Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2015, 7(2):237-242
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Removal of methylene blue dye from aqueous solution using alginate grafted polyacrylonitrile beads

Ahmed Salisu[a], Mohd Marsin Sanagi[a,b*], Ahmedy Abu Naim[a] and Khairil Juhanniabd Karim[a]

[a]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia*
[b]*IbnuSina Institute for Fundamental Science Studies, Nanotechnology Research Alliance, Universiti Teknologi Malaysia, Johor Bahru, Johor, Malaysia*

ABSTRACT

In this study, the removal of methylene blue (MB) dye using alginate graft-polyacrylonitrile beads was investigated. The effects of adsorption parameters such as initial pH, contact time, initial dye concentration and adsorbent dose were studied. The removal efficiency of the beads has been found to be depended on pH. The experimental equilibrium data was successfully fitted to Langmuir isotherm model with the maximum monolayer coverage of 3.51 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 in aqueous solution.

Keywords: Low-cost, sodium alginate, Langmuir model, methylene blue, trace

---

INTRODUCTION

Dye wastewaters are discharged by a wide variety of sources such as paper, textiles, leather and food industries [1-3]. Due their good solubility in water, the presence of trace amount of dyes in water (<1ppm for some dyes) is highly visible and damages the aesthetic nature of the environment. The release of dyes into the environment has become a major threat to the ecosystems.Many conventional methods are being used to remove dyes from wastewater such as adsorption, photocatalysis, oxidation, coagulation, evaporation, membrane separation etc. Adsorption is considered to be the most effective technology, because of simplicity of design and low cost [4-7]. The most widely used adsorbents are activated carbon [8], clay minerals [9], and polymers [10]. Recently, there has been considerable interest in the use of biomaterials as substitute for conventional adsorbents particularly biopolymers obtained from renewable sources due to their availability, biodegradability and low cost [11].Alginic acid or its salt called alginate is a polysaccharide obtained from seaweed species of brown algae [12].It is a linear copolymer consisting mainly the residue of β-1,4-linked-D-mannuronic acid (M-Block) and α-1,4-linked-L-guluronic acid (G-Block). The residues exist in the form of homopolymer block (M-block, G-block) or heteropolymer block (MG-block) [13]. The use alginate to remove toxic metals as well as to recover precious metals has been extensively studied [14]. The use of alginate for the removal of dyes from aqueous solution by magnetic alginate beads crosslinked with epichlorohydrin has been reported [15]. Tiwariand Kaushal reported the removal of

Rhodamine-B from aqueous solution by adsorption onto crosslinked alginate beads [16].In the present study, alginate grafted polyacrylonitrile copolymer wascrosslinked with calcium ions to form gel beads. The beads were then evaluated for removal methylene blue in aqueous medium.

MATERIALS AND METHODS

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

Graft copolymerization

Inthree-necked flask (250 mL) equipped with a reflux condenser, a predetermined weight of sodium alginate was dissolved in 100 mL distilled water. 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 selected amount of acrylonitrile was added. The reaction mixture was stirred with purged nitrogen gas. The polymerization flask was thermostat at 80°C temperature and the reaction was carried out for 4 h.. After the reaction time was over, the slurry was poured into methanol to induced precipitation. The precipitate was filtered, dried in a vacuum oven at 60°C until a constant weight and kept in a desiccator. The graft copolymer samples thus obtained were extracted for 24 h using DMF by Soxhlet extraction to remove the polyacrylonitrile homopolymer. The products were dried under vacuum at 60°C to a constant weight. The grafting percentage G (%) and grafting yield Y (%) were calculated using Equation (1) & (2), respectively, [17].

$$G\ (\%) = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

$$Y\ (\%) = \frac{W_2 - W_1}{W_3} \times 100 \qquad (2)$$

where W_1 is the initial weight of sodium alginate, W_2 is the weight of the graft copolymer after Soxhlet extraction and W_3 is the weight of methyl methacrylate.

The graft copolymer were characterized by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The maximum grafting percentagewas achieved using 1% w/v of sodium alginate, 7.53×10^{-1} M of acrylonitrile, 6.19×10^{-3} M of benzoyl peroxide, reaction temperature of 80°C and reaction time of 4 h.

Beads preparation

In the preparation of alginate-grafted polyacrylonitrile beads, 2 g of the material 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 formedcolloidal solution. The resultant colloidal solution was added dropwise into a $CaCl_2$solution (0.1 $molL^{-1}$) using a syringe with needle (1.2 × 38 mm) and the solution immediately formed solid 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.

Batch adsorption experiments

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 adsorbent 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 residualdye 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).The pH of the solution was adjusted by adding either HCl (0.1M) or NaOH (0.1M).

The percentage removal (%) was calculated using equation(3)

$$\text{Percent removal}\ (\%) = \frac{C_o - C_f}{C_o} \times 100 \qquad (3)$$

where $C_o$is the initial dye concentration (mgL^{-1}), and C_f is the residual dye concentration in the solution (mgL^{-1}).

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 optimum pH 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:

$$q_e(mg/g)= \left(\frac{C_o - C_e}{M\ (g)}\right) \times \text{Volume (L)}(4)$$

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)

RESULTS AND DISCUSSION

FTIR analysis was conducted to ascertain the presence of acrylonitrile peaks in the prepared Alg-*g*-PAN. The Spectrum of sodium alginate shown in Figure 1 (a) revealed a broad absorption band at around 3446 cm^{-1} which is assigned to O–H stretching vibration. The peak observed at 1600, 1407 and 1028 cm^{-1} is due to stretching vibrations of COO^- (asymmetric), COO^- (symmetric) and C−O respectively. The spectrum of alginate-grafted-polyacrylonitrile (Alg-g-PAN) (Figure 1 b) indicates the presence of nitrile functional group (− CN) at absorption band of 2243 cm^{-1}. Meanwhile C−H stretching vibration was observed at 2994 cm^{-1}.

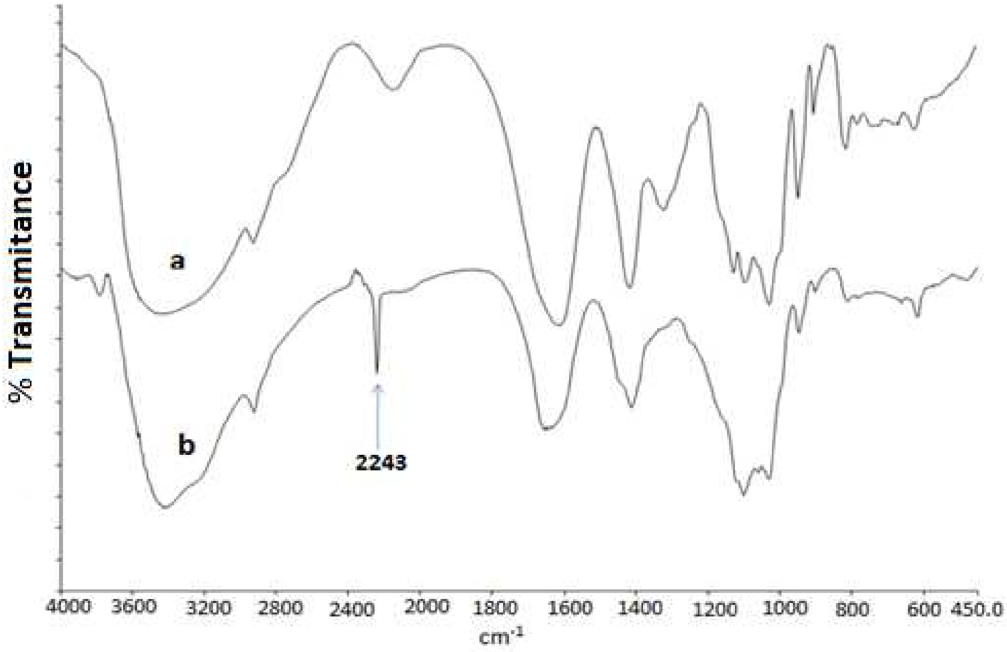

Figure 1 Infrared spectra of (a) sodium alginate and (b) the graft copolymer(Alg-*g*-PAN)

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 Fig. 2. The pH of the solution was varied from 5 to 10, the amount of adsorbent (0.1 g), dye concentration (6 mg L^{-1}) and contact time (40 min).The highest dye removal occurs at pH 7. Alginate possesses various functional groups such as hydroxyl and carboxyl groups together with long chains of polyacrylonitrile grafted onto it. 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 which does not favor the uptake of the dye due to electrostatic repulsion.

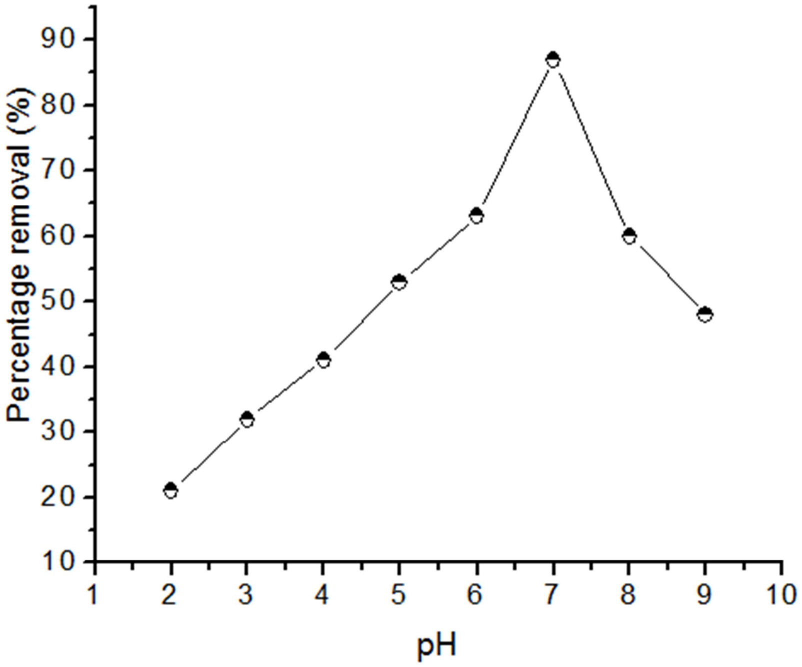

Fig. 2 Effect of initial pH on methylene blue removal

Effect of initial dye 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 used and agitated for 40 min,the result is shown in Fig. 3. The maximum percent removal occurred at 6 ppm concentration with maximum percentage removal of 85.34% and then steadily 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.

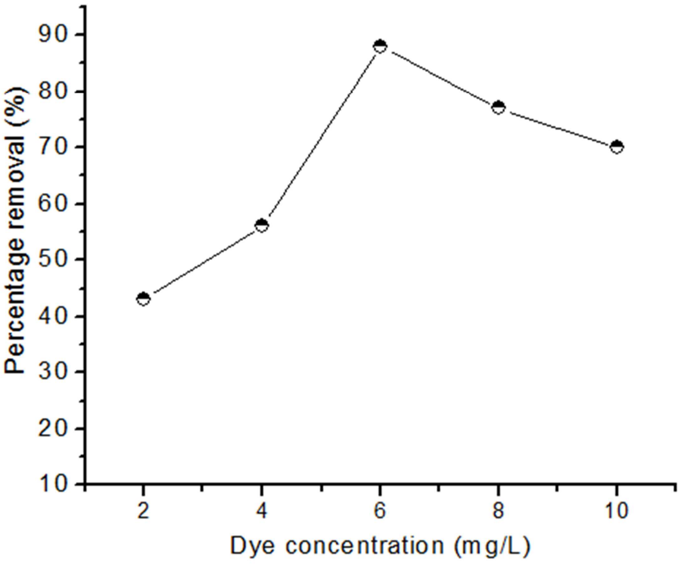

Fig. 3 Effect of initial dye concentration on methylene blue removal

Kinetics studies

Kinetic experiment was conducted and the experimental data were fitted to the pseudo-first-order and pseudo-second-order kinetic models.

Pseudo-first-order kinetic model

The pseudo-first-order equation is expressed as:

$$Log\ (q_e - q_t) = Log\ q_e - \frac{k_1}{2.303}\ t \qquad (5)$$

whereq$_e$ and q$_t$ are the amounts of dye adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, k$_1$ is the pseudo-first order rate constant (min^{-1}).

Pseudo-second-order kinetic model

The pseudo-second-order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2\ {q_e}^2} + \frac{1}{q_e}t(6)$$

where k$_2$ (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order. If this model is applicable, the plot of t/q$_t$ versus t should give a linear relationship. The pseudo-first-order and pseudo-second-order rate constants and correlation coefficients were calculated and are listed in Table 1. The high correlation coefficient of pseudo-second-order kinetics suitably represented the experimental data.

Table 1Kinetic parameters for the adsorption of MB blue onto Alg-*g*-PAN

Rate constants	Parameters	Value
Pseudo-first order	k$_1$ (min^{-1}) q$_e$ (mg g^{-1}) R^2	0.318 1.67 0.984
Pseudo-second order	k$_2$ (g mg^{-1} min^{-1}) q$_e$ (mg g^{-1}) R^2	0.0518 0.83 0.992

Adsorption isotherms studies

The adsorption isotherm represents the relationship between the amount adsorbed by a unit 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. The Langmuir model is valid for monolayer adsorption and expressed in the linear form as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} \times b} \qquad (7)$$

where Ce is the equilibrium concentration (mg L^{-1}), qe is the amount adsorbed at equilibrium (mg g^{-1}) per unit weight of the adsorbent; b is the Langmuir constant relating the free energy of adsorption (L mg^{-1}); qmax is the maximum monolayer uptake capacity of the adsorbent. The essential characteristics of the Langmuir adsorption can be expressed in terms of a dimensionless constant referred to as separation factor or equilibrium parameter for predicting whether an adsorption system is favorable or unfavorable. R$_L$ is calculated using the equation below:

$$R_{L=}\frac{1}{1+bC_o} \qquad (8)$$

where Co is the initial dye concentration (mg L^{-1}). If R$_L$ value lies between $0 < R_L < 1$, the adsorption is favorable

The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as:

$$\text{In qe} = \text{In } K_F + n\text{InCe} \qquad (9)$$

where K_F indicates adsorption capacity (mg g^{-1}) and n an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorption.

The equilibrium data fitted to Langmuir (R^2 = 0.992) model better than Freundlich model (R^2 = 0.981) indicating surface homogeneity of the adsorbent and monolayer adsorption. From Langmuir model, the maximum monolayer adsorption capacity (q_{max}) was found as 3.51 mg g^{-1} R_L and b were calculated to be 0.096 and 1.88 mg L^{-1} respectively thus adsorption is favorable. The Freundlich constant K_F and n were calculated to be 4.51 mg g^{-1} and 0.83, respectively. Correlation coefficients and equilibrium constants were summarized in Table 2.

Table 2 Equilibrium parameters and coefficients of determination of MB onto Alg-*g*-PAN

Model	Parameters	Value
Langmuir	q_{max} expt. (mg g^{-1})	3.51
	q_{max}cal. (mg g^{-1})	3.79
	R_L	0.096
	b(L mg^{-1})	1.88
	R^2	0.995
Freundlich	K_F	4.51
	n	0.83
	R^2	0.981

CONCLUSION

Cross-linked alginate-grafted polyacrylonitrile copolymer bead was prepared to selectively remove methylene blue dye from aqueous solution. The results indicated that the copolymer beads can be used as an alternative low-cost adsorbent to remove trace amount of methylene blue in aqueous solution.The optimum pH for maximum adsorption was observed at 7. The kinetic data followed well with pseudo-second-order model and Langmuir isotherm model satisfactorily fittedthe equilibrium data.

Acknowledgment

The authors are grateful to the UniversitiTeknologi Malaysia and the Ministry of Science, Tecnology and Innovation Malaysia (MOSTI) for financial support through research grant [No. RJ130000.7909.4S069].

REFERENCES

[1] D. Pokhrel, T. Viraraghavan *Sci Total Environ* **2004** 333, 37
[2] O. Tunay, I. Kabdasli, G. Eremektar, D. Orhon *Water SciTechnol**1996***, 34, 9
[3] A. Cassano, R. Molinari, M. Romano *J. MembrSci* **2001** 181,
[4] BH Hameed, DK. Mahmoud, AL. Ahmad *J Hazard mater*.**2008** 158, 65
[5] Q. Qingdon, MA. Jun, Keliu *J Hazard mater*.**2009** 162, 133
[6] C. Jerzy, Z. Anna,G. *Joana Adsorption**2010*** 16, 377
[7] V. Singh, AK. Sharma, DN. Tripathi, R. SanghiJ *Hazard mater* **2009** 161, 955
[8] JM. Dias, Alvim-Ferraz, CM. Maria, MF. Almeida, JS. Manuel *J Environ Management* **2007** 85, 833
[9] M. Dogan, A. Mahir, T. Aydin, O. YaseminJ *Hazard mater*. **2004** 109, 141
[10] NRM. Masque,F. *Borrull Trends* **1998**17, 384
[11] G. Crini *Bioresource Technol* **2006** 97, 1061
[12] H. Ertesvag, S. Valla *Polymdegrad Stab* **1998** 59, 85
[13] T. Matsumoto, M. Kawai, T. *Masuda Biorheology* **1992** 29, 411
[14] AD. Thomas, V. Bohumil, M. *AlfonsoWater Res*. **2003** 37, 4311
[15] A. Bee, V. Rocher, M. Jean, C. *Valeric Water Res* **2008** 42, 1290
[16] A. Tiwari, M. KaushalJ. *Disper Sci Technol* **2010** 31, 438
[17] K. Kaewtatip, V. Tanrattanakul *Carbohydr Polym* **2008** 73, 647