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Adsorption of methylene blue from aqueous solution using acetic acid modified rice bran

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Abstract : The capability of acetic acid modified rice bran (as a low cost adsorbent) for removal of methylene blue, a cationic dye, from aqueous solutions was studied. Batch experiments were conducted to study the effects of various experimental parameters such as initial solution pH, contact time, initial dye concentration and adsorbent dosage on dye adsorption and the optimal condition was selected. The kinetic data obtained from different batch experiments were analyzed using pseudo-second order equations. The applicability of the Langmuir and Freundlich models for the data was tested. Both the models adequately describe the experimental data of the adsorption of methylene blue. The equilibrium adsorption capacity (q_e) increases with increasing the initial concentration of dye and with increasing pH. The maximum adsorption capacity calculated from the Langmuir model is 25.1 mg/g for MB. The study has shown the effectiveness of modified rice bran in the removal of methylene blue from solutions.

Keywords : Modified rice bran, adsorption, methylene blue.

Introduction

Within the ecosystem, colored wastewater released in textile effluents is a dramatic source of pollution, eutrophication and perturbations in aquatic life. Dye ions, mainly from dyeing industries have become serious threats to human beings and the aquatic ecosystem, due to their toxicity and persistence after being released into the natural water[1,2]. Chemical oxidation, chemical coagulation, biological treatment and photodegradation are some of the most commonly practiced processes for the removal of dyes from industrial wastewater. However, these methods are non-economical and have many disadvantages such as high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. In addition, various dyes used in the industry are particularly difficult to remove by conventional methods as they are stable to light and oxidizing agents and resistant to aerobic digestion [3]. There is thus a need to search for new process that could remove dyes that are commonly used in the industry. Adsorption has been proven to be an excellent way of treating textile waste effluents, offering significant advantages, such as low cost, availability, profitability, ease of operation and efficiency over many conventional methods, especially from an economical and environmental point of view[4,5]. Activated carbon is the most popular and widely used adsorbent, but it is relatively expensive which limits its usage[6]. In addition its regeneration with refractory technique results in a 10–15% loss of the adsorbent and its uptake capacity. Thus, there has been intensive research exploring the potential of alternative low-cost, easily available materials as adsorbents for the dye removal[7,8]. For this purpose in recent years, various biological and industrial by-products have been investigated intensively for their ability to remove dye from aqueous solution as they can be obtained readily and are in great abundance, such as chitosan[9], waste coir pith[10], giant duckweed[11], powdered peanut hull[12], modified clays[13], fly ash[14], beer brewery waste[15], bentonite[16], eggshell[17], rice hull[18] and tree's leaves[19] have the potential of being used as alternative adsorbent for the removal of dyes from aqueous solutions.

Rice bran is an important agricultural waste generated during the milling of rice which is produced in high quantity each year. It contains different vitamins, carbohydrates, potassium, nitrogen and phosphorus compounds. These compounds are environmentally friendly and are nutritious to the plants. Therefore the use of rice bran to eliminate pollution from water and wastewater is interesting.

Adsorption of dyes onto various adsorbents demonstrated that the adsorption capacities are affected by operational parameters such as pH of the solution, contact time, initial dye concentration and adsorbent dosage. In the present study, we report the performance of acetic acid modified rice bran under various conditions as adsorbent for the cationic dye methylene blue (MB), the representative substance of dye compounds and study the optimum adsorption isotherm as well as the rate of adsorption kinetics.

Materials and methods :

Preparation of adsorbent :

The rice bran used in this study is a by-product of a rice factory in Shenyang, China. The rice bran was washed thoroughly with water to ensure the removal of dust and ash. It was then sieved to ~50 mesh size by passing the milled material through standard steel sieves to remove any large non-rice bran solids. Then, about 40 g grinded rice bran was mixed with 350 mL of 3.5 mol/L acetic acid. The mixture was placed in the oven at 60 °C for 24 h and subsequently heated at 100 °C for 90 min. After that, the modified rice bran was washed with distilled water until neutral pH and dried in the oven at 60 °C for 24 h.

Preparation of methylene blue solution :

Methylene blue ($C_{16}H_{18}N_3SCl{\bullet}3H_2O$, a cationic dye) was purchased from Sanaisi Reagent Ltd. (Shanghai, China) and used without further purification. The wavelength of maximum absorption (λ_{max}) of this dye is 664 nm. MB was dried at 110 °C for 2 h before use. All of the MB solution was prepared with distilled water. The stock solution of 1000 mg/L was prepared by dissolving MB in 1000 mL distilled water. The experimental solution was obtained by diluting the stock solution in accurate proportions to different initial concentrations with distilled water.

Batch adsorption experiments :

Batch techniques were used to investigate MB adsorption, which was examined via kinetic studies and adsorption isotherms, together with the effect of some operating parameters. All the batch experiments were carried out in duplicate and the results given are the means with a relative standard deviation of less than 5%. Control experiments without adsorbent were also carried out.

The adsorption capacity of modified rice bran was determined by batch adsorption isotherms at room temperature (20 ± 1 °C) in aqueous solution (initial pH values fixed at 3, 5 and 7). In several glass vials, 100 mL of solution containing various concentrations of MB (50, 100, 150, 200, 250 mg/L) were contacted with 5.0 g/L of modified rice bran. The vials were placed in a water bath at 20 °C and shaken at 150 r/min for approximately 8 h to ensure equilibrium was reached, and the pH was adjusted by adding 0.1 mol/L NaOH or HNO_3 until it remained constant (±0.10). The reaction mixture was then centrifuged at 3000 r/min for 10 min for phase separation. The MB concentrations of the various filtered solutions were analyzed by measuring the absorbance at the maximum wavelength 664 nm using a spectrophotometer (VIS-7220, Beijing, China). The amount of MB adsorbed was calculated from the following equation :

$$q_e = V(C_0 - C_e)/W \qquad (1)$$

where q_e is the amount adsorbed (mg/g); C_0 and C_e are the initial and equilibrium MB concentrations in the solution (mg/L), respectively; V is the solution volume (L); and W is the mass of modified rice bran (g).

The adsorption kinetic study was performed for MB in solution at pH 7.0 and room temperature (20 ± 1 °C). Several glass vials were used to hold 100 mL MB solution of known initial concentration (50, 100 and 200 mg/L) and 5.0 g/L of adsorbent at pH 7.0, and shaken at 150 r/min for a duration ranging from 0 to 360 min. At certain period of time, each vial was removed from the shaker, and the solution was then centrifuged at 3000 r/min for 10 min to measure the MB concentration.

To determine the effects of different parameters on MB adsorption, experiments were performed at various initial pH values ranging between 3 and 10. Initial concentration of 100 mg/L MB and 5.0 g/L of adsorbent were employed. The suspensions were shaken at 150 r/min for 1 h. Then the optimum initial pH 7.0 was identified. The effects of initial dye concentration, contact time, adsorbent dosage were also conducted.

Results and discussion

Effect of acetic acid modification of the rice bran on adsorption of methylene blue :

Fig. 1 shows the comparative removal rate of MB by unmodified and modified rice bran. It could be seen from

Fig. 1 that the adsorption of MB was enhanced when modified rice bran was used as the adsorbent. The adsorption capacity of modified rice bran for MB is about 1.5 times higher than that of unmodified rice bran. The presence of carboxyl groups in modified rice bran is believed to be primarily responsible for the adsorption of MB. Previous investigations have also postulated that the adsorption of positively charged species is due to the presence of binding sites such as carboxyl and hydroxyl groups on the surface[20,21].

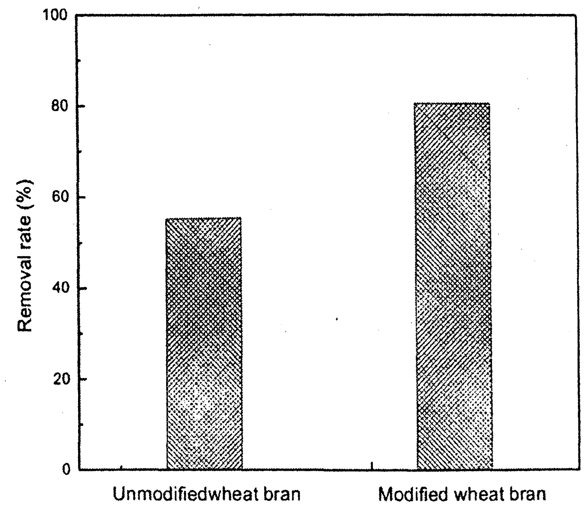

Fig. 1. Effect of acetic acid modification of the rice bran on the adsorption of MB (Experiment conditions employed : initial MB concentration 100 mg/L, adsorbent dosage 5.0 g/L, solution pH 7.0, adsorption time 1 h, agitation speed 150 r/min).

Effect of initial MB concentration on adsorption process :

Initial concentration is one of the effective factors on adsorption efficiency. Initial concentrations of MB solutions were changed (50, 75, 100, 150 and 200 mg/L) in order to determine proper MB adsorption keeping constant temperature (20 °C), solution pH (7.0), contact time (1 h) and adsorbent dosage (5.0 g/L). The experimental results were shown in Fig. 2. It can be seen that the MB removal rate decreased with the increase in initial MB concentration, the percentage adsorption of MB on modified rice bran decreased from 96.3 to 43.2% as the initial MB concentration was increased from 50 to 200 mg/L. At lower MB concentrations, the ratio of the available adsorption sites of adsorbent to the initial number of molecules of MB is large and subsequently the fractional

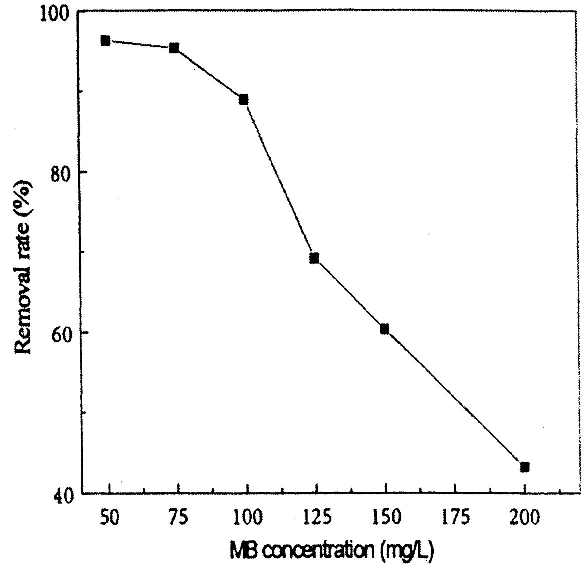

Fig. 2. Effect of initial MB concentration on the adsorption of MB (Experiment conditions employed : adsorbent dosage 5.0 g/L, solution pH 7.0, adsorption time 1 h, agitation speed 150 r/min).

adsorption becomes independent of initial concentration. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of MB which depends upon the initial concentration, decreases.

Effect of adsorbent dosage on adsorption process :

The effect of adsorbent dosage on adsorption of MB was shown in Fig. 3. The increase in adsorbent dosage from 1.0 to 7.0 g/L resulted in an increase from 25.2 to 91.3% in adsorption of MB. This is because of the availability of more and more adsorption sites (carboxyl groups) for MB adsorption during the adsorption reaction. A further increase in adsorbent dosage (>5.0 g/L) did not cause significant improvement in MB adsorption. This may be due to the adsorption of almost all MB to the adsorbent and the establishment of equilibrium between the MB molecules adsorbed to the adsorbent and those remaining unadsorbed in the solution. Thus 5.0 g/L of modified rice bran was chosen for next study.

Effect of initial solution pH on adsorption process :

The effect of initial solution pH on the adsorption process was investigated. Experiments of MB adsorption on modified rice bran were performed using various initial pH in the range of 3 to 10. The results were shown in Fig. 4.

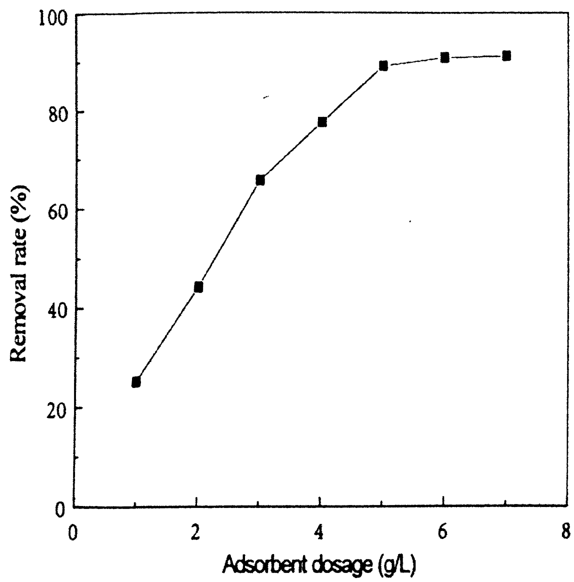

Fig. 3. Effect of adsorbent dosage on the adsorption of MB (Experiment conditions employed : initial MB concentration 100 mg/L, solution pH 7.0, adsorption time 1 h, agitation speed 150 r/min).

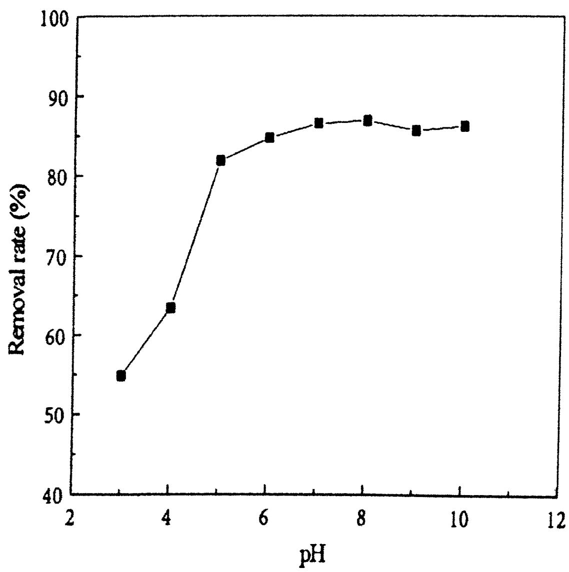

Fig. 4. Effect of pH on the adsorption of MB (Experiment conditions employed : initial MB concentration 100 mg/L, adsorbent dosage 5.0 g/L, adsorption time 1 h, agitation speed 150 r/min).

It is evident that the percentage of MB removal is highly depended on solution pH. The removal of MB increased with increasing pH value, which could be due to the surface charge of the adsorbent. In acidic media (low pH), the removal of MB was suppressed by H^+ ions that surrounded the surface of the adsorbent hindering the approach of MB to the carboxylate groups present on the surface of modified rice bran. The protonation of carboxylate groups would also reduce the MB adsorption. With increasing pH, the active site on the adsorbent is negatively charged and can adsorb MB as the result of electrostatic attraction between positively charged dye cations and negatively charged adsorption sites and an increasing in dye adsorption. The adsorption of MB would also become favorable due to the deprotonation of carboxyl groups, resulting in more adsorption sites available for binding with MB[10]. A further increase in solution pH (>7.0) did not cause significant improvement in MB adsorption, therefore, the pH 7.0 was chosen for the following experiments.

Effect of contact time on adsorption process :

Contact time is one of the effective factors in batch adsorption process. The effect of contact time on MB adsorption efficiency was shown in Fig. 5. As it was shown, the adsorption was very fast and equilibrium between the aqueous solution and modified rice bran was established within about 1 h. There was no significant change in MB removal rates after 1 h up to 3 h. Based on these results, 1 h was taken as the equilibrium time in adsorption experiments. The removal of MB from aqueous solutions by adsorption on modified rice bran in-

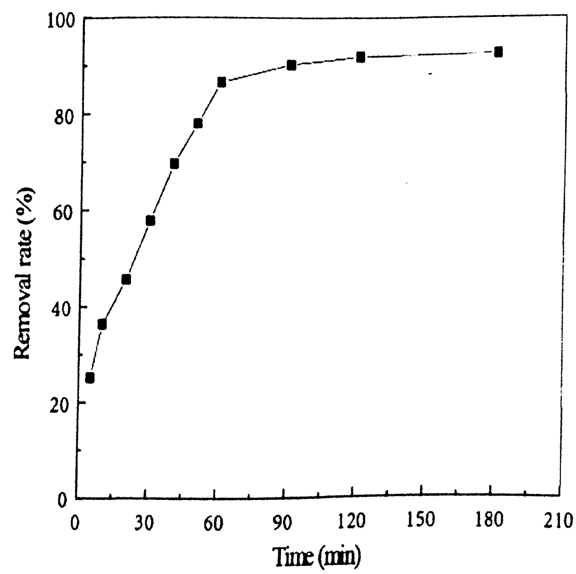

Fig. 5. Effect of contact time on the adsorption of MB (Experiment conditions employed: initial MB concentration 100 mg/L, adsorbent dosage 5.0 g/L, solution pH 7.0, agitation speed 150 r/min).

creases with contact time, till the equilibrium is attained. Similar results have been reported in literature for removal of dyes[22,23].

Adsorption isotherms :

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. Langmuir and Freundlich isotherm equations are the most widely used models to describe the experimental data of adsorption isotherms. Methylene blue adsorption isotherm obtained for modified rice bran was shown in Fig. 6. These isotherms represent the adsorption behavior of MB on the adsorbent as a function of increasing aqueous MB concentration for a contact time of 8 h at pH 7.0. The isotherm showed that the adsorption capacity increases with increasing equilibrium concentration of MB.

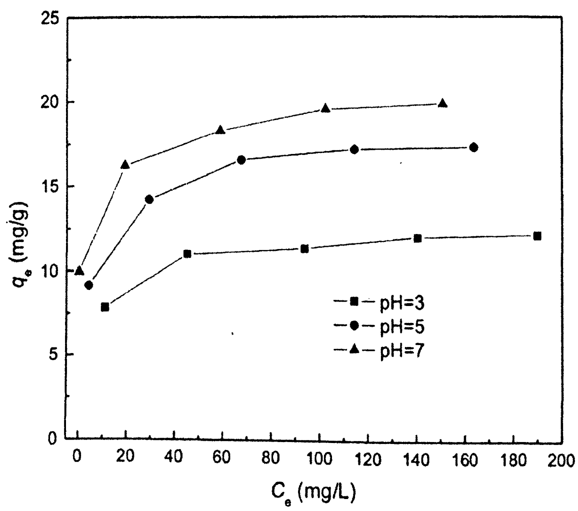

Fig. 6. Adsorption isotherms for MB by modified rice bran (Experimental conditions employed : adsorbent dosage = 5.0 g/L, adsorption time 8 h, agitation speed 150 r/min).

The results of MB adsorption on modified rice bran (Fig. 6) were analyzed by using the Langmuir model to evaluate parameters associated to the adsorption behavior. The linear form of Langmuir equation at a given temperature is represented by :

$$q_e = q_m \cdot b \cdot c_e/(1 + b \cdot c_e) \quad (2)$$

where c_e is the aqueous phase MB equilibrium concentration (mg/L), q_e is the amount of MB sorbet onto 1 g of the considered adsorbent (mg/g), b is the adsorption constant (L/mg) related to the energy of adsorption and represents the affinity between the adsorbent and adsorbate, q_m is the maximum adsorption capacity (mg/g).

Eq. (2) can be rearranged to obtain :

$$c_e/q_e = 1/(b \cdot q_m) + c_e/q_m \quad (3)$$

Experimental isotherm data acquired at different initial pH were correlated with the linear form of Langmuir model. The isotherm parameters related to the model were listed in Table 1. It could be seen that both q_m and b increased with increasing initial pH from 3.0 to 7.0. The maxima adsorption capacities (q_m) were 16.483, 21.864 and 25.092 mg/g at pH values 3.0, 5.0 and 7.0, respectively. High values of b were reflected in the steep initial slope of an adsorption isotherm, indicating desirable high affinity. Therefore, modified rice bran performed well in MB adsorption at initial pH 7.0 compared to other initial pH values examined.

The Freundlich isotherm model is also used to analyze the results of MB adsorption on modified rice bran (Fig. 6). The Freundlich model can be expressed by the following equation :

$$q_e = k_f \cdot c_e^{1/n} \quad (4)$$

where k_f and n are constants related to the adsorption capacity and affinity, respectively. The equation is conveniently used in the linear form by taking the logarithm of both sides as :

$$\log q_e = \log k_f + (1/n) \log c_e \quad (5)$$

Experimental isotherm data acquired at different pH were fit with the linear form of Freundlich model and the isotherm parameters related to the model were listed in Table 1. The data showed that the k_f constant was increased with the increase of initial pH values, at initial pH 7.0, k_f reached its corresponding maximum value, and $1/n$ value at initial pH 7.0 was smaller than that at other initial pH values. These implied that the affinity

Table 1. The parameters of Langmuir and Freudlich equation

Initial pH	Langmuir equation q_m (mg g^{-1})	b (L mg^{-1})	R^2	Freundlich equation $1/n$	K_f	R^2
3.0	16.483	0.1809	0.9997	0.1808	5.6863	0.9602
5.0	21.864	0.3172	0.9998	0.1506	7.3161	0.9806
7.0	25.092	0.6634	0.9994	0.1098	11.6268	0.9993

between the adsorbent and MB molecules was also higher than other initial pH values. The correlation coefficients (R^2) given in Table 1 also showed that Langmuir model and Freundlich model adequately describe the experimental isotherm data of the adsorption of methylene blue.

Kinetic study :

In order to define the adsorption kinetics of MB on the modified rice bran, the kinetics parameters for the adsorption process were studied for contact times ranging from 5 to 360 min by monitoring the removal percentage of MB at various initial MB concentrations (50, 100 and 200 mg/L), the results were shown in Fig. 7. It could be seen that the adsorption of MB increased rapidly with time as well as with the increase of the initial MB concentrations. However, the time to reach the adsorption equilibrium took longer with an increase in the concentration. The adsorption of MB reached to equilibrium state after 30 min reaction at initial MB concentration of 50 mg/L. For the initial MB concentration of 200 mg/L, the adsorption time reached to equilibrium state was more than 120 min.

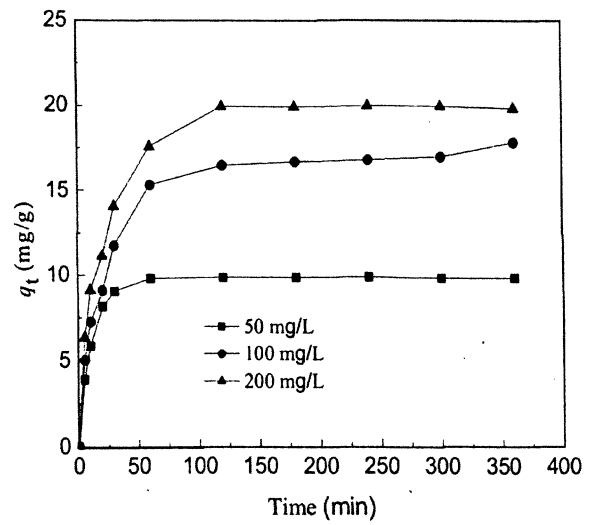

Fig. 7. Adsorption kinetics of MB by modified rice bran (Experimental conditions employed : pH 7.0, agitation speed 150 r/min, adsorbent dosage 5.0 g/L).

In order to investigate the mechanism of MB adsorption on the modified rice bran, the pseudo-second order rate equation model was applied to the kinetic experimental data. The pseudo-second order kinetic equation could be derived as[24] :

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (6)$$

Separating the variables in eq. (6) gave :

$$-d(q_e - q_t)/(q_e - q_t)^2 = k_2 \cdot dt \quad (7)$$

Integrating both sides for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ gave the integrated rate law for a pseudo-second order reaction,

$$1/(q_e - q_t) = 1/q_e + k_2 \cdot t \quad (8)$$

Eq. (8) could be rearranged to obtain :

$$t/q_t = 1/(k_2 \cdot q_e^2) + t/q_e \quad (9)$$

The kinetic constant, k_2, could be determined by plotting of t/q_t against t.

The kinetic experimental data of MB on the modified rice bran were simulated by pseudo-second order kinetic eq. (9). The results were listed in Table 2. Remarkably, the kinetic data could be described well by the pseudo-second order kinetic equation which was based on the assumption that the rate limiting step may be chemical sorption or chemisorptions involving valency forces through sharing or exchange of electron between adsorbent and adsorbate[25]. It could also be seen that the values of the pseudo-second order rate constant decreased with increasing the initial MB concentrations. This result was accordant with previous report[13]. However, Hu *et al.* showed that MB adsorbtion on other biosorbents follows Lagergreen's pseudo-first order rate equation[26].

Table 2. Kinetic parameters for MB adsorption by modified rice bran

C_0 (mg L^{-1})	q_e (mg g^{-1})	k_2 (L mg^{-1} min^{-1})	R^2
50	10.084	2.146×10^{-2}	0.9998
100	18.272	3.473×10^{-3}	0.9994
200	20.816	2.024×10^{-3}	0.9996

Conclusions :

The modification of rice bran by acetic acid significantly improved its adsorption capacity, and made this material a suitable adsorbent to remove MB, a basic dye from solutions. The adsorption capacity of modified rice bran for MB is about 1.5 times higher than that of unmodified rice bran. The amount of MB adsorbed was found to vary with initial solution pH, adsorbent dosage, contact time and initial MB concentration. The overall adsorption rate was illustrated by the pseudo-second order kinetic model. The equilibrium data obtained from this study was well presented by Langmuir and Freundlich models. As rice bran is readily available in great abundance in China, it can be considered as an attractive alternative to the more expensive technologies used in wastewater treatment containing dyes.

References

1. M. S. Tsuboy, J. P. F. Angeli, M. S. Mantovani, S. Knasmueller, G. A. Umbuzeiro and L. R. Ribeiro, *Toxicology in Vitro*, 2007, **21**, 1650.
2. S. Vinitnantharat, W. Chartthe and A. Pinisakul, *Water Sci. Technol.*, 2008, **58**, 1193.
3. K. S. Low, C. K. Lee and B. F. Tan, *Appl. Biochem. Biotech.*, 2000, **87**, 233.
4. S. J. Allen, Q. Gan, R. Matthews and P. A. Johnson, *J. Colloid Interface Sci.*, 2005, **286**, 101.
5. K. Ravikumar, B. Deebika and K. Balu, *J. Hazard. Mater.*, 2005, **122**, 75.
6. S. Hashemian, *Int. J. Phys. Sci.*, 2011, **6**, 6257.
7. R. Gong, Y. Jin, J. Chen, Y. Hu and J. Sun, *Dyes Pigments*, 2007, **73**, 332.
8. C. Namasivayam, D. Prabha and M. Kumutha, *Bioresour. Technol.*, 1998, **64**, 77.
9. T. K. Saha, N. C. Bhoumik, S. Karmaker, M. G. Ahmed, H. Ichikawa and Y. Fukumori, *J. Water Resource Protect.*, 2010, **2**, 898.
10. C. Namasivayam and D. Kavitha, *J. Dyes Pigments*, 2002, **54**, 47.
11. P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue and E. S. Upatham, *J. Environ. Pollut.*, 2003, **125**, 385.
12. R. Gong, Y. Ding, M. Li and C. Yang, *Dyes Pigments*, 2005, **64**, 187.
13. Z. Bouberka, S. Kacha, M. Kameche, S. Elmaleh and Z. Derriche, *J. Hazard. Mater. (B)*, 2005, **119**, 117.
14. S. Wang, Y. Boyjoo, A. Choueib and Z. H. Zhu, *Water Res.*, 2005, **39**, 129.
15. W. T. Tsai, H. C. Hsu, T. Y. Su, K. Y. Lin and C. M. Lin, *J. Hazard. Mater.*, 2007, **154**, 73.
16. S. Hashemian, *Main Group Chem.*, 2007, **6**, 97.
17. M. H. Ehrampoush, G. Ghanizadeh and M. T. Ghaneian, 2011, **8**, 101.
18. S. T. Ong, P. S. Keng, A. W. Chong, S. L. Lee and Y. T. Hung, *J. Environ. Sci.*, 2010, **6**, 244.
19. R. P. Han, W. H. Zou, W. H. Yu, S. J. Cheng, Y. F. Wang and J. Shi, *J. Hazard. Mater.*, 2007, **141**, 156.
20. P. L. Tang, C. K. Lee, K. S. Low and Z. Zainal, *Environ. Technol.*, 2003, **24**, 1243.
21. K. K. Wong, C. K. Lee, K. S. Low and M. J. Haron, *Process Biochem.*, 2003, **39**, 437.
22. N. Kannan and M. M. Sundaram, *Dyes Pigments*, 2001, **51**, 25.
23. M. Sarioglu and U. A. Atay, *Global NEST Journal*, 2006, **8**, 113.
24. Y. S. Ho and G. McKay, *Adsorpt. Sci. Technol.*, 1998, **16**, 243.
25. Y. S. Ho and G. McKay, *Water Res.*, 2000, **34**, 735.
26. C. W. Hu, J. L. Li, Y. Zhou, M. Li, F. Xue and H. M. Li, *J. Health Sci.*, 2009, **55**, 619.