Removal of methylthioninium chloride dye from aqueous solution using cogon grass as adsorbent

N M M Isa, N S M Yatim* and N A Zabanor

Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, Sungai Chucuh, 02100 Padang Besar, Perlis, Malaysia

E-mail: nursuhaili@unimap.edu.my

Abstract. The aim of this study was to investigate the removal Methylthioninium Chloride dye using cogon grass to treat the effluent. The effects of various parameters such as adsorbent dosage, dye concentration and contact time were studied. Functional group properties of cogon grass had been characterized using Fourier transform infrared spectroscopy (FTIR). The adsorption process attained equilibrium around 50 minutes. The maximum adsorption capacity was calculated to be 46.30 mg/g with optimized condition of adsorbent dosage 0.1 g at temperature 30 ℃ for 50 minutes. The adsorption kinetics of Methylthioninium Chloride with cogon grass suit into non-linear pseudo-second order reaction model that refers to the amount of adsorbate and amount of solute adsorbed on adsorbent surface at equilibrium. It was also found that the Langmuir isotherm fit better (R² = 0.9959) compare to the Freundlich isotherm (R² = 0.4093). The high levels of color removals were achieved with low contact times; and the cogon grass can be effectively used as adsorbent of methylthioninium chloride in aqueous solutions. These results prove that cogon grass is highly potential to be used as low-cost adsorbent for the dye removal from industrial wastewater.

1. Introduction
Wastewater is a mixture of water with pollution from sources like dye, municipal solid waste and chemical waste which have bumped into the sewage or river from the domestic and industrials. One of the dyes that is commonly used in industry is Methylthioninium Chloride (MC). MC is usually used in industrial colouring, medical field and methemoglobinemia treatment. However, the disposal of MC is not properly managed, hence affected both human and environment, especially, the ecosystem lakes, rivers and oceans [1]. Such effluent pollution has since become a global issue. Several wastewater treatments have been introduced, liquid membrane filtration, coagulation, and flotation as well as adsorption by activated carbon to name a few. Among all these methods, adsorption seems the most frequently used technique in wastewater management. Adsorption is a physical process involving the transfer of solute from the liquids to a solid matrix surface. The adsorbents are easy to handle, and they have high surface area which help to maximize adsorption per unit weight. The most used adsorbent commercially is none other than the expensive commercial activated carbon. The application of biomass as an adsorbent is widely investigated due to their good adsorption capacity. Biomass such as cogon grass (Imperata Cylindrica) is proposed to minimize the cost of adsorbent investment. Cogon grass is a grassy weed which is easy to grow through seed germinate and it is abundantly available with no economic value. Domestically, the usage of activated carbon is extensively used for the removal of water contaminants. However, it requires a high capital cost to buy activated carbon which limits their usage. Therefore, many researchers have since focused on a new adsorbent which is cheaper and environmental
friendly, where it was from organic matter such as fruit peel, rice husk and grass such as cogon grass [2]. Thus, cogon grass can be altered to an adsorbent, consequently can be used in MC waste treatment. Therefore, cogon grass was used as adsorbent to remove the Methylthioninium Chloride in aqueous solution [2] and a few parameters such as effect of contact time, initial dye concentration and adsorbent dosage were investigated.

The aim of this research work is to study the adsorption of Methylthioninium Chloride by using cogon grass as an adsorbent and to evaluate the characterization of adsorbent using Fourier Transform Infrared Spectroscopy (FTIR). Kinetic and isotherm of Methylthioninium Chloride by cogon grass have also been evaluated.

2. Methodology
2.1. Sample collection and adsorbent preparation
The cogon grass was collected from abandoned land near to Campus Uniciti Alam, Universiti Malaysia Perlis (UniMAP). It was washed to remove the impurities such as soil and dirt that attach on the surface of cogon grass. Trunk and leaves of cogon grass were dried in an oven at 100°C for 24 hours prior to grinding and sieving at 250um and were kept for further analysis [2].

2.2. Methylthioninium Chloride dye stock solution
1g of MC dye was dissolved in 1000 mL of distilled water to prepare 1000 mg/L of Methylthioninium Chloride dye solution [33]. 20, 40, 60, 80 and 100 mg/L of Methylthioninium Chloride concentration were diluted with distilled water to prepare stock solution. Then, the absorbance value of stock solution concentration was determined by using UV Spectrophotometer. The percentage of absorbance was determined by UV-Vis Spectrophotometer ($\lambda_{max}$=665 nm).

2.3. Experimental method and measurement
The adsorption tests were placed in batch system at temperature of 30°C with constant initial pH of solution. The 100 mL of conical flasks were used in this study. A 0.1g/L adsorbent was mixed with 50 mL of fixed concentration of dye stock solution in conical flask. Then, the conical flasks were placed for 50 minutes in a water bath shaker at 130 rpm. The shaker speed rate was kept constant. The Methylthioninium Chloride concentration was measured by using UV Spectrophotometer at 665 nm maximum wavelength. During different batch experiments, several parameters such as initial dye concentration (20-100mg/L), adsorbent dosage (0.1-0.6g) and contact time were varied (10-80 min). In each parameter, the test was conducted in triplicate. The five different ranges of each parameter were conducted at the same time [3]. The adsorption capacity of cogon grass, $Q_t$ and colour removal percentage was determined by using Equation (1) and Equation (2), respectively:

$$q_t = \frac{(C_o-C_t)V}{W}$$

(1)

$$\text{Colour Removal (\%)} = \left(\frac{C_o-C_t}{C_o}\right) \times 100$$

(2)

Where V is the solution volume (L), $C_o$ is the initial concentration of Methylthioninium Chloride (mg L$^{-1}$), $C_t$ is the concentration of Methylthioninium Chloride at times (mg L$^{-1}$), t and W is the mass of cogon grass (g) [2].

2.4. Fourier Transform Infrared (FTIR) Analysis
The FTIR Spectrophotometer was used to determine the of adsorbent functional group. A spectrum of 4000-400 cm$^{-1}$ in the mid-infrared region (IR) range with a resolution of 1 cm$^{-1}$ will be collected 4].
3. Result and discussion

3.1. Effects of parameter (contact time, initial dye concentration and adsorbent dosage)

3.1.1. Effect of various contact time. Figure 3.1 illustrates the amount of Methylthioninium Chloride dye adsorbed at time range from 10 to 80 minutes with constant parameter initial concentration of 40 mg/L of Methylthioninium Chloride dye, 0.1 g of the absorbents and at temperature 30°C. This was to ascertain the adsorption equilibrium time for the removal of Methylthioninium Chloride from the solution. The adsorption process increased with contact time and reaches to equilibrium after 50 minutes, which there is no significant uptake in the percentage of Methylthioninium Chloride that was removed. The highest amount of percentage of Methylthioninium Chloride removal achieved at 89% exposed for 50 minutes. The percentage during the initial 10 minutes was high due to many binding vacant sites were available on the surface of the adsorbent. However, incoming time the percentage of Methylthioninium Chloride removal became slow as most of the binding sites were already occupied with other dye molecules. It reached constant at time 50 minutes where the dye molecules unable to diffuse more deeper as the binding site was fully occupied with other dye molecules [5]. By analysing the data of percentage dye removal from 10 up to 50 minutes, the percentage gap shown that there was not much gap or double percentage value from each time interval. This might be due to the adsorbate can be adsorbed on monolayer only (chemisorption). Once one dye molecule had taken over a site, there can be no further adsorption were taken place on that site. Thus, the percentage Methylthioninium Chloride removal obtained from each time interval not so much different as the dye molecules did not have many binding sites to be diffused on the surface of the adsorbent. These confirmed that the adsorption kinetics depend on the rate of adsorbate transported from the bulk solution to the adsorbent surface [6].

![Figure 3.1](image-url).

**Figure 3.1.** Graph of percentage colour removal (%) of Methylthioninium Chloride from solution versus contact time (minute).
3.1.2 Effect of initial dye concentration. The percentage removal of the dye, Methylthioninium Chloride over cogon grass adsorbent was investigated at initial concentration ranges from 20 to 100 mg/L for 50 minutes. For the adsorption of Methylthioninium Chloride, the maximum uptake was reached in a dye concentration range of 20 to 60 mg/L where the percentage of Methylthioninium Chloride removal decreased from 94% to 93.58%. The uptake became more decreased when dye concentration was higher than 60 mg/L and stayed constant about 90.6% at dye concentration of 100 mg/L [7]. From Figure 3.2, it was found that the percentage of dye removal decreased with an increase in the initial dye concentration. This is due to the saturation of adsorption sites on the adsorbent surface as well as due to the high driving force at a high initial dye concentration after 50 minutes [8]. The result shown that the data is almost consistent from 20 mg/L to 100 mg/L of initial dye concentration. For example, at concentration of 20 mg/L, the percentage of Methylthioninium Chloride removal was 94% and at next concentration interval of 40 mg/L, the percentage of Methylthioninium Chloride removal is 93.75%. This is because many dye molecules were presented, however the availability of binding site is low. Therefore, only small amount of dye molecules could be diffused into binding site. Even though, as more dye concentration was added, the ability for the adsorbent to adsorb the dye molecules may still limited. It can be related to quicker Methylthioninium Chloride saturated the binding site on the adsorbent surface.

![Figure 3.2](image_url)  

**Figure 3.2.** Graph of percentage colour removal (%) of Methylthioninium Chloride from solution versus initial dye concentration (mg/L).

3.1.3 Effect of adsorbent dosage. A study of adsorbent amount of cogon grass used during the removal of dye was achieved by different adsorbent dosage from 0.1 to 0.6 g with an initial concentration of Methylthioninium Chloride solution of 20 mg/L is presented in Figure 3.3. The removal efficiency is increased rapidly from 67.5% to 82.5% as adsorbent dosage increased from 0.1 to 0.6 g. The adsorption saturation is reached at adsorbent dose above 0.5g. The increasing removal efficiency in this range of adsorbent 0.1 to 0.5 g is due to an increase in surface area and the availability of more binding sites for adsorption. The quantity of sorption sites at the surface of adsorbent increased by increasing the amount of the adsorbent [8][9]. The percentage gap shown that there was not much gap or double percentage value from each dosage interval. This was due to the adsorbate can be adsorbed on monolayer only (chemisorption). Once one dye molecule had taken over a site, there can be no further adsorption were taken place on that site. Thus, the percentage Methylthioninium Chloride removal obtained from each
time interval not so much different even though the amount of dosage was added 0.1 g for each dosage interval. This is because low ability for the adsorbent to adsorb more dye molecules.

![Graph](image)

**Figure 3.3.** Graph of percentage colour removal (%) of Methylthioninium Chloride from solution versus adsorbent dosage (g).

3.2. Characterization of adsorbent

3.2.1. Fourier Transform Infrared Spectroscopy (FTIR). The spectrum of cogon grass powder obtained by Fourier Transform Infrared Spectroscopy (FTIR) in the 4000 – 400 cm\(^{-1}\) wavelength range. Figure 3.4(a) and 3.4(b) showed the FTIR spectra of the raw cogon grass and cogon grass after adsorption, respectively. Characteristic peaks of cogon grass were found at 2341.48 cm\(^{-1}\) which indicated the functional group Nitriles, C≡N stretch, N=O bend of Nitromethane shown at the wavenumber 1640.77 cm\(^{-1}\), 1343.23 cm\(^{-1}\) is deformation alcohols,−OH with C−OH bend and Bromo group with C−Br stretch found at wavelength 582.45 cm\(^{-1}\). It was clear that the adsorbent displays a number of adsorption peaks, reflected the complex nature of the cogon grass adsorbent.
Based on the FTIR spectrum shown in Figure 3.4(b), the functional groups on the surface of cogon grass after adsorption were observed at wavenumber 3417.12 cm⁻¹ (Hydrogen bonded O-H stretch, shifted wavenumber from 3426.01 cm⁻¹ to 3417.12 cm⁻¹) due to presence of moisture in the Methylthioninium Chloride dye, spectrum shown peak of similar functional group get weak and almost disappearance of band at wavenumber 2359.83 cm⁻¹ (Nitriles, C≡N stretch, weak peak). Wavenumber 1640.77 cm⁻¹ (N=O stretch, medium peak) and 1513.64 cm⁻¹ (H-CH bends, medium peak) was assigned to the bending vibration of C-H group linked in cellulose and lignin molecules [5]. These changes in functional group peak position and strength of the cogon grass- Methylthioninium Chloride dye complex provided evidence of Methylthioninium Chloride dye adsorption onto the cogon grass surface. The interaction sites in the cogon grass and Methylthioninium Chloride dye macromolecule were identified from the functional groups that were negatively charged such as -CN-, -CH₂- and -OH- at the surface of cogon grass interact with positively charged site =N⁺ (CH₃)₂ of the Methylthioninium Chloride dye molecules [2].

3.3. Adsorption Kinetics

Three simplified kinetic model have been adopted in order to understand the adsorption mechanism process depending on the order of the rate constants [6]. First, kinetic adsorption was analysed by the non-linear pseudo-first order and pseudo-second order kinetic models are depicted by Equation (3) and (4). On the other hand, the non-linear Elovich kinetic model is expressed by Equation (5).

\[ q_t = q_e (1 - e^{-kt}) \]  \hspace{1cm} (3)

\[ q_t = \frac{kq_e^2 t}{1+kq_e t} \]  \hspace{1cm} (4)

\[ q_t = \frac{1}{\beta} \ln \ln (\alpha \cdot \beta) + \frac{1}{\beta} t \ln ln (t) \]  \hspace{1cm} (5)

where \( t \) (min) is the adsorption time, \( k \) (min⁻¹) is the adsorption rate, and \( q_e \) (mg g⁻¹) is the adsorption capacity at a time \( t \). \( \alpha \) (mg g⁻¹ min⁻¹) is the initial adsorption rate at time \( t \) (min) and \( \beta \) (g mg⁻¹) is a
surface coverage rate and activation energy parameter correlated with chemisorption process [36]. Table 3.2 shown the parameters of non-linear pseudo-first order, pseudo-second order and Elovich kinetic models. Figure 3.5 shows the experimental and predicted results of the (a) non-linear pseudo-first order, (b) pseudo-second order and (c) Elovich kinetic models for Methylthioninium Chloride adsorption to the cogon grass adsorbent. The kinetic fit well with non-linear pseudo-second kinetic model, as demonstrated by the higher correlation coefficients, $R^2 = 0.9968$ than pseudo-first order and Elovich model. This showed that the process rate is regulated by the chemical reaction between the adsorbent and adsorbate, indicating interactions dependent on the amount of active binding sites. Hence, a chemical reaction is the controlling step in the process of Methylthioninium Chloride adsorption. This suggested that the binding site occupation rate in the cogon grass is proportional to the number of sites that are not occupied the sites. As a result, it can be assumed that Methylthioninium Chloride binds to a single binding site in the adsorbent structure [6].

**Table 3.1.** Parameters of non-linear pseudo-first order, pseudo-second order and Elovich kinetic models.

| Pseudo-First Order | $R^2$ | \(K_1 \text{ (min}^{-1}\)) | \(q_e \text{ (mg g}^{-1}\)) |
|--------------------|-------|---------------------------|-----------------------------|
|                    |       | 0.8970                    | 5.9520                      |
| Pseudo-Second Order | $R^2$ | \(K_2 \text{ (min}^{-1}\)) | \(q_e \text{ (mg g}^{-1}\)) |
|                    |       | 0.9968                    | 0.0215                      |
| Elovich            | $R^2$ | \(\beta \text{ (g mg}^{-1}\)) | \(0.9537\) |

![Figure 3.5(a) Graph of Adsorption Kinetics non-linear Pseudo-First Order.](image-url)
3.4. Adsorption Isotherm

Adsorption isotherm provides a better understanding of the adsorption mechanism and indication of the surface properties, affinity and adsorption capacity of the adsorbent. The equilibrium adsorption data have been analysed using the well-known Langmuir and Freundlich models [10]. Equation (6) and (7) express the Langmuir Isotherm and Freundlich Isotherm, respectively.

\[ q = \frac{q_o c}{K + c} \]  
\[ q = Kc^n \]  

Where \( q_o \) is kg adsorbate/kg solid, \( K \) is kg/m³, \( q \) (mg/g) is a solvent adsorbent per adsorbent and \( c \) is solute concentration in solution. Plot \( 1/q \) versus \( 1/c \), \( Kq_o \) is the slope and \( 1/q_o \) is the intercept. \( K \) and \( n \) are constants and a log-log plot for \( q \) versus \( c \) and must be determined experimentally. As seen in Figure 3.6, the Langmuir isotherm represents the adsorption process very well; the \( R^2 \) values was 0.9959 while Freundlich isotherm was 0.4093. The scattered data points of \( C_e/q_e \) versus \( C_e \) plot has been shown. The best fit line with their equation is also represented there. Five gradual increasing initial concentrations (20, 40, 60, 80 and 100 mg/L) of Methylthioninium Chloride dye were considered for this plot. The slope and intercept of the best fit line were employed to determine the Langmuir isotherm parameters such as \( Q_o \) and \( K_L \) were found to be 46.30 mg/g and 4.41 L/mg, respectively [2]. The fact that the Langmuir isotherm fits the experimental data very well may be due to the homogeneous distribution of sites onto the cogon grass surface. Once one dye molecules have taken over a site, there can be no further adsorption on that site. It is worth to mention here that adsorptive removal of Methylthioninium Chloride dye by other adsorbents obtained from agricultural waste such as wheat straw, cottonseed hull and cotton stalk has also been found to obey Langmuir isotherm [8].
4. Conclusion
This study examined cogon grass as an agriculture-based waste material can be used as an adsorbent for the removal of Methylthioninium Chloride from aqueous solution. The characterization of cogon grass was determined by using FTIR. FTIR shown the changes peak position and strength after adsorption process. The functional groups on the surface of cogon grass after adsorption was observed at wavenumber 3417.12 cm\(^{-1}\) (Hydrogen bonded O-H stretch, shifted wavenumber from 3426.01 cm\(^{-1}\) to 3417.12 cm\(^{-1}\)) due to presence of moisture in the Methylthioninium Chloride dye, spectrum shown peak of similar functional group get weak and almost disappearance of band at wavenumber 2359.83 cm\(^{-1}\) (Nitriles, C≡N stretch, weak peak). Wavenumber 1640.77 cm\(^{-1}\) (N=O stretch, medium peak) and 1513.64 cm\(^{-1}\) (H-CH bends, medium peak) was assigned to the bending vibration of C-H group linked in cellulose and lignin molecules. It was found that the amount of dye adsorbed differed with contact time, dosage of adsorbent and initial concentration of dye. The colour removal percentage improved with an improvement in time and reached equilibrium with 89% colour removal after 50 minutes. Similarly, with increased adsorbent dosage, the removal efficiency of Methylthioninium Chloride increased and became constant at 0.5 g adsorbent dosage, which was achieved by 82.5% dye removal. However, the removal efficiency of Methylthioninium Chloride decreased with increase in dye concentration. At 20 mg/L of dye concentration gave the highest colour removal which was 94%. The adsorption of Methylthioninium Chloride dye followed the non-linear pseudo-second order model. The pseudo-second model refers to the amount of adsorbate and amount of solute adsorbed on adsorbent surface at equilibrium. The adsorption process was favourably described by the Langmuir isotherm (R\(^2\) = 0.9959), confirmed the monolayer adsorption capacity of 46.30 mg/g. These finding shown that cogon grass is a potential low-cost adsorbent for the dye removal from industrial wastewater.
References

[1] Santhi T, Manonmani S, Vasantha, S, and Chang, Y T 2016 A new alternative adsorbent for the removal of cationic dyes from aqueous solution. *Arabian Journal of Chemistry* 9 466–474

[2] Su C X H, Teng T T, Alkarkhi A F M and Low L W 2014 Imperata cylindrica (cogongrass) as an adsorbent for Methylthioninium Chloride dye removal: Process optimization. *Water, Air, and Soil Pollution* 225(5)

[3] Danish M, Shakeel Iqubal S M, Pin Z, Ziyang L, Ahmad M, Majeed S and Ahmad T 2018 Use of banana trunk waste as activated carbon in scavenging Methylthioninium Chloride dye: Kinetic, thermodynamic, and isotherm studies. *Bioresource Technology Reports* 3(July) 127–137

[4] Bulgariu L, Escudero L B, Bello O S, Iqbal M, Nisar J, Adegoke K A and Anastopoulos I 2019 The utilization of leaf-based adsorbents for dyes removal: A review. *Journal of Molecular Liquids* 276 728–747

[5] Shakoor S and Nasar A 2016 Removal of Methylthioninium Chloride dye from artificially contaminated water using citrus limetta peel waste as a very low cost adsorbent. *Journal of the Taiwan Institute of Chemical Engineers* 66 154–163

[6] Vilela P B, Matias C A, Dalalibera A, Becegato V A and Paulino A T 2019 Polyacrylic acid-based and chitosan-based hydrogels for adsorption of cadmium: Equilibrium isotherm, kinetic and thermodynamic studies. *Journal of Environmental Chemical Engineering* 7(5) 103327

[7] Yagub M T, Sen T K, Afroze S and Ang H M 2014 Dye and its removal from aqueous solution by adsorption: A review. *Advances in Colloid and Interface Science* 209 172–184

[8] Jarusiripot C 2014 Removal of Reactive Dye by Adsorption over Chemical Pretreatment Coal based Bottom Ash. *Procedia Chemistry* 9 121–130

[9] Sharma P and Kaur H 2011 Sugarcane bagasse for the removal of erythrosin B and Methylthioninium Chloride from aqueous waste. *Applied Water Science* 1(3–4) 135–145

[10] Singh N B, Nagpal G and Agrawal S 2018 Environmental Technology & Innovation Water purification by using Adsorbents: A Review. *Environmental Technology & Innovation* 11 187–240

Acknowledgment
Authors wishing to acknowledge lab staff in Faculty of Chemical Engineering Technology UniMAP for their assistance in the research analysis and appreciation to colleague mates for sharing their pearls of wisdom during this research.