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KINETIC STUDIES AND ABSORPTION ISOTHERMAL OF METHYLENE BLUE BY USING N,O-CARBOXYMETHYL CHITOSAN

(Kajian Kinetik dan Isoterma Serapan Metilena Biru Menggunakan N,O-Karboksimetil Kitosan)

Putri Amirah Solehin Sulizi and Nadhratun Naiim Mobarak*

Department of Science Chemistry, Faculty of Science and Technology
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

**Corresponding author: nadhratunnaiim@ukm.edu.my*

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Abstract

The potential of carboxymethyl chitosan as a low-cost and effective adsorbent for removal of methylene blue (MB) from aqueous solution has been investigated. N,O-carboxymethyl chitosan (N,O-CMCTS) was synthesized by reacting chitosan with monochloroacetic acid. The presence of a carboxymethyl group on carboxymethyl chitosan structure was demonstrated by Fourier Transform Infrared (FTIR) spectroscopy, with the presence of peaks at 1587 cm^{-1} and 1408 cm^{-1} assigned to the asymmetrical and symmetrical stretching vibrations of carboxylate anions ($-COO^-$). ^1H nuclear magnetic resonance (NMR) results confirm that *O-*, *N-* substituted carboxymethyl chitosan was synthesized, as the presence of peaks at 3.987 and 3.275 ppm that represent the substitution of carboxymethylation occurred at both hydroxyl and amino groups of chitosan. The influence of parameters such as initial dye concentration, sorbent dosage and sorption time on the sorption capacity were studied using the batch method. The results showed that maximum sorption capacity N,O-CMCTS was 0.549 mg/g. The concentration of methylene blue and the quantity of N,O-CMCTS were important in the absorption process, as the kinetic data followed pseudo second order. The sorption of methylene blue on N,O-CMCTS was via chemisorption, as in the isothermal studies, it followed Freundlich model.

Keywords: N,O-carboxymethyl chitosan, methylene blue, isotherms, kinetic

Abstrak

Potensi karboksimetil kitosan sebagai penjerap kos rendah dan efektif untuk menyingkirkan metilena biru (MB) dalam larutan akueus telah dikaji. N,O-karboksimetil kitosan (N,O-CMCTS) telah di sintesis melalui tindak balas kitosan dengan asid monokloroasetik. Kehadiran kumpulan karboksimetil pada struktur karboksimetil kitosan telah dibuktikkan dengan keputusan spektroskopi inframerah transformasi Fourier (FTIR) di mana kehadiran puncak pada 1587 cm^{-1} dan 1408 cm^{-1} yang menunjukkan getaran regangan asimetri dan simetri bagi anion karboksilat ($-COO^-$). Keputusan ^1H resonans magnet nukleus (NMR) mengesahkan penggantian *O-*, *N-* karboksimetil kitosan telah di sintesis dengan kehadiran puncak pada 3.987 dan 3.275 ppm yang menunjukkan penggantian pengkarboksimetil terjadi pada kedua-dua kumpulan hidroksil dan amino pada kitosan. Parameter yang mempengaruhi seperti kepekatan awal pewarna, dos penjerap dan masa erapan terhadap kapasiti erapan telah dikaji menggunakan kaedah kelompok. Keputusan menunjukkan kapasiti erapan maksima N,O-CMCTS adalah 0.549 mg/g. Dari kajian ini, kepekatan metilena biru dan kuantiti N,O-CMCTS adalah penting bagi proses serapan di mana data kinetik mengikut tertib pseudo kedua. Selain itu, erapan metilena biru pada N,O-CMCTS secara jerapan kimia serta ujian isoterma mengikut model Freundlich.

Kata kunci: N,O-karboksimetil kitosan, metilena biru, isoterma, kinetik

Introduction

It is estimated that over 10,000 different dyes and pigments are used industrially, while over 7 x 10^5 tons of synthetic dyes are annually produced worldwide [1]. In the textile industry, up to 200,000 tons of these dyes are lost to effluents every year. It is estimated that approximately 15% of dye stuffs are lost in industrial effluents during manufacturing and processing operations [2]. Unfortunately, most of these dyes escape conventional wastewater treatment processes and persist in the environment as a result of their high stability to light, temperature, water, detergents, chemicals, soap and other parameters such as bleach and perspiration [3]. The removal of dye pollutants from wastewater effluents is vital, because even a small quantity of dye in water is toxic and highly visible. Moreover, their degradation products may be mutagenic and carcinogenic. Methylene blue is widely used in the textile industry and may cause discoloration, coldness, redness or dryness when contact with skin if it exceeds World Health Organization (WHO) or United States Environmental Protection Agency (US-EPA) limits. Ingestion of methylene blue may result in gastrointestinal irritation, discoloration of oral mucosa, irritation of lips, mouth and throat, paleness of complexion, insufficient coordination or drowsiness [2]. International Organization of Standardization 16265 (ISO 16265) for the determination of the methylene blue active substances (MBAS) has an index which ranges from 0.05 mg/l to 0.5 mg/l and 0.5 mg/l to 5.0 mg/l in various water samples (e.g. ground water, drinking water, surface water, waste water and leachates) [4]. Major problems associated with colored effluent include lowering light penetration, photosynthesis and damages the aesthetic nature of the water surface [5]. It is challenging to treat the dye effluents, as they are mostly biologically non-degradable and stable to light and heat. Most dyes are of synthetic origin and have a complex aromatic structure.

Nowadays, there is great interest in finding inexpensive, biodegradable, non-toxic and an environment friendly material for the removal of dyes [6]. Many non-conventional low-cost adsorbents have been studied for the removal of methylene blue, including natural materials, biosorbents and waste materials from agriculture and industry [7]. Among the natural polymeric materials, chitosan is the most attractive polymer due its low cost and ready availability. Chitosan is a linear copolymer composed of (1-4)-linked D-glucosamine and N-acetyl-D-glucosamine and is obtained by alkaline hydrolysis of chitin (second abundant polymer in nature after cellulose) [8]. Chitin is obtained from crustaceans (crab, krill, crayfish) primarily because a large amount of crustacean exoskeletons is available as a by-product of food processing. Chitosan is widely used for removal of heavy metals, transition metals and dyes as a well-known sorbent. Chitosan based biosorbents show high affinity for various dyes and have wide range of applications in the biomedical, cosmetic, food and textile industries [9]. Even though chitosan can adsorb the anionic dyes, as it is cationic in nature, some chemical modifications of chitosan are necessary to enhance their properties and consequently their applications [10, 11]. Various modification on chitosan as adsorbents have been examined, such as grafting, cross-linking and functionalization for forming composite for adsorption of dyes in aqueous media [12]. Carboxymethylation of chitosan is a very attractive method as it introduces active carboxyl (-COOH) groups into the molecule. This is lead to an increase in the adsorption capacity of chitosan for dyes, transition and heavy metals [13].

The present work deals with a series of experiments that focus on higher concentrations of methylene blue, ranging from 1000-1800 mg/l [14]. In this study, we focused removal at low concentration of methylene blue on N,O-CMCTS. Therefore, the aim of this study was to investigate N,O-carboxymethyl chitosan as an effective sorbent for removal of methylene blue in detail. The effects of initial dye concentration at lower concentration, sorbent dosage and sorption time were investigated. The sorption kinetics and isotherms for methylene blue onto N,O-carboxymethyl chitosan have also been measured.

Materials and Methods

Materials

Chitosan was obtained from Chito-Chem Sdn. Bhd., Malaysia. Monochloroacetic acid was purchased from Sigma Aldrich. Other reagents used were of analytical grade and used without further purification.

Methylene blue stock solution

Methylene blue, also known as 3,7-bis (dimethylamino) phenazathionium chloride, λ_{max}= 664 nm is a basic dye. It was purchased from Sigma Aldrich. The molecular formula and molecular mass of methylene blue are $C_{16}H_{18}N_3SCl$

and 319 g mol^{-1}, respectively. Methylene blue stock solution of 1000 mg/L was prepared by dissolving 1 g of the dye into 1000 mL distilled water. The stock solution was used throughout the whole experiment by fresh dilution.

Preparation of N,O-carboxymethyl chitosan

N,O-carboxymethyl chitosan (N,O-CMCTS) was prepared according to the previous report [3] with slight modification. Briefly, 10 g of chitosan was swelled in 50 mL isopropanol and water mixture (1:1 v/v ratio) contained 10 g sodium hydroxide at a 25℃ for 1 hour. Then, 15 g monochloroacetic acid dissolved in 20 mL isopropanol was added drop-wise into the reaction mixture over the period of 30 min. The reaction was continued with constant stirring for another 4 hours at 55℃. Finally, the reaction was stop by adding 70% ethyl alcohol. The product was filtered and washed with 80% ethyl alcohol to remove salt and water. The N,O-CMCTS was dried in a desiccator overnight.

Characterization of N,O-carboxymethyl chitosan

N,O-CMCTS was characterized by Fourier transform infrared spectroscopy (FTIR) Perkin Elmer, USA. The infrared spectrum was recorded at the frequency range of 4000-800 cm^{-1}. The infrared spectrum analysis was done to determine the functional groups on chitosan and carboxymethyl chitosan. In order to confirm the structure of the products, analysis of ^{1}H NMR was performed using Bruker Avance 111 600 MHz. chitosan and carboxymethyl chitosan were dissolve in D_2O solvent.

Equilibrium adsorption and sorption isotherm studies

Batch adsorption experiments were performed in conical flask and stirring with a magnetic stirrer at a speed of 200 rpm. The effects of sorbent dosage on dye sorption were measured with different masses (0.05, 0.10, 0.15, 0.20 and 0.25 g) in 25 mL of dye solution (2 mg/L) at 25℃ for 30 minutes. For effect of initial dye concentrations, 50 mg of N,O-CMCTS was added to 25 mL of an aqueous solution of methylene blue at known concentrations in a 250 mL conical flask for 30 minutes. The adsorbent was separated by centrifuge and the dye content in the remaining aqueous was analyzed by using a UV-vis spectrophotometer at 664 nm corresponding to a maximum absorbency of methylene blue. The amount of absorption, q (mg/g) was calculated by the following equation:

$$q = \frac{(C_o - C_t)V}{W} \quad (1)$$

where C_o and C_t (mg/L) are the concentration of dye at initial and at time t, respectively. V is the volume of solution (L) and W is the mass of dry adsorbent used (g).

The experimental data were processed using two adsorption isotherm models, namely the Freundlich isotherm model and Langmuir isotherm model, in order to obtain information about the adsorption capacity, the degree of affinity and the surface characteristics of N,O-CMCTS, as well as to establish the equilibrium relationship and mechanism of methylene blue adsorption onto the N,O-CMCTS as adsorbent.

The sorption data were interpreted by Langmuir and Freundlich isotherm equations [15]. The Langmuir isotherm model estimates the maximum adsorption capacity corresponding to complete monolayer coverage on the sample surface. The linear form of Langmuir adsorption isotherm could be represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \quad (2)$$

where K_L was constant of the sorption equilibrium (L/mg) and q_{max} was the maximum dye sorption capacity (mg/g). The values of q_{max} and b could be obtained from linear plot of C_e/q_e versus C_e.

The Freundlich isotherm model for sorption takes place in heterogenous systems and assumed that the sorption occurs on sites with different sorption energies. The model gives a representation of equilibrium between the amount of adsorbate in solution and that on the surface of the adsorbent. This involves the sorption occur in multilayer and the Freundlich isotherm equation as follows:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

This equation could be written in its linearized form:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (4)$$

where K_F and n were the Freundlich constants, which represent sorption capacity and sorption intensity respectively. K_F and n were obtained from intercept and slope of a linear plot of log q_e against log C_e.

Kinetic adsorption studies

The influence of contact time on the adsorption of dye by N,O-CMCTS was studied in batch experiments, mixing 0.05 g of N,O-CMCTS and 25 mL of methylene blue (2mg/L) at a temperature of 25℃ for time intervals ranging from 30 to 300 minutes. Finally, the adsorbent was separated via centrifuge and the dye content in the remaining aqueous was analyzed using a similar procedure to that of the equilibrium studies.

To examine the kinetic mechanism of the absorption process of MB on N,O-CMCTS, the pseudo-first-order and the pseudo-second-order kinetics models were used for analyses. The pseudo-first-order rate equation of Lagergren model for the absorption of solid/liquid systems [3] as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

The pseudo-second-order rate equation was as below [3]:

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

where q_e and q_t were the absorption capacity (mg/g) at equilibrium and at time t (min), respectively. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) the absorption rate constants of pseudo-first-order and pseudo-second-order absorption rates, respectively.

Results and Discussion

Characterization of carboxymethyl chitosan by FTIR

Figure 1 shows the FTIR spectra of chitosan and carboxymethyl chitosan (CMCTS). The chitosan spectra showed the basic characteristic peaks of chitosan at 3281 cm^{-1} (O-H stretch and N-H stretch), 2923 and 2883 cm^{-1} (C-H stretch), 1645 cm^{-1} (NH-CO stretch), 1576 cm^{-1} (N-H bend), 1152 cm^{-1} (bridge-O- stretch) and 1028 cm^{-1} (C-O stretch). It was observed that a broad absorption band and strong stretch was attributed to O-H, while N-H stretching vibrations were noticed for carboxymethyl chitosan at approximately 3350 cm^{-1} after carboxymethylation. A sharp and intense peak at 1587 cm^{-1} indicated the bending vibration of an amide for CMCTS [16]. The presence of absorption band at 1631 cm^{-1} assigned for carboxylic group of carboxymethyl chitosan. The bands at 1587 cm^{-1} and 1408 cm^{-1} were assigned to the asymmetrical and symmetrical stretching vibrations of carboxylate anions ($-COO^-$) while the bands at 1321 cm^{-1} was characteristic of CH_2 scissoring in the carboxymethyl group [17].

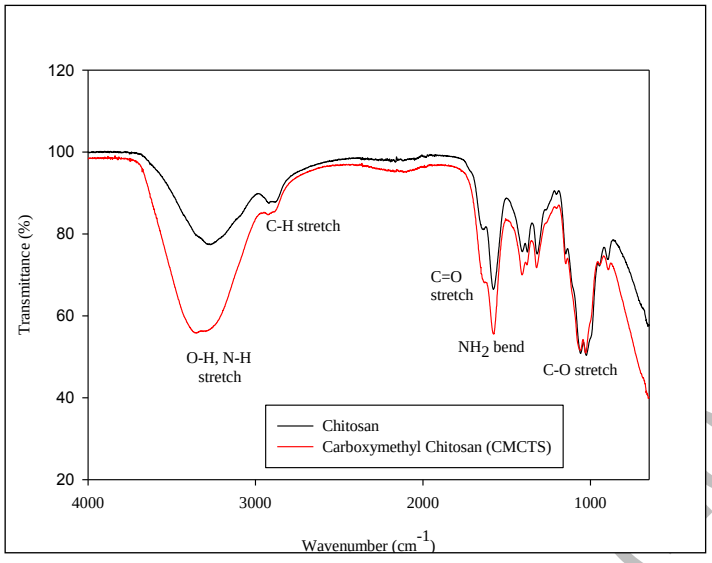

Figure 1. FTIR spectrum of chitosan and carboxymethyl chitosan (CMCTS)

Characterization of N,O-carboxymethyl chitosan by ^{1}H NMR

Figure 2 shows the ^{1}H NMR spectra of chitosan and carboxymethyl chitosan respectively (chemical shift ranging between δ = 1 and 5 ppm). The ^{1}H NMR chemical shifts of chitosan assigned as follows: ^{1}H NMR (D_2O): δ = 3.09 (H2) and δ = 3.64-3.84 (H3, H4, H5, H6). While the ^{1}H NMR chemical shifts of carboxymethyl chitosan could be assigned as follows ^{1}H NMR (D_2O): δ = 3.10-3.28 (H2) and δ = 3.65-4.00 (H3, H4, H5, H6) [17, 18]. The results confirmed that *O*-, *N*- substituted carboxymethyl chitosan was synthesized, as the presence of peaks at 3.99 and 3.28 ppm shows that the substitution of carboxymethylation occurred at both hydroxyl and amino groups of chitosan, respectively [16].

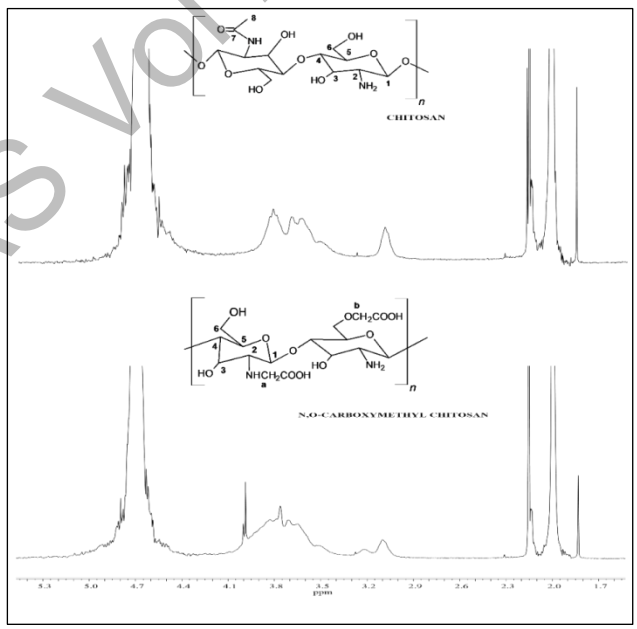

Figure 2. ^{1}H NMR spectra of chitosan and N,O-carboxymethyl chitosan

Effect of adsorbent dosage on methylene blue sorption

Previous literature had reported that chitosan was able to remove 99% of methylene blue from 10 ppm solution at dosage of 0.1 g; however, they do not clearly showed proof in terms of data [19]. Other literature has reported that chitosan cannot uptake cationic dye such as methylene blue and modification should be done to chitosan for adsorb cationic dyes [20]. It can be observed from Figure 3 0.05 g of N,O-CMCTS was able to remove 73% of methylene blue with a capacity sorption of methylene blue of 0.55 mg/g. However, that the sorption capacity sharply decreased as the mass of adsorbent increased due to the saturation of the system.

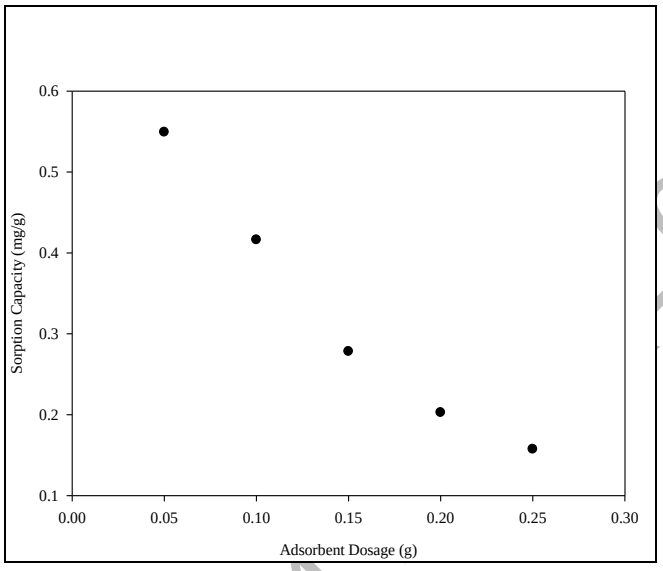

Figure 3. Effect of adsorbent dosage on methylene blue sorption by N,O-CMCTS

Effect of initial dye concentration on methylene blue sorption

Figure 4 shows that the sorption capacity of sample increased from 0.133 mg/g to 0.899 mg/g with an increase in initial dye concentration from 0.3 mg/L to 2.0 mg/L. The sorption capacity of MB on N,O-CMCTS was increased with increased concentrations of MB. This was due to presence of available active sites in N,O-CMCTS for the sorption of the MB [21]. The -OH, $-NH_2$ and -COOH groups of N,O-CMCTS were involve in sorption process between MB and N,O-CMCTS through chemical interaction and electrostatic attraction [14].

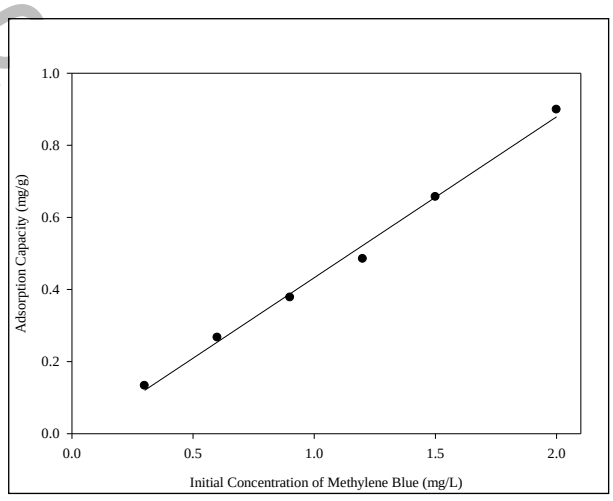

Figure 4. Effect of initial dye concentration on methylene blue sorption by N,O-CMCTS

Sorption Isotherm

Sorption isotherms were important to describe how molecules of methylene blue interact with the N,O-CMCTS surface. Hence, the correlation of equilibrium data using either a theoretical or empirical equation was essential for the sorption interpretation and prediction of the extent of sorption.

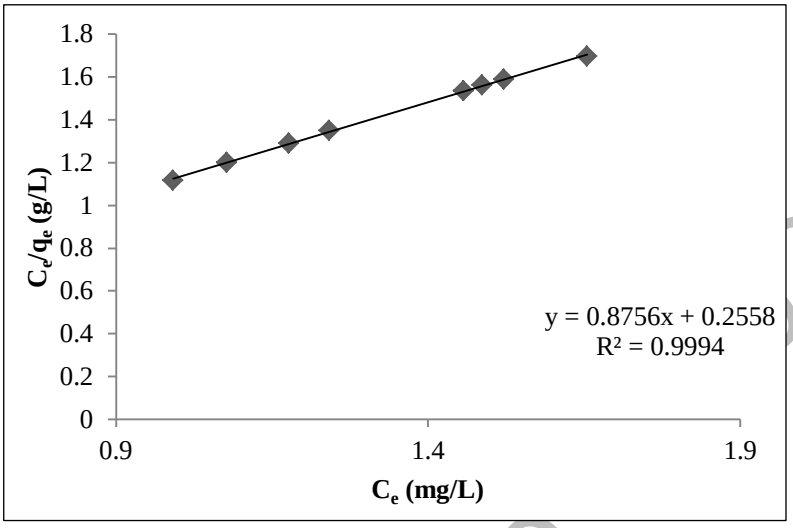

Figure 5. The linearized Langmuir adsorption isotherm for sorption of methylene blue on N,O-CMCTS

A linear plot of C_e/q_e versus C_e for the Langmuir model of sorption of methylene blue on N,O-CMCTS is shown in Figure 5 and corresponding parameters are listed in the Table 2. The affinity between the adsorbate and adsorbent could be obtained from the Langmuir parameter with the help of the dimensionless separation factor (R_L) as below [3]:

$$R_L = \frac{1}{1+a_L C_i} \tag{7}$$

According to the criteria of R_L in Table 1, R_L could be used to predict whether a sorption system was favorable or unfavorable. Based on Table 2 the R_L value for this sorption system was 0.1275, which was lower than 1 and higher than zero. These suggested that the sorption of methylene blue onto N,O-CMCTS was favorable at the range of concentration in these studies. The degree of favorability is generally related to the irreversibility of the system, giving a qualitative assessment of the N,O-CMCTS-MB interactions. The degrees tended toward zero (the completely ideal irreversible case) rather than unity (which represents a completely reversible case).

Table 1. Characteristics of the Langmuir adsorption isotherms

Separation Factor (R_L)	**Types of Isotherms**
R_L >1	Unfavorable
R_L =1	Linear
0>R_L< 1	Favorable
R_L= 0	Irreversible

The Freundlich isotherm model the sorption takes place on heterogenous systems; the data are given in Table 2. When the value 1/n was between 0.1 less than equal to 0.5, the sorption process was favorable. If the value was between 0.5 and 1 the process is easy to adsorb and if value greater than 1 it was difficult to adsorb [22]. From our

study the value 1/n (1/n = 0.1316) which was between 0.1 less than equal to 0.5 and we can assume that the sorption was favorable or easy to adsorb. Moreover, the value of n was greater than 1 (n =7.5987), indicating that the sorption process was favorable in high and low concentration in the range of concentration being studied.

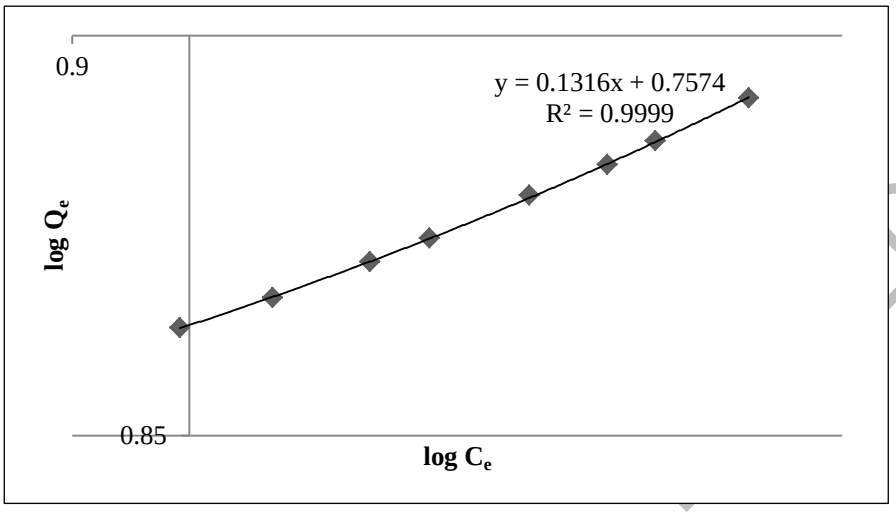

Figure 6. The linearized Freundlich absorption isotherm for sorption of methylene blue on N,O-CMCTS

Based on the correlation coefficient (R^2) values in Table 2 of the linearized form of Langmuir and Freundlich sorption equations indicated that sorption fitted to the Freundlich absorption model for the experimental equilibrium sorption data. From correlation coefficient (R^2) value for Freundlich model was close to 1 which was 0.9999 compared to correlation coefficient (R^2) value of Langmuir model. This suggests that sorption of methylene blue occur at multilayer on the N,O-CMCTS with non-uniform distribution of sorption heat and affinities over the heterogenous surface [23]. These proved that the sorption of methylene blue to N,O-CMCTS were through an absorption mechanism.

Table 2. The Langmuir and Freundlich isotherms model constants and their respectively correlation coefficients R^2 for the sorption of methylene blue by N,O-CMCTS

Experimental	**Langmuir**				**Freundlich**		
q (mg/g)	**q_{max} (mg/g)**	**K_L (L/mg)**	**R_L**	**R^2**	**K_F (g mg^{-1} min^{-1})**	**1/n**	**R^2**
0.975	1.1421	3.4229	0.1275	0.9994	5.7200	0.1316	0.9999

Absorption kinetics

The adsorption kinetic study was important in predicting the mechanisms (chemical reaction or mass-transport process) that control the rate of the pollutant removal and retention time of adsorbed species at the solid-liquid interface [24]. Figure 7 shown the absorption of MB onto N,O-CMCTS as a function of time. As observed in Figure 4, the absorption capacity of MB on N,O-CMCTS increased within 240 minutes, after that it decreased. The increase probably occurred due to the availability of more active sites on N,O-CMCTS, which acts as an absorbent. After that, the active sites were decreased by the occupancy of absorbent at 300 minutes. Under our experimental conditions, the assumption that the system reached the equilibrium time for absorption of methylene blue on N,O-CMCTS was 240 minutes.

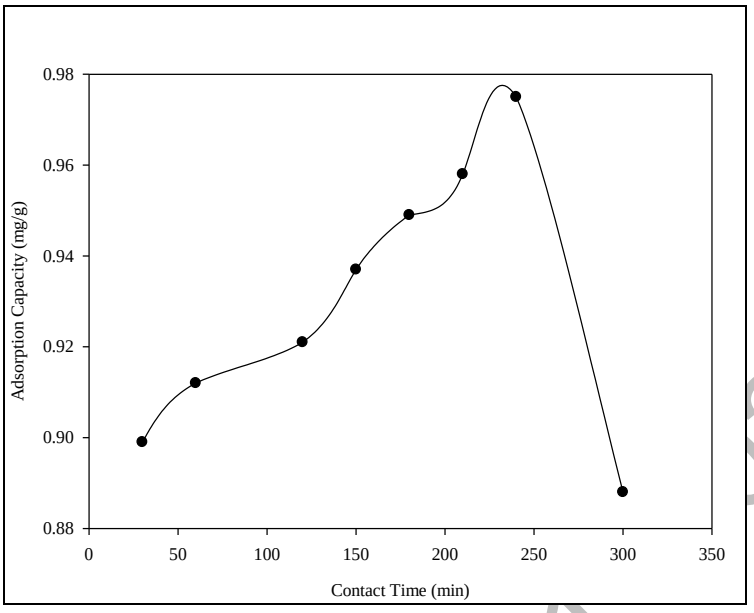

Figure 7. Absorption of methylene blue by N,O-CMCTS as a function of time

The linear plot of $\log(q_e-q_t)$ versus t for pseudo-first-order model in Figure 8 and that of (t/q_t) versus t for pseudo-second-order model in Figure 9 were shown. The values of q_e and the rate constants k_1 and k_2 could be obtained from the plot of experimental data.

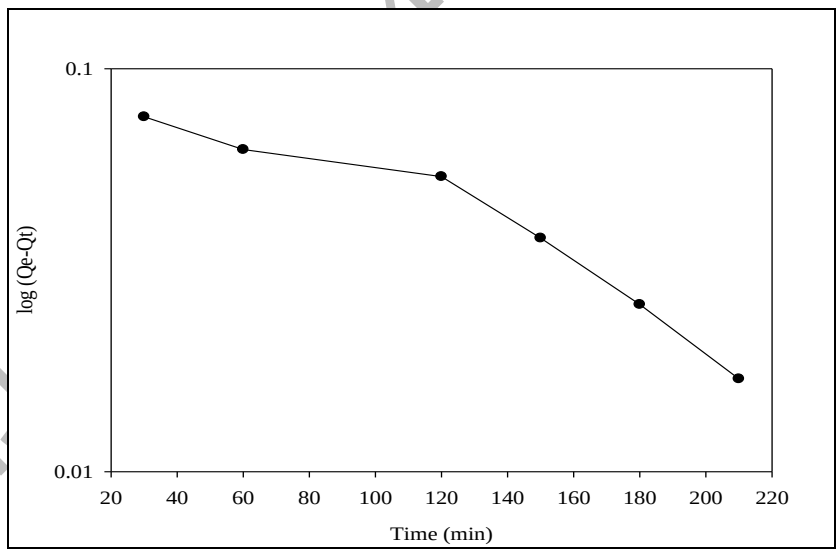

Figure 8. Linearized pseudo-first-order plot for absorption of methylene blue by N,O-CMCTS

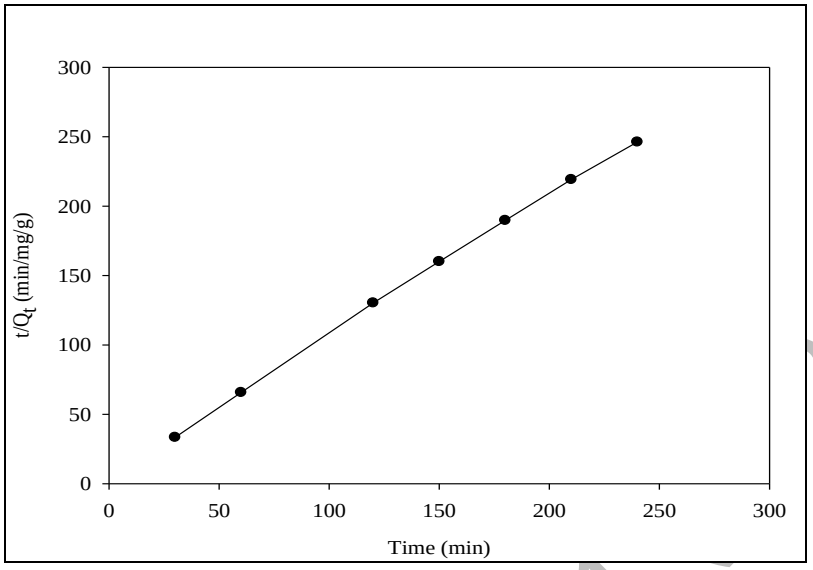

Figure 9. Linearized pseudo-second-order plot for absorption of methylene blue by N,O-CMCTS

Table 3. Theoretically determined constants of the pseudo-first-order and pseudo-second-order reaction kinetics based on the absorption of methylene blue

Experimental q (mg/g)	**Pseudo-first-order constants**			**Pseudo-second-order constants**		
	q_e (mg/g)	**k_1 (min^{-1})**	**R^2**	**q_e (mg/g)**	**k_2 (g mg^{-1} min^{-1})**	**R^2**
0.975	1.216	6.909×10^{-4}	0.9142	0.983	0.202	0.9993

The calculated q_e, the rate constants and the correlation coefficients for two kinetic models of N,O-CMCTS are shown in Table 3. The values of correlation coefficient (R^2) of pseudo-first-order and pseudo-second-order models were 0.9142 and 0.9993, respectively. The calculated q_e value of the pseudo-second-order model was 0.983 mg/g, which is close to the experimental data of 0.975 mg/g. Table 4 showed the comparison of maximum adsorption capacities for methylene blue by different adsorbents. The higher value of correlation coefficient (0.9993) and the close calculated q_e value indicated that these data was well fitted for pseudo-second-order model. Thus, it may be suggested that the absorption of methylene blue obeyed the pseudo-second-order kinetic, indicating that the absorption mechanism depended on the N,O-CMCTS and methylene blue [25].

Table 4. Comparison of maximum adsorption capacities for methylene blue by different adsorbents

Adsorbents	**Maximum Capacities (mg/g)**	**References**
Natural clay	15.40	[26]
Corncob based activated carbon	0.84	[27]
Fir wood activated carbon	1.21	[27]
Clay	6.30	[28]
Glass	2.24	[29]

Conclusion

Modified N,O-Carboxymethyl chitosan (N,O-CMCTS) has been prepared under heterogenous condition. The FTIR and NMR characterizations have shown that N,O-carboxymethyl chitosan was successfully synthesized. Sorption tests of Methylene Blue on N,O-CMCTS were carried out at various parameters including sorbent dosage, initial dye concentration and contact time, The results obtained showed that sorbent dosage 0.05 g exhibited the highest sorption capacity. The kinetics studies showed that the absorption process followed the second-order-kinetic model rather than the first-order-kinetic model. By comparing the correlation coefficient value of Langmuir and Freundlich model for each linear formed of isotherm analysis, Freundlich model properly described the absorption equilibrium of MB on N,O-CMCTS. Therefore, it may be concluded that N,O-CMCTS has shown strong potential in wastewater treatment in removal of dye. However, other parameters such as pH may be examined in order to enhance the potential of N,O-CMCTS as adsorbent for different type of dyes.

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