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Kinetic and thermodynamic of adsorption of methylene blue (MB) by CuFe_2O_4 /rice bran composite

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The adsorption of methylene blue (MB) dye onto activated rice bran and CuFe_2O_4 /rice bran (CRB) composite was investigated. Activated rice bran was prepared by treating with NaCl. The CuFe_2O_4 /rice bran was prepared by chemical co-precipitation method. The adsorbents were characterized by XRD and SEM analyses. The adsorption of MB was strongly dependent on the pH (pH 12). The process was very fast initially and maximum adsorption was attained within 60 min of contact time. The specific surface area (BET method) of rice bran, activated rice bran and CuFe_2O_4 /rice bran were 0.44, 35 and 68 $\text{m}^2 \text{g}^{-1}$, respectively. The adsorption isothermal data could be well interpreted by the Langmuir isotherm model. The adsorption process follows pseudo second-order kinetics and rate constant 0.112 for ARB and 0.17 for CRB ($\text{g mg}^{-1} \text{min}^{-1}$). Thermodynamic parameters were evaluated.

Key words: Adsorption, composite, methylene blue, kinetic, rice bran.

INTRODUCTION

One of the major problems concerning textile wastewaters is colored effluent. This wastewater contains a variety of organic compounds and toxic substances, which are harmful to fish and other aquatic organisms (Ramakrishna and Viraraghavan, 1997). Methylene blue (MB) dye causes eye burns, and may be responsible for permanent eye injury in humans and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, painful micturition and methemoglobinemia (Reife, 1993; Douglas and Considine, 1984; Kannan and Sundaram, 2001). Therefore, the treatment of effluent containing such dyes is of interest due to its esthetic impact on receiving waters. There are several methods used to treat wastewaters which contain organic pollutants and dyes. These methods include physical and chemical processes, such as chemical coagulation (Sadri Moghaddam et al., 2010), ozonation (Oguz et al., 2005; Tapalad et al., 2008) and adsorption (Hashemian, 2007; Hashemian et al., 2008). Adsorption has been proved 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 (Ravikumar et al., 2005; Allen et al., 2005; Mittal et al., 2005; Arami et al., 2005). Activated carbon is widely used as an adsorbent due to its high surface area and high adsorption capacity; however, it is relatively expensive which limits its usage (Özcan et al., 2004; Gupta et al., 2003; Gupta et al., 2004, 2003). For this reason, many researchers have investigated low-cost, locally available, biodegradable substitutes from natural sources to remove dyes from wastewater (Gupta et al., 2004; Mittal et al., 2005; Srivastava, 1987; Özer et al., 2007; Hameed et al., 2007; Gong et al., 2005).

Many of the starting materials for these replacement adsorbents are themselves agricultural or industrial by-products. Rice bran is considered a food waste. Part of the waste is used as fodder and as fertilizer; however, most of the rice bran is unused. Rice bran is carbonaceous and has the potential to be converted into a carbonaceous adsorbent. This conversion to secondary adsorbents could contribute to reducing the volume of waste, while producing an adsorbent with a lower cost. The use of rice bran as an adsorbent has been tried in the removal of pesticides and dyes (Kesarwani et al., 2000; Adachi et al., 2001; Gong et al., 2006; Gong et al.,

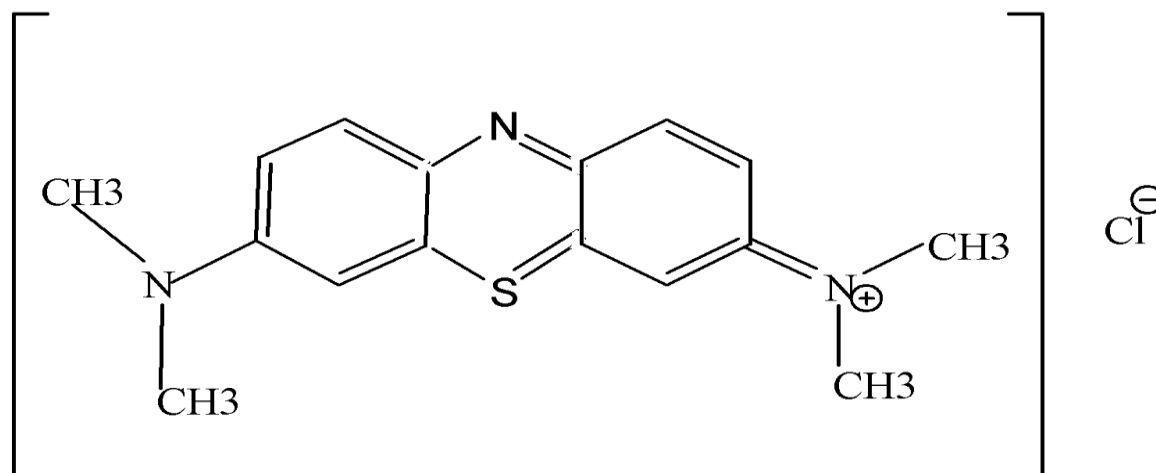


Figure 1. Chemical structure of M.

2007).

Recently, considerable attention has been focused on the application of magnetic composite (Wu et al., 2004; Vadivelan and Vasanth, 2005; Sheha and Metwally, 2007; Wu et al., 2005). It is known that copper ferrite is a magnetic material (Qu et al., 2007). In this study, first CuFe_2O_4 /rice bran magnetic composite was prepared and the adsorption characteristics of CuFe_2O_4 /rice bran to remove methylene blue were demonstrated.

MATERIALS AND METHODS

Rice bran as a raw material was purchased from a local market. It is an agricultural by-product from farms in northern Iran. It was extensively washed with water to remove soil and dust, and then air dried. The rice bran was dried in an oven at 65°C for a period of 3 h. Finally, it was ground and sieved using mesh 35. For preparation of activated rice bran, natural rice bran was mixed with NaCl (1 M) with ratio 1:10 (bran/comp, w/v) and stirred for 24 h. After stirring, the modified rice bran was washed with distilled water to remove residual compounds and then the wet modified rice bran was dried at 50°C until constant weight, and preserved in a desiccator as sorbent for further use (Hashemian et al., 2008).

Analytical grade copper (II) chloride dehydrates and ferric chlorides were obtained from Merck. CuFe_2O_4 was prepared using a co-precipitation method. The rice bran was added to a 400 ml solution containing copper (II) chloride (0.02 mol) and ferric chloride (0.04 mol) at room temperature. The amount of rice bran was adjusted to obtain a CuFe_2O_4 /rice bran mass ratio of 1:10 under vigorous magnetic stirring. The pH was slowly raised by adding NaOH (5 mol L^{-1}) solution to around 10 and stirring was continued for 30 min, then, stopped. The suspension was heated to 95 to 100°C for 2 h.

Methylene blue is a heterocyclic aromatic chemical compound with molecular $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$. MB was purchased from Merck and used without further purification. The stock solution of MB was prepared with distilled water (100 mg l^{-1}). The chemical structure of MB is shown in Figure 1.

The surface area charge (Q) and the pH_{pzc} of the adsorbent in aqueous phase was analyzed with different system pH values by

using the titration method (Ozcan et al., 2005). 0.1 g adsorbent was taken in 50 ml 0.1 M KNO_3 solution and agitated with magnetic stirrer. Then, the pH of solution was measured after an equilibrium time of 10 min. The titration was carried out with 0.1 M NaOH and 0.1 M HCl, respectively.

The crystalline structure of CuFe_2O_4 was determined using the X-ray powder diffraction method with a Philips PW1840 diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation and wavelength 1.54°A . Scanning electron microscopy was carried out using a Hitachi S-3500 Scanning Electron Microscope. The concentration of MB solutions were estimated using UV-Vis spectrophotometer Shimadzu 160 A at 595 nm. An infrared (IR) diffuse reflectance infrared spectrum of activated rice bran (ARB) was determined using a Shimadzu 270 IR spectrophotometer. Adsorption studies were performed in glass vessels with agitation provided by a shaker. The temperature was controlled at 25°C by an air bath. The pH was adjusted by addition of HCl or NaOH of 0.1 M. The suspensions containing 0.1 g of the composite with varying amounts of MB were shaken in an orbital shaker at 130 rpm. The adsorbent and dye solutions were separated by filter paper.

RESULTS AND DISCUSSION

Characterization of the composite

The composite was prepared by the chemical co-precipitation method of CuFe_2O_4 onto the rice bran surface. The magnetism test with a permanent magnet (2300 G) showed that the material was magnetic and completely attracted to the magnet. The X-ray diffraction (XRD) analysis of activated rice bran (ARB), CuFe_2O_4 and CuFe_2O_4 /rice bran (CRB) are shown in Figure 2a to c. In rice bran, SiO_2 is the main phase ($2\theta = 27^\circ$ $d = 3.34^\circ\text{A}$). The XRD of CuFe_2O_4 indicated that the metal oxides mainly occurred in the form of the spinel structure of CuFe_2O_4 ($2\theta = 36^\circ$ $d = 2.527^\circ\text{A}$). The sharp diffraction peaks ($d = 3.69^\circ\text{A}$) observed may be related to the presence of some impurities (Qu et al., 2007). For composite, these peaks appear weaker. In the diffraction peaks of composite, some impurities were observed.

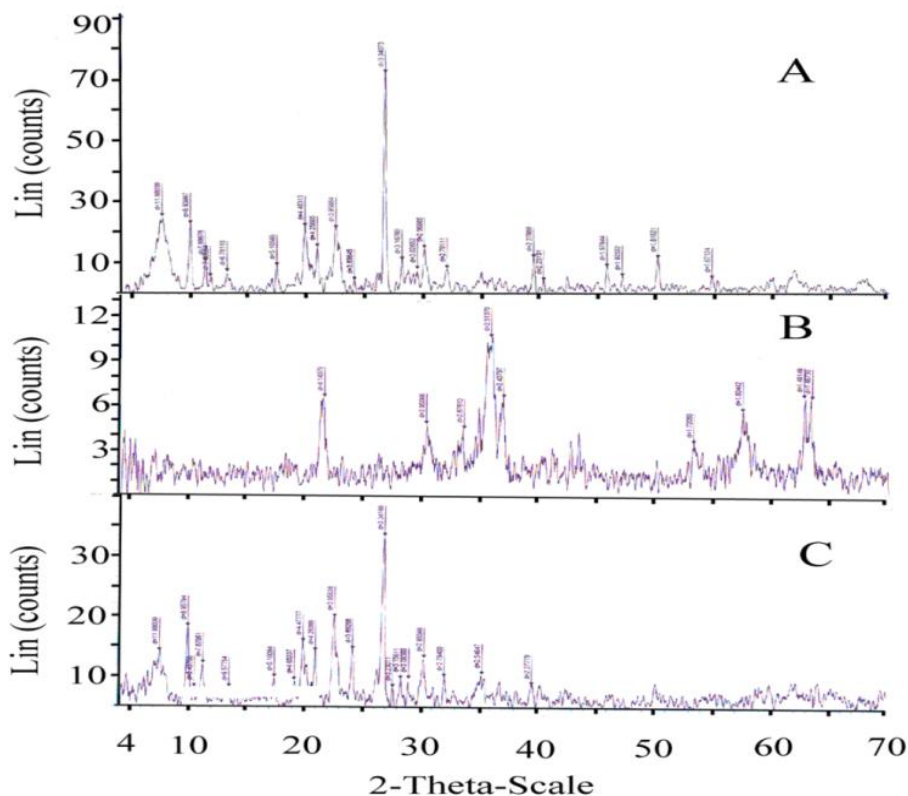


Figure 2. XRD powder diffraction for (a) activated rice bran (ARB), (b) CuFe_2O_4 , (c) CuFe_2O_4 /rice bran (CRB).

The surface structure of rice bran, activated rice bran, CuFe_2O_4 /rice bran composite and CuFe_2O_4 /rice bran adsorbed dye were studied by scanning electronic microscopy (SEM). Figure 3a to d shows the views of rice bran, activated rice bran, CuFe_2O_4 /rice bran composite and CuFe_2O_4 /rice bran adsorbed, respectively. The micrographs clearly reveal the presence of cylindrical structures with different diameters. Although, the surface of sorbents were similar, but CRB was the best when compared with RB and ARB for removing of MB. The CuFe_2O_4 does not change on the cylindrical structures of the surface of RB and may be acting as a catalyst. From Figure 3, agglomeration was not done.

The specific surface area (BET method) of rice bran, activated rice bran particles and CuFe_2O_4 /rice bran composite were 0.44 , 35 and $68 \text{ m}^2 \text{ g}^{-1}$, respectively. Although, this surface area is much smaller than that of activated carbon, an adsorbent commonly used for the removal of volatile organic compounds and metal ions in aqueous samples, which presents a very large surface area ($> 700 \text{ m}^2 \text{ g}^{-1}$) (Qu et al., 2007), but the ability of the potential in dye removal was comparable to activated carbon. This may be due to the presence of CuFe_2O_4 on the surface that can act as a catalyst for removing of dye. Particle diameters in the CuFe_2O_4 /rice bran composite samples were estimated to be in the range of 0.145 to

0.450 nm , with an average particle diameter of 0.340 nm .

The activated rice bran IR-spectrum showed four bands, around 3380 , 2920 , 1635 to 1660 and 1040 cm^{-1} . The broad band around 3380 cm^{-1} was attributed to the surface hydroxyl groups and chemisorbed water. The bands at 2920 and 1635 to 1660 cm^{-1} were assigned to C-H stretches of the methyl and methylene groups and carbonyl stretching frequencies, respectively. The stretching band of the Si-O was observed at 1040 cm^{-1} . Therefore, the activated rice bran IR-spectrum indicated the presence of ionizable functional groups that are able to bind with dye ions (Özcan et al., 2004; Ozcan et al., 2005; Montanher et al., 2005). In the composite, the same peaks also appear. It shows that the presence of CuFe_2O_4 on the surface of rice bran do not change the structure of rice bran.

The surface charge Q of the adsorbent was calculated from the experimental titration data according to the following equation (Kiefer et al., 1997):

$$Q = 1/W (C_A - C_B - [\text{H}^+] - [\text{OH}^-]) \quad (1)$$

where W is the dry weight of adsorbent in aqueous system (g L^{-1}), C_A is the concentration of added acid in aqueous system (mol L^{-1}), C_B is the concentration of added base in aqueous system (mol L^{-1}), $[\text{H}^+]$ is the

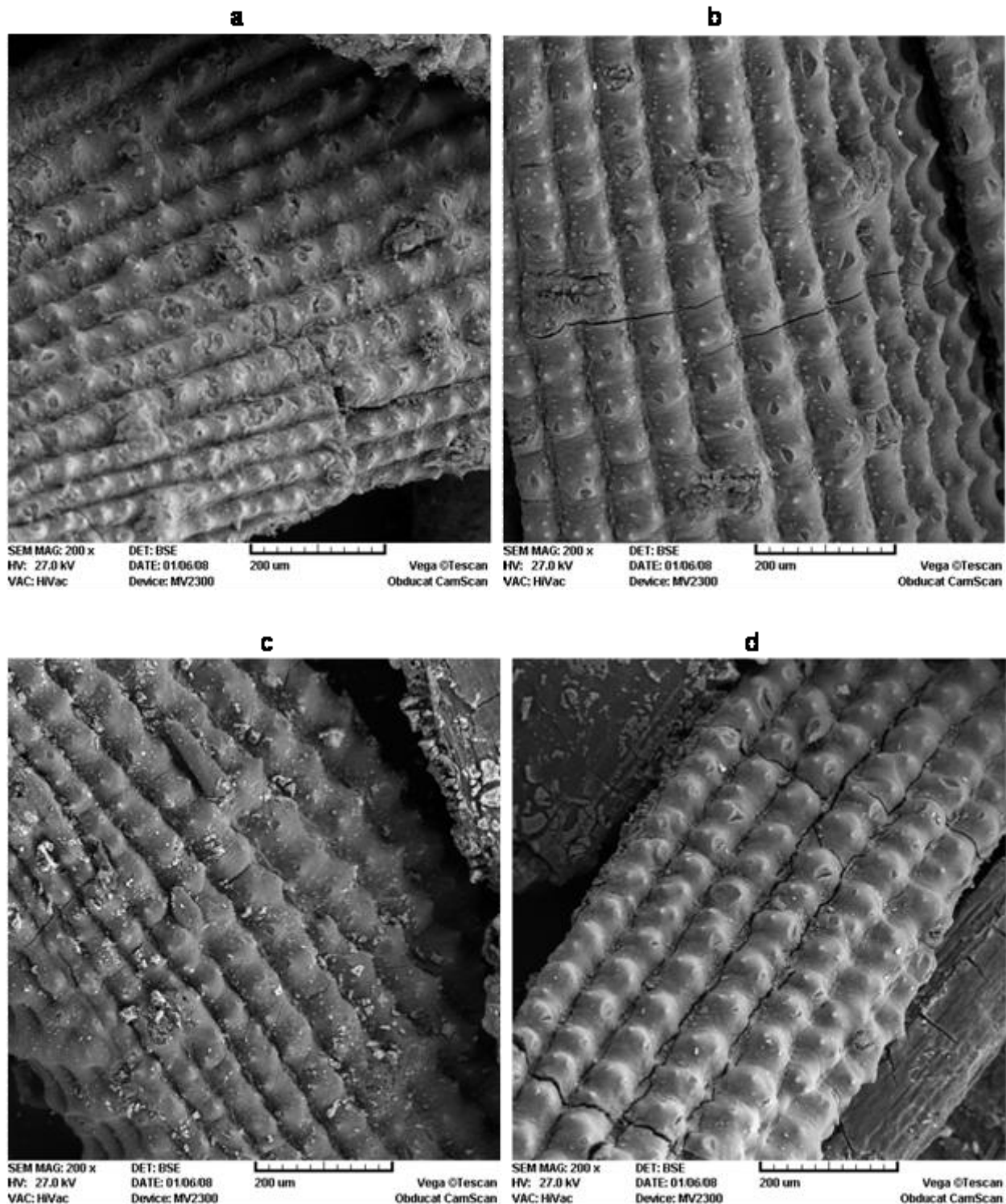


Figure 3. SEM micrographs of (a) rice bran, (b) activated rice bran, (c) CuFe_2O_4 / rice bran, (d) CuFe_2O_4 / rice bran and adsorbed dye.

concentration of H^+ (mol L^{-1}) and $[\text{OH}^-]$ is the concentration of OH^- (mol L^{-1}). Then, the pH value at the point of zero charges was determined by plotting Q

versus pH. Figure 4 shows the surface charge of the adsorbent as a function of pH. From Figure 5, it is obvious that the surface charge of the adsorbent at pH

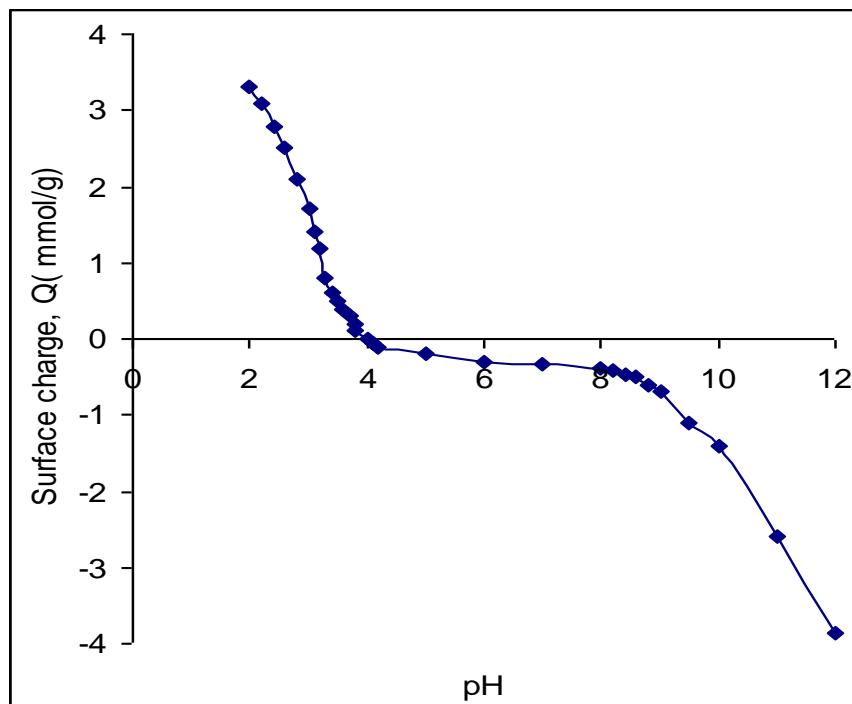


Figure 4. Surface charge of adsorbent as a function of pH.

4.2 ± 0.2 is zero. Therefore, the pH pzc of the composite adsorbent CRB is 4.2 ± 0.2 .

Effect of pH

The pH is one of the most important factors controlling the adsorption of dye onto suspended particles. In the experiments, 30 ml of initial concentration of MB 10 mg L^{-1} and 0.1 g adsorbents of ARB and CRB were used and initial pH varied from 2 to 12. Figure 5a shows the effect of pH on the adsorption of MB onto ARB and CRB. The adsorption removal increased with increasing pH of the solution. The maximum adsorption removal of MB on adsorbents was observed at pH 12. The effect of pH on MB removal from activated rice bran (ARB) and $\text{CuFe}_2\text{O}_4/\text{rice bran}$ (CRB) were similar. The pH_{pzc} value of CRB is found to be 4.2 (Figure 4). At $\text{pH} < \text{pH}_{\text{pzc}}$, sorbent surface may get positively charged due to the adsorption of H^+ . This could be explained by the fact that at low pH, more protons will be available to protonate hydroxyl groups, reducing the number of binding sites for the adsorption of MB. When pH is increased, the adsorbent surface is more negatively charged, resulting in increase of adsorption, since electrostatic repulsion between MB and the surface is decreased. Therefore, the adsorption behavior showed that adsorption of MB onto adsorbents is governed by electrostatic interactions. The influence of pH on the adsorption removal showed decreasing affinity with increasing electrostatic repulsion between MB and

the adsorbent with a maximum value at pH 12.

Effect of dye concentration

The influence of initial concentrations of MB on the percentage adsorption was investigated using 30 ml of MB 2 to 20 mg L^{-1} initial concentration at pH 12. As shown in Figure 5b, when the initial dye concentration was increased from 2 to 20 mg L^{-1} , the adsorption removal decreased for ARB from 76 to 45% and for CRB from 97.5 to 78.6%, respectively. The maximum adsorption of dye occurred at low concentrations. This indicates that the initial dye concentrations played an important role in the adsorption removal of MB on the rice bran and $\text{CuFe}_2\text{O}_4/\text{rice bran}$. The similar result for MB removal by wheat straw was seen (Gong et al., 2008). This was due to the saturation of the sorption sites on adsorbents.

Effect of adsorbent concentration

Figure 5c shows the plot between the percent of dye adsorbed against adsorbent concentration (g). It was observed that the amount of dye adsorbed varied with varying adsorbent mass and increased with increasing adsorbent mass, whereas the percentage color removal increased from 55 to 75% for ARB and 77 to 96.5% for CRB with an increase in adsorbent mass from 0.05 to 2 g. This can be attributed to increased adsorbent surface

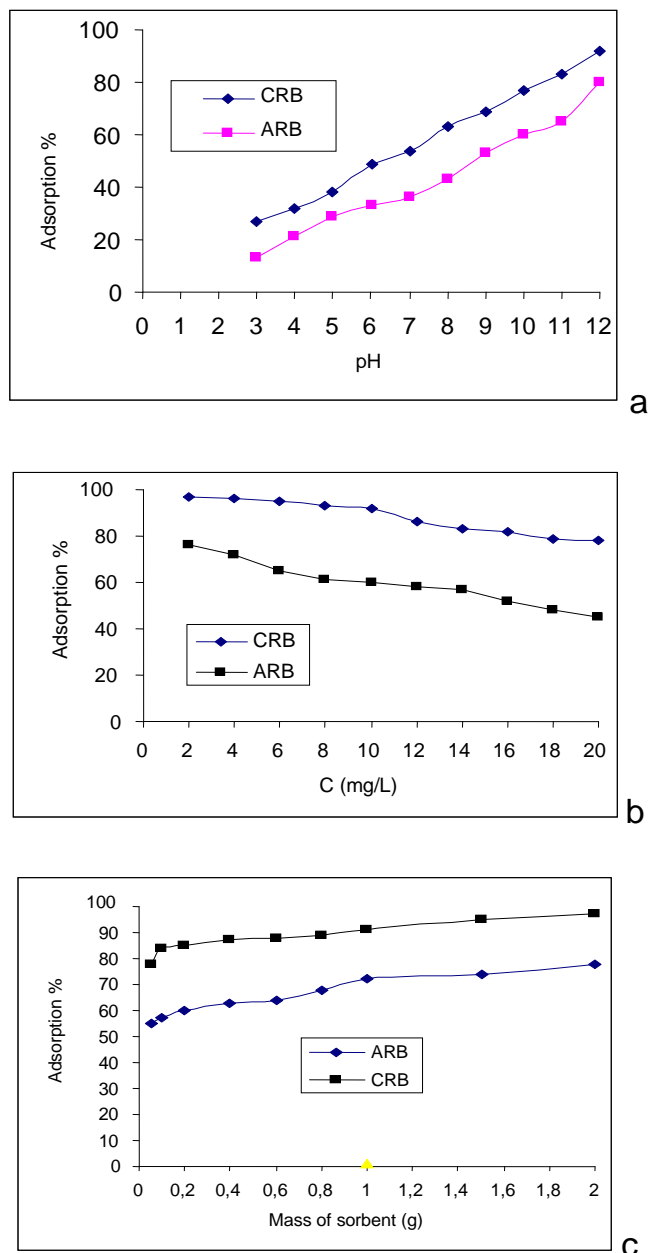


Figure 5. (a) Effect of adsorption (%) of MB versus pH, (b) Effect of initial dye concentration on adsorption, (c) Effect of adsorbent mass on adsorption for 30 ml of 10 mg L^{-1} MB onto ARB and CRB at room temperature.

area and availability of more adsorption sites resulting from the increase dosage of the adsorbent (Gong et al., 2008).

Adsorption kinetics

In order to predict adsorption kinetic models of MB dye solutions, pseudo-first order and pseudo-second-order kinetic models were applied to the data. The pseudo-first

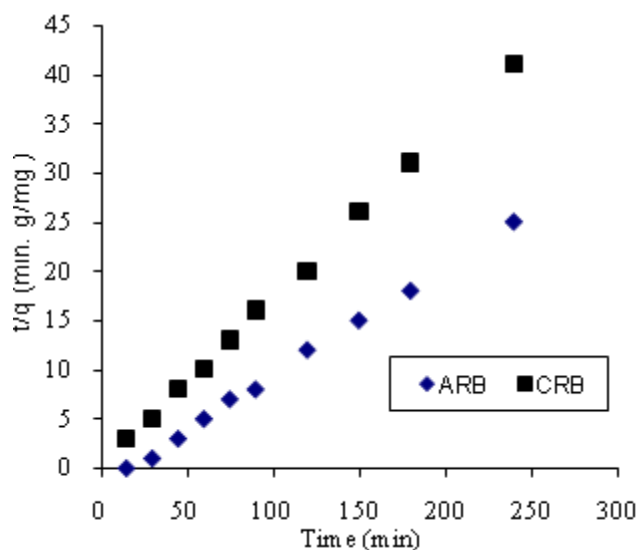


Figure 6. Pseudo-second order kinetic of MB onto ARB and CRB at room temperature at pH 12 and 25°C .

order model assumes that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and amount of solid uptake with time (Uddin, 2009; Akcay, 2004).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

where q_e and q_t are the amounts of dye adsorbed per unit mass of the adsorbent (mg g^{-1}) at equilibrium and time t , respectively and k_1 is the rate constant of adsorption (min^{-1}). When $\ln(q_e - q_t)$ was plotted against time, a straight line should be obtained with a slope of k_1 , if the first order kinetics is valid.

The pseudo-second order model as developed (Akcay, 2004; Ho and McKay, 1998) has the following form:

$$t/q = t/q_e + 1/(k_2 q_e^2) \quad (3)$$

where q_e and q represent the amount of dye adsorbed (mg g^{-1}) at equilibrium and at any time. k_2 is the rate constant of the pseudo-second order equation ($\text{g mg}^{-1} \text{min}^{-1}$). A plot of t/q versus time (t) would yield a line with a slope of $1/q_e$ and an intercept of $1/(k_2 q_e^2)$, if the second order model is a suitable expression.

The plot between $\log(q_e - q_t)$ versus time t shows the pseudo-first order model and the plot of t/q versus time t shows the pseudo-second order model (Figure 6). The kinetic model with a higher correlation coefficient r^2 was selected as the most suitable one.

It was found that application of pseudo-second order kinetics provides better correlation coefficient of experimental data than the pseudo-first order model for the MB on adsorbent. In addition, the equilibrium sorption capacities determined from the first order kinetic model

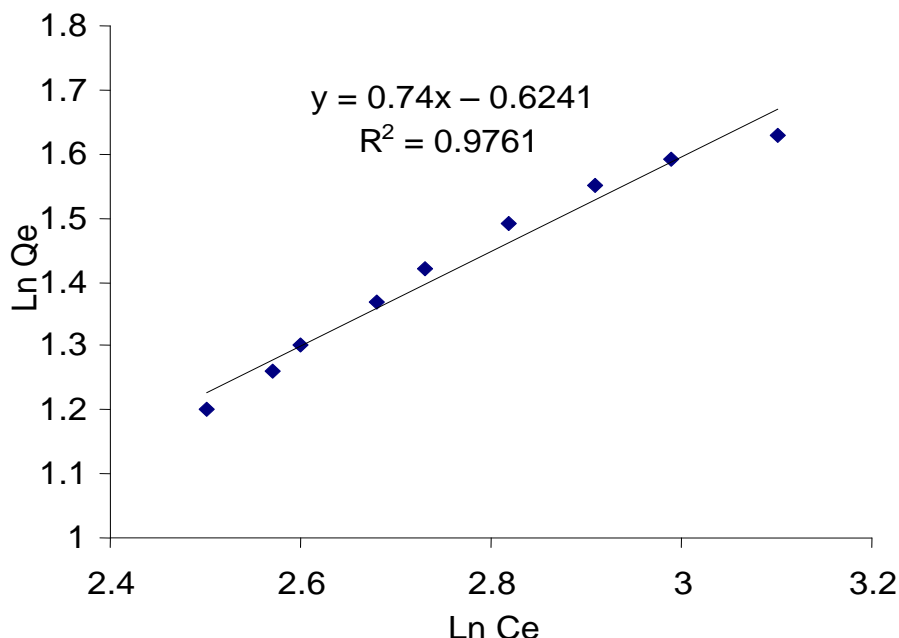


Figure 7. Freundlich plot for MB sorption onto CuFe₂O₄/rice bran.

were lower than those determined experimentally. It thus appears that the system under study is more appropriately described by the pseudo-second order model (Wu et al., 2010).

The values of rate constant were calculated from the slope of the Figure 6, as 0.112 for activated rice bran ($r^2 = 0.998$) and 0.17 for CuFe₂O₄/rice bran ($r^2 = 0.999$) ($\text{g mg}^{-1} \text{min}^{-1}$), respectively. The high rate constant of CuFe₂O₄/rice bran, indicates the high affinity for this dye, consistent with its high adsorption. Similar trends were observed in the adsorption of acid dye yellow 4 GL (Adachi et al., 2002) and BB3 and RO16 12 (Bouberka et al., 2005). The good correlation coefficients were obtained by fitting the experimental data to Equation 3, indicating that the adsorption process on rice bran and CuFe₂O₄/rice bran is pseudo-second order.

Adsorption isotherm of MB

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 (Ong et al., 2007). The adsorption of MB was performed by shaking 0.1 g of CRB in 30 ml of MB at 30°C and pH 12. The Langmuir adsorption model is given as:

$$q_e = q_m K_L C_e / (1 + K_L C_e) \quad (4)$$

The linearized form of Langmuir can be written as follows:

$$C_e / q_e = 1/q_m K_L + C_e / q_m \quad (5)$$

where q_e is the solid phase equilibrium concentration (mg g^{-1}); C_e is the liquid equilibrium concentration of dye in solution (mg L^{-1}); K_L is the equilibrium adsorption constant related to the affinity of binding sites (L mg^{-1}) and q_m is the maximum amount of dye per unit weight of adsorbent for complete monolayer coverage (mg g^{-1}).

The Freundlich adsorption isotherm model, which is an empirical equation used to describe heterogeneous adsorption systems, can be represented as follows:

$$q_e = K_F C_e^{1/n} \quad (6)$$

where q_e and C_e are defined as the previous description, K_F is the Freundlich constant representing the adsorption capacity (mg g^{-1}), and n is the heterogeneity factor depicting the adsorption intensity. In most references, Freundlich adsorption Equation 4 may also be expressed as Equation 5.

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (7)$$

Figures 7 and 8 show the adsorption equilibrium data fitted to Freundlich and Langmuir isotherm expression, respectively. It is evident from Figures 7 and 8 that the equilibrium data were better represented by Langmuir isotherm equation than done by the Freundlich equation. The best fit of equilibrium data in the Langmuir isotherm expression predicts the monolayer coverage of MB onto composite particles. It is known that the Langmuir isotherm is used on the supposition that the surface of

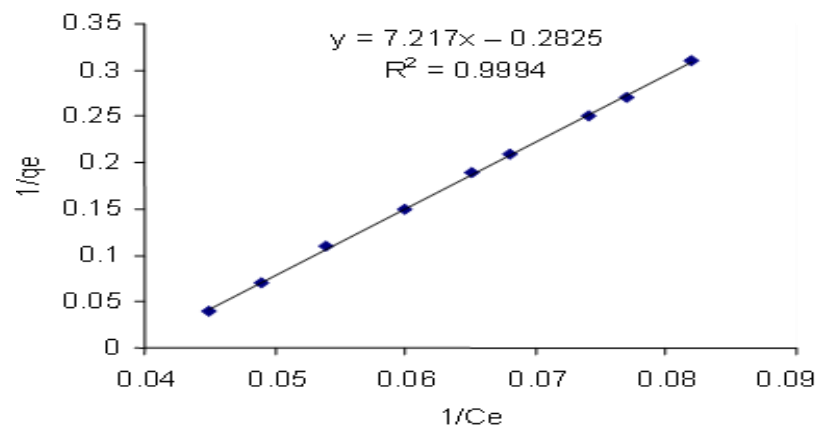


Figure 8. Langmuir plot for MB adsorption onto CuFe₂O₄/rice bran.

Table 1. Adsorption parameters for methylene blue by alternative adsorbent.

| Adsorbents | Surface area(m ² g ⁻¹) | Adsorption capacity (mg g ⁻¹) | Contact time | pH | Isotherm model | Reaction order | Number reference |
|---|---|---|--------------|--------|----------------|----------------|---------------------------|
| Sawdust -walnut | - | 59.17 | 60 - 180 min | - | - | - | (Uddin et al., 2009) |
| Sawdust- cherry | - | 39.84 | 60 - 180 min | - | - | - | (Uddin et al., 2009) |
| Coal | - | 250 | 6 h | - | - | - | (Tapalad et al., 2008) |
| Rice husk | - | 40.583 | - | 8 | Langmuir | 2 | (Mittal et al., 2005) |
| Bamboo-based activated carbon | 18.96 | 454.2 | 6 h | - | Langmuir | 2 | (Iqbal and Ashiq, 2007) |
| Peanut hull | 1.85 | - | 250 min | - | Langmuir | 2 | (Ho and McKay, 1998) |
| perlite | 1.22 | 25.97 | 30 | 11 | - | 2 | (Srivastava et al., 1987) |
| Zeolite | - | 0.5 | 90 - 60 min | 9 | - | - | (Wu et al., 2005) |
| wheat shells | 0.67 | - | 50 - 25 min | 9 | Langmuir | 2 | (Tapalad et al., 2008) |
| wheat straw | - | - | 6 h | 4 > pH | Langmuir | 2 | (Özca and Özca, 2005) |
| activated | 35 | - | 60 min | 12 | Langmuir | 2 | In this study |
| Rice bran | - | - | - | - | - | - | - |
| CuFe ₂ O ₄ /rice bran | 68 | - | 15 min | 12 | Langmuir | 2 | In this study |

the adsorbent is a homogenous surface, whereas the Freundlich isotherm applies to the adsorption process on a heterogeneous surface.

A comparison between the adsorption parameters and isotherms for methylene blue by alternative adsorbents are presented in Table 1.

Adsorption of MB onto different adsorbent also, were obeyed by the Langmuir equation (Hameed et al., 2007; Vadivelan and Vasanth, 2005;

Table 2. Thermodynamic parameters for the adsorption of MB onto CuFe₂O₄/rice bran.

| <i>T</i> (°C) | <i>K_C</i> | ΔG° (kJ mol ⁻¹) | ΔH° (kJ mol ⁻¹) | ΔS° (J mol ⁻¹) |
|---------------|----------------------|--|--|---|
| 20 | 1.2 | -0.23 | | |
| 25 | 1.21 | -0.47 | -26.4 | -3.5 |
| 30 | 1.25 | -0.57 | | |
| 40 | 1.3 | -0.7 | | |
| 50 | 1.41 | -0.9 | | |

Ozcan, 2005; Jin et al., 2008).

Thermodynamic parameters

In any adsorption process, entropy consideration must be taken into account in order to determine what process will occur spontaneously. Values of thermodynamic parameters are the actual indicators for practical application of a process. The amount of dye adsorbed at equilibrium at different temperatures 20, 25, 30, 40 and 50°C, have been examined to obtain thermodynamic parameters for the adsorption system. The thermodynamic parameters, change in the standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) associated with the adsorption process and these were determined using the following equations (Dogan et al., 2004):

$$\Delta G^\circ = -RT \ln K_C \quad (8)$$

where ΔG° is the standard free energy change, R is the universal gas constant (8.314 J.mol⁻¹ K⁻¹), T the absolute temperature and K_C is the equilibrium constant. The apparent equilibrium constant of the sorption, K_C , is obtained from:

$$K_C = C_A / C_S \quad (9)$$

where K_C is the equilibrium constant, C_A is the amount of dye adsorbed on the adsorbent of solution at equilibrium (mg L⁻¹), C_S is the equilibrium concentration of dye in the solution (mg L⁻¹). K_C values were calculated at different temperature to allow the determination of the thermodynamic equilibrium constant (K_C) (Iqbal and Ashiq, 2007; Bulut and Aydin, 2006). The free energy changes are also calculated by using the following equations:

$$\ln K_C = -\Delta G^\circ / RT = -\Delta H^\circ / RT + \Delta S^\circ / R \quad (10)$$

ΔH° and ΔS° were calculated from the slope and intercept of van't Hoff plots of $\ln K_C$ versus $1/T$. The results are given in Table 2.

The small negative value of the standard enthalpy change (-26.4 kJ mol⁻¹) indicates that the adsorption is physical in nature involving weak forces of attraction and

is also exothermic, thereby demonstrating that the process is stable energetically (Safa et al., 2004; Özcan et al., 2004). The overall standard free energy change during the adsorption process was negative for the experimental range of temperatures corresponding to a spontaneous physical process of MB adsorption and the system did not gain energy from an external source. When the temperature was increased from 20 to 50°C, the magnitude of the standard free energy change shifted to a low negative value, suggesting that the adsorption was rapid and more spontaneous at low temperature. The negative standard entropy changes (ΔS°) correspond to a decrease in the degree of freedom of the adsorption species (Özcan and Ozcan, 2005).

Conclusions

In this study, ability of activated rice bran and CuFe₂O₄/rice bran for methylene blue removal from aqueous solution were studied. CuFe₂O₄/rice bran magnetic adsorbents were successfully prepared by a chemical co-precipitation method. The particles were characterized using XRD, SEM and IR. The magnetic phase formed in the composite was spinel CuFe₂O₄. The presence of copper ferrite on the surface of the rice bran did not significantly decrease the micro porosity of the bran. The copper ferrite present on the surface of rice bran plays an important role in the catalytic adsorption of MB adsorbed on to the composite.

The amount of dye adsorbed was found to vary with initial pH, adsorbent dose and initial concentration of MB. The amount of dye removal was found to increase with increasing pH (12), and with an increase in adsorbent mass from 0.05 to 2 g of ARB and CRB. The results indicated that the sorption of MB data were found to follow pseudo-second order kinetics with rate constant 0.112 for activated rice bran and 0.17 for CuFe₂O₄/rice bran (g mg⁻¹ min⁻¹), respectively. The Langmuir and Freundlich adsorption models were used to express the sorption phenomenon of MB. The adsorption was best defined by the Langmuir isotherm model at the optimum conditions, confirming the monolayer sorption of MB. The thermodynamic constants of adsorption were also evaluated. The negative value of ΔG° confirms the spontaneous nature adsorption process.

It can be concluded that the CuFe₂O₄/rice bran (CRB) is

an efficient adsorbent for the removal of MB from aqueous solution and the magnetic adsorbent can be used repeatedly.

REFERENCES

- Adachi A, Takagi S, Okano T (2002). Adsorption and adsorption mechanism of rice bran for chloroform from tap water. *Chemosphere*, 46: 87- 92.
- Adachi A, Takagi S, Okano T (2001). Studies on removal efficiency of rice bran for pesticides. *J. Health. Sci.*, 47: 94–98.
- Akcaay M (2004). Characterization and determination of the thermodynamic and kinetic properties of p-CP adsorption onto organophilic bentonite from aqueous solutions. *J. Colloid Interface Sci.*, 280: 299–304.
- Allen SJ, Gan Q, Matthews R, Johnson PA (2005). Kinetic modeling of the adsorption of basic dyes by kudzu. *J. Colloid Interface Sci.* 286: 101–109.
- Arami M, Limaee NY, Mahmoodi NM, Tabrizi NS (2005). Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies. *J. Colloid Interface Sci.*, 288: 371–376.
- Bouberka Z, Kacha S, Kameche M, Elmaleh S, Derriche Z (2005). Study of an acid dye from an aqueous solution using modified clays. *J. Hazard. Mater.*, B119: 117-124.
- Bulut Y, Aydin H (2006). A kinetic and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination*, 194: 259-267.
- Dogan M, Alkan MA, Türkyilmaz Y (2004). Kinetics and mechanism of removal of methylene blue by adsorption onto perlite. *J. Hazard. Mater.*, B109:141-148.
- Douglas M, Considine PE (1984). *Encyclopedia of chemistry*, 4th edition, p. 336.
- Gong R, Ding Y, Li Yang M, Liu CH, Sun Y (2005). Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. *Dyes Pigments*, 64: 187-192.
- Gong R, Jin J, Youbin Chen F, Liu JZ (2006). Enhanced malachite green removal from aqueous solution by citric acid modified rice straw. *J. Hazard Mater.*, 137(2): 865-870.
- Gong R, Jin Y, Chen Hu JY, Sun J (2007). Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw. *Dyes Pigments*, 73(3): 332-337.
- Gong R, Zhu S, Zhang D, Chen J, Ni S, Guan R, (2008). Adsorption behavior of cationic dyes on citric acid esterifying wheat straw. *Desalination*, 230: 220-228.
- Gupta V K, Mittal A, Krishnan L, Gajbe V (2004). Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. *Purification Technol*, 40: 87–96.
- Gupta VK, Ali I, Hubbard AT (2003). Adsorbents for water treatment: low cost alternatives to carbon. In: A.T. Hubbard, *Encyclopaedia of Surface and Colloid Science*, Marcel Dekker, New York, pp. 1–34.
- Gupta VK, Suhasl, Ali I, Saini VK (2004). Removal of rhodamine B, fast green, and methylene blue from wastewater using red mud, an aluminum industry waste. *Ind. Eng. Chem. Res.*, 43: 1740–1747.
- Gupta VK, Suhas I, Mohan D (2003). Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents. *J. Colloid Interface Science*, 265: 257–264.
- Hameed BH, Din ATM, Ahmad AL (2007). Adsorption of methylene blue onto bamboo-based activated carbon: Kinetic and equilibrium studies. *J. Hazard. Mater.*, 141: 819-825.
- Hashemian S, Dadfarnia S, Nateghi MR, (2008). Sorption of acid red 138 from aqueous solutions onto rice bran. *Afr. J. Biotechnol.*, 7 (5): 600-605.
- Hashemian S (2007). Study of adsorption of acid dye from aqueous solutions using bentonite Main Group. *Chemistry*, 6 (2): 97-107.
- Ho Y S, McKay G (1998). Pseudo –Second order model for sorption process. *Chem. Eng. J.*, 70: 115-124.
- Iqbal MJ, Ashiq MN (2007). Adsorption of dyes from aqueous solutions on activated charcoal. *J. Hazard. Mater.*, B 139: 57-66.
- in X, Jiang M Q, Shan X Q Z, Pei G, Chen Z, (2008). Adsorption of J methylene blue and orange II onto unmodified and surfactant-modified zeolite

Wu J, Zhang H, He PJ, Yao Q, Shao LM (2010). Cr (VI) removal from aqueous solution by dried activated sludge biomass, J. Hazard. Mater., 176(1-3): 697- 703.

Wu R, Qu J, Chen Y (2005). Magnetic powder MnO-Fe₂O₃ composite- A novel material of azo-dye from water, Water Res., 39: 630-638.