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The Kinetic Study of Methylene Blue Adsorption over MgO from PVA Template Preparation

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ABSTRACT

Magnesium oxide (MgO) was prepared by using polyvinyl alcohol (PVA) as template and the resulting MgO was then used as adsorbent in Methylene Blue (MB) adsorption. The effect of pH, temperature, the kinetic of adsorption and adsorption isotherm were investigated. The $Mg(NO_3)_2.6H_2O$ and PVA were dissolved, then mixed these solution together. An aqueous ammonia (NH_4OH) was precipitant. The precipitate was washed, filtrated, dried and calcined to obtain MgO. The MB uptake over MgO showed clearly that at lower pH, the higher adsorption capacity was occurred. This might be because the surface of MgO produced more -OH group. In term of temperature, at higher temperature could induce more MB adsorption since the higher mass transfer. Moreover, the adsorption is an endothermic process and the order of adsorption process was suggested to be Pseudo-second order. The experimental data was fitted with Freundlich and Langmuir equation, the more linearity relationship was shown in Freundlich model. Therefore, the Freundlich isotherm was fitted better than Langmuir isotherm.

Key words: MgO, methylene blue, PVA, adsorption, kinetic study, freundlich isotherm, Langmuir isotherm

INTRODUCTION

Now-a-days, the technology is rapidly developed and this is the main cause in environmental problem. Dyes have been applied in many industries such as textiles, printing and publication, pulp mills, leather, food and plastics, etc. The effluent from these industries normally contains some of dyes. The estimation of 10,000 different commercial dyes and pigments exist and more than 7×10^5 tons are produced per year world-wide. It has been about 10-15% of these dyes are released aft dyeing process (Al-Degs *et al*., 2008). Since many organic dyestuffs are harmful to human being and toxic to animal and microorganism. The dye removal has been in considerable attention over the past decades for dye treatment in the waste before release to natural stream.

Various dye removal process have been used such as coagulation, chemical oxidation, membrane separation, electrochemical process, biological treatment (Durai and Rajasimman, 2011) and adsorption techniques. All techniques have their own advantages and limitations such as the adsorption process, the cost and recycling are the limitation. However, adsorption was recognized to be an effective process for removal of dyes from waste effluents (Orthman *et al*., 2003) which are the easiness in separation after process and high effective in dye removal. Many kinds of adsorbents have been developed for various applications such as activated carbon (Iqbal and Ashiq, 2007), spent activated clay (Weng and Pan, 2007), sand (Rauf *et al*., 2008), soil

(Cheng *et al.*, 2008), kaolin (Nandi *et al.*, 2009), biomass from *Calotropis procera* leaf (Ali and Muhammad, 2008), natural resin (Clinoptilolite) (Moazed, 2008) and Mg-Al-CO_3 layers (El-Gaini *et al.*, 2009) etc.

Magnesium oxide (MgO) has been widely used in many application such as catalyst, catalyst support and destructive adsorbent for a large number of pollutants. The structure of MgO is a simple sodium-chloride structure and is very stable thermally and stoichiometrically. The highly active MgO nanoparticles with high surface area have been obtained with specific preparation method and the MgO prepared from different routes has different morphologies and properties. These could lead to different activities and selectivity of resulting MgO. MgO prepared by using PVA as template for the precipitation with NH_4OH was reported by Meshkani and Rezaei (2009) could produce nano size of MgO. This would relate in high surface area of MgO and it could enhance the high adsorption capacity. This research aimed to study the optimization conditions which were pH and temperature of MB adsorption over MgO from PVA template preparation. The data were then analyzed to investigate the adsorption model and order of adsorption process to understand the adsorption on the surface.

MATERIALS AND METHODS

The present study was conducted at Department of Chemistry, Faculty of Science, Mahasarakham University during the academic year 2010.

MgO preparation: It has been proposed by Meshkani and Rezaei (2009) to obtain nano-scaled MgO. Firstly, polyvinyl alcohol (PVA, MW: 70000) which commercial grade from ACROS organics was completely dissolved in DI water under stirring at 60°C. The $Mg(NO_3)_2.6H_2O$ (Ajex Finechem) was also dissolved in water in round bottom under stirring at 60°C, then added PVA solution into round bottom and waited until temperature was maintained at 60°C. And then, NH_4OH (analytical grade from AnalaR®) was added drop wise to the mixture until the precipitation was completed. PVA and NH_4OH were used as precipitant and polymeric surfactant, respectively. The mixture was then stirred at 60°C for further 3 h and then filtrated and washed with enough amount of hot DI water to prevent the PVA precipitation over the resulted cake. The cake was dried at 100°C for 12 h and calcined at 500°C for 4 h.

Adsorption measurement and Kinetic study: MB which obtained from Asia Pacific Specialty is the cationic dye and the formula process of MB adsorption study using MgO was described as follow: (1) prepared a concentration of MB at 2.5×10^{-5} M; (2) MB solution was then adjusted pH to 3 by using either 1 M HCl and 1 M NaOH. The pH was measured by Metrohm 713 pH Meter (3) distributed 500 ml of MB solution into round bottle under well stirring in oil bath which set temperature at 45°C; (4) weighted MgO and loaded into MB solution in ratio 1 g L^{-1}; (5) stirring the mixture for 5 h to obtain the saturation adsorption (6) at the completion of 5 h, the samples were interval sampling out 20 mL from 500 mL round bottle every 10-15 min (7) centrifuged immediately the sampling mixture at 5000 rpm for 10 min to obtain the clear blue solution; (8) determined the residual MB concentration in the supernatant by UV-Vis spectrophotometer (Perkinelme, Lambda 25) at wave number 650 nm. The structural formula of MB is shown in Fig. 1.

The effect of pH on adsorption was also studied by maintaining pH at 3, 7, 8, 9 and 10 by using 1 M Hcl and 1 M NaOH in step 2 and the effect of temperature on adsorption process was

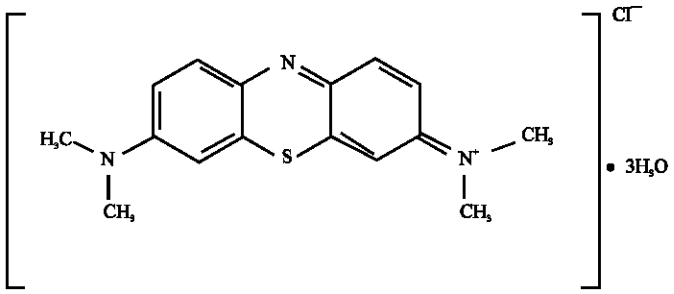

Fig. 1: Formular structure of MB (Liu *et al.*, 2010)

conducted under isothermal at 0, 30, 38, 45 and 60°C. The desired temperature was achieved by using oil bath (Digital hotplate, V. GO) with temperature probe controller. The other parameters were similarly such as adsorption time, volume of MB solution, MB initial concentration and adsorbent amount.

Calculation: The initial dye concentration, C_0 (M) and equilibrium dye concentration, C_t (M) were calculated from peak height at wave number 650 cm^{-1} of UV-vis spectra by using standard curve of MB. The dye removal per unit weight of MgO at time t, q_t (mg g^{-1}) were obtained from Eq. 1:

$$q_t = (C_0\text{-}C_t)\ V/M \quad (1)$$

where, V is the volume of dye solution in adsorption process (l) and M is the mass of MgO (g).

Adsorption model: Langmuir and Freundlich isotherms were applied to determine the adsorption model of MB onto MgO. The Langmuir equation is shown in Eq. 2:

$$C_t/q_t = 1/(Q_0.K_L)+(1/Q_0)\ C_t \quad (2)$$

where, Q_0 (mg g^{-1}) is the maximum adsorption capacity of the dye (monolayer formation) per gram of adsorbent. K_L is a constant related to the affinity of the binding sites (l/mg).

The empirical Freundlich isotherms is also shown in Eq. 3:

$$\ln q_t = \ln K_f+(1/n)\ln C_t \quad (3)$$

Adsorption kinetics model: Pseudo-first-order kinetic model assume that the adsorbate uptake to the surface with time was directly proportional to difference in saturation concentration and the adsorbent amount (Lagergren, 1898).

Pseudo-second-order model with proposed by Ho and Mckay (1999).

RESULTS

Effect of pH and temperature on the adsorption: Figure 2 shows the effect of pH on the adsorption kinetics of MB onto MgO at 45°C with solid concentration 1 g L^{-1} and initial concentration of dye 2.5×10^{-5} M. The adsorption was slightly taken place until 100 min, then adsorption became slower and almost reached equilibrium in 180 min for pH 3-10. The adsorption

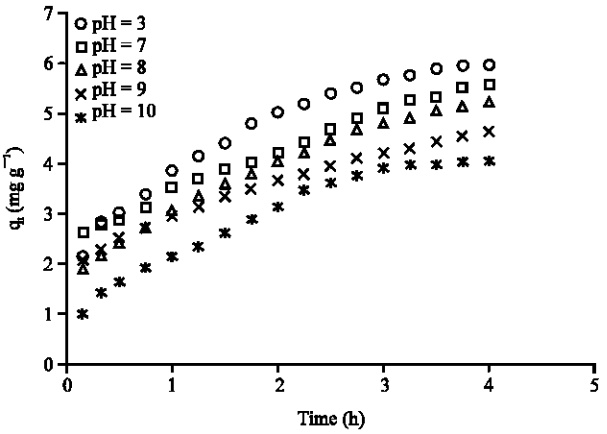

Fig. 2: Effect of pH on the adsorption of MB over MgO at 45°C

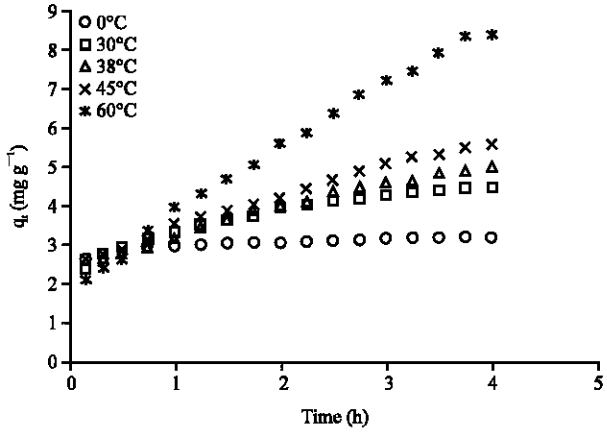

Fig. 3: Effect of temperature on the adsorption of MB over MgO at pH 7

of MB by MgO at pH 3 and pH 8 was about 5.75 and 3.83 mg g^{-1}, respectively. It was found that at lower pH, the higher adsorption capacity was achieved.

Figure 3 shows the effect of temperature on adsorption of MB onto MgO at pH 7 with solid concentration 1 g L^{-1} and initial concentration of dye 2.5×10^{-5} M. At initial for all temperatures, there was a low uptake of MB of temperature between 0-60°C. At higher temperature, the adsorption was occurred more rapid and reached equilibrium slower. At 0°C, the equilibrium was reached within 30 min whereas at 60°C, the equilibrium was obtained at about 220 min. From Fig. 5, it was clearly that at higher temperature, the adsorption was higher.

Adsorption model: The experimental data were plotted in 2 different adsorption isotherm of Langmuir and Freundlich model as shown in Fig. 4a and b, respectively. The fitted results were clearly linear relationship in the Freundlich model in Fig. 4b whereas the Langmuir plot (Fig. 4a) is not a linear relationship.

Adsorption kinetics model: In order to investigate the kinetic of process such as the mechanism of adsorption and potential rate controlling steps, basically the order of process has to be studied.

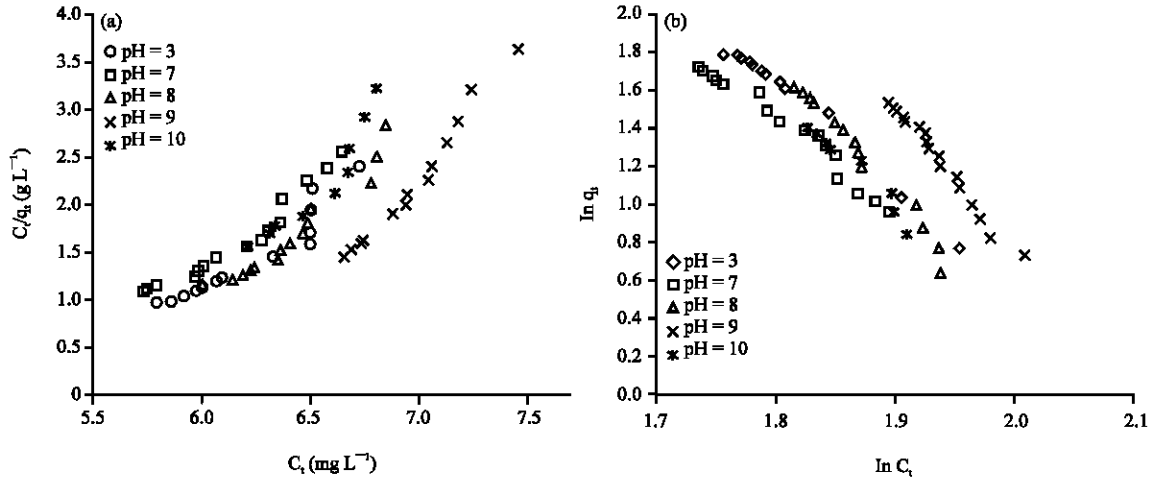

Fig. 4: Langmuir (a) and Freundlich (b) adsorption isotherms for the adsorption of MB over MgO at 45°C

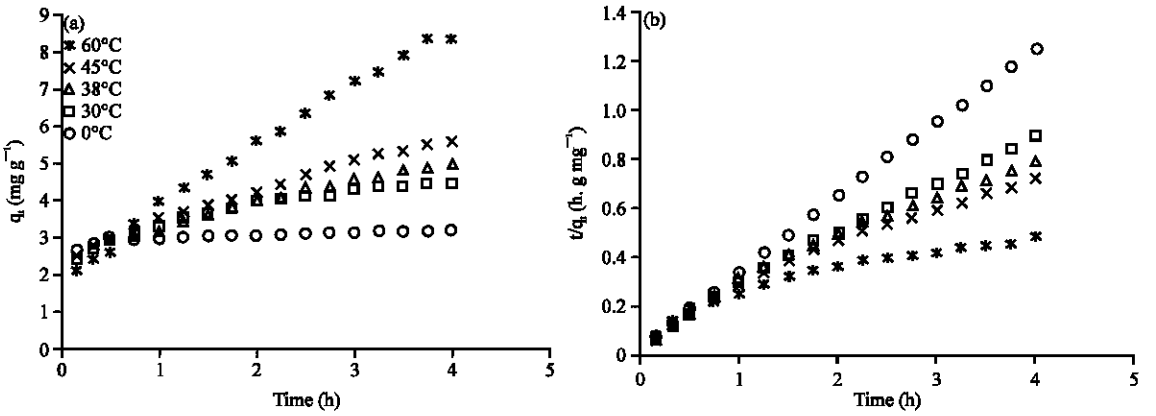

Fig. 5: First-order (a) Psuedo-second-order (b) kinetic model for the adsorption of MB over MgO at 0°C and pH 7

Figure 5b shows the relationship between t/q_t and time which is the relationship of Psuedo-second order model. Figure 5b shows more linear plot of MB adsorption onto MgO than first order model in Fig. 5a.

DISCUSSION

Figure 2 shows that pH of initial MB solution could affect the adsorption property of MgO. The lower pH causes the enhancement of adsorption capacity. Mostly case of MB adsorption over solid adsorbent, the pH could clearly enhance adsorption capacity of solid supports by increasing pH (Dogan *et al.*, 2004; Bulut and Aydin, 2006; Dogan *et al.*, 2009; Franca *et al.*, 2009; Sener, 2008). However, pH could affect in the different routes when using the different adsorbents for MB removal such as found in Bhattacharyya's reports (Bhattacharya and Sharma, 2005). They reported the MB adsorption on Neem (*Azadirachta indica*) leaf powder (NLP) by varying adsorbate

concentration, adsorbate amount, pH and temperature. For the influence of pH, the results showed that pH of medium did not affect any significant effect on uptake of MB by this leaf powder. Ho *et al.* (2001) studied the extent of removal of a basic red 18 by activated clay under pH between 3-10. They found that the dye uptake was clearly reduced when pH was increased from 3-5 and remained constant within pH range 5-10. It was suggested that the increase of sorption depended on the properties of the adsorbent surface and type of dyes. In addition, they also suggested that the influence of pH might also be explained on the basis of surface hydroxylation and the electrostatic interaction between dye and adsorbent.

In the present study, the effect of pH might be explained on the basis of 2 possible mechanisms: (i) this could relate to the increasing of -OH group at the surface of MgO at lower pH and -OH group might be the active adsorption site for MB molecules. The precipitation of Mg salt with PVA produced $Mg(OH)_2$ soaked with water. Then, the soaked precipitate was calcined at 500°C for 4 h, resulting in the decomposition of $Mg(OH)_2$ to MgO as previous study by Kumari *et al.* (2009). Therefore, over surface of MgO before treated with MB solution was lacked of -OH group. When the MgO was soaked with strong acid solution, the protonation of H^+ to surface of MgO to obtain $Mg(OH)_2$ might be occurred. MB is cationic dye which is more favour adsorbed over anionic potential site which might be -OH group. (ii) chemical reaction between -OH group of active component over MgO surface (from (i)) and the reactive group Cl^- in MB, resulting in MB adsorbed over MgO surface and eliminated HCl in solution (Bhattacharya and Sharma, 2005).

The effect of temperature on the adsorption kinetics was investigated under isothermal conditions in the temperature range of 0-60°C. The experimental results indicated that magnitude of adsorption was related to the temperature of reaction as shown in Fig. 3. The results were also supported by Weng and Pan (2007), Al-Degs *et al.* (2008) and Pengthamkeerati *et al.* (2010). It could be explained by the enhancing of higher mass transfer or intraparticle diffusion of MB molecules to the adsorption site of adsorbent. This could increase the adsorption property of MB to MgO. Therefore, the adsorption is the endothermic process.

Figure 4a and b show the adsorption isotherm plot which referred to Langmuir and Freundlich model, respectively. Refer to Eq. 2 and 3, the plot has to be straight line to investigate the type of adsorption isotherm. It is clearly that Fig. 4a was not straight line whereas Fig. 4b is. This could be supported that the adsorption isotherm was Freundlich model. Some of dye adsorption studies over various solid adsorbents were also showed the best fitted data with Freundlich adsorption isotherm as found by Iqbal and Ashiq (2007), Rauf *et al.* (2008) and Gomez *et al.* (2007). However, there were some of adsorption studies supported the different adsorption isotherm such as Langmuir and Tempkin adsorption model (Franca *et al.*, 2009; Bulut and Aydin, 2006; Bhattacharya and Sharma, 2005; Hameed *et al.*, 2007). Therefore, the adsorption isotherm was independence due to the solid adsorbent and dyes.

In order to investigate that the adsorption is Pseudo-first-order, the data will be plotted between log $(q_e\text{-}q_t)$ and t to obtain the straight line with slope and Y-intercept of $-k_1/2.303$ and log q_e, respectively. However, the Pseudo-first-order is normally plot in the exponential type of Lagergren first-order equation as shown in Eq. 4 (Pengthamkeerati *et al.*, 2010):

$$q_t = q_e (1\text{-}e^{-k1t}) \quad (4)$$

Therefore, the exponential plot is the relationship between q_t and t as shown in Fig. 5a. The plot shows clearly that it is the straight line which is not fitted with the exponential type of Eq. 4. Therefore, the adsorption process is not support with first order process.

In other hand, the experimental data was plotted between t/q_t and t (Fig. 5b). The straight line should be obtain to confirm that the adsorption process is the Pseudo-second-order, the slope and Y-intercept will be $1/q_e$ and $1/k_2q^2_e$, respectively. Figure 5 shows that it is straight line with related to Pseudo-second-order. Thus, this adsorption process was fitted well with the Pseudo-second-order. Many publications were also studied the kinetic order of adsorption process onto solid support which could use as primary data to propose the possible adsorption mechanism, leading to understanding of adsorption nature of dye onto solid support. They were investigated various dyes and solid adsorbents. It has been supported that the adsorption kinetic model was fitted well with pseudo second order as the present study (Hameed *et al.*, 2007; Dogan *et al.*, 2009; Dogan *et al.*, 2004; Bulut and Aydin, 2006; Franca *et al.*, 2009).

CONCLUSIONS

The present study resulted that MB adsorption took placed on the surface of MgO from the precipitation of Mg nitrate salt by PVA. The pH and temperature could affect the MB adsorption capacity which was at higher temperature and lower pH could enhance the adsorption of MB onto surface of MgO. The adsorption isotherm was fitted well with Freundlich model and the kinetic adsorption model was revealed to Psuedo-second order.

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