Preparation of Lignin-Based Magnetic Adsorbent From Kraft Lignin for Adsorbing the Congo Red

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INTRODUCTION

Due to the impact of environmental issues of dye wastewater from printing and dyeing mill on public health, it has become a global concern (Liu J. et al., 2018). Most of these dyes are soluble in water, complex in composition, and high in organic pollutants (Liu L. et al., 2018). Most of them are difficult to biodegrade and even cause “Triple induction” (carcinogenic, teratogenic, mutagenic) (Konicki et al., 2018; Sham and Notley, 2018). Therefore, the dye wastewater must be properly treated and protected, otherwise it will cause harm to aquatic species and the environment (Ghaedi et al., 2012; Gu et al., 2021). Congo red is a typical biphenyl amine azo dye, which will produce toxic substances in an anaerobic environment and easily accessible to water bodies during industrial

The utilization of lignin from different lignocellulosic biomass is the hot topic for the biorefinery of biomass. In this paper, magnetic lignin nanoparticles (MLN) were prepared by kraft lignin from bamboo residue and Fe₃O₄ with different ratios via Mannich reaction. The surface morphology and structure of magnetic lignin were characterized and analyzed by X-ray powder diffraction, Fourier transform infrared spectroscopy, and transmission electron microscopy, which confirmed that the MLN were successfully prepared. The performance of MLN adsorbents was evaluated by adsorbing Congo red solution at different initial concentrations and contact times. The results showed that Fe₃O₄@lignin (1:0.5) had the best adsorption effect on Congo red solution. When the concentration of Congo red reached 0.6 g/L, Fe₃O₄@lignin (1:0.5) had the best adsorption effect on Congo red, reaching 95.5% in only 30 min. As lignin is modified by Fe₃O₄, it can be recovered by magnetic substances after adsorption and has good reuse performance. The results of adsorption kinetics and adsorption isotherm showed that except for the adsorption process of Fe₃O₄@lignin (1:0.5), which is consistent with the chemical adsorption of the multimolecular layer, the adsorption process of other adsorbents is in accordance with the chemical adsorption of the monomolecular layer. In terms of environmental protection and adsorption efficiency, and MLN has become an ideal adsorbent for Congo red dyes due to its simple preparation, superior performance, and convenient recovery.

Keywords: kraft lignin, Mannich reaction, Congo red, magnetic adsorbent, preparation
production and use (Zhao et al., 2018). It is one of the representative pollutants in printing and dyeing wastewater. At present, the treatment methods of dye wastewater include radiation method, magnetic separation method, an adsorption method, membrane separation method, and photocatalytic oxidation method (Holkar et al., 2016; Cui et al., 2018; Wang et al., 2018b). Adsorption method is a common method for wastewater treatment because it is efficient, simple, recyclable, produces less secondary pollution, and does not change the structure of pollutants in dye wastewater (Yang et al., 2019).

In recent years, several adsorbents such as activated carbon, zeolite, ion exchange materials, and bentonite have been widely used in dye adsorption. However, due to the problems of difficult recovery, difficulty in regeneration and reuse, high price, and low adsorption efficiency of these adsorbents, if these adsorbents are used for large-scale treatment of dye wastewater adsorption, the cost is relatively expensive (Hassan and Carr, 2018).

As a renewable biomass material, lignin is one of the main components in nature plants, with a wide range of sources (Klapiszewski et al., 2017a; Pei et al., 2020; Zheng et al., 2021). In industry, lignin is mainly separated and extracted from black liquor discharged during the pulping and papermaking process, and can be processed into various functional materials with high value and applied (Kai et al., 2016; Dong et al., 2020a). Lignin contains a large number of functional groups such as benzene ring, hydroxyl group, carbonyl group, carboxyl group, methoxy group, and unsaturated bond (Gall et al., 2017; Dong et al., 2020b). It has the ability of ion exchange and adsorption, which is more advantageous than other adsorbents such as activated carbon, macromolecule resin, and minerals, and has attracted extensive attention (Upton and Kasko, 2016). However, lignin is difficult to separate and recover, and its application is greatly restricted (Humpert et al., 2016). It can be solved by combining with magnetic materials to produce magnetic lignin nano-materials. The magnetic components are mainly nickel, iron, cobalt, iron, and alloy oxides such as γ-Fe₂O₃ and Fe₃O₄. Fe₃O₄ is widely used as the magnetic component of magnetic polymer materials due to its advantages of simple preparation process, stable performance, and low toxicity (Siyasuk et al., 2018; Wang et al., 2018a; Lou et al., 2020, 2021). MLN, such as Fe₃O₄@lignin, can be prepared by Mannich reaction, which is a condensation reaction between amine compounds and aldehydes and containing active hydrogen atoms in lignin (Wang B. et al., 2018). The Mannich reaction usually involves the formation of N-hydroxymethyl amines by the reaction of the amine group with the aldehyde group, and condensation of the hydrogen atoms by the substitution of the amine group, namely, the amine methylation reaction (Jiao et al., 2019).

This reaction is particularly useful for the synthesis of β-aminocarbonyl derivatives (Kobayashi et al., 2011). In the Mannich reaction, the crosslinking agent between fatty amine and lignin consists of an aldehyde group, and formaldehyde is currently the most widely used aldehyde (Gao et al., 2020). Because the Mannich reaction is simple, effective, and without by-products, it is widely used in the synthesis of new materials (Guo et al., 2020). Luo et al. (2017) recovered lignin from black liquor, modified the lignin by Mannich reaction with triethylenetetramine (TETA), and then chelated iron to the aminated lignin to obtain a highly efficient phosphate adsorbent. The magnetic lignin prepared can be simply recovered by using a magnetic substance. Therefore, lignin can be fully utilized, and lignin can be recycled and reused through magnetic properties, thereby improving the economic value of lignin (Calvo-Flores and Dobado, 2010). In the current research, few people load lignin on magnetic nanoparticles of Fe₃O₄ and use the MLN for dye adsorption, which is also the starting point of our work.

In this study, the magnetic Fe₃O₄ with good performance was prepared by co-precipitation method, and then it reacted with ethylsilicate (TEOS) and (3-aminopropyl) triethoxysilane (APTES) to obtain the aminated Fe₃O₄. Then, the aminated Fe₃O₄ was reacted with lignin to obtain a green recyclable MLN adsorbent. The surface morphology and phase composition of magnetic lignin were characterized and analyzed by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), and apply it to the removal of Congo red. In addition, the adsorption kinetics and adsorption isotherm of MLN for adsorbing the Congo red were also evaluated.

**MATERIALS AND METHODS**

**Materials**

Kraft lignin was obtained from black liquor of bamboo residues via acid precipitation. The textile dye Congo red was purchased from China National Pharmaceutical Holding Chemical Reagent Co., Ltd. and was used without further purification. All other chemicals were also used without any other purification.

**Preparation of Fe₃O₄**

Fe₃O₄ was prepared by the co-precipitation method, based on the principle of Fe²⁺+2Fe³⁺+8OH⁻ = Fe₃O₄+4H₂O. Specifically, 6.1 g FeCl₃·6H₂O and 4.2 g FeSO₄·7H₂O were dissolved in 100 ml of deionized water, added into a 250-ml three-necked flask. Then the solution was heated to 85°C in an oil bath under an argon atmosphere and mechanically stirred at 300 rpm. When at 70°C, 10 ml ammonia water was added and continued to heat for 1 h at 85°C. After the reaction was finished, the black precipitate was separated from the reaction medium by an external magnetic field and ultrasonically washed three times with deionized water until the pH is neutral, to obtain Fe₃O₄ particles.

**Preparation of Fe₃O₄ @lignin Composites**

Fe₃O₄ nanoparticles prepared by the aforementioned method were dispersed in 150 ml of ethanol/water (4:1, v/v) solution, and then the mixture was dispersed uniformly in ultrasonic to form magnetic fluid and added into a 250-ml three-necked flask. Then 5 ml of tetraethyl orthosilicate (TEOS) was added, and ammonia water was used to adjust the pH to 9.0. Then the solution was heated to 45°C for 16 h in an oil bath under an argon atmosphere and mechanically stirred at 300 rpm. After 16 h, different proportions of lignin solution (1.0:5, 1.1: ,1.2:1.3), 7 ml formaldehyde, and 10 ml
of 496 nm to determine the concentration of Congo red. Further, for 5 h. The absorbance value of supernate was measured at λ = 510 nm. The absorption value of supernate was measured at 496 nm to determine the concentration of Congo red. Further, the adsorption rate and the absorption capacity were calculated.

In all experiments, the equilibrium adsorption amount qe (mg/g) was determined by the mass balance of the dye:

\[ q_e = \frac{(C_o - C_e) \times V}{m} \]  

The initial concentration and adsorption equilibrium concentration of the dyes were C_o (mg/L) and C_e (mg/L), respectively. V (ml) is dye solution's volume and m (g) is adsorbent's amount.

**Adsorption Kinetics**

To study the control mechanism of the adsorption process, such as mass transfer or chemical reaction, the pseudo-first-order, pseudo-second-order dynamic models and the intraparticle diffusion model given in Eqs. 2–4 were used respectively.

\[ \log q_e - q_t = \log q_e - \frac{k_1}{2.303} t \]  

\[ \frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \]  

\[ q_t = k_i t^{1/2} + C \]

q_t (mg/g) is the adsorption capacity at t (min); q_e (mg/g) is the adsorption capacity when equilibrium is reached, t is the adsorption time, and C is a constant related to the boundary layer thickness; k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are pseudo-first-order and pseudo-second-order kinetic adsorption rate constants, respectively, and k_i (mg/g min^{1/2}) is the intraparticle diffusion rate constant. q_e and k_1, k_2, and k_i can be determined from the experimental data by equations.

**Adsorption Isotherm**

The adsorption equation of the Langmuir model is shown in Eqs. 5 and 6:

\[ \frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \]  

\[ R_L = \frac{a}{(1 + b C_o)} \]

q_e: Adsorption mass (mg/g) during adsorption equilibrium of Congo red solution

C_e: equilibrium concentration of Congo red solution (mg/L)

q_m: maximum adsorption value of adsorbent (mg/g)

b: Langmuir adsorption constant (L/mg)

Adsorption equation of Freundlich model is shown in Eq. 7:

\[ \ln(q_e) = \ln(K_f) + \frac{1}{n} \ln(C_e) \]

q_e: Adsorption mass (mg/g) during adsorption equilibrium of Congo red solution

C_e: equilibrium concentration of Congo red solution (mg/L)

K_f: Freundlich equilibrium constant, roughly indicating the adsorption capacity of the adsorbent (mg/g)

\( \frac{1}{n} \): Heterogeneity factor, related to adsorption strength. When 0 < 1/n < 1, the adsorption is advantageous; if
1/n = 1, the adsorption is linear, there is no interaction between adsorbates; when l/n > 1, the adsorption is negative (Wang et al., 2018b).

RESULTS AND DISCUSSION

Characterization of Adsorbents

In this paper, through the Mannich reaction, the magnetic Fe₃O₄ reacted with TEOS and APTES in turn, and finally reacted with lignin to obtain MLN. The specific mechanism is shown in Figure 1. Characterization analysis was performed on Fe₃O₄@lignin to understand the structural characteristics of the samples.

The morphology and particle size distribution of the Fe₃O₄ and Fe₃O₄@lignin composites were carried out by transmission electron microscope (TEM). It can be seen from Figure 2 that the average particle size of Fe₃O₄ is about 20 nm, which is spherical. The particles in Fe₃O₄ have a strong agglomeration phenomenon. This is due to the large specific surface area of Fe₃O₄ nanoparticles, the surface energy is in an unstable state, and the intermolecular force, hydrogen bond, static electricity, and other forces make it agglomerate together. When Fe₃O₄ nanoparticles are loaded with lignin, Fe₃O₄@lignin has an obvious core–shell structure, and lignin is present on the outer layer of Fe₃O₄. At the same time, the particle agglomeration phenomenon is suppressed to a certain extent and has a good dispersion performance. This may be due to the decrease of the surface energy of the composite magnetic particles after Fe₃O₄ is loaded with lignin and the reduction of the interaction force between the particles, thereby improving the dispersion performance. In addition, the particle size of Fe₃O₄@lignin is equivalent to that of Fe₃O₄, indicating that Fe₃O₄ modified APTES and lignin has almost no effect on the size of magnetic nanoparticles. The magnetite–lignin hybrid materials obtained by Klapiszewski et al. (2017b) also have the same aggregation tendency.

X-ray diffraction (XRD) was used to study the phase and crystal structure of the sample. The XRD patterns of five samples lignin and Fe₃O₄@lignin composites nanoparticles are shown in Figure 3. According to the literatures (An et al., 2017; Wang et al., 2019; Jia et al., 2021) that three diffraction peaks appear on the spectrum of Fe₃O₄ nanoparticles at 30.1°, 35.5°, and 42.9°, which were attributed to the (220), (310), and (401) crystal planes of inverse spinel Fe₃O₄, respectively. For lignin, only a broad diffraction peak appears around 20°, which is the diffraction peak in the amorphous region of lignin. When lignin is loaded with Fe₃O₄, the obtained magnetic lignin Fe₃O₄@lignin composites also show three crystal plane diffraction peaks of inverse spinel Fe₃O₄, and the position of the diffraction peaks does not shift, indicating that in the process of loading lignin to Fe₃O₄, it did not change its crystals.

When lignin is loaded on the outer layer of Fe₃O₄ nanoparticles, it will not only directly affect the iron distribution of the particles, but also have a great influence on the magnetic strength of the particles (Mikhaylova et al., 2004). In addition, the magnetic strength of the magnetic adsorbent will directly affect the recovery process of the material. Therefore, the magnetic strength of Fe₃O₄@lignin was evaluated and shown in Figure 4. It can be seen that the hysteresis loops of the four Fe₃O₄@lignin composites all cross the origin and are symmetrical, which shows that the coercivity of the magnetic lignin is zero. At the same time, no remanence and hysteresis were found in these 4 hysteresis loops, indicating that the prepared magnetic Fe₃O₄@lignin composites all showed good superparamagnetism. Specifically, the saturation magnetization of Fe₃O₄@lignin with ratios of 1:0.5, 1:1, 1:2, and 1:3 was 23, 21, 16, and 15 emu g⁻¹, respectively.
The results indicated that the Fe$_3$O$_4$ loaded by a greater amount of lignin could decrease its magnetic strength. The reason for this phenomenon can be explained by the fact that the coating of lignin is a non-magnetic polymer. More coatings will increase the dipole moment of Fe$_3$O$_4$ particles and decrease the magnetic content, which will lead to a decrease in magnetic properties (Deatsch and Evans, 2014). In general, the results of the hysteresis curve show that the obtained Fe$_3$O$_4$@lignin composite material has good magnetic properties and can be easily recovered when used as an adsorbent under an external magnetic field.

Infrared spectroscopy was used to analyze the structure of the prepared Fe$_3$O$_4$@lignin. It can be seen from Figure 5 that the lignin samples show typical signal peaks of the lignin benzene ring structure at 1,598, 1,510, and 1,420 cm$^{-1}$ (Jiang et al., 2019). In addition, the peak at 1,360 cm$^{-1}$ is attributable to the absorption peaks of lignin syringyl and condensed guaiacyl, and the peak at 1,118 cm$^{-1}$ is attributable to the “S” type lignin absorption peak. The peak at 1,034 cm$^{-1}$ indicates the vibration
The iron content of magnetic Fe₃O₄@lignin is analyzed and shown in Table 1. According to Table 1, the iron content of the samples Fe₃O₄@lignin (1:0.5), Fe₃O₄@lignin (1:1), and Fe₃O₄@lignin (1:2) gradually increased. For Fe₃O₄@lignin (1:2), the iron content is the highest, and Fe₃O₄@lignin (1:3) is decreased. This is because the content of Fe₃O₄ in the prepared raw material is constant, and the maximum grafting number of Fe₃O₄ and lignin is fixed.

**Table 1 | Iron content of magnetic lignin nanoparticles.**

| Sample             | Iron concentration (mg/g) |
|--------------------|---------------------------|
| Fe₃O₄@lignin (1:0.5) | 2.71                      |
| Fe₃O₄@lignin (1:1)  | 3.41                      |
| Fe₃O₄@lignin (1:2)  | 5.28                      |
| Fe₃O₄@lignin (1:3)  | 3.97                      |

*Iron concentration (mg/g) is defined as the mass of iron ions (mg) per gram of sample.*
Based on the analysis of the initial concentration and adsorption time, it can be found that Fe₃O₄@lignin (1:0.5) is superior than other MLN to adsorb Congo red. Moreover, the adsorption capacity of 0.6 g/L Congo red solution by Fe₃O₄@lignin (1:0.5) for 30 min is the equilibrium adsorption amount, which is the focus of this study.
Intraparticle diffusion model

k

Pseudo-second order

q

Figure 7

adsorption mechanism of prepared MLN, which is shown in different concentrations of dyes were used to investigate the Adsorption isotherms play an important role in understanding Adsorption Kinetics

The pseudo-first-order kinetic equation assumes that the adsorption process is controlled by diffusion. The pseudo-second-order kinetic equation assumes that the adsorption rate of Fe

TABLE 2 | Kinetic parameters for the adsorption of Congo red dye on lignin and magnetic lignin composites.

| Kinetics model                  | Parameter       | Lignin   | Fe

0.5 @lignin | 1:0.5 | 1:1 | 1:2 | 1:3 |
|-----------------|---------------|---------|-------|
| Pseudo-first order | q_{exp} (mg/g) | 37.43   | 237.69 | 152.44 | 25.78 | 26.73 |
|                 | q_{cal} (mg/g) | 34.52   | 236.60 | 136.43 | 21.14 | 24.66 |
|                 | k_{1} (x 10^{-2}/min) | 0.10 | 17.90 | 6.30 | 4.10 | 2.40 |
|                 | R^2           | 0.89 | 0.99 | 0.68 | 0.49 | 0.83 |
| Pseudo-second order | q_{exp} (mg/g) | 37.43 | 237.69 | 152.44 | 25.78 | 26.73 |
|                 | q_{cal} (mg/g) | 32.67 | 261.13 | 148.27 | 22.28 | 28.21 |
|                 | k_{2} (x 10^{-2} g/mg min^{-1}) | 0.06 | 0.12 | 0.07 | 0.33 | 0.11 |
|                 | R^2           | 0.93 | 0.98 | 1.00 | 0.64 | 0.99 |
| Intraparticle diffusion model | k_{i} (mg/g min^{-1/2}) | 2.45 | 1.57 | 4.59 | 1.04 | 1.21 |
|                 | C (mg/g)      | 1.90 | 216.00 | 80.18 | 8.48 | 7.50 |
|                 | R^2           | 0.94 | 0.46 | 0.94 | 0.94 | 0.97 |

Adsorption isotherms play an important role in understanding the adsorption mechanism for different adsorbent. In this study, different concentrations of dyes were used to investigate the adsorption mechanism of prepared MLN, which is shown in Figure 7.

The pseudo-first-order kinetic equation assumes that the adsorption process is controlled by diffusion. The pseudo-second-order kinetic equation assumes that the adsorption rate is controlled by a chemical adsorption mechanism (Nair et al., 2014). This chemisorption involves electron transfer or electron pairing between the adsorbent molecules and the adsorbates. For the intraparticle diffusion equation, if there is intraparticle diffusion, q

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TABLE 3 | Adsorption isotherm model parameters.

| Parameters                | Lignin | Fe

0.5 @lignin | 1:0.5 | 1:1 | 1:2 | 1:3 |
|------------------------|--------|-------|
| Langmuir               |        |       |
| q_{m} (mg/g)           | 28.72  | 470.02 | 206.29 | 25.30 | 27.10 |
| b (x 10^{-2} L/mg)     | 1.10   | 0.11  | 0.28  | 2.27  | 2.33 |
| R^2                    | 0.96   | 0.98  | 0.98  | 0.97  | 0.93 |
| R_b = 1/(1+bC_0)       | 0.90   | 0.98  | 0.97  | 0.78  | 0.81 |
| Freundlich             |        |       |
| K_f (L/g)              | 2.28   | 0.42  | 0.74  | 1.97  | 1.99 |
| 1/n                    | 0.41   | 0.98  | 0.95  | 0.44  | 0.44 |
| R^2                    | 0.80   | 1.00  | 0.98  | 0.89  | 0.82 |

(Fang et al., 2018). Jiang et al. (2019) showed that the adsorption rate was generally controlled by three stages. The first stage is the initial stage of the reaction, which is the diffusion stage of the dye in the boundary layer, where the adsorption capacity increases faster. As the reaction continues, the adsorption capacity in the second stage still increases, but the increase rate slows down. The reaction process in this stage is controlled by intraparticle diffusion. In the third stage, the adsorption reaches equilibrium. It can be seen from Figure 7D that the adsorption rate of Fe

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O_4@lignin (1:0.5) is faster, and the figure shows the three stages of the adsorption process. While the adsorption rate of the other samples is slower, the figure only shows the second step between the initial rapid external diffusion stage and the equilibrium stage in the adsorption process. The adsorption rate of the second step is relatively stable to each sample, so the second step is chosen to characterize the rate parameters corresponding to diffusion.

The calculated k_{i} values for each initial concentration are shown in Table 2. It can be seen that the R^2 values of the lignin and Fe

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O_4@lignin (1:1) (1:2) (1:3) for the diffusion model were all above 0.9. This indicated that the adsorption process could be followed by an intra-particle diffusion after around 10 min (Liu L. et al., 2018). In contrast, the R^2 value of the adsorption process also includes complex mechanism pathways.
An, L., Si, C., Bae, J. H., Jeong, H., and Kim, Y. S. (2020). One-step silanization and the adsorption capacity increased with the increase of between heterogeneous multilayer molecules and adsorbates, to the formation of a single layer; the adsorption is an interaction adsorption isotherm describes reversible adsorption not limited on its surface is equal. Adsorption migration did not occur after Langmuir adsorption isotherm adsorption. The Freundlich adsorption isotherm assumes that the adsorbate adsorbs on the monolayer of the surface of the homogeneous adsorbent, and adsorption activation energy of each molecule adsorbed on its surface is equal. Adsorption migration did not occur after Langmuir adsorption isotherm adsorption. The Freundlich adsorption isotherm derives reversible adsorption not limited to the formation of a single layer; the adsorption is an interaction between heterogeneous multilayer molecules and adsorbates, and the adsorption capacity increased with the increase of the concentration.

From the correlation coefficient (R^2) in Table 3, it can be seen that Fe₃O₄@lignin (1:0.5) Freundlich isotherm model R^2 is closer to 1 than the Langmuir isotherm model R^2. The Freundlich isotherm R^2 for Fe₃O₄@lignin (1:1) is consistent with the Langmuir model R^2. Other adsorbents perform better on Langmuir isotherms than Freundlich isotherms, indicating that except for Fe₃O₄@lignin (1:0.5), (1:1), the process of adsorbing Congo red is multilayer adsorption, and the adsorption processes of other adsorbents are all monolayer adsorption. What is more, the value of the separation factor R_l is greater than 0 and less than 1, which results demonstrated that the adsorption process is favorable. This result is consistent with the results of Li et al. (2019) that showed the adsorption of Congo red is more consistent with the Langmuir model, indicating that the adsorption process of Congo red is monolayer adsorption.

The value of theoretical maximum of adsorption capacity (q_m) of the lignin and MLN of Fe₃O₄@lignin (1:0.5), Fe₃O₄@lignin (1:1), Fe₃O₄@lignin (1:2), and Fe₃O₄@lignin (1:3) derived from the Langmuir model were 28.72, 470.02, 206.29, 25.30, and 27.10 mg/g, respectively, of which lignin, Fe₃O₄@lignin (1:2), and Fe₃O₄@lignin (1:1) were consistent with the corresponding experimental values. The q_m values of Fe₃O₄@lignin (1:0.5) and Fe₃O₄@lignin (1:1) were higher than the experimental data, indicating that these two samples do not conform to the Langmuir model, which is consistent with previous conclusions. According to the Freundlich model, 1/n values of lignin, Fe₃O₄@lignin (1:2), and Fe₃O₄@lignin (1:3) are greater than 0 and less than 1, showing that the adsorption is advantageous. 1/n values of Fe₃O₄@lignin (1:0.5) and Fe₃O₄@lignin (1:1) are close to 1, showing that the adsorption is linear and there is no interaction between adsorbates. The reason for this phenomenon might be due to the high adsorption efficiency of Fe₃O₄@lignin (1:0.5) and Fe₃O₄@lignin (1:1), which leads to inaccurate adsorption model.

CONCLUSION

Studies have shown that MLN is an effective Congo red adsorbent with good adsorption performance, simple preparation, and easy recovery, which is an ideal adsorbent for Congo red dye. For the prepared MLN with different ratios of Fe₃O₄@lignin, Fe₃O₄@lignin (1:0.5) showed the best adsorption performance on Congo red with adsorption rate of 95.5% and adsorbing ability of 229 mg/g. The kinetics and isothermal models show that adsorption process of Fe₃O₄@lignin (1:0.5) belonged to the chemical adsorption of the multimolecular layer, and the adsorption process of other adsorbents is in accordance with the chemical adsorption of the monomolecular layer.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

LF: investigation. HW and YT: supervision. YS: writing. QY: writing—review and editing. All authors contributed to the article and approved the submitted version.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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