Adsorption Of Methylene Blue Onto Xanthogenated-Modified Chitosan Microbeads

Zurhana Mat Hussin
Mardhiah Ismail
Megat Ahmad Kamal Megat Hanafiah
Siti Nadzifah Ghazali
Sarah Laila Mohd Jan
Siti Norhafiza Mohd Khaazai
Siti Raihan Zakaria

ABSTRACT

Methylene Blue (MB) is thiazine dyes that is widely used to color product in many industry such as textile, printing, leather, cosmetic and paper. Xanthogenated-Modified Chitosan Microbeads (XMCM) is used to observe the new alternative adsorbent in removing MB from water body through adsorption process. The interactions between MB and functional group in XMCM were confirmed by Fourier Transform Infrared (FT-IR) Spectra. Several parameters that influence adsorption ability such as the effect of adsorbent dosage of XMCM and the effect of initial pH of MB aqueous solution were studied. This study was done at an optimum condition which is at pH 4 of initial pH of MB solution, 0.01 g of initial XMCM dosage, 6 hours stirring time and temperature of (30 ± 2°C). The adsorption data fitted well Langmuir model more than Freundlich model. Based on Langmuir model, the maximum monolayer adsorption capacity of MB was 21.62 mg g^{-1} which indicated that XMCM can be a new alternative adsorbent for removing MB.

Keywords: *methylene blue, chitosan, xanthogenate, adsorption*

Introduction

Colored (dye) pollution is highlighted as one of the common leading hazards due to its characteristics that gives harmful effects on human and the nature (Wang et al., 2011). Dye pollution in industrial waste are from textile, leather, food processing, cosmetics and dye manufacturing industries, with textile known as the leading contributor (Rafatullah et al., 2010). In textile industry itself, there are a few types of dye pollutant such as reactive, direct, acid, and basic dyes (Vargas et al., 2011). The most common effluent found in textile industry is called methylene blue (MB) which is classified as a basic dyestuff and widely used for dyeing cotton, silk and wool (Rafatullah et al., 2010). Even though MB is not classified as hazardous pollutant as heavy metal, but the chronic exposure of excessive amount of this chemical can lead to adverse effect to human health and microorganisms. Instant contact via inhalation of MB can lead to breathing difficulties, while direct contact with MB may lead to permanent eye injuries, burning sensations, excessive sweating, mental confusion, cyanosis, convulsions, tachycardia and methemoglobinemia disease (Cazetta et al., 2011; Hameed & Ahmad, 2009). The toxicity and carcinogenic characteristics of MB also influence the ecological system by contaminated water with dyes inhibitory to aquatic life (Vargas et al., 2011).

There are a varieties of method used in terms of treating wastewater due to industrial discharge of dye pollution, which is adsorption, membrane separation, oxidation and ozonation, coagulation and flocculation, as well as electro-coagulation. However, adsorption has been found to be the most favorable technique due to its potential technique to remove dye. Adsorption of dyes was found to be effective and economical compared to the use of other conversational techniques (Wang et al., 2011). Activated carbon was introduced in the past as the most effective adsorbent to remove coloring materials because of its large surface area and functional groups on its structure that makes adsorption possible in high capacity (Vargas et al., 2011). However, activated carbon requires high operating cost (Weng et al., 2009).

Chitosan is widely used as an adsorbent in adsorption process due to its ability to remove dyes and heavy metal ions even at low concentration (Wan Ngah et al., 2008). The presence of high amine and hydroxyl groups in chitosan chain makes chitosan to have strong chelating ability (Kannamba et al., 2010; Zhu et al., 2012). This adsorbent is a natural biopolymer that formed from deacetylation of chitin which comes from seafood cells such as crabs and prawns (Wan Ngah et al., 2011). It is also known as an ideal natural support for enzyme immobilization due to its hydrophilicity, biodegrablility, biocompatibility, non-toxic and adsorption properties characteristic (Wan Ngah et al., 2011). Cross-linking agent has been applied to improve the solubility of chitosan to become insoluble in acid solution and to increase its mechanical properties for better function against MB (Wan Ngah et al., 2011).

The main objectives of this study are to prepare and evaluate the potential of xanthogenate modified chitosan microbeads as an adsorbent for MB. A series of experiments were then carried out to investigate the changes in functional groups and MB adsorption properties of the raw and xanthogenated modified chitosan.

Materials and Methods

Adsorbents and other Chemicals

All reagent used were analytical grade chemicals, and distilled water was used throughout this study. 1000 ppm MB stock solution was prepared by dissolving 0.1357 g of MB in 100 mL distilled water. Initial pH of MB was adjusted by using 0.1 M NaOH and 0.1 M NaCl solutions. pH meter (Cyberscan 500) with a combined pH electrode (EUTECH Instrument) was used for pH measurement. MB concentration was determined using UV-Vis spectroscopy (Shimadzu, Model UV 1601, Japan) at 664 nm of absorbance wavelength.

Preparation of Xanthogenated Modified Chitosan Microbeads (XMCM)

Modifications of chitosan were performed by modifying the methods used by (Kannamba et al., 2010; Wan Ngah et al., 2013; Zhou et al., 2011). 2.0 g chitosan powder was soaked in 75 mL of 5% (v/v) acetic acid and was stirred for 3 hours to make sure the chitosan completely dissolved. The dissolved adsorbent was neutralized by dropping the adsorbent gel into 500 mL of 0.5 M NaOH solution under continuous stirring. White beads were left for 3 hours under continuous stirring. The beads were washed with distilled water for several times to remove the excess NaOH. The modified chitosan microbeads were treated with 100 mL of 14% NaOH solution and were stirred for 2 hours. Then, 1 mL of carbon disulphide (CS_2) was added into the solution continuously and was stirred for 2 hours. Next, 10 mL of 0.42 M $MgSO_4$ was added into the mixture and was stirred for another 1 hour. The Xanthogenate Modified Chitosan Microbeads (XMCM) were filtered and rinsed with distilled water. Lastly, the resulting beads were air-dried and sieved to obtain adsorbent size of < 212 μm.

Characterization of XMCM

FTIR

The Infrared Spectra of adsorbent were obtained by using a Fourier Transform Infrared Spectrometer (Perkin Elmer, 1600 Model). 0.1 g of XMCM was added into 10 mg/L MB solution and was stirred for 24 hours. After the stirring process completed, the solution was filtered. The adsorbents after adsorption was air dried and the effect of chemical treatments was determined by comparing any shift of band before and after adsorption. The functional groups present in chitosan flake, XMCM before and after adsorption with methylene blue were confirmed by using FTIR-ATR by scanning the samples at 400-4000 cm^{-1} with the resolution of 4 cm^{-1}.

pH_{slurry}

pHslurry was used to identify the acidity or an alkalinity of adsorbent using pH meter. The initial pH of distilled water was checked by using pH meter. After that, 0.1 g of adsorbent was added into 100 mL distilled water and the mixture was stirred for 24 hours. After the stirring process completed, the pH of the solution was determined by using pH meter.

pH_{zpc}

The pH of zero point charges (pH_{zpc}) of the adsorbent was determined by modified addition method described by Ngah and Fatinathan (2010). NaCl solution was transferred into a series of conical flask. The initial pH (pH_i) of 50 mL of 0.01 M NaCl in each conical flask was adjusted to a value between 3 to 9 by adding 0.1 M HCl or 0.1 M NaOH. 0.1 g adsorbent was added to each conical flask and the mixture was stirred for 24 hours. After the stirring process had completed, the solution was filtered and the final pH (pH_f) of the solution was measured. The acidity or alkalinity of the adsorbent was identified by plotting pH against ΔpH (pH_i - pH_f). The pH_{zpc} can be determined from the point of intersection of the curve to pH_i axis.

Batch Mode Study

Effect of Adsorbent Dosage

The optimum dosage was determined by adding various doses of XMCM into 50 mL of 10 mg L^{-1} of MB. The pH of MB was fixed at pH 6. The adsorbent dosages used were 0.01 g, 0.02 g, 0.03 g, 0.05 g and 0.1 g. The mixture was stirred at 120 rpm stirring rate for 6 hours. After the process was completed, the solution was centrifuged at 3000 rpm for 5 min. The solution was analyzed by using UV-Vis Spectrometer. The optimum adsorbent dosage of the XMCM was determined by plotting adsorption capacity (qe) against adsorbent dosage.

Effect of Initial pH

The optimum pH for methylene blue adsorption on Xanthogente-Modified Chitosan Microbeads was determined by adding 0.01 g of XMCM into 50 mL of 10 mg L^{-1} of MB. The pH of adsorbate was adjusted from pH 3 to 9 by adding 0.1 M HCl and 0.1 M NaOH. The mixture was stirred for 6 hour at 120 rpm. After the adsorption process had completed, the solution was centrifuged at 3000 rpm for 5 minutes and then it was analyzed by using UV-Vis spectrophotometer. The optimum pH of the adsorbate was determined by plotting adsorption capacity (qe) against pH.

Isotherm Study

For the isotherm study, the concentration of adsorbate was varied ranging from 10 to 100 mg L^{-1}. Each of the adsorbate was adjusted to pH 4. A mass of 0.01 g XMCM was added into each of solution. All solutions were stirred at 120 rpm for 6 hours. This study was done at 30 °C. After the stirring process had completed, the solution was centrifuged at 3000 rpm for 5 minutes and then was analyzed by using UV-Vis spectrophotometer. The data obtained from this study were analyzed by using Langmuir and Freundlich models.

Results and Discussion

Adsorbent Characterization

pH_{zpc} is used to show the tendency of a surface of adsorbent to become either positively or negatively charged (Kamal et al., 2010). The value of pH_{zpc} of XMCM was 9.80 which indicate that the adsorbent is basic. Kamal et al. (2010) stated that when the pH of adsorbate is greater than pH_{zpc}, the surface of adsorbent will carry negative charge and vice versa. Hence, cationic dye adsorption study is more effective if the initial

pH of adsorbate is higher than pH_{zpc} value. pH_{zpc} is closed to the pH of aqueous slurry (pH_{slurry}), which matched the previous finding that the pH_{zpc} is equal to pH_{slurry} (Kamal et al.,2010).

The FTIR spectrum of chitosan before and after treatment and XMCM before and after MB loaded shown in Figure 1. The appearance of many peaks indicates the presence of various type of functional group in XMCM. From chitosan spectrum, a broad peak at 3272 cm^{-1} corresponds to the presence of O-H stretching in either alcohol or carboxylic group which might overlap with N-H stretching in amine as reported by Kamari and Ngah (2009). The C-N bending absorption appears at 1744 cm^{-1}. Peak located at 1636 and 1560 cm^{-1} represent the deformation of amine which similar to peak (around 1650 cm^{-1}) observed by Kamari et al. (2009). The appearance sharp adsorption peak at 1453 cm^{-1} indicates present of $-NH_2$. Peak located at 1298, 1229 and 1147 cm^{-1} can be assigned as C-O-C asymmetrical stretching vibration which is a characteristic of chitosan's saccharide structure (Kamari and Ngah., 2009, Zhu et al., 2012, and Azlan et al., 2009). After modification process with xanthogenate, several changes in XMCM spectra were observed. Peaks at 3455 and 3187 cm^{-1} indicate the OH in $Mg(OH)_2$ which is due to the side reaction during the magnesium substitution process with CS_2 results in $Mg(OH)_2$ percipitation (Deang et al., 2012). A new peak appear at 1654 cm^{-1} indicate the present of imine bond (C=N). NH_2 peak of chitosan was found to be shifted to the right (1445 cm^{-1}) and increase the intensity due to modification with xanthogenate. The high intense peak at 1429 cm^{-1} can be assign to C=S group. From FTIR spectra XMCM-MB, there is a new peak appear at 1546 cm^{-1} after adsorption process which proved that a chemical interaction between XMCM and MB occurred. The reduction of intensities of peak that observed at 1464 and 1370 cm^{-1} and also shift to the left compared to peak 1445 cm^{-1} (N-H group in amine) and 1429 cm^{-1} (–C=S group) before adsorption process indicated that nitrogen and sulphur has an interaction with MB. Therefore, the main functional groups that participate in adsorption process of MB onto XMCM were amino and sulphur group.

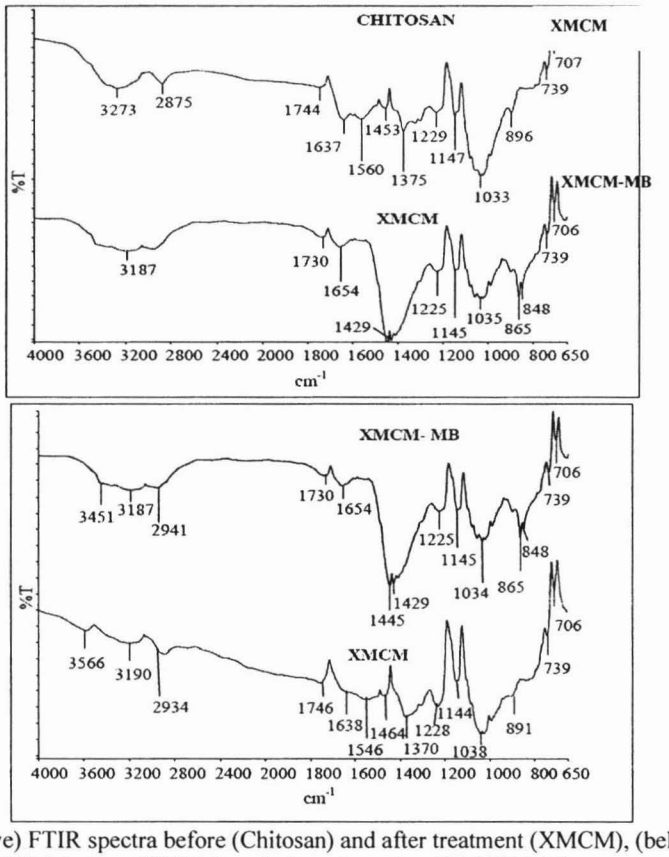

Figure 1 : (above) FTIR spectra before (Chitosan) and after treatment (XMCM), (below) FTIR spectra of XMCM before (XMCM) and after adsorption (XMCM-MB).

Effect of Adsorbent Dosage

The relationship between adsorption of MB with adsorbent dosage of XMCM is shown in Figure 2. The percentage removal of MB increased with the increasing of absorbent dosage. The surface area will be directly proportional to the mass of adsorbent in the solution as the particle size range used in this study was constant. However, the adsorption capacity decreases. According to Özer et al. (2007), the increase in the adsorption of MB with the adsorbent dosage can be associated with the increase of surface area and the sorption sites. The decrease of the effective surface area explained the reduction in adsorption capacity.

Effect of initial pH

pH of initial solution plays an important role in the adsorption process. Initial pH of the solution also affects the adsorption of other ions (Han et al., 2011). Therefore, the adsorption of MB dye was studied at different pH. This study was performed at pH 3 to 7. Figure 3 shows that the adsorption capacity increases from 2.24 to 6.83 mg g^{-1} between pH 3 and 4 due to the reaction of cationic dye with negative charge adsorbent surface. However, it decreases from pH 4 onward.

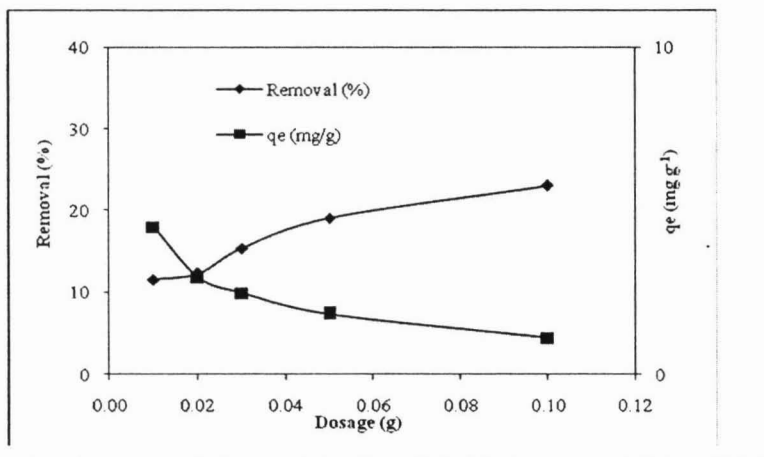

Figure 2 : Effect of adsorbent dosage on the adsorption of MB onto XMCM

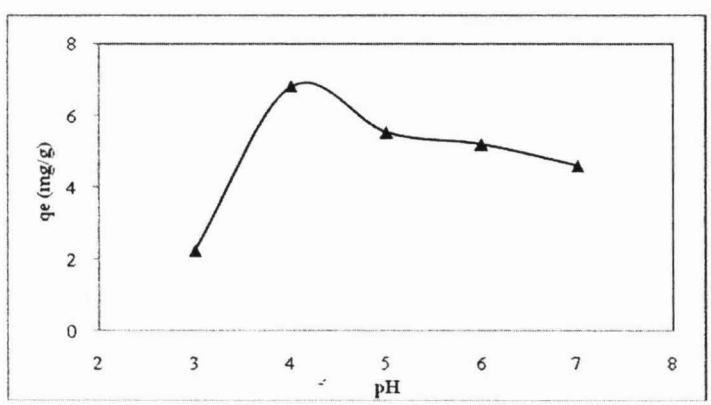

Figure 3 : Effect of pH on the adsorption of MB onto XMCM

Adsorption Isotherm

Isotherm study relates the amount of adsorbate adsorbed per unit weight of adsorbent and it also give the information about surface properties, adsorption mechanisms and affinity of an adsorbent towards adsorbate ions (Kamal et al. 2010). The general isotherm plot of MB onto XMCM (Figure z) shows that adsorption capacity increase with the increasing of initial MB concentration and can be classified as "H" type of isotherm plot based on Giles classification which indicates that the adsorption is chemical adsorption and have strong adsorbate and adsorbent interactions (Kamal et al., 2010).

Isotherm data was further analysed using Langmuir and Freundlich model. Langmuir equation is written as:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} b} + \frac{C_e}{Q_{max}}$$

Where q_e is the amount of MB adsorbed at equilibrium (mg g^{-1}), Q_{max} is the theoretical maximum adsorption capacity per unit weight adsorbent (mg g^{-1}). b is the Langmuir adsorption constant related to the affinity of

binding sites (L mg^{-1}) and a measure of the energy of adsorption, and C_e is the equilibrium MB concentration (mg L^{-1}). Langmuir plot (plot not shown) gives straight line. A similar adsorption isotherm was also found in the adsorption studies of MB onto a various type chitosan carried out by (Liu et al., 2010; Fan et al., 2012; Huang et al., 2011; Wang et al., 2011). The R^2 value (table 1) demonstrated that XMCM is a favourable adsorbent. (Kamari et al., 2009).
Freundlich model assume that the adsorption spots are scattered exponentially with respect to the adsorption temperature. This model is given by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where K_F and n are Freundlich constant that represents adsorption capacity (mg g^{-1}) and adsorption intensity (unit less). This Freundlich constant value and n can be obtained by plotting a linear Freundlich plot of log qe versus log Ce. Where and n are related to intercept and slope, respectively.

The summary of the maximum adsorption capacity, adsorption intensity, and correlation coefficient value obtained from this study is shown in Table 1. The isotherm data followed well with the Langmuir model since the Q_{max} of Langmuir is closed to the experimental value Q_{exp}.

Table 1: Adsorption isotherms parameters for MB adsorption on XMCM

Q_{exp} (mg/g)	Langmuir			Freundlich		
	Q_{max} (mg/g)	b (L/mg)	R^2	K_F (mg/g)	n	R^2
19.80	21.60	0.13	0.989	1.59	1.23	0.935

By comparing adsorption capacities of various type of adsorbents (Table 2), it can be concluded that XMCM is one of the effective low cost adsorbent used for the MB adsorption.

Table 2: Comparison of the maximum monolayer capacities of MB on various adsorbents

Adsorbent	Q_{max} (mg/g)	Reference
Xanthate modified chitosan microbeads (XMCM)	21.60	This study
Coir pith carbon	5.87	Hamdaoui (2006)
Activated carbon	9.81	Basava Rao and Ram Mohan Rao (2006)
Banana peel	20.80	Annadurai *et al.* (2002)
Hazelnut shell	38.22	Dogan and Alkan (2008)

Conclusion

The feasibility of XMCM used in treating wastewater was assessed based on XMCM characterization, its effects on MB adsorption that are due to the XMCM volume used during the experiment, its initial pH value, adsorption isotherm, as well as Langmuir and Freundlich isotherm. The chemical process and uptake rate of XMCM against MB were assessed and compared to the other adsorbents proved that XMCM could be the best chitosan-based adsorbent available in treating polluted wastewater.

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ZURHANA MAT HUSSIN, MARDHIAH ISMAIL, MEGAT AHMAD KAMAL MEGAT HANAFIAH, SITI NADZIFAH GHAZALI, SARAH LAILA MOHD JAN, SITI NORHAFIZA MOHD KHAAZAI, SITI RAIHAN ZAKARIA.
Universiti Teknologi MARA(Pahang).
zurhana_mhussin@pahang.uitm.edu.my,mardhiahismail@pahang.uitm.edu.my,
makmh@pahang.uitm.edu.my,nadzhifahghazali@yahoo.com,sarahlaila@pahang.uitm.edu.my,
ctnorhafiza@pahang.uitm.edu.my, sitiraihan@pahang.uitm.edu.my.