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Utilization of Powdered Rice Husk for The Adsorption of Methylene Blue from Aqueous Solution

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Abstract : This study investigate the potential use of untreated rice husk (URH) and base treated rice husk (BRH) for the removal of methylene blue (MB) from aqueous solution. Effect of initial dye concentration, contact time and sorbent dose on sorption were studied. The base treated rice husk had higher adsorption capacities compared to the untreated rice husk. Equilibrium data were fitted to the Freundlich and Langmuir isotherm equations and the equilibrium data were found to be well presented by the Langmuir isotherm equation. The value of q_m from the Langmuir model was 25.64 mg $g^{-1}$and 111.11 mg g^{-1} for untreated rice husk and base treated rice husk respectively. Pseudo-first order and pseudo-second order kinetic model were employed to describe the adsorption mechanism. The kinetic data were found to fit pseudo-second order kinetic model with good correlation coefficient. The experimental data obtained in this study indicate that rice husk could be employed as low cost adsorbents in waste water treatment for dye removal.

Keywords: rice husk, kinetic, methylene blue, adsorption, isotherm

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Introduction

Dyes are widely used in textile, food, cosmetic, paper and printing industries to colour their final products. The released of these coloured effluent to the waterways could give harmful effect as it is known to be carcinogenic and highly toxic to living things. Dyes generally consists of complex aromatic complexes which provide stability against biodegradation in aquatic ecosystems [1]. Dyes are highly visible material and may cause the appearance of colour when release to the environment. Colour in the water may hinder light penetration and retards photosynthetic activities [2]. The dyes also have tendency to sequester metal and may cause microtoxicity to fish and other microorganism. Therefore the removal of dyes from wastewater is of major environmental concern. A range of conventional methods has been applied for the removal of dyes including chemical coagulation, carbon adsorption, reverse osmosis, aerobic and anaerobic treatment and electrolysis [3]. Among these technique, adsorption by activated carbon has been widely used for the removal due to its microporous structure, high surface area, high adsorption capacity and high degree of surface reactivity. Nevertheless, the application of activated carbon for wastewater treatment is not feasible due to its high price and cost associated with the regeneration as a result of high degree of losses in real process [4]. Thus, there is a need to find an alternative adsorbent to replace the costly activated carbon. Some low cost materials used as sorbent for dye removal from wastewater investigated were cotton waste [5], tea waste [6], peanut shell [7], and jackfruit peel [8].

Rice husk an agricultural waste produced as by-product of the rice milling industry and 96% of this is generated in developing country. The main component of rice husk are carbon and silica which makes it has a potential to be used as adsorbent. In Malaysia, large quantities of rice husk are generated as agricultural waste and disposal of this material has become an issue. The use of rice husk as adsorbent would help to reduce cost of disposal and provide potentially cheap alternatives to existing commercial activated carbon. The objective of this study was to investigate the feasibility of rice husk as adsorbent to remove methylene blue (MB) from aqueous solution. MB is a cationic dye that is widely used in dyeing industry. Acute exposure to MB will cause increased heart rate, vomiting and shock [9]. Thus there is a need to remove MB before disposal to the environment. In this study, rice husk was modified with NaOH in order to investigate whether base modification increase the capacity of MB removal. The results were then compared to those for AC for reference. High concentration of MB solution (up to 500 mgL^{-1}) was used in this study. The effect of various parameters on adsorption such as contact time, initial concentration and sorbent dose were also studied.

Materials and Method

Preparation of Adsorbent and Adsorbate

The rice husk used in this study was obtained from a rice mill in Permatang Pauh Pulau Pinang. The rice husk was soaked with distilled water to remove dirt and impurities and dried in oven at 60 °C to constant weight. It was ground and screened through a set of sieves to obtain a particle size of ≤ 80 μm. The sieved fiber was kept dry in a closed container until required. The base modified rice husk was prepared by placing 25.0 g of rice husk in 0.1 M NaOH, with constant stirring for 4 hours. It was then filtered, and washed with distilled water to a neutral pH, and dried at 105 °C for 24 hours to constant weight. The AC used in this study was sieved and prepared in sizes ≤ 80 μm to standardize it with the size of the RH. MB stock solution was prepared by dissolving required amount of dye in distilled water which was later diluted to the required concentration. All reagents used were of analytical grade.

FTIR Analysis

The surface structure of the materials were investigated with FTIR. The IR spectra of each sample were recorded by Perkin Elmer 2000 spectrometer to check the functional group of the sample surface for untreated and base treated rice husk in the form of KBr disc.

Batch Adsorption Experiment

In order to evaluate the feasibility of adsorption, batch studies were carried out using 250 mL conical flask containing 0.50 g of adsorbent with 100 mL aqueous solution of methylene blue of known concentration between 50 -500 mg L^{-1}. The sample was agitated by using orbital shaker at constant speed of 200 rpm. Samples were withdrawn at pre-determined time and filtered to separate the adsorbent from dye solution. The concentration of dye solution was determined spectrometrically by UV-Vis spectrophotometer (Perkin Elmer-Lambda 35). The experimental parameter studied were; contact time (5-180 min), initial concentration (50-500 mg L^{-1}) and the adsorbent dosage (0.2- 1.0 g). Comparison study on the removal of MB by URH and BRH with activated carbon (AC) was carried out at various concentrations.

Study of Adsorption Isotherm

Adsorption isotherm study was carried out with different initial concentration where 0.5 g of adsorbent were mixed with 100 mL MB solution with concentration ranging between 50-500 mg L^{-1}. At the end of the adsorption period, the solution was filtered and analyzed to determine the concentration of MB unadsorbed. The isotherm data were fitted to Langmuir and Freundlich equations.

Kinetic Studies

The rate of adsorption of MB was studied at different time interval. 0.5 g of adsorbent was mixed with 100 mL of 100 mg L^{-1} MB solution. The mixture was agitated with orbital shaker at 200 rpm and several mL of reaction solution was sampled at interval between 0 and 180 min of adsorption. The sample solution was filtered and analyzed for methylene blue concentration

Results and Discussion

Infrared Spectra

The infrared spectra for untreated rice husk (URH) and base treated rice husk (BRH) are presented in Figure 1. The spectra display a number of adsorption peaks indicating the complex nature of the adsorbents. Identification on the most important peak is based on previous studies on oil palm fibre empty fruit bunch [10] sugarcane bagasse and maize corncob [11]. The strong broad band observed at 3387.86 cm^{-1} for URH and 3369.83 cm^{-1} for BRH was due to the stretching of OH band which indicates the existence of free and intermolecular bonded hydroxyl group present in cellulose, hemicellulose and lignin. The peak at 2924.36 cm^{-1} and 2918.76 for URH and BRH respectively is attributed to C-H stretching vibration. The band around 1739.86 cm^{-1} for URH corresponds to absorption of carbonyl group in methyl ester and carboxylic acid present in hemicellulose. This region is to be expected from a conjugated carbonyl or carboxyl structure. Interestingly, the dissappearance of the band at around 1730 cm-1 for URH suggest the removal of hemicellulose. These findings are in agreement with those reported by Kostic et al. (2010) [12]. The peak attributed to the C=C stretching of lignin was observed at1655.34 cm^{-1} for URH and 1642.55 cm^{-1} for BRH. The band observed at 1051.33 cm^{-1} and 1050.22 cm^{-1} correspond to C-O band due to OCH_3 group which confirms the existence of lignin.

Effect of Contact Time and Initial Concentration

The adsorption of MB on rice husk was observed at different contact times as shown in Figure 2. The initial uptake of MB increased rapidly for the first 10 min (first stage) and equilibrium (second stage) was reached after 120 min. At the initial stage, the rate of adsorption was fast due to the availability of free surfaces. However, as time passed, they were gradually occupied by the dye molecules and a decrease in the adsorptive sites for the residual dye molecules in the solution was observed [13]

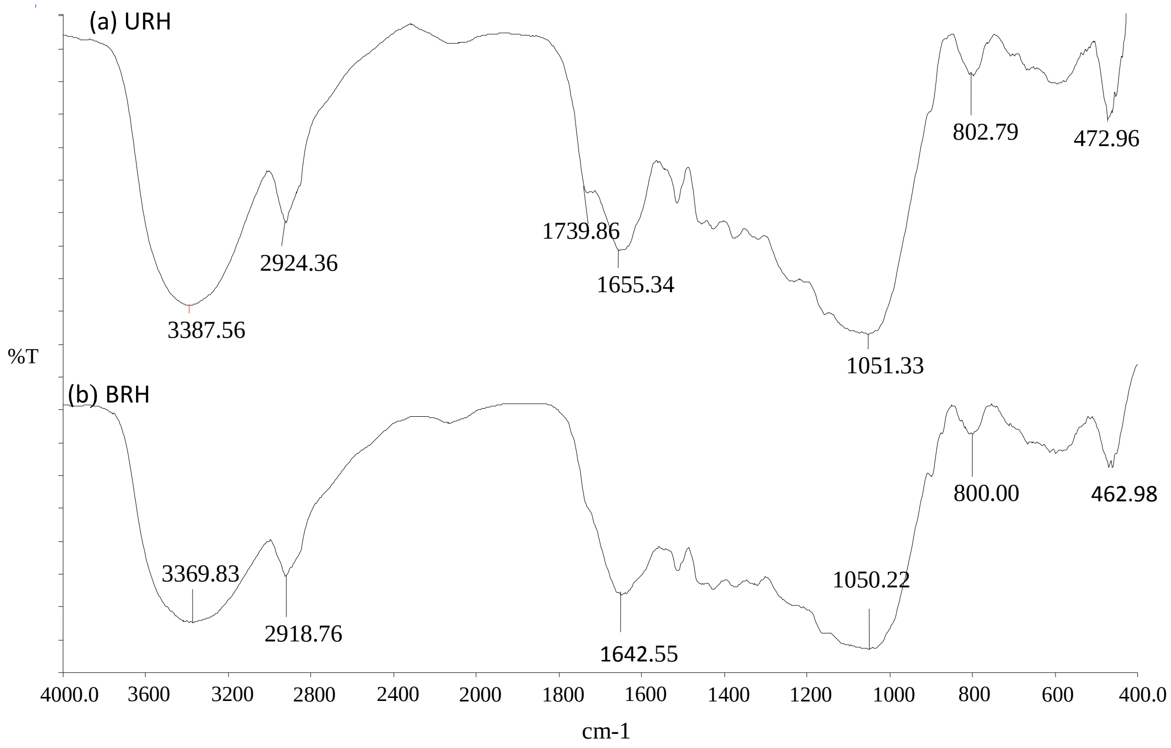

Figure 1 : Infrared spectra of URH and BRH

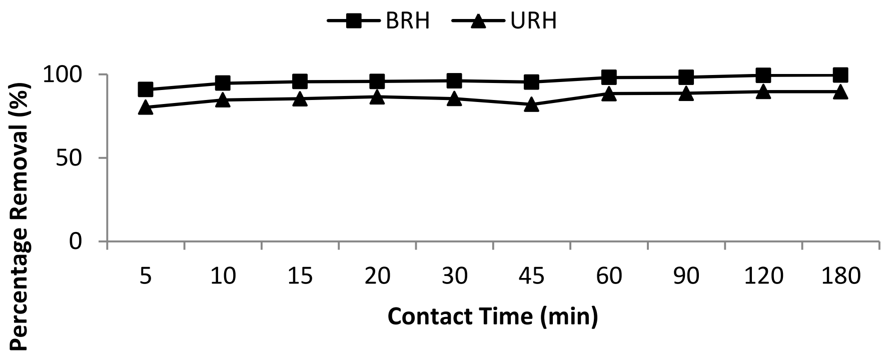

Figure 2 : Effect of contact time on removal of methylene blue using URH and BRH

The effect of concentration on the removal of MB by rice husk is shown in Figure 3. It is observed that when the concentration of MB was increase from 50 to 500 mgL^{-1}, the percentage of dye removal decreases. At higher dye concentrations, lower dye removal was observed which is due to the saturation of sorption sites. As the concentration increased, more MB will compete for available surface site which result in more MB left unadsorbed [14]. BRH did not show significant decrease on the percentage removal of MB when the concentration was increased which shows that BRH gives better removal of MB compared to URH. This maybe due to the removal of hemicellulose during the base treatment which cause the fiber to become less dense and less rigid which enable easier penetration of larger quantity of molecules into the structure [10]

Figure 4 shows the comparison on the removal of MB by URH and BRH with that by activated carbon. As expected, AC gives higher removal of MB because of its large surface area and pore volume which gives it a unique adsorption capacity[15]. The results also indicate that, at concentration of 50 -250 mgL^{-1}, BRH are capable of removing up to 97% of MB which is almost comparable with the removal by activated carbon.

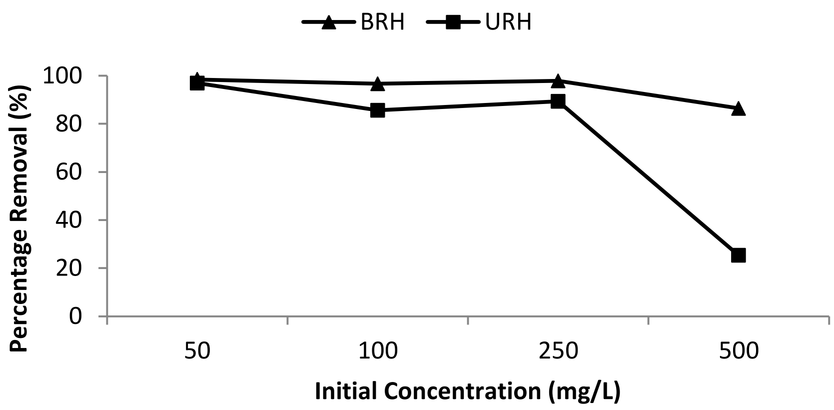

Figure 3 : Effect of concentration on removal of MB by URH and BRH

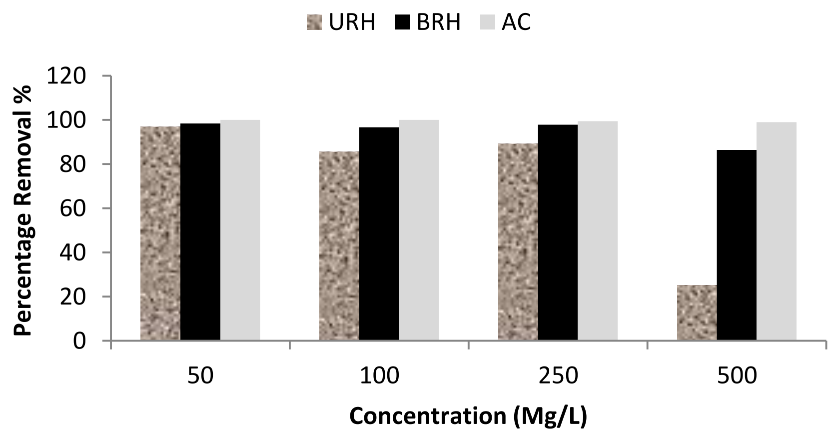

Figure 4 : Comparison of the percentage removal of MB by URH, BRH and AC

Effect of Adsorbent Dosage

Figure 5 illustrates the effect of adsorbent dosage towards the removal of MB by URH and BRH. It can be observed that the increase of URH dose resulting in increase of MB removal. This is due to the presence of a greater surface for adsorption and thus more available sites for MB to be adsorbed [16] . There is no significant changes on the percentage removal of MB by BRH as the adsorbent dosage increase from 0.25 g to 1.00 g. This shows that even at low adsorbent dosage, BRH can effectively remove MB up to 98.80%.

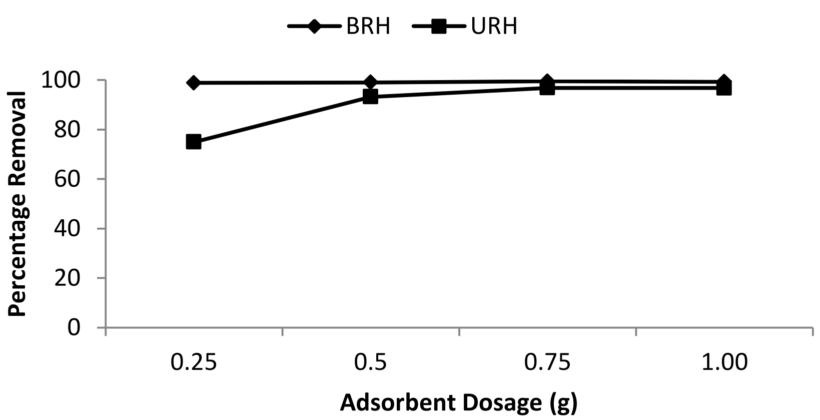

Figure 5 : Effect of adsorbent dosage on removal of MB by URH and BRH

Adsorption Isotherm

Adsorption isotherm indicates the partition of adsorbate between solution and adsorbent when the adsorption process reaches an equilibrium state. Adsorption isotherm is basically important to describe how solutes interact with adsorbent and is critical in optimizing the use of adsorbents [17]. Two isotherm models; the Langmuir and Freundlich were carried out for adsorption isotherm study. The applicability of the isotherm models to the adsorption study done was compared by judging the correlation coefficients, R^2 values. Expressions of the model can be written as follows:

Langmuir : $\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{C_e}{Q_o}$ (1)

Freundlich : $\log q_e = \log K_f + \frac{1}{n} \log C_e$ (2)

The results are well in lined with the Langmuir models (Figure 5, Figure 6 and Table 1). This indicate that adsorption of methylene blue onto URH and BRH demonstrated the formation of monolayer coverage of dye molecules at the outer surface of RH. The Langmuir constant b and Q_O were calculated from this isotherm and their values are given in Table 1. The value of R_L is found to be 0.0297 and 0.0184 for URH and BRH respectively. Thus suggesting the isotherm to be favorable at the concentration studied.

For Freundlich isotherm,K_F and n are Freundlich constants with n giving an indication of how favorable the adsorption process. Values of n >1 represent favorable adsorption condition [18]. The values of K_f and n are calculated from the intercept and slope of the plot of ln qe versus ln Ce and were represented in Table 1.

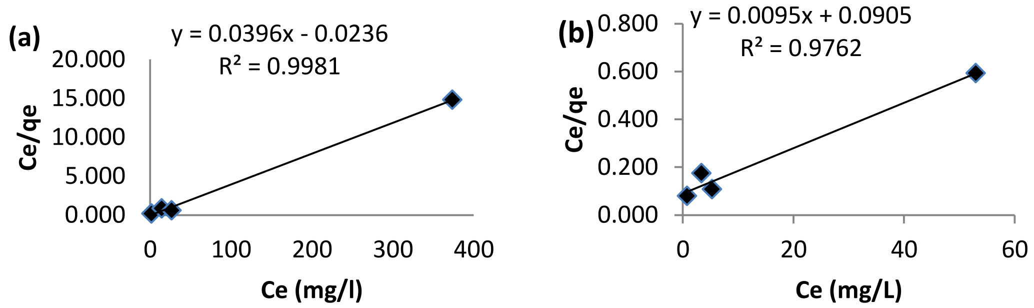

Figure 6 : Langmuir isotherm for the removal of methylene blue by adsorption of (a) URH (b) BRH

Table 1 : Langmuir and Freundlich Isotherm Constant and Correlation Coefficient for Adsorption of MB

Isotherms	**Constants**			
<u>Langmuir</u>	q_m	b	R_L	R^2
URH	25.64	0.06	0.01	0.998
BRH	111.11	0.11	0.17	0.976
<u>Freundlich</u>	K_f		n	R^2
URH	**11.82**		5.45	0.415
BRH	**12.65**		1.89	0.893

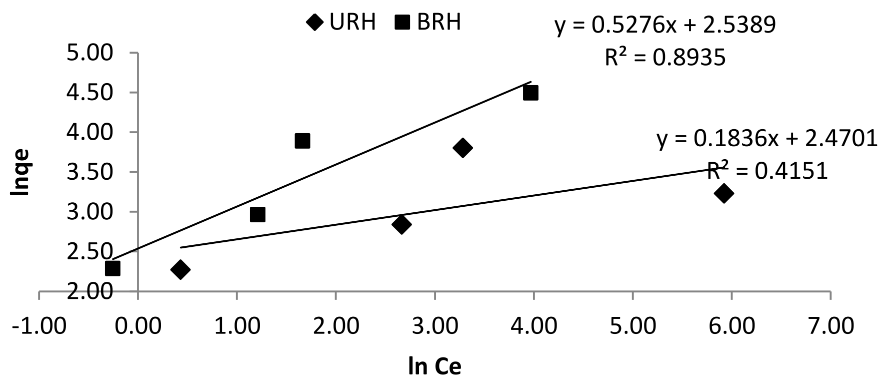

Figure 7 : Freundlich isotherm for the removal of methylene blue by adsorption of (a) URH (b) BRH

Adsorption Kinetics

Pseudo first order and pseudo second order kinetic models were applied to test the experimental data for the adsorption process as illustrated in Figure 8 and Figure 9. The equations are generally represented as follows:

Pseudo first order :$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$ (4)

Pseudo second order: $\frac{t}{q_t} = \frac{1}{k_2 q^2_e} + \frac{t}{q_e}$ (5)

The calculated constant of both equations with the R^2 values are presented in Table 2. The linear plot for first order equation is of low R^2 values as shown in Table 2. Moreover, the values of calculated adsorption capacities (qe cal) shows a large difference from experimental data suggesting that the adsorption reaction is not of pseudo-first order. High R^2 values are obtained for the pseudo-second order equation as shown in Figure 9 and Table 2. The pseudo-second order kinetic model better represented the adsorption kinetics and the calculated values of adsorption capacities also agree well with experimental values. This suggest that the adsorption of MB on RH follows second-order kinetic.

The pseudo-sesond order is based on the assumption that sorption follows a second order mechanism, with chemisorption as the rate limiting step. So the rate of occupation of adsorption site is proportional to the square of the number of unoccupied sites [19].

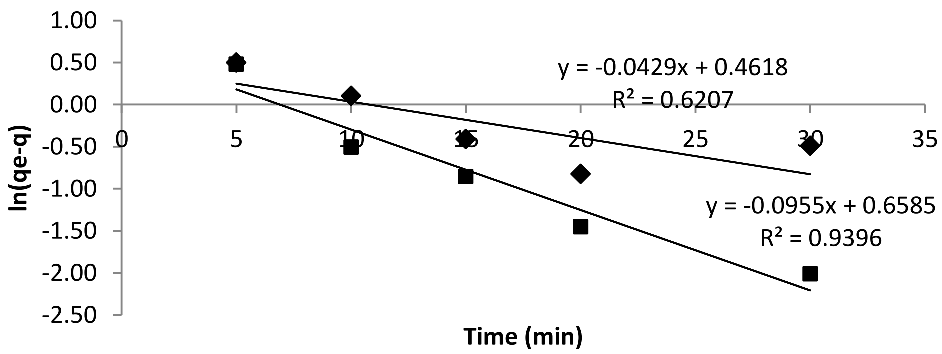

Figure 8 : Pseudo-first order kinetic for the adsorption MB onto URH and BRH

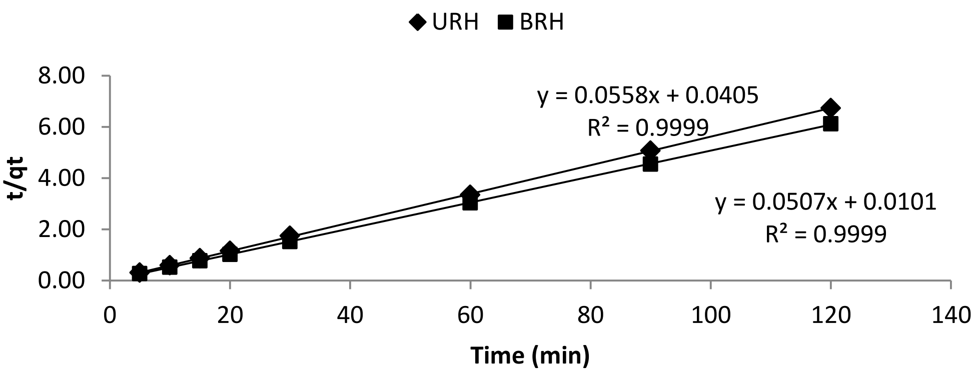

Figure 9 : Pseudo-second order kinetic for the adsorption MB onto URH and BRH

Table 2 : Kinetic Studies on MB adsorption

Sample	**First-order-kinetic model**			
	q_e (exp) (mg/g)	k_1 (min^{-1})	q_e (cal) (mg/g)	R^2
Unmodified RH	17.76	0.07	1.58	0.620
Base modified RH	19.80	0.38	1.93	0.934
	Second-order-kinetic model			
	k_2 (g/mg min)		q_e (cal) (mg/g)	R^2
Unmodified RH	0.0749		18.18	0.999
Base modified RH	0.0714		20.00	0.999

Conclusion

This study reveals that both URH and BRH has the capabilities of removing MB. BRH shows better MB removal compared to the URH with more than 95% percentage removal up to 500 mg L^{-1} MB concentration. Base treated rice husk can be considered as alternative dye adsorbent to replace the costly activated carbon. The equilibrium data were found to be fitted well with langmuir isotherm conforming to the monolayer adsorption capacity of MB onto rice husk. The adsorption process also conformed to the pseudo second order kinetic model.

References

1. Gong, R., Ding, Y., Li, M., Yang, C., Liu, H., & Sun, Y. (2005) Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. *Dyes and Pigments*, **64(3)**, 187-192
2. Gong, R., Jin, Y., Chen, J., Hu, Y., & Sun, J. (2007) Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw. *Dyes and Pigments*, **73(3)**, 332-337
3. Lata, H., Garg, V. K., & Gupta, R. K. (2007). Removal of a basic dye from aqueous solution by adsorption using Parthenium hysterophorus: An agricultural waste. *Dyes and Pigments*, **74(3)**, 653-658.
4. Park, D., Yun, Y., Jo, J. H., Park, J. M. (2006) Biosorption process for treatment of electroplating wastewater containing Cr(VI): Laboratory-Scale Feasibility Test. *Industrial Engineering Chemical Research*, **45**, 5059–5065.
5. Ertas, M., Acemioglu, B., Alma, M. H., Usta, M. (2010) Removal of methylene blue from aqueous solution using cotton stalk, cotton waste and cotton dust. *Journal of Hazardous Material*, **183**, 421-427.
6. Tamez, M. U., Akharatul Islam, M., Shaheen, M., Rukanuzzaman, M. (2009) Adsorptive removal of methylene blue by tea

waste. *Journal of Hazardous Material* , **164**, 53-60.

7. Sakalar, N., Hilal, B. M., Acemioglu, B., Alma, M. H. (2010) Adsorption of basic red 2 onto peanut shell : batch and column studies. *Asian Journal of Chemistry*, **22**, 5649-5662.
8. Hameed, B. H. (2009) Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low cost sorbent. *Journal of hazardous Material*, **162**, 344-350.
9. Vadivelan V., Kumar K. V. (2005) Equilibrium, kinetics, mechanism and process design for the sorption of methylene blue onto rice husk. *Journal of Colloid Interface Science*, **286**, 90-100
10. Misson, M., Haron, R., Kamoroddin, M. F. A., Amin, S. N. A. (2009) Pretreatment of empty palm fruit bunch for production of chemicals via catalytic pyrolysis. *Bioresource Technology*, **100**, 2867–2873.
11. Garg, U., Kaur, M. P., Jawa, G. K., Dhiraj, S., Garg, V. K. (2008) Removal of Cd(II) from aqueous solutions by adsorption on agricultural waste biomass. *Journal of Hazardous Material*, **154**, 1149–1157.
12. Kostic, M. M., Pejic, B. M., Asanovic, K. A., Aleksic, V. M., Skundric, P. D. (2010) Effect of hemicelluloses and lignin on the sorption and electric properties of hemp fibers. *Industrial Crops and Products*, **32(2)**, 169-174.
13. Malekbala, M. R., Hosseini, S., Kazemi Yazdi, S., Masoudi Soltani, S. (2012) The study of the potential capability of sugar beet pulp on the removal efficiency of two cationic dyes. *Chemical Engineering Research and Design,* **90**, 704-712.
14. Deniz, F., Karaman, S. (2011) Removal of an azo-metal complex textile dye from colored aqueous solutions using an agro-residue. *Microchemical Journal*, **99**, 296-302.
15. Hasnain Isa, M., Lang, S, M., Asaari, F. A. H., Aziz, H. A., Azam Ramli, N., Dhas, J. P. A (2007) Low cost removal of disperse dyes from aqueous solution using palm ash. *Dyes and Pigments*, **74(2)**, 446-543.
16. Moussavi, G., Khosravi, R. (2011) The removal of cationic dyes from aqueous solutions by adsorption onto pistachio hull waste. *Chemical Engineering Research and Design*, **89**, 2182-2189.
17. Tan I. A. W., Hameed B. H., Ahmad A. L. (2007) Equilibrium and kinetic studies on basic dye adsorption by oil palm fiber activated carbon, *Chemical Engineering Journal*, **127**, 111-119.
18. Hameed B. H., Krishni R. R., Sata S. A. (2009) A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solutions, *Journal of Hazardous Material*, **162**, 305-311.
19. Ho Y. S., Mckay G. (1998) Sorption of dye from aqueous solution by peat, *Chem Eng J* **70**, pp 115-124.
20. Lata, H., Garg, V. K., & Gupta, R. K. (2008) Adsorptive removal of basic dye by chemically activated Parthenium biomass: equilibrium and kinetic modeling. *Desalination*, **219(1–3)**, 250-261.
21. Antunes W. M., Luna A. S., Henriques C. A., Costa A. C. A. (2003) An evaluation of copper biosorption by a brown seawed under optimized condition, *Electronic Journal of Biotechnology*, **6**, 174-184.