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การดูดซับมาลาไคต์ กรีนในสารละลายด้วยแกลบดัดแปรด้วยความร้อน

Adsorption of Malachite Green in Aqueous Solution by the Thermally Modified Rice Husk

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บทคัดย่อ

แกลบดัดแปรด้วยความร้อนถูกนำมาประเมินเพื่อเป็นวัสดุดูดซับราคาถูกเพื่อดูดซับสีย้อมที่เป็นพิษ (มาลาไคต์ กรีน)ในสารละลายด้วยการทดลองแบบกะ ผลของความเข้มข้นเริ่มต้นและเวลาต่อการดูดซับมาลาไคต์โดยแกลบดัดแปรด้วยความร้อนได้ถูกศึกษา กรีนกับแกลบปรับปรุงด้วยความร้อน เวลาที่เหมาะสมของการดูดซับคือ 1 ชั่วโมง ไอโซเทอร์มการดูดซับของแลงเมียร์และฟรอยน์ดลิชได้ถูกใช้เพื่อศึกษาข้อมูล ณ จุดสมดุลของการดูดซับ การดูดซับตามแบบไอโซเทอร์มของแลงเมียร์แสดงให้เห็นว่าการดูดซับเป็นแบบชั้นเดียว โดยมีความจุสูงสุดของการดูดซับที่ 50 มิลลิกรัมต่อกรัม จากผลการทดลองชี้ให้เห็นว่าแกลบดัดแปรด้วยความร้อนสามารถใช้เป็นวัสดุดูดซับเพื่อกำจัดมาลาไคต์ กรีน จากสารละลายได้

ABSTRACT

The thermally modified rice husk (TMRH) was evaluated as a low cost adsorbent for adsorption of toxic dye, malachite green, from aqueous solution in batch adsorption experiments. The effect of initial dye concentration and contact time of malachite green on TMRH adsorption was studied. The optimal time for malachite adsorption was reached in 1 h. Langmuir and Freundlich isotherms were used to investigate the equilibrium data. The Langmuir isotherm model showed good fit to the equilibrium adsorption data, showing a monolayer adsorption. The maximum monolayer adsorption capacity was found to be 50 mg g^{-1}. The result indicated that TMRH was an adsorbent for the removal of malachite green from aqueous solution.

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คำสำคัญ: แกลบ มาลาไคต์ กรีน การดูดซับ ไอโซเทอร์มการดูดซับ

Keywords: Rice husk, Malachite green, Adsorption, Adsorption isotherm

Introduction

Malachite green (MG) is a synthetic dye, containing the *N*-methyl diaminotriphenyl methane. It is widely used as colorant for the textile industries (Ahmad and kumar, 2010). It is also applied for being the biocide in the aquaculture. Beside the biocide, When MG is applied in the aqua cultural farms, it is highly accumulated in edible fish tissues. In addition, the waste water discharged from dying process from textile factory most likely contains the MG at approximately 10-200 mg/ml of dyestuffs (Neill et al., 1999). Despite its wide use, MG is considered to be a risk for human. It may cause the adverse effects on the immune and reproductive systems and also shows the carcinogenic and genotoxic properties. It could promote the tumor in liver as well (Srivastava et al., 2004). Moreover, MG strongly absorbs the sunlight ultimately reduce the penetration through the phytoplankton, affecting its photosynthesis. Therefore, contamination of MG in natural reservoir may affect to the living system and ecosystem (Arellano-Cardenas et al., 2013). MG also has a tendency to chelate metal ions which result in micro-toxicity to fish and other organisms (Malik et al., 2007). Therefore, removal of MG is needed to reduce the harmful impact for environment and is also a big challenge for industries.

There are many treatment methods have been developed to remove dyes from waste water. Those methods are based on the physical, chemical and biological methods such as photo-degradation (Nogueira et al., 2005, Sayılkan et al., 2007), and adsorption (Zhang et al., 2008). Adsorption techniques have potential for removing organic and inorganic pollutants from wastewater due to their high efficiency and ability to separate a wide range of compounds.

Activated carbon is perhaps the most widely used as adsorbent to remove chemical dye from industrial waste. However, the high operational costs and problems with regeneration may hamper the application in large-scale (Tsai et al., 2007). Thus, the alternative materials posses a low cost has been focus intensively. There are many by-products from agricultural activity showed the potential to be alternative absorbents e.g. neem leaf powder, hazel nut shells, rice hull, wood shavings (Bhattacharyya and Sarma, 2004), cedar sawdust (Pengthamkeerati et al., 2008), banana peel (Annadurai et al,. 2002), and pineapple stem (Hameed et al,. 2009). However, the data regarding the rice husk has not been extensively studied.

Rice husk (RH) is another type of agricultural by-product from rice and abundantly available in the Southeast Asia, where rice is the main source of carbohydrate. Globally, approximately 600 million tons of rice is produced annually and 22% of husk is produced during production of the paddy milled rice. This RH is normally dumped as a waste or burnt out in the open area, resulting in air pollution. Therefore, maximally utilize the rice husk is the challenge. The compositions of RH are mainly cellulose and it derivatives. It has been reported that RH consists of cellulose, hemicelluloses and lignin at 32.24, 21.44, and 21.34%, respectively (Mahvi et al., 2004). The presence of cellulose and hemicelluloses provide the benefit to be the adsorbent. However, those compositions are associated tightly to each other, forming a stable matrix. In addition, the inner surface of rice husk is coated by wax and natural fats. The presence of such coated lipids may retard the adsorption properties by neither chemical nor physical mechanisms (Ndazi et al., 2007). Therefore, the removal of other impurities from the rice husk is necessary to improve the adsorption properties.

Modification the surface of rice husk has been reported to increase the ability to adsorb the heavy metals of untreated RH (Yeneneh et al., 2011). Modification of RH can be made by chemical treatment, which hydrochloric acid, sodium hydroxide and sodium carbonate are commonly used. Those chemicals could remove lignin, breakdown the linkage, and reduce crylstalinity of cellulose, resulting in an increase the porosity (Yeneneh et al., 2011). Although chemical treatments are useful for surface improvement, the chemical management and complicated processes are still limited for practical. Chakrborty et al., (2011) reported that the pretreatment of RH by autoclave before chemical modification. However, the data regarding modification of RH by only physical methods e.g. high pressure has been not wildly available and should be investigated. The obtained data would be useful for developing the practical method to modify RH for being the alternative absorbent to remove synthetic dye from waste water from aqua culture and textile industries. Therefore, the aim of this research was to study the structure of rice husk modified under the autoclave condition as well as its adsorption properties toward malachite green were also evaluated.

Materials and methods

Adsorbate

Malachite green (MG) as commercial grade was from Sigma-Aldrich. The formula weight of MG was 365 mole g^{-1} with the chemical formula of $C_{23}H_{25}N_2Cl$. The stock solution was prepared at 1,000 mg L^{-1} by dissolving the dye in double-distilled water

(DI-water) and working concentrations were further diluted from stock solution.

Preparation of adsorbent

Rice husk used was obtained from a local rice mill factory at Nong Song Hong, Nongkhai province, Thailand. It was washed repeatedly with water until the washing was clear. The washed husk was dried overnight at 60°C. The dried sample was mixed with water at the weight ratio of husk to water of 1:15 and autoclaved at 10 psi for 15 min. The autoclaved sample was washed thoroughly with water until the washing was close to 7.0. The treated rice husk was dried overnight in an oven at 60 °C before grinding to be the powder. The obtained powders were sieved through the pore size of 300 μm. The obtained powder was then stored in sealed plastic containers and used as the thermally modified rice husk (TMRH) adsorbent throughout the study.

Surface structure of adsorbent

The surface structure of TMRH was evaluated by scanning electron microscopy (SEM) using a scanning electron microscope (Hitachi, Model S-3000N, Japan). The samples were gold coated using a sputter coater prior to analyze at an electron acceleration voltage of 5 kV.

Fourier transform infrared spectrophotometry

The functional groups of the adsorbent were also analyzed using a Fourier Transform Infrared Spectrophotometer (Spectrum One model Spectrometer, Perkin-Elmer, England). The sample was mixed with KBr and pressed as a pellet before scanning the spectra in the range of 4,000- 450 cm^{-1}.

Batch adsorption study

The adsorption of MG on TMRH was studied in batch equilibrium experiment. All batch experiments were carried out in Erlenmeyer flasks (250 mL) containing a mixture of TMRH (0.2 g) and 20 mL of MG solution at various concentrations of 100, 200, 300, 400 and 500 mg L^{-1}. The flasks were shaken at a constant speed of 200 rpm for different times of 1, 3, 6, 12 and 24 h in an incubator shaker (Model VS-8480SFN, Vision Scientific, Korea) at 30 °C. Samples were collected from the flasks at the desired adsorption. The concentration of MG in the solution at studied time was estimated by the

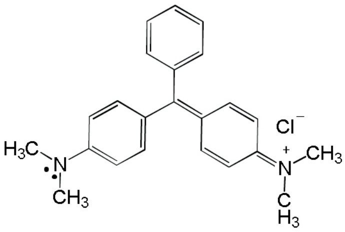

Figure 1. Structure of malachite green (Arellano-Cardenas et al, 2013)

the absorbance of MG at 618 nm using the Visible spectrophotometer (Model CE1021, Cecil Instruments, England). The amount of adsorption at equilibrium, q_e (mg g^{-1}) was calculated according to the method described by Hameed et al. (2007) as shown in Equation (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

where C_0 is the initial dye concentration (mg L^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), V is the volume of the solution (L), W is the weight of the TMRH (g). All the experiments were performed in triplicate and the average value were reported.

Results and discussion

Microstructure of TMRH

The microstructure of TMRH was observed by SEM and the result shown in Fig. 2. The SEM structure of TMRH provided the insight morphology of the rice husk upon treatment. The surface of rice husk was cracked and broken down. This evidence was caused by thermal treatment. An increase in surface area would be occurred, providing more contraction to other chemicals. Chakraborty et al. (2011) reported that the conical protrusions of rice husk surface were also cracked by thermo-chemical treatment, resulting in an increase in surface roughness. The thermo-chemical treatment would likely removed the cementing materials of the inter fibrillar region (mainly hemicelluloses and lignin). Although the surface of rice husk has been modified, the fibrous network of rice husk was still retained. It has been reported that modification of rice husk surface was involved by only the introduction of amine group onto the surface. In addition, this adsorbent is non-porous materials, due to the absence of pores and cavities.

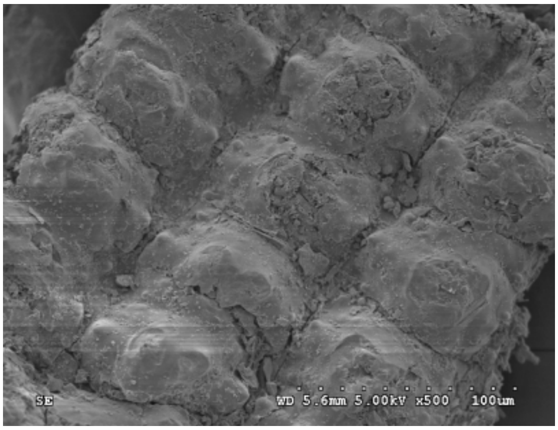

Figure 2 Scanning electron micrograph of TMRH

FI-IR spectrum of TMRH

The FTIR technique is powerful tool to identify the characteristic functional groups of biomaterial. The information would be benefit to identify the binding mechanism of TMRH to the MG. The FTIR spectra of the rice husk after thermal treatment is presented in Figure 3.

The FTIR spectrum showed the stretching vibration in the region of 3200-3600 cm^{-1} and the band assignment of each peak has been summarized in Table 1. The band stretching from OH vibrations showed the adsorption peak around 3433 cm^{-1}. This indicated the existence of free hydroxyl groups. The C-H stretching vibration was also observed at around 2927 cm^{-1}, indicating the alkane groups (Samah et al., 2012). The C=C stretching vibrations between 1546-1652 cm^{-1} were also found and indicated the signal from alkenes and aromatic groups. In addition, the aromatic groups were also showed in the peak around 1508 cm^{-1}. The presence of CH_2 was evidenced by the peaks around 1459 cm^{-1}, while that for CH_3 was at 1366 cm^{-1}. The carboxyl-carbonate structures was reported at 1399 cm^{-1} and also found in TMRH. The peaks around 1237, 1102, 1020 and 862-476 cm^{-1} were from the CHOH stretching, Si-O-Si stretching, Si-O stretching and Si-H groups, respectively.

According to the FTIR results, more functional groups were available in the TMRH surface and would likely facilitate the adsorption of the organic dye.\

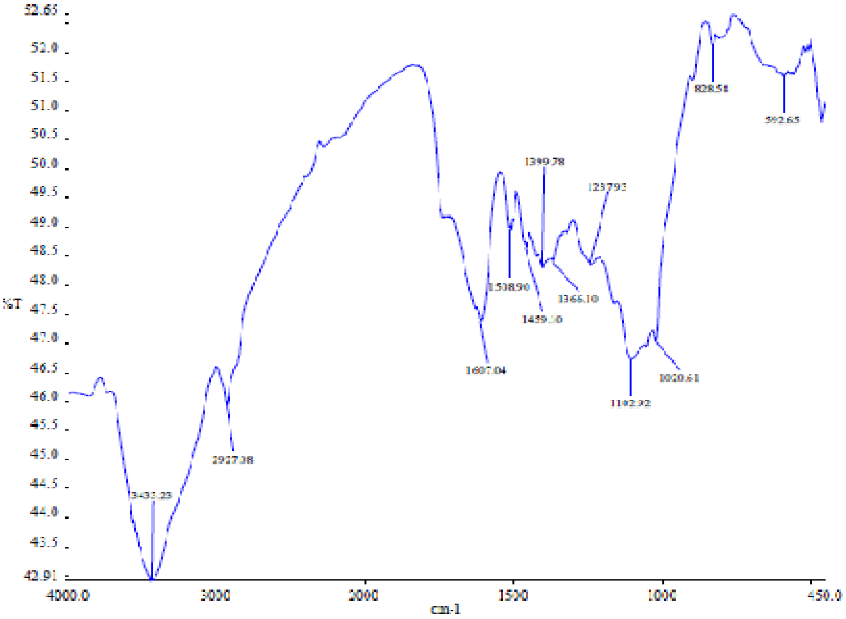

Figure 3 FTIR spectrum of TMRH

Table1. Peak Identification of FT-IR Spectrum of TMRH

Wave number (cm^{-1})	Functional group
3433	-OH and Si-OH
2927	C-H stretching of alkanes
1546-1652	C=C stretching of alkenes and aromatic
1508	Aromatic region
1459	CH_2 and CH_3
1399	Aromatic CH
1366	Aromatic CH and carboxyl-carbonate
1237	CHOH stretching of alcohol group
1102	Si-O-Si stretching
1010-1090	Si-O-Si
1020	Si-O stretch
828	Si-H groups
592	$-OCH_3$

Batch adsorption study

The effect of contact time between MG and TMRH was carried out at 30 °C at different concentration ranging from 100-500 mg L^{-1} (Fig. 4). The contact time was necessary for MG to be adsorbed by TMRH and the amount of MG adsorbed onto TMRH increases with increasing time. At the certain time, the amount of the MG desorbing from the TMRH was in the dynamic equilibrium with the amount of the MG is being adsorbed. The time required to attain this state is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time was considered as the maximum adsorption capacity of the TMRH under studied condition. The equilibrium time was observed at 1 h when the initial concentrations were at 100–300 mg L^{-1}. However, at high initial concentrations (400–500 mg L^{-1}), longer equilibrium time of 6 h was required. Ahmad and Kumar (2010) reported that the treated ginger waste required only 15 min to contract with MG to reach the adsorption equilibrium. However, the organically modified clay showed longer time for 6 h (Arellano-Cardenas et al., 2013). Thus, the equilibrium time for MG adsorption was relied on the types of adsorbent. The adsorption capacity at equilibrium increased from 9 to 49 mg g^{-1} when the initial dye concentration increased from 100 to 500 mg L^{-1}. The initial rate of adsorption was increased rapidly due to a large number of binding sites. Upon the adsorption, the saturation of the binding sites was occurred, resulting in a reduction of equilibrium rate. The similar phenomenon was observed by Khattri and Singh (2009), who carried out the adsorption of MG by neem sawdust. The rate of adsorption is a function of the initial concentration of the dye. It was evidenced by an increase adsorption capacity upon increasing the initial concentration of MG from 100 to 500 mg L^{-1}. The adsorption capacity increased with increasing of initial concentration (Zhang et al., 2008).

Adsorption isotherm

The adsorption isotherm for MG adsorption by TMRH is shown in Fig. 5. This value indicates the distribution of MG between the liquid and solid phase at the equilibrium state. There are several models used to explain the behavior but the suitable for each system was important for application. The data in Fig. 5 are considered according to the two isotherms, Langmuir and Freundlich.

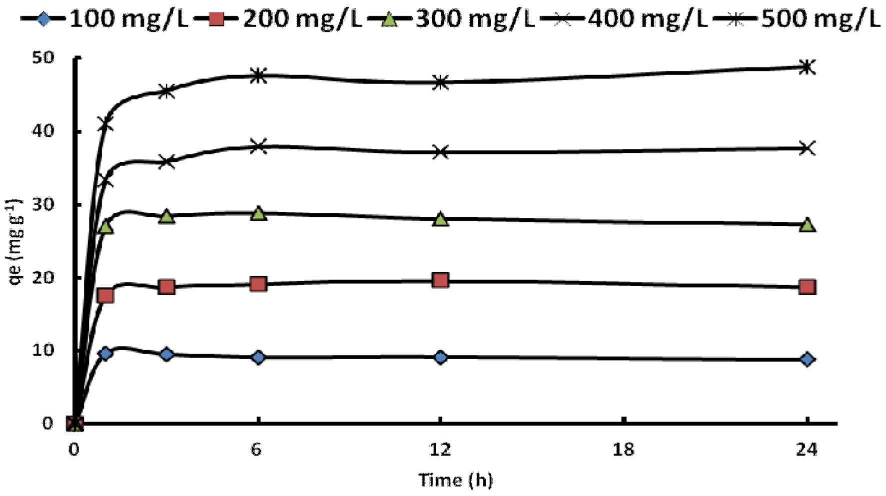

Figure 4 The variation adsorption capacity with contact time at various initial MG concentrations at 30 °C

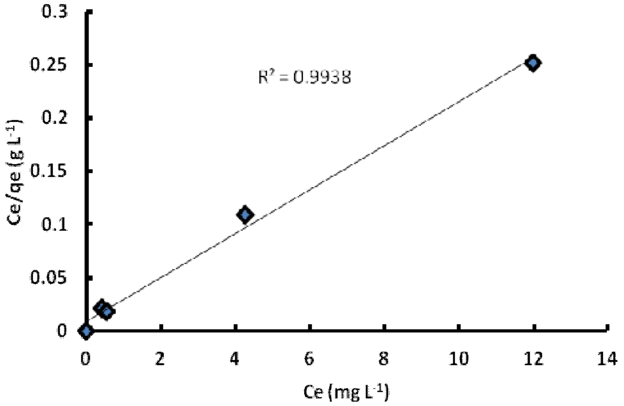

Figure 5 Langmuir adsorption isotherm of MG onto TMRH at 30 °C.

Langmuir isotherm was based on the assumption of monolayer adsorbed onto a surface containing a certain number of adsorption sites without the transmigration of adsorbate to the plane of surface. The acceptability of the isotherm model is based on the correlation coefficients, R^2. The linear form of Langmuir's isotherm model is given by the following equation (2):

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \left(\frac{1}{Q_0}\right)C_e \qquad (2)$$

where C_e is the equilibrium concentration of the adsorbate (MG) (mg L^{-1}), q_e the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}), and Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When C_e/q_e was plotted against C_e, straight line with slope $1/Q_o$ was obtained (Fig. 5), indicating that the adsorption of MG on TMRH obeys the Langmuir isotherm.

The Langmuir constants 'b' and 'Q_o' were calculated and their values are listed in Table 2.

Information regarding the Langmuir isotherm model indicated the homogeneous surface of adsorbent. This allowed the MG adsorb onto the surface by the formation of monolayer coverage. The similar results were observed in the cases of acid orange 10 dye adsorbed by activated carbons prepared from bagasse (Tsai et al., 2001) as well as the adsorption of direct dyes by activated carbon prepared from sawdust (Malik, 2004).

The specific characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L), which is defined by equation (3):

$$R_L = \frac{1}{1 + bC_0} \qquad (3)$$

where b is the Langmuir constant and C_0 the highest dye concentration (mg L^{-1}). The value of R_L indicated the type of the isotherm to be either unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$) or irreversible ($R_L=0$). Value of R_L was found to be $9.00\text{x}10^{-4}$. This confirmed that the TMRH is favorable for adsorption of MG dye under the studied condition.

Table 2. Adsorption isotherm constants for sorption of MG on to TMRH at 30 °C

Isotherms	Parameters	Value
Langmuir isotherm	Q_0 (mg g^{-1})	50.00
	b (mg^{-1})	2.222
	R^2	0.993
	R_L	9.00E-04
Freundlich isotherm	1/n	0.324
	K_F [(mg g^{-1})(mg^{-1})]1/n	24.29
	R^2	0.849

Freundlich isotherm was based on the heterogeneous surface energies and the energy term in Langmuir equation varies as a function of the surface coverage as given by the following equation (4):

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

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (MG) and K_F and n are Freundlich constants, n giving an indication of how favorable the adsorption process and K_F (mg g^{-1}(l mg^{-1})n) is the adsorption capacity of the adsorbent. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of MG adsorbed onto TMRH for a unit equilibrium concentration. The slope 1/n ranging between 0 and 1, is a measurement of adsorption intensity or surface heterogeneity. The more heterogeneous is observed as its value gets closer to zero (Haghseresht and Lu, 1998).

Basically, the value of 1/n is below unity, indicating a normal Freundlich isotherm. On the other hand, if the 1/n above unity, it indicates the cooperative adsorption (Fytianos et al., 2000). The plot of log q_e versus log C_e gives straight lines yield the slope of '1/n' (Fig. 6), which shows that the adsorption of MG also follows the Freundlich isotherm. Accordingly, Freundlich constants (K_F and n) were calculated as summarized in Table 2.

The values for the parameters obtained from both isotherm models and the related correlation coefficients were used to consider the applicability of the model. According to the data in Table 2, the Langmuir model yielded a better correlation (R^2 = 0.993) than the Freundlich model (R^2 = 0.849) due to the higher correlation coefficients. In addition, the adsorption is also favorable as indicated by the 1/n value at 0.324.

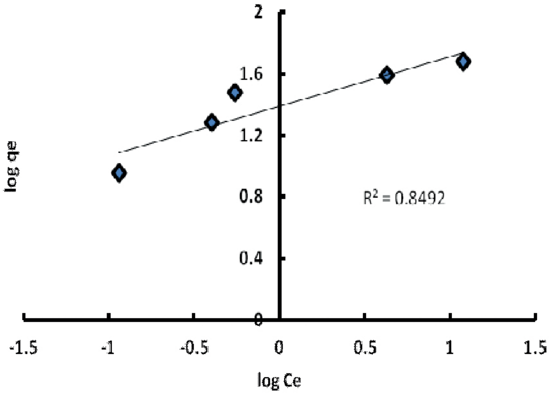

Figure 6 Freundlich adsorption isotherm of MG onto TMRH at 30 °C

Adsorption mechanism

The major challenge in an adsorption study is to elucidate the adsorption mechanism. To understand the adsorption mechanism, there are two points to be considered, which are the structure of the adsorbate and the surface properties of adsorbent. It must be pointed out that MG is a cationic dye, having amine groups in its structure (Chakraborty et al., 2011). In addition, thermal treatment also changed the rice husk morphology. According to those properties, ionic interactions or hydrogen bonding between the exposed hydroxyl groups on the TMRH surface and the cationic ion of MG would be theoretically favorable. Therefore, the dye ions could penetrate to adsorb on the surface of TMRH easily.

According to the presented data, the possible adsorption mechanism of MG onto TMRH may be proposed by the following steps:

- Migration of dye from bulk of the solution to the surface of the adsorbent
- Diffusion of dye through the boundary layer to the surface of the adsorbent
- Adsorption of dye on the surface of TMRH, which may be due to the formation of surface hydrogen bonds between the hydroxyl groups on the rice husk surface and the nitrogen atoms of MG as suggested in Fig. 7 or through a possible mechanism of a dye–hydrogen ion exchange process as shown below:

$$\text{Rice husk–OH} \rightleftharpoons \text{rice husk–O}^{-} + \text{H}^{+}$$

$$\text{Rice husk–O}^{-} + \text{MG}^{+} \rightleftharpoons \text{rice husk–O–MG} + \text{H}^{+}$$

- Intraparticle diffusion of dye into the interior surface of the adsorbent

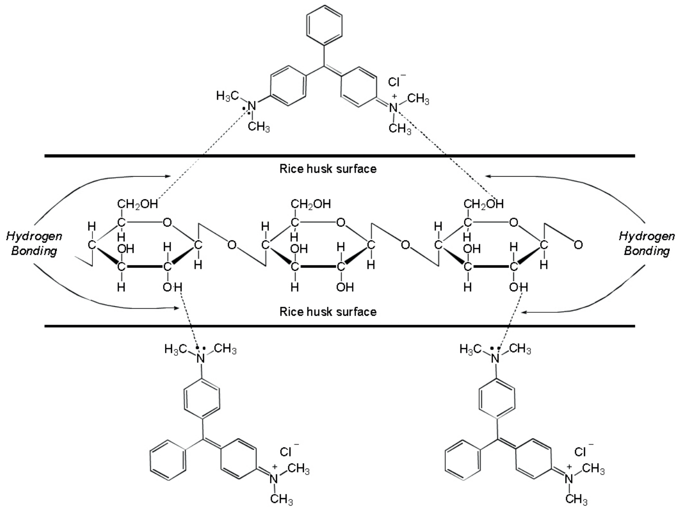

Figure 7 Schematic representation of hydrogen bonding between nitrogen atoms of MG and hydroxyl group of TMRH surface, cellulose unit.(Modified from Chakraborty et al., 2011)

Table 3 Comparison of the maximum adsorption capacity of MG on TMRH with various adsorbents

Adsorbent	Maximum adsorption capacity (mg g^{-1})	Reference
Treated ginger waste	84.03	Ahmad and Kumar, 2010
Coconut coir AC	63.85	Sharma et al., 2009
Neem sawdust	4.35	Khattri and Singh, 2009
Rattan sawdust	62.72	Hameeda et al., 2008
Arundo donax root	8.69	Zhang et al., 2008
Groundnut shell AC	222.22	Malik et al., 2007
Basic treated rice husk AC	56.50	Rahman et al., 2005
TMRH	50.00	This study

From this study, it is interesting that the thermal treatment could be a useful technique to modify the adsorption ability of rice husk. The adsorption capacity of TMRH for MG was also higher than neem sawdust and arundo donax root as shown in Table 3. The abundant available as well as the cheap price would drive the rice husk to be the alternative adsorbent for removing the toxic dye, generated from dying process. The implication of this study may be used as basic knowledge to design the way to remove dye from the waste water from dying of silk, especially from the small and medium enterprise (SME) spreading around the North eastern part of Thailand. In addition, the treatment of natural reservoir for the aquaculture by the TMRH would also be possible. Thus, the use of TMRH as an adsorbent is a thoughtful and economic strategy for wastewater treatment processes.

Conclusion

TMRH showed an effective adsorbent for removal of MG dye from aqueous solution. The initial dye concentration affected the dye uptake capacity of adsorbent. Based on the equilibrium data, the Langmuir isotherm showed higher correlation for dye adsorption than that did by the Freundlich adsorption isotherm. The isotherm constants were calculated successfully and used to compare the adsorptive capacities of adsorbent. Rice husk, agricultural waste, had a potential to utilize as an alternative adsorbent. Modification by thermal treatment provided an alternative method to improve capacity of adsorbent to remove the dye from aquacultural reservoir or waste water. This implied the economic treatment to remove dye from dyeing step generated by textile industries.

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References

Ahmad, R. and Kumar, R. (2010). Adsorption studies of hazardous malachite green onto treated ginger waste. Journal of Environmental Management 91(4):1032–1038.

Annadurai, G., Juang, R. and Lee, D. (2002). Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. Journal of Hazardous Materials 92(3): 263-274.

Arellano-Cardenas, S., Lopez-Cortez, S., Cornejo-Mazon, M. and Mares-Gutierrez, J. C. (2013). Study of malachite green adsorption by organically modified clay using a batch method. Applied Surface Science 280: 74–78.

Bhattacharyya, K.G. and Sarma, A. (2004). Kinetics and thermodynamics of methylene blue adsorption on neem (*Azadirachta indica*) leaf powder. Dyes and Pigments 65(1): 51-59.

Chakraborty, S., Chowdhury, S., and Saha, P. D. (2011). Adsorption of Crystal Violet from aqueous solution onto NaOH-modified rice husk. Carbohydrate Polymers 86(4): 1533-1541.

Fytianos, K., Voudrias, E. and Kokkalis, E. (2000). Sorption–desorption behavior of 2,4-dichlorophenol by marine sediments. Chemosphere 40(1): 3–6.

Haghseresht, F. and Lu, G. (1998). Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents. Energy and Fuels 12(6): 1100–1107.

Hameed, B.H., Din, A.T.M. and Ahmad, A.L. (2007). Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies. Journal of Hazardous Materials 141(3): 819-825.

Hameed, B.H., Krishni, R.R. and Sata, S.A. (2009). A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solution. Journal of Hazardous Materials 162(1): 305-311.

Hameeda, B.H. and El-Khaiary, M.I. (2008). Malachite green adsorption by rattan sawdust: Isotherm, kinetic and mechanism modeling. Journal of Hazardous Materials 159(2-3): 574–579.

James, J. and Rao, M. S. (1986). Characterization of silica in rice husk ash. Bulletin of the American Ceramic Society 65(8): 1177–1180.

Khattri S.D. and Singh, M.K. (2009). Removal of malachite green from dye wastewater using neem sawdust by adsorption. Journal of Hazarous Materials 167(1-3): 1089-1094.

Mahvi, A. H., Maleki, A. and Eslami, A. (2004). Potential of rice husk and rice husk ash for phenol removal in aqueous system. American Journal of Applied Science 1(4): 321-326.

Malik, R., Ramteke, D. S. and Wate, S. R. (2007). Adsorption of malachite green on groundnut shell waste based powdered activated carbon. Waste Management 27(9): 1129-1138.

Ndazi, B. S., Karlsson, S., Tesha, J. V. and Nyahumwa , C. W. (2007). Chemical and physical modifications of rice husks for use as composite panels. Composites (A) 38(3): 925–935.

Neill, C. O., Hawkes, F. R., Hawkes, D. L., Lourenco, N., Pinheiro, H. M. and Delee, W. (1999). Colour in the textile effluents sources, measurements discharge consents and simulation: a review. Journal of Chemical Technology and Biotechnology 74(11): 1009-1018.

Nogueira, R.F.P., Silva, M. R. A. and Trovo, A. G. (2005). Influence of the iron source on the solar photo-Fenton degradation of different classes of organic compounds. Solar Energy 79(4): 384–392.

Pengthamkeerati, P., Satapanajaru, T. and Singchan, O. (2008). Sorption of reactive dye from aqueous solution on biomass fly ash. Journal of Hazardous Materials 153(3): 701-708.

Rahman, I.A., Saad, B., Shaidan, S. and Sya Rizal, E.S. (2005) Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical–thermal process. Bioresource Technology 96(14): 1578–1583.

Sayılkan, F., Asilturk, M., Tatar, P., Kiraz, N., Arpac,, E. and Sayılkan, H. (2007). Photo catalytic performance of S_n-doped TiO_2 nanostructured mono and double layers thin films for malachite green dye degradation under UV and vislights. Journal of Hazardous Materials 144(1-2): 140–146.

Sharma, Y.C. and UmaUpadhyay, S.N. (2009). Removal of a cationic dye from wastewaters by adsorption on activated carbon developed from coconut coir. Energy and Fuels 23(6): 2983–2988.

Srivastava, S., Sinha, R. and Roya, D. (2004). Review toxicological effects of malachite green. Aquatic Toxicology 66(3): 319–329.

Sudova, E., Machova, J., Svobodova, Z. and Vesely, T. (2007). Negative effects of malachite green and possibilities of its replacement in the treatment of fish eggs and fish: a review. Veterinarni Medicina 52(12): 527–539.

Tsai, W.T., Hsu, H.C., Su, T.Y., Lin, K.Y. and Lin, C.M. (2007). Removal of basic dye (methylene blue) from wastewaters utilizing beer brewery waste. Journal of Hazardous Materials 154(1-3): 73-78.

Yeneneh, A.M., Maitra, S. and Eldemerdash, U. (2011). Study on Biosorption of Heavy Metals by Modified Lignocellulosic waste. Journal of Applied Sciences 11 (21):3555-3562.

Zhang, J., Li, Y., Zhang, C. and Jing, Y. (2008). Adsorption of malachite green from aqueous solution onto carbon prepared from Arundo donax root. Journal of Hazardous Materials 150(3): 774–782.

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