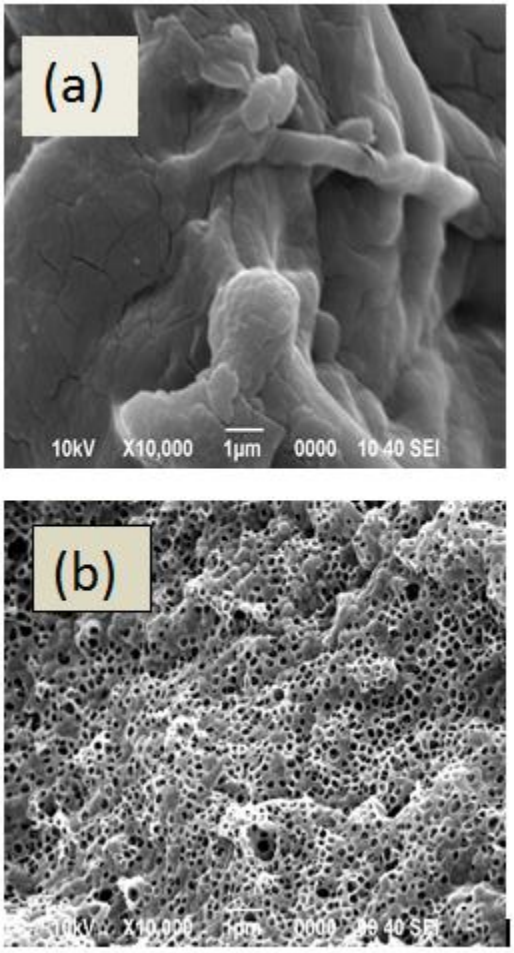


Figure 4 SEM images of (a) sodium alginate (b) Alg-g-PMMA graft copolymer

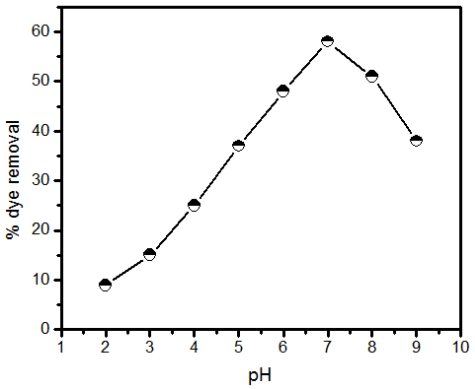


Figure 5 Effect of initial pH on adsorption of MB onto Alg-g-PMMA

3.4 Effect of Initial Concentration

The amount of dye adsorbed is highly depended on the initial dye concentration. To study the effect of initial dye concentration, adsorbent dose (0.1 g) was added into a 50-mL beakers containing different initial dye concentrations and the mixture was stirred for, 1 h the result is shown in Figure 6. The maximum percent removal occurred at 6 mg L^{-1} concentration and then progressively decreased. This may be due to the saturation of the adsorption sites on the adsorbent surface, which indicates the possibility of the formation of monolayer coverage of the dye molecules at the interface of the adsorbent.

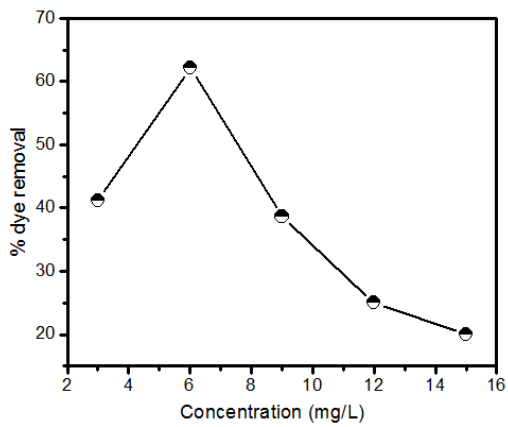


Figure 6 Effect of initial concentration on adsorption of MB onto Alg-g-PMMA

3.5 Kinetic Studies

In order to investigate the equilibrium time and the possible mechanism of the adsorption, two kinetic models were selected to examine the mechanism of the adsorption process. First, the kinetics of adsorption was analyzed by the pseudo-first-order equation given Langergren [15] as:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_e and q_t are the amounts of dye adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively and k_1 (min^{-1}) is the rate constant. Value of k_1 was calculated from the plot of ln ($q_e - q_t$) versus t (Figure not shown). The coefficient of determination (R^2) was relatively small and the experimental qe value did not agree with the calculated value obtained from the linear plot as shown in (Table 2).
On the other hand, the pseudo-second-order kinetic model has been applied to many adsorption systems as was reported by Mckay and Ho [16], the kinetic equation is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2\ q_e{}^2} + \frac{1}{q_e} t \quad (3)$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order adsorption. If the second order kinetics is applicable, then the plot of t/q_t versus t should give a linear relationship. The value of k_2 and q_e were calculated from the intercept and slope of the plot (Figure 7). The linear plot of t/q_t versus t showed closed agreement between experimental and calculated q_e value (Table 2). The coefficient of determination for the pseudo-second model is greater than 0.99 indicating the applicability of this kinetic equation. This suggested that chemosorption might be the rate limiting step controlling the adsorption process.

Table 2 Adsorption kinetic models and kinetic parameters for MB adsorption onto Alg-g-PMMA

Pseudo-First Order model				Pseudo-Second-Order model			
q_eExp (mg/g)	q_eCal (mg/g)	K_1 (min^{-1})	R^2	q_eExp (mg/g)	q_eCal (mg/g)	K_2 (g/mg/min)	R^2
2.00	1.81	0.02	0.944	2.00	2.10	0.05	0.999

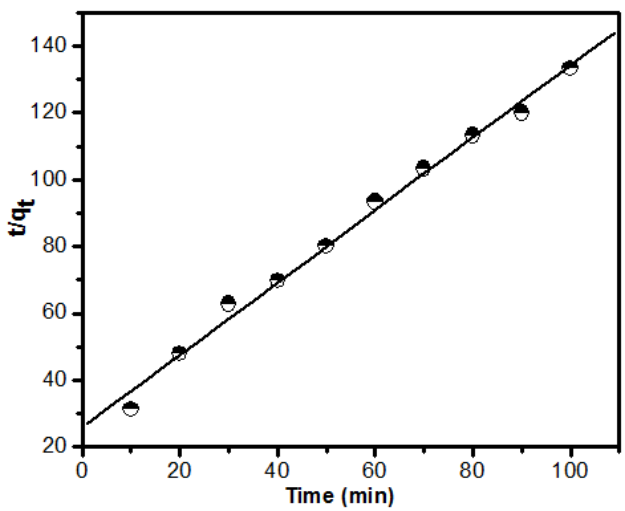


Figure 7 Pseudo-second-order kinetics for adsorption of MB onto Alg-g-PMMA

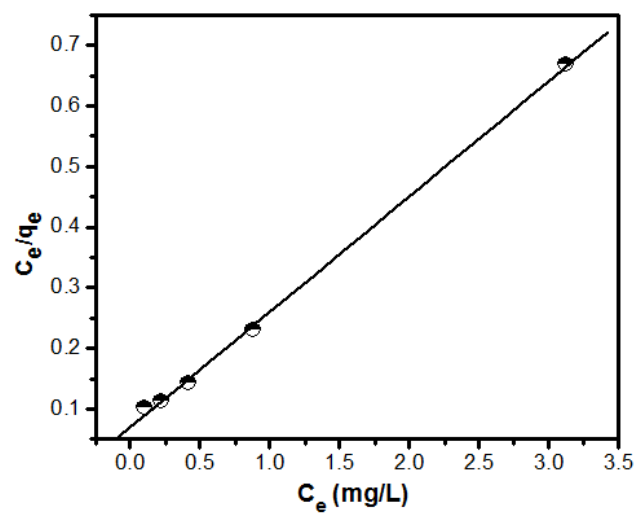


Figure 8 Langmuir adsorption isotherm of MB onto Alg-g-PMMA

3.4 Adsorption Isotherms Analysis

The adsorption isotherm represents the relationship between the amount adsorbed by a unit mass of adsorbent and the amount of adsorbate remaining in the solution at equilibrium. The Langmuir and Freundlich isotherms models were selected for adsorption isotherms studies.

3.4.1 Langmuir Isotherms Analysis

Langmuir isotherm assumes monolayer adsorption onto surface containing a finite number of adsorptive sites. The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} + \frac{C_e}{q_{max}} + \frac{1}{q_{max} \times b} \quad (4)$$

where C_e is the equilibrium concentration (mg L^{-1}) , q_e is the amount adsorbed at equilibrium (mg g^{-1}) per unit mass of the adsorbent, b is the Langmuir constant relating the free energy of the adsorption (L mg^{-1}), q_{max} is the maximum monolayer uptake capacity of the adsorbent. When C_e/q_e was ploted against C_e , a straight line with slope of $1/q_{max}$ was obtained as shown in Figure 8.

The essential characteristics of the Langmuir isotherm can be express in terms of dimensionless equilibrium parameter (R_L) [17], which is defined by:

$$R_L = \frac{1}{1+b\,C_o} \quad (5)$$

where b is the Langmuir constant and C_o is the initial dye concentration (mg L^{-1}). The value of R_L indicates the type of the isotherm: unfavorable ($R_L > 1$) and favorable ($0 < R_L < 1$).

3.4.2 Freundlich Isotherms Analysis

The Freundlich in the other hand assumes that adsorption takes place on heterogeneous surfaces, can be expressed as

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (6)$$

where q_e is the amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg g^{-1}) and C_e is the equilibrium concentration of dye in solution (mg L^{-1}). K_F and *n* are isotherms constants which indicate the capacity and the intensity of the adsorption, respectively [18].

The isotherm plot of C_e/q_e versus C_e for the adsorption of methylene blue is shown in Figure 8. It was observed that the equilibrium data fitted to Langmuir (R^2 = 0.999) model better than Freundlich model (R^2 = 0.9509) indicating surface homogeneity of the adsorbent and monolayer adsorption. From Langmuir model, the maximum monolayer adsorption capacity (q_{max}) was found as 5.25 mg g^{-1}. The value of R_L and b were calculated to be 0.068 and 2.70 mg L^{-1} respectively thus adsorption is favorable. The Freundlich constant K_F and *n* were calculated to be 4.021 mg g^{-1} and 1.83, respectively. Correlation coefficients and equilibrium constants were summarized in Table 1.

4.0 CONCLUSION

In this study, alginate-grafted poly(methyl methacrylate) copolymer was successfully prepared using benzoyl peroxide initiator. The graft copolymer was further crosslinked with calcium ions to form beads, which was evaluated for the removal of methylene blue dye from aqueous solution. The

results indicated that the graft copolymer beads can be used as an adsorbent to remove trace amount of methylene blue in aqueous solution. The kinetic of the adsorption process was found to follow pseudo-second-order model and the equilibrium data were best described by Langmuir isotherm model, with maximum monolayer adsorption capacity of 5.25 mg g^{-1}.

Acknowledgement

The authors are grateful to Universiti Teknologi Malaysia and the Ministry of Science, Tecnology and Innovation Malaysia (MOSTI) for financial support through research grant No. RJ130000.7909.4S069. The authors also thank the Ministry of Education Malaysia for financial support through research grants No. Q.J130000.2509.09H84.

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