Materials Research Express

PAPER

Enhancement the rhodamine 6G adsorption property on Fe₃O₄-composited biochar derived from rice husk

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Keywords: Fe₃O₄ nanoparticle composites, rice husk biochar, adsorption, rhodamine 6G

Abstract

Magnetic biochars were prepared using Fe₃O₄ nanoparticle composites onto the surface of biochar derived from rice husk. The characteristics of magnetic biochar were characterized by scanning electron microscope, x-ray powder diffraction and Fourier-transform infrared techniques. The removal of rhodamine 6G dye by magnetic biochar, compared to pristine biochar was studied. The effects of pyrolysis temperature on rhodamine 6G adsorption was evaluated. Kinetic, isotherms and thermodynamic studies were carried out to investigate the adsorption mechanism of rhodamine 6G dye on magnetic biochar surface. The rhodamine 6G removal efficiency of Fe₃O₄-composited biochar (pyrolyzed at 500 °C) is higher than that of pristine biochar with maximum efficiency of 94% removal. The adsorption isotherm and kinetic studies indicated that the langmuir model, pseudo-first order and pseudo-second order models described well the rhodamine adsorption onto magnetic Fe₃O₄-biochar.

Abbreviations

| Symbol | Description |
|--------|-------------|
| BC     | Biochar     |
| C₀     | Initial dye concentration (mg/L) |
| Cₑ     | Equilibrium concentration of dye (mg/L) |
| ΔG⁰    | The Gibbs free energy and f |
| ΔH⁰    | The change of enthalpy |
| MB     | Magnetic biochar |
| qₑ     | Adsorbed dye amount per gram of sorbent at equilibrium (mg/g) |
| qₑ,cal | Calculated amount of dye adsorbed per gram of adsorbent at equilibrium (mg/g) |
| qₑ,exp | Experimental amount of dye adsorbed per gram of adsorbent at equilibrium (mg/g) |
| qₜ     | Adsorbed dye amount per gram of adsorbent at time t (mg/g) |
| K      | Thermodynamic equilibrium constant |
| KₑL    | Langmuir isotherm equilibrium constant representing the energy of sorption (L/mg) |
| KₐF    | Freundlich constant representing sorption capacity ((mg/g)(L/mg)/n) |
| k₁     | Pseudo-first order rate constant (1/min) |
| k₂     | Pseudo-second order rate constant (g/mg-min) |
| n      | Freundlich isotherm constant representing sorption intensity |
| R      | The ideal gas constant (8.314 J mol⁻¹·K⁻¹) |
1. Introduction

The fluorescent dyes have been used as an ingredient in products such as paper, cosmetics, plastics, glowing product, forensic, biotechnology, food, and colourant in textile and the developments of these industries lead to the discharge of fluorescent dyes contaminated in wastewater which causes serious pollutions to the environment and human in direct or indirect ways [1, 2]. Most dyes have complex properties such as aromatic structure and high stability. These dyes are difficult to be degraded or decomposed by physical, chemical or biological treatments. Among the various dyes classified, the cationic dyes are presumed to present the highest toxicity [3]. One of the cationic dyes is the rhodamine 6G which has been considered as a highly fluorescent rhodamine family dye, as shown in figure 1, and a highly water-soluble agent. Rhodamine 6G has been used in a wide range of applications such as biotechnologies (ELISA), forensic technologies (Dye stain, reagent powder, laser dye, etc) and industries [4, 5]. Even though rhodamine 6G is not strongly hazardous, its long-term exposure by inhalation or skin contact can cause serious health problems or symptoms such as increasing heart rate, vomiting, skin cancer, lung cancer and teratogenic effect (delay in physiological development) [6, 7]. Hence, the elimination of rhodamine 6G from wastewater streams before discharging into the environment is important to reduce the water pollution and human health impacts.

There have been many reports of various techniques applied to remove dye contaminated in wastewater, including oxidation process, chemical precipitation, electrochemical method, ion exchange, membrane separations, and adsorptions. However, each of these referred techniques has its own limitation. Among the available techniques, adsorption has received much attention compared to other technologies because of its higher removal efficiency, lower-cost, simpler operation, and lower sensitivity to the toxic agents in wastewater [7]. In recent years, the utilization of agricultural wastes to produce low-cost and eco-friendly biochar has been reported. Biochar, prepared by the pyrolysis of biomass in an oxygen-limited atmosphere, is a porous and carbonaceous product with high porosity. Biochar has been employed for many applications such as soil amendment, fertilizer or removal of contaminants from wastewater [8–10]. Hence, the use of biochar derived from agricultural waste as an adsorbent is an alternative choice for the removal of dye from contaminated water. The adsorption property of biochar not only depends on the biomass used but also on the pyrolysis conditions because the surface area, porosity, chemical content and surface chemistry such functional group of the biochar are significantly affected by pyrolysis temperature [8–10].

In this work, we used the agricultural residue of rice husk to produce biochar by slow pyrolysis process. The pyrolysis temperatures were varied at 400 °C–600 °C. The obtained biochar was used as adsorbent for rhodamine 6G removal. Moreover, in order to increase the adsorption efficiency, facilitate the treatment of spent biochar after adsorption process and enable the biochar in various applications and fields for the removal of contaminants in water, we developed the magnetic property of biochar with the attachment of metallic ions on the surface of biochar. to increase its magnetic effect [9, 10]. The removal of rhodamine 6G from aqueous solution by modified biochar compared with pristine biochar was reported. The adsorption mechanism was also explained in this study by fitting the experiment results to the adsorption isotherm model, kinetic model and thermodynamic parameters models.

2. Experiments

2.1. Materials and equipment

The rice husk RD6 gene sample used as raw material for preparing the biochar (BC) materials in this study was collected from the local agricultural wastes in Chiang Rai, Thailand. The slow pyrolysis in an electrical muffle furnace (Nabertherm, model L3/11/B170, Germany) was used to prepare the biochar and magnetic biochar samples [8, 9]. A stock solution of rhodamine 6G with a concentration of 100 mg l⁻¹ was obtained by dissolving accurately weighed 0.1 g rhodamine 6G, as received from Aldrich, USA, in 1000 ml of deionized water. The pH for adsorption studies was adjusted to around 7 using either 1 M NaOH or 1 M HNO₃ and monitored with a pH meter (pH/ORP Bench meter model AD1040). Adsorption studies were carried out at 220 rpm in an
incubator shaker (SI4–2 SHEL LAB) at a controlled temperature. Rhodamine 6G concentration of the supernatant was determined using a UV–vis spectrophotometer (Perkin Elmer model Lambda 35).

### 2.2. Biochar and magnetic biochar preparations

Rice husk biomass (1 kg) was firstly washed two times with tap water, three times with distilled water. The rice husk biomass was dried in the air for 1 day and was then dried in an oven at 80 °C for 6 h. Measured quantities of rice husk biomass were then placed in covered crucibles and heated in a furnace under oxygen-limited conditions at the pyrolysis temperatures 400 °C–600 °C, with a heating rate of 5 °C min⁻¹, for 2 h to obtain biochar (BC) materials. BC400, BC500 and BC600 were produced by pyrolysis temperature at 400, 500 and 600 °C, respectively. After the pyrolysis process, the BC materials were washed several times with distilled water to remove fine particulates, water-soluble organic residuals, and impurities. The BC (20 g) was then dried in an oven at 80 °C for 2 h. The BC was ground and stored in closed vessels [9–13].

Magnetic biochar (MB) derived from rice husk was prepared from BC materials according to the method described by Karunanayake, et al [9] to obtain MB400, MB500 and MB600 by pyrolyzed at 400, 500 and 600 °C, respectively. Briefly, BC 5 g was immersed in distilled water 40 ml. The aqueous solution of FeCl₂ (2.52 g, 10 ml) and FeCl₃ (3.24 g, 10 ml) was mixed and vigorously stirred at 60 °C for 10 min [8, 9]. The mixture of FeCl₂ and FeCl₃ solutions was slowly poured into the BC solution and slowly stirred (50 rpm) at room temperature for 30 min. The 4 M NaOH solution was added dropwise into the mixture until a pH reach ~9–10 and then mixed by vigorously stirring at 70 °C for 30 min [14]. The mixture was then stirred in ultrasonic bath at 60 °C for 30 min for precipitation iron hydroxides as tiny particles adhering to the biochar surfaces. The resulting material was filtered by suction filtration (Whatman filter paper, pore size 11 μm), washed several times with distilled water. This was then dried in an oven at 80 °C for 2 h. The materials were re-pyrolyzed according to the pyrolysis temperature of selected BC (400 °C–600 °C) for 1 h and then washed several times with distilled water to remove fine particulates and impurities. The MB materials were separated from distilled water using magnet, and then filtered by suction filtration (Whatman filter paper, pore size 11 μm). The obtained MB materials were dried in an oven at 80 °C for 2 h [15–17].

### 2.3. Biochar and magnetic biochar characterization

The BC samples were dried and kept in a desiccator. Elemental analysis was performed using a CHNS/O analyzer (Flash 2000, ThermoScientific, Italy). The mineral compositions in rice husk and BC materials were determined by x-ray fluorescence (XRF) (S2175 Ranger, Bruker., Germany). The surface morphology (SEM) of dried rice husk as raw materials and BC materials was characterized using scanning electron microscopy (SEM, Zeiss (LEO) 1450VP) at 5 kV and the SEM of MB materials was performed using field scanning electron microscope (SEM, FEI Apreo) at 5 kV. The sample for SEM analysis was coated on a gold stub attached to carbon tape and then was mounted into a sample holder for analysis. The x-ray diffraction (XRD) pattern (PAN analytical, X’ Pert Pro MPD) of MB500 was further performed for confirmation of Fe₃O₄ structure composited to BC surface. The functional groups of BC were determined using Fourier transform infrared (FT-IR) analysis (Perkin Elmer model Spectrum GX) and the KBr pellet method. The spectra were recorded in the wavenumber range of 400–4000 cm⁻¹ [18].

### 2.4. Adsorption experiments

The adsorption potential of BC and MB materials for removal of rhodamine 6G was assessed from batch experiments. The effect of contact time on the adsorption process of BC and MB materials was investigated. The initial concentration of dye was fixed at 100 mg l⁻¹. A 10 ml dye sample was transferred to a 15 ml centrifuge tube along with 0.1 g of BC or MB adsorbents. The solution was mixed at 220 rpm in incubator shaker for a
controlled time from 5 to 120 min at 25 °C. The spent BC materials after adsorption of dye were removed from solution using suction filtration (Whatman filter paper, pore size 2.5 μm) and spent MB after adsorption of dye were removed from solution using magnet. The removal percentage (% removal) of rhodamine 6G dye was analyzed by monitoring the change in the absorbance at 552 nm recorded by a UV–vis spectrophotometer. All the experiment was replicated thrice and the averaged results are reported. The removal efficiency of rhodamine 6G was calculated using the following equation (1) and the adsorption capacity \( q_e \) was calculated based on the equation (2) [19, 20].

\[
\text{Removal} \% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)
\]

\[
q_e = \frac{(C_0 - C_e)V}{m} \quad (2)
\]

2.5. Adsorption isotherm study

Adsorption isotherm study was carried out to investigate the adsorption performance and the relationship between the liquid phase rhodamine 6G adsorbed onto the surface of Fe3O4 composited biochar (MB500) [20]. A 10 ml dye sample was transferred to a 15 ml centrifuge tube along with 0.1 g of MB500. The solution was mixed at 220 rpm in incubator shaker for 30 min at 25 and 40 °C. The spent MB500 after adsorption of dye was removed from the solution using magnet. The adsorption capacity of rhodamine 6G dye was analyzed by monitoring the change in the absorbance at 552 nm recorded by a UV–vis spectrophotometer. Different isotherm models were applied in adsorption experimental data to evaluate the adsorption mechanism, surface properties and adsorbent affinities of rhodamine 6G on MB500 [21–25].

2.6. Adsorption kinetic study

In order to describe the rates and mechanism of adsorption dynamics of rhodamine 6G onto the surface of Fe3O4 composited biochar, the adsorption kinetic study of MB500 was carried out. A 10 ml dye (100 mg l−1) sample was transferred to a 15 ml centrifuge tube along with 0.1 g of MB500. The solution was mixed at 220 rpm in incubator shaker for a controlled time from 5 to 120 min at 25 and 40 °C. The spent MB500 after adsorption of dye was removed from solution using magnet. The absorbance change at 552 nm was monitored by a UV–vis spectrophotometer. In this work, pseudo-first order and pseudo-second order models were used for representing the adsorption kinetics of rhodamine 6G dye onto MB500 [26–28].

2.6.1. Pseudo-first-order model

The pseudo-first order kinetic model is given by equation (3).

\[
\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (3)
\]

2.6.2. Pseudo-second-order model

The sorption data were also analyzed in terms of the pseudo-second order model. The pseudo-second order equation is based on the sorption capacity of the solid phase and expressed follows equation (4).

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)
\]

If the initial adsorption rate, \( h \) (mg g−1 min) is explained in equation (5).

\[
h = k_2 q_e^2 \quad (5)
\]

Then, equations (4) and (5) become the equation (10).

\[
\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (6)
\]

2.7. Adsorption thermodynamics

The study of adsorption thermodynamics can provide the effect of temperature on the behavior and feasibility of the adsorption of rhodamine 6G dye onto magnetic biochar. MB500 is the representative for the magnetic biochar adsorbent for this experiment. The thermodynamic parameters including the Gibbs free energy change (\( \Delta G^0 \), kJ/mol), the enthalpy change (\( \Delta H^0 \), kJ/mol) and the entropy change (\( \Delta S^0 \), kJ/mol), were used for explanation the adsorption process. The thermodynamic parameters can be obtained from the following equation (7) [18, 20]:

\[
\Delta G^0 = -nRT \ln \left( \frac{q_e}{V} \right) \quad (7)
\]

\[
\Delta H^0 = \frac{-\Delta S^0}{\beta} \quad (8)
\]

\[
\Delta S^0 = -nRT \ln (1 - \alpha) \quad (9)
\]

\[
\beta = \frac{C_p}{\Delta H^0} \quad (10)
\]

\[
\alpha = \frac{C_0 - C_e}{C_0} \quad (11)
\]

\[
\beta = \frac{\Delta S^0}{\Delta H^0} \quad (12)
\]

\[
\Delta G^0 = -RT \ln K \quad (13)
\]

\[
K = \frac{C_e}{C_0} \quad (14)
\]

\[
\Delta G^0 = -RT \ln (1 - \alpha) \quad (15)
\]

\[
\Delta H^0 = -\frac{\Delta S^0}{\beta} \quad (16)
\]

\[
\Delta S^0 = nR \ln (1 - \alpha) \quad (17)
\]

\[
\beta = \frac{nR \Delta H^0}{\Delta S^0} \quad (18)
\]

\[
\Delta S^0 = nR \ln \frac{C_e}{C_0} \quad (19)
\]

\[
\beta = \frac{1}{C_e} - \frac{1}{C_0} \quad (20)
\]

\[
\Delta G^0 = -RT \ln \left( \frac{C_e}{C_0} \right) \quad (21)
\]

\[
K = \frac{C_e}{C_0} \quad (22)
\]

\[
\Delta H^0 = -\frac{\Delta G^0}{\beta} \quad (23)
\]

\[
\Delta S^0 = \frac{nR \Delta H^0}{\Delta G^0} \quad (24)
\]

\[
\beta = \frac{\Delta S^0}{\Delta H^0} \quad (25)
\]

\[
\Delta G^0 = -RT \ln \frac{q_e}{V} \quad (26)
\]

\[
\Delta H^0 = \frac{-\Delta G^0}{\beta} \quad (27)
\]

\[
\Delta S^0 = nR \ln \frac{q_e}{V} \quad (28)
\]

\[
\beta = \frac{nR \Delta G^0}{\Delta H^0} \quad (29)
\]
\[ \Delta G^0 = -RT \ln K \]  
(7)

where, \( K = q_{\text{max}} \times K_1 \) and \( \Delta H^0 \) and \( \Delta S^0 \) can be derived using the Van’t Hoff equation (8).

\[ \ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]  
(8)

According to the equation (8), the plotting of \( \ln K \) and \( 1/T \) would obtain the \( \Delta H^0 \) and \( \Delta S^0 \) values [29].

Moreover, the experimental set-up for the studies of adsorption property of rhodamine 6G onto BC and MB material surface was demonstrated in figure S1 is available online at stacks.iop.org/MRX/7/025511/mmedia in the supplementary information.

3. Results and discussion

3.1. Characterization of biochar

From the pyrolysis process at 400 °C–600 °C, BC400, BC500 and BC600 were obtained in yields 47.19, 44.64 and 43.73%, respectively. The physical characteristics and chemical composition of BC materials were determined with SEM, elemental analysis, XRF and FT-IR techniques. The SEM images of the rice husk, BC400, BC500 and BC600 exhibit the rough surface morphology and porosity structure (figures 2 and S2). The surface morphology in the rice husk is quite smooth and compact as shown in figure 2(a). After pyrolysis, the mesoporous surface with the various sizes of small canals was observed in BC materials as shown in figures 2(b)–(d) [8]. For the SEM images, these mainly depend on the effect of pyrolysis temperature on the surface characteristics of BC materials such as the number of pore structures and large cavities presented on the surface which was increased with the increasing pyrolysis temperature. Generally, surface and porosity construction of biochar was not fully developed at the low pyrolytic temperatures [10, 11, 21]. The observation of developing the rough surface and porosity on BC materials was employed by increase the pyrolysis temperature to improve the surface morphology for adsorption application including the surface areas, pore volumes and pore sizes. Hence, the huge cavities in mesopore size were formed on the surface of BC500 and BC600 (figures 2(c) and 1(d)).

The elemental composition of BC materials is given in table 1. The results show that carbon is the major component of BC materials derived from rice husk (~41%–44%wt), which confirms the carbonaceous nature of the obtained BC materials. However, at the low-pyrolysis temperature at 400 °C, the carbonous biochar was obtained in higher yield with the higher oxygen and volatile-matter components, compared to the biochar produced at the high-temperature pyrolysis. The increasing pyrolysis temperature reduced biochar yield and its volatiles content [30, 31]. At increasing temperature of pyrolysis (500 and 600 °C), the percentage of carbon is increased and oxygen content is obviously decreased. The mineral components in BC500 and BC600 compared to rice husk (Table S1 in supplemental information) were screened with XRF technique and shown in table 2 and table S2 (in supplemental information), respectively. For the mineral composition of BC500 (table 2), silicon is the main inorganic content in biochar (18.71%) which was observed in form of silicon dioxide (SiO₂) in 40.02%. This result correlates with the presence of the Si–O–Si peak in FT-IR spectrum (figure 3). The rhodamine 6G adsorbed onto biochar surface was also screened with SEM technique, The surface morphology of BC after

**Figure 2** Scanning electron microscopy images of rice husk (a), BC400 (b), BC500 (c) and BC600 (d) surfaces, in 10 micrometer.
adsorption of rhodamine 6G can be observed in figure S3 in supplemental information, showing morphological changes due to rhodamine 6G precipitation in the original pore and surface structures of BC materials. These can be observed as very small particles widely distributed and also aggregated in some areas.

The FT-IR spectra of rice husk, BC and MB materials were shown in figures 3 and S4. In figure 3(a) the FT-IR spectra of BC400, BC500 and BC600 are consistent with the chemical composition changes with the increasing pyrolysis temperature. The FT-IR spectrum of MB500 compared to BC500 was also shown in figure 3(b) and the details of peak assignments were explained in table 3 [18, 32]. The main surface functional groups in rice husk were observed in FT-IR spectrum including the vibrations of –OH group, C–H, C–O stretching in aliphatics/ aromatics, C=C stretching in alkenes/aromatics, CH2 and CH3 bending, CH–OH stretching of alcohol group, C=O group in lactones, and Si–O–Si stretching in SiO2 [32]. The main functional groups of BC500 were observed including the vibrations of –OH stretching, C–H, C=O, and C=C stretching in aliphatic/aromatic carbons, C–O stretching, and Si–O–Si stretching in SiO2 and C–H stretching. The disappearances of some functional groups were related to the decomposition of the pristine material during the pyrolysis process, such as the vibrations of CH2 and CH3 stretching and bending in aromatic, –OH stretching of the alcohol group. The oxygen and hydrogen of the biomass material in H2O, CO2 and CO forms were eliminated by dehydration and decarboxylation as well. And the oxygen and hydrogen contents in biochar were dramatically decreased with the increasing pyrolysis temperature as shown in figure 3(a) [33]. Hence, the protein-like substances, lipids, polysaccharides and cellulos in the rice husk gradually decomposed during the biochar preparation process. In figure 3(b), the main functional groups in MB500 are quite similar to those of BC500, but some functional groups, such as Fe–O bond, were formed during the development of magnetic biochar process by adding the Fe3O4 nanoparticle composites on the biochar surface [8, 16].

XRD patterns of MB500 correlating with SEM image of Fe3O4 nanoparticles compositied on biochar surface were shown in figure 4. Moreover, the SEM images of MB materials pyrolyzed at different temperatures were shown in figure S5. Figure 4(a) demonstrated the Fe3O4 nanoparticles compositied on some areas of the MB500 surface. Multiple iron oxide phase peaks appear in the 2θ range from 5 to 90°, proving that the iron oxide present is primarily Fe3O4. The peaks of the standard diffraction pattern for the Fe3O4 corresponding to the 29.54°, 35.05°, 36.44°, 42.4°, 52.5°, 55.98°, 61.42°, and 72.66° [34, 35]. In figure 4(b), all these peaks appear again in the XRD spectrum of MB500 and some peaks of the MB500 shifted such as 30.05°, 43.48°, and 56.50°. The major peak at 35.83 of MB500 is correlated with the peak at 35.05° of standard which is for a crystalline plane with Miller indices of (311) [9, 35]. Therefore, the iron oxide precipitation by thermal process, Fe3O4 is formed. With adding NaOH dropwise, the pH was increased. The first Fe(OH)3 and then Fe(OH)2 were precipitated onto the biochar surface and the Fe(OH)2 can be oxidized to Fe(OH)3 by dissolved oxygen as well. These processes

| Table 1. | Elemental analysis for biochar derived from rice husk comparing with the other biomass. |
| Material | C | H | N | S | O | Ash |
|---------|---|---|---|---|---|-----|
| Rice husk | 36.02 | 5.16 | 0.51 | 0.17 | 35.99 | — |
| BC400 | 41.90 | 3.77 | 0.59 | < 0.01 | 22.66 | 26.5 |
| BC500 | 44.38 | 2.00 | 0.76 | < 0.01 | 11.07 | 33.8 |
| BC600 | 44.56 | 1.56 | 0.68 | < 0.01 | 7.46 | 35.4 |

| Table 2. | Mineral composition (%wt) of BC500 by XRF technique. |
| Element | Conc. (%) | Element | Conc. (%) |
|---------|-----------|---------|-----------|
| C       | 44.381    | Mn      | 0.049     |
| O       | 33.003    | Fe      | 0.037     |
| Si      | 18.708    | Al      | 0.036     |
| H       | 1.999     | Cl      | 0.014     |
| N       | 0.765     | Na      | 0.011     |
| K       | 0.430     | Zn      | 0.007     |
| Ca      | 0.195     | Rb      | 0.005     |
| P       | 0.175     | Cu      | 0.004     |
| Mg      | 0.128     | Cr      | 0.003     |
| S       | 0.049     |         |           |
lead to the formation of mixed iron oxide/hydroxide (FeOOH) and magnetite (Fe₃O₄) during the pyrolysis condition [9, 34–36]. Furthermore, the broad band at ~20°–30° indicates that the majority of biochar remains as amorphous in the MB nanocomposite materials.

Table 3. The surface functional group of Rice husk, BC500, and MB500.

| Rice husk (cm⁻¹) | Functional group | BC500 (cm⁻¹) | Functional group | Before adsorption | After adsorption | Difference | MB500 (cm⁻¹) | Functional group |
|-----------------|-----------------|--------------|-----------------|-------------------|------------------|-----------|--------------|-----------------|
| 3419            | −OH             | 3416         | −OH             | —                 | 3413             | 0         | —            | −OH             |
| 2925            | C−H             | 2930         | C−H             | 1617              | 1619–1615        | ±2        | C=O, C=C     |
| 1591–1731       | C=O, C=C        | 1591         | C=O, C=C        | 1087              | 1050             | −6        | C−O, Si−O−Si  |
| 1532            | N−H             | 1088         | C−O, Si−O−Si    | 796               | 780              | −16       | Si−H         |
| 1452            | C−H             | 795          | Si−H            | 586               | 562              | −24       | Fe−O         |
| 1389            | C−H             | 795          | Si−H            | 586               | 562              | −24       | Fe−O         |
| 1229            | C−O             | 795          | Si−H            | 586               | 562              | −24       | Fe−O         |
| 1037–1099       | C−O, Si−O−Si    | 795          | Si−H            | 586               | 562              | −24       | Fe−O         |

Figure 3. FT-IR spectra of rich husk, BC500 (a) and MB500 (b).
3.2. Adsorption study

The adsorption time and the initial concentration of rhodamine 6G are important factors influencing the adsorption capacity, as shown in figure 5. The pH of adsorption can affect the surface charge, ionization degree and the speciation of dye in solution, hence all batch adsorption experiments were controlled at pH 7 [17]. The removal efficiency of rhodamine 6G by biochars (BC 400, BC500 and BC600) increased consistently with time (figure 5(a)). The kinetic study showed that the adsorption of rhodamine 6G with different initial concentrations (5–100 mg l⁻¹) by BCs and MBs (MB400, MB500, and MB600) reached the equilibrium at different times (figure 5(b)). Rapid adsorption was observed in the first stage (0–5 min). After BCs were composited by Fe₃O₄ nanoparticles, the equilibrium adsorption capacities of MBs were increased in which MB500 show the highest adsorption with qₑ 9.42 mg g⁻¹ as shown in figure 5(c). Figure S6 also showed the increasing removal percentage of rhodamine 6G by MB materials compared to those of BC materials in which the composites of Fe₃O₄ nanoparticles on BC400, BC500 and BC600 surfaces enhance the removal percentage of rhodamine 6G by MB400, MB500 and MB600 in 39.28%, 79.88% and 60.33%, respectively. With the highest value of increasing removal percentage of rhodamine 6G by MB500, therefore, MB500 was selected as representative of Fe₃O₄ magnetic biochar for the following adsorption studies to provide insights on understanding the adsorption mechanism.

The interaction between the adsorbate and the adsorbent surface, the maximum adsorption capacity of the adsorbent material and the dynamic equilibrium of adsorption system were investigated using the adsorption isotherm models [21]. From figure 6, the isotherm experiment is fitted to the data of Langmuir and Freundlich models according to the equations (9) and (10), respectively.

**Figure 4.** SEM of Fe₃O₄ nanoparticles composited on biochar surface (a) and XRD pattern confirming the Fe₃O₄ nanoparticles in MB500 materials (b).
Figure 5. The adsorption capacity (mg/g) of rhodamine 6G by BC (a) and MS materials (b) at the contact time (min) rhodamine 6G dye adsorption on BC and MB at 25 °C (c).

\[
\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}}
\]  

(9)
The adsorption isotherms for rhodamine 6G adsorption by MB500 at 25 and 40 °C are shown in Figure 6, along with the fits by Langmuir and Freundlich models. The fitting parameters are listed in Table 4, with the coefficient of determination for Langmuir ($R^2 \approx 0.996$) models at 25 and 40 °C. The Langmuir model gave a better fit suggesting that the adsorption of rhodamine 6G by MB500 was mainly to a monolayer [17]. From Table 4, the $K_L$ is larger than 1 ($K_L = 2.019 \ (25 ^\circ C)$, $K_L = 1.680 \ (40 ^\circ C)$), so the adsorption of rhodamine 6G by...
MB500 was favorable [37]. For Freundlich isotherm, the $1/n = 0.1$ to 0.5 (adsorption process is magnificent): $1/n = 0.5$ to 1 (process is easy to absorb); $1/n > 1$ (process is difficult to absorb). In the study, $1/n$ value is more than 1, indicating the Freundlich adsorption process is difficult for rhodamine 6G adsorption on MB500 and mainly in monolayer [19, 21, 22].

The kinetic mechanism for the adsorption of rhodamine 6G dye on magnetic biochar is an important study to provide information on the reaction pathway and the rate-controlling mechanism of exchange reactions [19]. The adsorption kinetics of rhodamine 6G in solution by MB500 at 25 and 40 °C are shown in figure 7. As the temperature increased, the maximum rhodamine 6G adsorption capacity was slightly decreased. The fits of the pseudo-first and pseudo-second order kinetic models to rhodamine 6G adsorption by MB500 are summarized in table 5. At the initial concentration of dye (100 mg l$^{-1}$), the adsorption of rhodamine 6G by MB500 is on the monolayer surface of MB500 and participated with the diffusion-controlled relating with external liquid film diffusion, surface adsorption and intra-particle diffusion of rhodamine 6G in MB500. The rate-limiting step and the linear form of pseudo-second order kinetic model confirm chemisorption in which liquid film diffusion, ion-exchange, intra-particle diffusion, and surface adsorption affected rhodamine 6G adsorption rates [38, 39].

For adsorption thermodynamic study, the thermodynamic parameters including Gibbs free energy ($\Delta G^o$), enthalpy ($\Delta H^o$) and entropy ($\Delta S^o$) play a significant role in the determination of the behavior of the adsorption process (endothermicity or exothermicity). Therefore, these parameters can provide information on the influence of the temperature on the adsorption property of rhodamine 6G dye on Fe$_3$O$_4$ magnetic biochar [21]. The calculated thermodynamic parameters were listed in table 6. From table 6, the negative value of $\Delta G^o$ (~7.30
at 25 °C and −7.15 at 40 °C) and negative value of $\Delta H^0$ (−10.32) were observed which confirm the spontaneous and slightly exothermic adsorption processes of rhodamine 6G onto the Fe$_3$O$_4$ magnetic biochar (MB500) [17]. And, the negative value of $\Delta S^0$ (−0.010) might feature that adsorbate molecules lose at least one degree of freedom when they get adsorbed on the MB surface. It also validates that decreased randomness at the solid-liquid interface during the adsorption process [40, 41].

The proposed mechanism of rhodamine 6G absorption on MB500 was confirmed by the change in some functional groups. The FT-IR spectra of rhodamine 6G adsorbed on MB500 was shown in figure 8 and the detail of virations of the surface functional groups was also presented in table 3. In figure 8, FT-IR result was therefore used for preliminary qualitative analysis of the change in major functional groups present on pristine biochar surface after rhodamine 6G adsorption, and the FT-IR spectra and detail of MB500 comparing with rhodamine 6G adsorbed on MB500 were presented in figure 8 and table 3. When rhodamine 6G molecules were adsorbed onto the magnetic biochar (MB500) surface, some peaks of functional groups in the MB500 were shifted or weaken, such as stretching vibrations of C=O at 1617 cm$^{-1}$ (shifted to 1619–1615 cm$^{-1}$), C–O at 1087 cm$^{-1}$ (shifted to 1050 cm$^{-1}$) and Fe–O in Fe$_3$O$_4$ moiety at 586 cm$^{-1}$ (shifted to 562 cm$^{-1}$). Therefore, the functional

| Table 5. Kinetic model fitting to rhodamine 6G dye adsorption by MB500. |
|-----------------------------|---------------------|------------------------|
| Pseudo-first order          |                      |                        |
| Temp. | $q_e$, exp | $q_e$, cal | $k_1$, 1/min | $R^2$ |
| 25 °C | 9.76       | 10.09       | 0.367       | 0.9999 |
| 40 °C | 9.71       | 8.28        | 0.453       | 0.9956 |
| Pseudo-second order         |                      |                        |
| Temp. | $q_e$, exp | $q_e$, cal | $k_2$, g/mg·min | $R^2$ | h |
| 25 °C | 9.76       | 10.31       | 0.178       | 0.9980 | 18.96 |
| 40 °C | 9.71       | 9.92        | 0.587       | 0.9995 | 57.70 |

| Table 6. Thermodynamic parameters of rhodamine 6G adsorption on Magnetic biochar (MB). |
|-----------------------------|---------------------|------------------------|
| Temp., °C | $\Delta G^0$, kJ/mol | $\Delta H^0$, kJ/mol | $\Delta S^0$, kJ/(mol·K) |
| 25     | 19.011       | −7.30       | −10.32       | −0.010   |
| 40     | 15.574       | −7.15       |                     |          |
groups on the surface of magnetic biochar participate in the binding of biochar and rhodamine 6G molecule through hydrogen bonding, ion exchange, surface complexation and cation–π interaction [17–19].

4. Conclusion

In the study, biochar from agricultural waste biomass of rice husk RD6 was prepared by the slow pyrolysis process. Rice husk biochar exhibits the surface morphology. The materials of Fe₃O₄ nanoparticles composited on biochar show better adsorption capacity for rhodamine 6G dye removal compared with pristine biochar. The presence of Fe–O functional groups on the surface of the magnetic biochar which changes in the FT–IR wavelength upon the binding with rhodamine 6G confirming Fe₃O₄ composited on biochar surface plays an important role for rhodamine 6G removal. The adsorption isotherm study indicates that the Langmuir isotherm model agreed well with the experimental data which describes the adsorption process is favorable and mainly on monolayer of magnetic biochar adsorbent. The adsorption kinetic study was described by the pseudo-first order and pseudo-second order kinetic models in which the adsorption process is controlled by various chemisorption mechanisms. Hence, this can be concluded that the adsorption processes are contributed to both chemical and physical processes. The thermodynamic study also reviews the exothermic reaction of rhodamine 6G on magnetic biochar. From this study, the low-cost and abundantly available adsorbent from rice husk which was improved by Fe₃O₄ composited on biochar shows considerable adsorption efficiency on the removal of rhodamine 6G dye in aqueous solution. And this adsorbent can be used alternatively as an eco-friendly adsorbent for wastewater treatment.

Acknowledgments

This work was supported by the grants from Mae Fah Luang University (No. DR256201012009). The authors also acknowledge the extensive help given by the Office of Scientific Instrument and Testing, Prince of Songkla University and Scientific and Technological Instrument Center, Mae Fah Luang University for assistance with relevant experimental analysis.

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