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Research paper

Adsorption Studies of Methylene Blue by Encapsulated Nano-Carbonaceous Alginate Beads

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Abstract

Two different nano-carbonaceous materials namely, multi-walled carbon nanotubes and graphene oxide were encapsulated with biopolymer alginate and employed as adsorbents for the removal of methylene blue dye from aqueous solution. To evaluate the performance of synthesized adsorbents, several parameters including adsorbent dosage, sample volume, stirring speed, sample pH, contact time and initial dye concentration were optimized. The optimum conditions were found as follow: 0.1g adsorbent dosage, 400 rpm stirring speed, 10 mL of sample volume, 180 minutes contact time, pH 11 and 20 mg/L initial concentration of methylene blue. From the results, the encapsulated Alginate-carbonaceous beads gave higher removal percentage as compared to pristine alginate beads. This could attribute by additional hydrophobic and π-π interaction contributed from aromatic rings of carbonaceous material towards methylene blue molecular structure. Whilst, kinetic studies showed that the adsorption process accurately represented by a pseudo second-order model.

Keywords: *adsorption; alginate; graphene oxide; multiwall carbon nanotubes*.

1. Introduction

Dyes have been extensively used in various industries such as textile, leather, paper, cosmetics, plastic, pharmaceutical rubber and food [1]. The extensively used of dyes in various industries and improper disposal has lead series of pollution problems significantly towards aquatic system. Molecular of dye which mainly aromatic structure are biological non-biodegradable, stable to light oxidation, prevent sunlight and oxygen, thus disturb the photosynthesis process in aquatic systems [2]. They also can be degraded to carcinogenic, toxic, and mutagenic compound that will effect on living organisms [3]. Therefore, technologies are needed for the removal of dyes from aqueous solution.

Numerous technologies including ultrafiltration, ion exchange, photocatalysis, adsorption, electro-dialysis, chemical oxidation, chemical precipitation and coagulation have been implemented for the treatment of dyes contaminant [4]. Among these, adsorption technology is the most preferable technique due to easy access, simple operation without entail sludge formation, effectively remove both organic and inorganic pollutants and regeneration of adsorbent [5]. However, improving adsorption efficiency is a great challenges and various adsorbents have potential to lower dyes concentration in aqueous solution such as fly ash [6], saw dust [7], activated carbon, zeolite [8] calcined animal bones [9], mesoporous silica [10], magnetic nanomaterials [11] and graphene oxide [12].

In recent years, carbonaceous materials have been extensively used for adsorption applications such as activated carbon due to their good chemical stability, structural diversity, low density and suitability for large scale production [13]. Carbon nanotubes (CNTs) serve as excellent adsorbents because of their hollow, layered structure and large surface area [14]. The CNTs adsorbents can be grouped into three sorts that are single-walled CNTs (SWCNTs), multi-walled CNTs (MWCNTs) and functionalized CNTs [15]. MWCNTs exhibit excellent adsorption for heavy metal ions, radioactive elements, dye, pesticide and other organic pollutants in the water since its possess small radial size, excellent mechanical properties, outstanding electrical conductivity and thermal conductivity [16]. Another fascinating nanomaterial is graphene oxide (GO), have great attracted attention in wastewater treatment [17]. Owing to massive quantities of oxygen-containing functional groups in carboxyl, epoxy, and have large specific surface area, it could be an excellent choice for the adsorption of various organic molecules such as organic dye, heavy metals and aromatic compounds [18-19].

However, nanoscale MWCNTs and graphene oxide are too small and light to isolate from effluent and these materials are insoluble and easily to clump due to strong inter-tube Van der Waals forces which might tend to give difficulty in adsorption [20]. Therefore, to facilitate phase separation of MWCNTs and GO by functionalize and coupling with superior performance materials. Recently, development encapsulation of carbon materials and biopolymers have been made and represent an interesting option for the removal pollutants due to it can increase hydrophobic sites, surface area and the porosity of the materials. This approach can retain the structure and original properties after modification [21-22].

Alginates are well known in development of adsorbents as well as encapsulation in cell immobilization and drugs delivery due to its nontoxicity, biodegradability and chemical versatility [23]. Alginate is a biopolymer extracted from brown algae and consists of edible polysaccharides with homopolymeric blocks of 1-4 linked *d*-mannuronate and *L*-guluronate [24]. Alginate has been explored as supporting material by encapsulating with activated carbon

[25], carbon [17], synthetic polymer [26] and maghemite nanoparticles [27] to form as adsorbents for heavy metals, dyes and other pollutants [1, 28].

To the best of our knowledge, there are only few investigations focused on comparison adsorption studies towards dyes removal by carbonaceous materials with alginate. Within this framework, the present study focuses on the synthesis and adsorption properties of the encapsulated MWCNTs and GO within alginate in the form of beads. The adsorption performance and kinetic studies have been evaluated to observe the effects of various parameters such as medium acidity, contact time and initial concentration of methylene blue (MB) removal

2. Experimental section

2.1. Materials

Graphene oxide was purchased from GO Advanced Solution Sdn Bhd and multiwalled carbon nanotubes (MWCNTs) was obtained from Sun Nanotech (Jiangxi, China). Other chemicals such as methylene blue ($C_{16}H_{18}N_3SCl.3H_2O$), acetic acid (CH_3COOH), sodium hydroxide (NaOH, sodium alginate ($C_6H_7NaO_6$), calcium chloride and methanol used were purchased from Sigma Aldrich.

2.2. Instrumentation

Chemical characteristics of the prepared materials were examined using Fourier Transform Infrared (FTIR) spectroscopy model Perkin Elmer. The morphology of materials was viewed by scanning electron microscopy (SEM) of a TM3030 PLUS instrument. While, Ultra Violet Visible (UV-Vis) Spectrometer (Perkin Elmer Lamda 35, Deuterium Lamp, 190-110 nm) was used to evaluate the adsorption activities of prepared materials toward methylene blue.

2.3. Procedure

2.3.1. Preparation of solutions

A 1000 mg/L of MB dye solution was prepared as stock solution and 100 mg/L of MB dye was prepared for working solution. Series of initial MB dye concentration 5, 10, 15, 20 and 25 mg/L was prepared from 100 mg/L solution. Then, the standard solution was observed via UV-Vis spectrometer at λmax 659 nm to obtain the calibration curve.

2.3.2. Preparation of alginate beads

An aqueous solution of 3% w/v alginate (Alg) was prepared by dissolving the subsequent amount of sodium alginate in deionized water and was vigorously stirred ate constant temperature 60 °C for 1 h. The solution was then dripped into 0.1 M of calcium chloride ($CaCl_2$) solution by using micropipette to form the Alg beads. The Alg beads was filtered, washed thoroughly with deionized water and dried at 60 °C for overnight.

2.3.3. Preparation of alginate-multiwalled carbon nanotubes and alginate-graphene oxide beads

Preparation of Alginate-Multiwalled Carbon Nanotubes (Alg-MWCNT) and Alginate-Graphene Oxide (Alg-GO) were adapted from previous study [23] with minor modification. 3 g of sodium alginate powder was dissolved in 60 °C of 70 mL deionized water and stirred using magnetic stirrer. A mixture of 0.3 g of carbonaceous material (MWCNTs or GO) was dispersed using sonication with 30 mL deionized water for 30 minutes. Then, this solution was mixed with alginate solution and sonicate for further 30 minutes. The mixture was then dripped into 0.1M of CaCl2 solution using micropipette and the carbonaceous encapsulated in alginate beads were form upon contact. The beads were filtered, washed with deionized water and dried at 60 °C for overnight.

2.3.4. Batch Adsorption Experiment

Adsorption experiments were carried out at room temperature using batch process on a shaker (400 rpm). **Effect of Medium Acidity.** A series of MB solution (10 mL, 20 mg/L) were adjusted to pH 3, 5, 7, 10, 11 and 12 by adding either HCl or NaOH solution. Into every MB solution, 0.1 g adsorbent beads were added, the mixture was shaken for 60 min, and followed by the phase separation using gravity filtration. The residual MB solution was determined with UV-Vis. **Adsorption Kinetics.** Into a series MB solution (10 mL, 20 mg/L) at optimum pH 10, 0.10 g of adsorbent beads was added, shaken for various contact times the range 30 – 300 min and followed by the phase separation using gravity filtration. The residual MB in every solution was determined with UV-Vis. **Adsorption Isotherm.** Adsorption isotherm was conducted by using a series of 10 mL MB solution with various concentration at optimum pH. Into every MB solution, 0.10 g of adsorbent beads was added, shaken for optimum contact time, and followed by the phase separation. The MB concentration in the solution was determined with UV-Vis.

3. Results and discussion

3.1. Characterization of adsorbents

The Alg beads formed in yellowish color while, Alg-MWCNT and Alg-GO beads adsorbents obtained in black color. The prepared beads have spherical in shape with bead diameter size < 0.2 cm.

FTIR analyses were carried out to ascertain the functional groups present in prepared adsorbents. Major absorption bands of Alg, Alg-MWCNT and Alg-GO beads were summarized in Table 1. A slight variation was observed in -OH stretching bands (3348-3263 cm^{-1}) and C-H stretching for aromatic rings (2140-2109 cm^{-1}) indicating intermolecular hydrogen bonds occurred between aromatic proton of carbonaceous with the backbone of alginate [29]. While shifting of vibration bands in the range 1423-1417 cm^{-1} (COO- stretching), 1080-1030 cm^{-1} (C-O stretching) and 942-940 cm^{-1} (C-O-C stretching) proved a good miscibility of Alg-carbonaceous matrix through π–π stacking and electrostatic interactions [22, 30-31].

Table 1: Comparison FTIR absorption bands of Alg, Alg-MWCNT and Alg-GO beads

Adsorption stretching bands	**Wavelength (cm^{-1})**		
	Alg	**Alg-MWCNT**	**Alg-GO**
O-H	3348	3345	3263
C-H	2140	2109	2118
COO^-	1423	1420	1417
C-O	1080	1070	1030
C-O-C	942	940	941

The morphologies of prepared adsorbent were studied by SEM as shown in Fig. 1. Pristine Alg beads possess smooth outer surface with minimal small pores observed at high magnification, which similar as reported in previous study [32]. While, Fig 2(b-c) show multilayer of MWCNTs and black graphite thick planar sheets of GO were observed over the exterior surface of alginate indicating high compatibility of carbonaceous within alginate matrix [33-34]. Interestingly, the present of carbonaceous material onto Alg matrix will increased the surface area as well as the adsorption sites of the adsorbents [35].

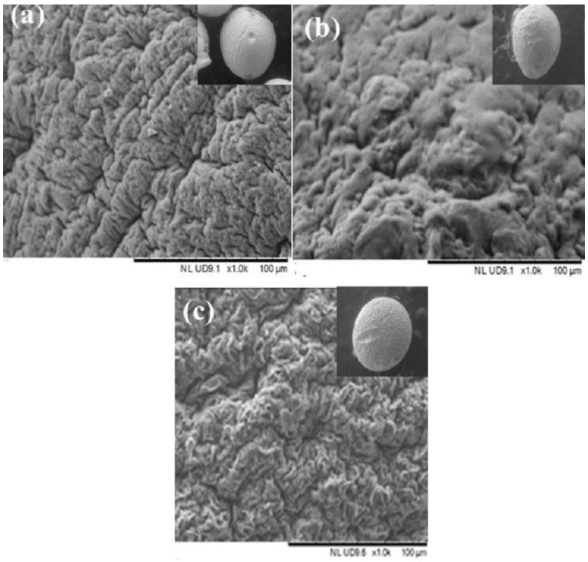

Fig 1: SEM micrograph of beads Alg at (a), Alg-MWCNT (b) and Alg-GO (c)

3.2. Adsorption studies

3.2.1. Effect of medium acidity

Medium acidity is expected to significantly influence the efficiency of dyes removal. In this work, different pH values in the range of 3-12 were investigated by adjusting the sample solution with 1.0 M HCl and 0.1 NaOH solution. Fig. 2 shows the adsorption of MB dye significantly increases from pH 3 to 10. The differences in adsorption behavior under various pH values can be explained due to electrostatic forces between the surface of beads and MB dyes. At pH below than 5, the carboxylate groups of alginate tend protonated, leading to less electrostatic forces between the MB and adsorbents molecular structure. Also, under acidic conditions, massive quantities of H_3O+ ions existed, which can compete with dye cations adsorbing on the active sites, resulting in the lower removal percentage [36-38]. While, at mild acid to basic medium, the alginate presence at natural structure. Thus, the interaction between at their optimum condition due to contribution of electrostatic, hydrophobic and π-π interaction form both alginate and aromatic rings of carbonaceous materials [22]. Therefore, pH 10 of aqueous solutions was suggested for subsequent experiment to get high percentage removal of MB.

3.2.2. Effect of contact time

Contact time is an important parameter to determine the equilibrium time and kinetics of adsorption process. Thus, in this study, the effect of contact time on adsorption MB was determined by exposing the prepared beads in aqueous sample for different lengths of time in the range of 30-300 min. The results as shown in Fig. 3 revealed that the adsorption activities significantly increased with contact time of up to 180 min, beyond which it gradually decreased [39]. It is clearly show that the adsorption process of MB on Alg-MWCNT and Alg-GO adsorbents has adsorption capacity higher than Alg adsorbents. This could be attributed to the considerable hydrophobic and hydrophobic and π-π interaction of abundance of aromatic rings in the nano-carbonaceous materials [18, 40]. It was observed that adsorption of MB onto Al-GO 20% higher than adsorption of Al-MWCNT. This phenomena could be explained by presence of graphite planar sheet and massive quantities oxygen-containing functional groups of GO at exterior surface of the beads provide easy pathway for the adsorption to occurred [41]. However, nature of multi layered wall of porous MWCNTs might be difficult for the MB structure to pass through, thus inhibit the adsorption to occurred between layer.

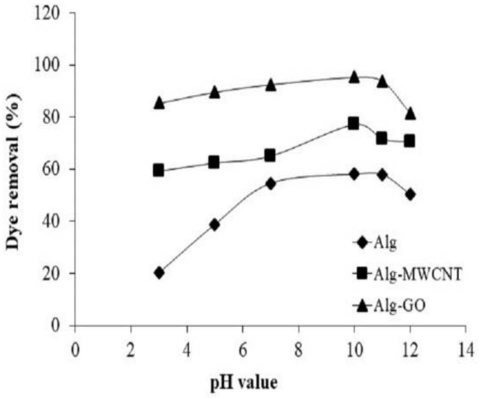

Fig. 2: Effect of medium acidity on the removal of MB by prepared adsorbents at 27 °C, stirring speed 400 rpm, 0.10g adsorbents, initial concentration 20 mg/L and contact time 30 min.

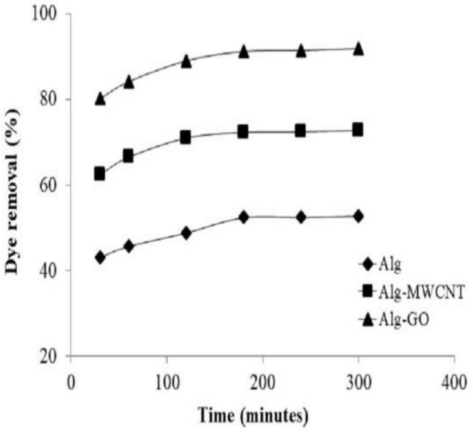

Fig. 3: Effect of contact time on the removal of MB by prepared adsorbents at 27 °C, stirring speed 400 rpm, 0.10g adsorbents, initial concentration 20 mg/L and optimum pH 10.

3.2.3. Adsorption kinetics

The kinetic study of MB adsorption onto Alg and Alg-GO adsorbents were determined using three common models being pseudo-first-order model (Eq. 1), pseudo-second-order model (Eq. 2), and intraparticle diffusion model (Eq. 3), respectively.

$$\log (q_e - q_t) = \log q_e - (k_1 t / 2.303) \quad (1)$$

$$(t / q_t) = (1 / k_2 q_e^2) + (t / q_e) \quad (2)$$

$$q_t = k_3 t^{1/2} + C \quad (3)$$

where qt (mg/g) and qe (mg/g) represent the adsorption capacities at time t and at equilibrium respectively; k_1 (g/(mg.min)), k_2 (g/(mg.min)) and k_3 (g/(mg.min$^{1/2}$) are the first-order, second-order, and intraparticle diffusion rate constants, respectively; C is the intercept of intraparticle diffusion model. The fitting results are summarized in Fig. 4 and Table 2. The suitability was determined by introducing the correlation coefficient (R^2). The closer the value R^2 to 1, the more applicable the model was. For all MB concentration (20, 40, 60, 80 and 100 mg/L), the correlation for pseudo-second-order model (0.9995) was much larger than that for the pseudo-first-order model (0.9143), indicating that MB adsorption onto Alg beads, Alg-MWCNT and Alg-GO beads can be described as pseudo-second-order model. The adsorption capacities calculated by pseudo-second-order model were close to those determined by the experiments. As conclusion, MB adsorption on Alg, Alg-MWCNT and Alg-GO beads can be described as pseudo-second-order model which described the chemical adsorption behavior.

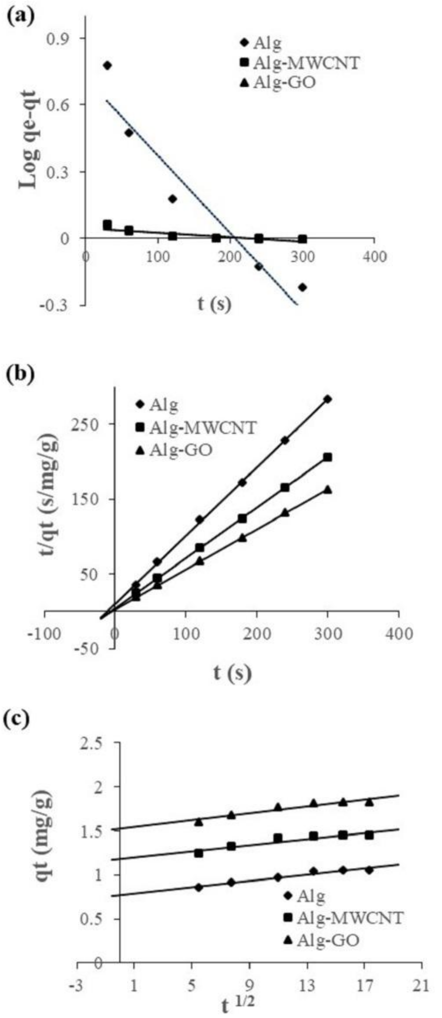

Fig. 4: Adsorption kinetics of MB on Alg, Alg-MWCNT and Alg-GO beads fitted to the pseudo-first order rate model (a), pseudo-second order rate model (b) and intraparticle diffusion (c)

Table 2: Calculated values of parameters for pseudo-first-order, pseudo-second-order and the intraparticle diffusion model of the Alg, Alg-MWCNT and Alg-GO beads

Model	Parameter	Adsorbents		
		Alg	Alg-MWCNT	Alg-GO
pseudo-first-order	q_e (mg g^{-1})	5.29	1.31	1.12
	k_1 (min^{-1})	8.06×10^{-3}	5.43×10^{-4}	4.61×10^{-4}
	R^2	0.914	0.743	0.794
pseudo-second-order	q_e (mg g^{-1})	1.10	0.98	1.88
	k_1 (min^{-1})	8.552×10^{-2}	9.35×10^{-2}	9.193×10^{-2}
	R^2	0.999	1	1
intraparticle diffusion	C (mg g^{-1})	0.78	1.39	1.53
	K_3 (min^{-1})	1.75×10^{-2}	1.99×10^{-2}	1.980×10^{-2}
	R^2	0.940	0.864	0.903

3.2.4. Effect of initial concentration

The influence of initial dye concentration in equilibrium uptake of MB dye by Alg, Alg-MWCNT and Alg-GO adsorbents were presented Fig. 5. The initial dye concentrations were varied from 20 100 mg/L while keeping the other parameters as constant. From observation, the percentage removal of dye decreases with more than 20 mg/L MB concentration. This might be due to limitation of adsorbents capacity, where it become saturated at particular concentration [27]. As such at higher concentrations, more MB dye molecules are left unabsorbed in the solution resulting in decreased of dye removal percentage.

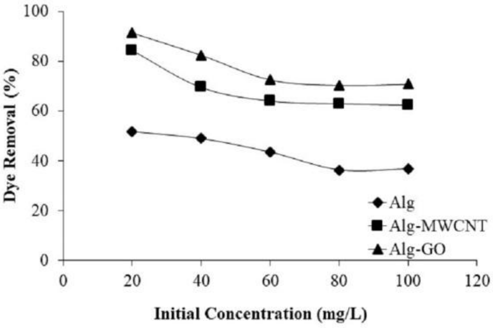

Fig 5: Effect of initial concentration on the removal of MB by prepared adsorbents at 27 °C, stirring speed 400 rpm, 0.10g adsorbents, at optimum pH 10 and 180 min contact time.

3.2.5. Adsorption Isotherm

In order to determine quantitatively the adsorption of MB onto Alg, Alg-MWCNT and Alg-GO, Langmuir and Freundlich models were utilized to describe the sorption isotherms of MB on prepared adsorbents. The Langmuir isotherm model presented that a monolayer adsorption specify that the adsorbent has a finite capacity for adsorbate to be adsorbed onto the adsorbent, all the sites are energetically equilibrium, and there is no interaction between the adsorbed molecules [42]. The Freundlich model is a multilayer adsorption on heterogeneous surfaces with interaction between adsorbed molecules where the energy is reduced upon completion of the sorption sites of the adsorbent [43].The linear form of Langmuir and Freundlich equations were expressed in (Eq. 4) and (Eq.5) respectively.

$$(C_e / q_e) = (1 / q_{max} K_L) + (C_e / q_{max}) \quad (4)$$

$$\log q_e = \log K_F + (1 / n) \log C_e \quad (5)$$

where q_{max} is defined as the capacity of adsorbent (mol/g), q_e is the equilibrium adsorptive quantity of the adsorbate per gram of adsorbent (mol/g), C_e is the equilibrium adsorbate concentration (mg/L). K_L and K_F is the Langmuir and Freundlich adsorption constant respectively and n is the Freundlich exponential coefficient.

Adsorption isotherms of MB on Alg, Alg-MWCNT and Alg-GO are summarized in Table 3. All three adsorbents gave correlation coefficient for Freundlich equation (R^2 > 0.9716, 0.9604 and 0.9752, which were better than Langmuir equation (R^2 > 0.9434, 0.8223 and 0.8867) respectively. It is indicating that, the adsorption of MB onto these adsorbents may occurs in a multilayer adsorption on varied surfaces with possible interactions taking place between the adsorbed molecules and that the adsorption energy depletes upon equilibrium. Thus, isotherm adsorption equation of MB onto these adsorbent fitted better to the Freundlich isotherm model.

Table 3: Calculated values of parameters in Langmuir and Freundlich equations.

Model	Parameter	Adsorbents		
		Alg	Alg-MWCNT	Alg-GO
Langmuir	q_{max} (mol/g)	5.886	8.599	8.361
	K_L(L/mol)	1.265	0.272	0.140
	R^2	0.943	0.822	0.887
Freundlich	K_F (mol/g)	0.268	0.885	1.392
	n	1.592	1.976	2.236
	R^2	0.972	0.960	0.975

All data on the effect of medium acidity, contact time and initial concentration for adsorption capacity (qt) and percentage dye removal (% R) for prepared adsorbents were Tabulated in Table 4.

Table 4: Summarized data on the effect of medium acidity (pH) on removal of MB by Alg, Alg-MWCNT and Alg-GO beads.

Parameter	**Adsorption capacity, qt (mg/g), (Dye removal, %)**		
Acidity (pH)	**Alg**	**Alg-MWCNT**	**Alg-GO**
3	0.40 (20)	1.18 (59)	1.71 (85)
5	0.67 (33)	1.25 (62)	1.80 (90)
7	1.09 (54)	1.03 (65)	1.85 (92)
10	1.16 (58)	1.54 (77)	1.91 (95)
11	1.16 (58)	1.43 (72)	1.88 (94)
12	1.00 (50)	1.41 (71)	1.63 (81)
Time (min)	**Alg**	**Alg-MWCNT**	**Alg-GO**
30	0.86 (43)	1.25 (62)	1.60 (80)
60	0.91 (46)	1.33 (66)	1.68 (84)
120	0.98 (49)	1.42 (71)	1.78 (89)
180	1.05 (52)	1.45 (72)	1.82 (91)
240	1.05 (52)	1.45 (72)	1.83 (91)
300	1.05 (52)	1.45 (72)	1.83 (91)
Initial conc. (ppm)	**Alg**	**Alg-MWCNT**	**Alg-GO**
20	1.04 (52)	1.69 (84)	1.83 (91)
40	1.97 (49)	2.78 (70)	3.30 (82)
60	2.61 (44)	3.84 (64)	4.35 (73)
80	2.90 (36)	5.03 (63)	5.63 (71)
100	3.66 (35)	6.23 (62)	7.08 70)

4. Conclusion

Three adsorbents Alg, Alg-MWCNT and Alg-GO were successfully prepared and was confirm by FTIR and SEM analysis. The effects of experimental parameters on the MB removal were investigated by conditions optimization of adsorbents contact time, sample pH, and initial concentration of MB. The optimum conditions obtained as follow; 180 minutes contact time, 20 mg/L of initial concentration at sample pH 10.

The encapsulated carbonaceous alginate beads provide higher percentage MB removal as compared to alginate beads due to additional hydrophobic and π-π interaction contributed from aromatic rings of MWCNTs and GO. The freundlich and langmuir models were used to describe the isotherms and the freundlich model was shown to provide the best fitting. From kinetic studies, it showed that the adsorption process was more accurately represented by a pseudo second-order model.

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