Magnetic lignin-based carbon nanoparticles and the adsorption for removal of methyl orange

Ying-zhi Ma\textsuperscript{a}, Da-feng Zheng\textsuperscript{*a,}\textsuperscript{b}, Zhen-ye Mo\textsuperscript{a}, Rui-jing Dong\textsuperscript{a}, and Xue-qing Qiu\textsuperscript{a,}\textsuperscript{b}

\textsuperscript{a} Guangdong Engineering Research Center for Green Fine Chemicals, College of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China

\textsuperscript{b} State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, China

**GRAPHICAL ABSTRACT**

![Graphical Abstract](image)

**ABSTRACT**

In order to expand the application of lignin, magnetic lignin-based carbon nanoparticles (MLBCN) were synthesized using a precipitation-carbonization process and the structure was confirmed by FTIR, XRD, Raman, BET, SEM, DLS and VSM. The adsorption of MLBCN for methyl orange was consistent with the Langmuir model and pseudo-second-order model, showing monolayer...
adsorption, with a maximum adsorption capacity of 113.0 mg/g and chemisorption being the rate-controlling step. This process was exothermic and of entropy reduction, showing spontaneous below 35°C. MLBCN could be used under near neutral conditions and easily regenerated. This study demonstrates that MLBCN is promising as an efficient, sustainable absorbent.

**Keywords:**
Magnetic lignin-based carbon nanoparticles
Characterization
Adsorption
Methyl orange
Regeneration

1. **Introduction**

Magnetic materials are widely used in a wide variety of applications such as magnetic fluids [1], drug [2], separation [3], nuclear magnetic resonance [4], and trace detection [5]. Functionalization of magnetic materials by various polymers is an important way to increase the range of applications, and has become a major focus of magnetic material research [6, 7]. The primary functionalization methods used are adsorption, in situ synthesis, and indirect modification. By adjusting pH the polymer surfaces become charged, allowing their adsorption onto the surface of magnetic nanoparticles via electrostatic attraction. Peng et al. [8] studied the adsorption of bovine serum albumin (BSA) on Fe₃O₄ nanoparticles at different pH and salt concentrations. The results illustrated that at the isoelectric point, there was minimum repulsion between BSA and the Fe₃O₄ nanoparticles and the adsorption of BSA onto the nanoparticles was at a maximum. In-situ synthesis is another one of the common synthesis methods for polymer-modified magnetic nanoparticles. The advantage of this method is the magnetic particles are not easily agglomerated in solution. Mornet, et al. [9] first formulated a DNA-bound Fe²⁺ and Fe³⁺ salt complex then produced DNA-modified Fe₃O₄ composite nanoparticles by adding aqueous ammonia. The third method involves introducing reactive functional moieties such as amino, sulfhydryl, and hydroxyl groups onto the magnetic nanoparticle carrier first, then combining these groups with modifiers. Xu et al. [10] used dopamine as a chelator to introduce amino groups on the surface of magnetic iron oxides, then grafted proteins
to these particles via peptide bonds.

In recent years, studies on carbon nanomaterials had also been of great interest, especially in the application of adsorption. Norouzi et al. [11] reported an activated carbon prepared from Date Press Cake. It showed high specific surface area and microporous texture. The resulting activated carbon successfully adsorbed Cr(VI) from aqueous solutions with maximum monolayer adsorption capacities as high as 282.8 mg/g (pH=2) and 198.0 mg/g (pH=5). Kumar et al. [12] prepared a nano zero valent iron stacked activated carbon (NZVI-AC), which exhibited efficient performance in malachite green dye biosorption properties. It had a Langmuir adsorption capacity of 187.3 mg/g and was recommended for the removal of dyes from industrial effluent. Kong et al. [13] produced activated carbon from hide waste (HWAC) and high-pressure steaming hide waste (HWSAC), then studied the adsorption of Ni(II). The results indicated that the adsorption capacity of Ni(II) for both HWAC and HWSAC increased with the increase in pH value, Langmuir isotherm and Pseudo-second order model fitted well for both the two adsorbents. Tiwari et al. [14] prepared nitrogen enriched carbon adsorbent by carbonizing the low-cost urea formaldehyde resin. The highest adsorption capacity of 2.43mmol/g for CO₂ for this adsorbent was obtained at 303 K under pure CO₂ flow. The heterogeneity of the adsorbent surface was confirmed from the Langmuir and Freundlich isotherms fits. Zhang et al. [15] studied the adsorption behaviors of five typical volatile organic compounds (VOCs) onto a commercial activated carbon (CAC). The adsorption capacities of these five kinds of typical VOCs, including acetone, ethyl acetate, propyl acetate, butyl acetate, and isopropanol, were 289.8, 389.4, 443.7, 467.4, and 474.3 mg/g⁻¹, respectively. The Boltzmann model and the Banham percent adsorption equation could well fit the data of the selected sorption periods. When used in the adsorption, carbon materials demonstrate excellent chemical resistance and superb interface properties [16]. However, to our knowledge, common adsorbents are not easy to recover from the aqueous solutions. Additionally, direct discard can increase the treatment cost and produce secondary pollution. Magnetic materials can solve the above difficulty easily. As a result, combination of carbon nanomaterials and magnetic materials would generate new materials which could be much more easily used in the field of adsorption and magnetic separation. Zhou et al. [17] synthesized carbon-Fe₃O₄ core–satellite nanospheres through successive steps of impregnation, ammoniation and carbonization. The nanoparticles exhibited the efficient removal of Rhodamine B from an aqueous solution. Zhou et al. [18] prepared Fe₃O₄@polydopamine core–shell
NPs by coating a layer of polydopamine (PDA) onto the surface of magnetic Fe₃O₄ NPs, and then carbonized Fe₃O₄@PDA to obtain Fe₃O₄@C NPs. Both NPs were tested as magnetic adsorbents for cationic and anionic dyes. The results showed that the removal efficiency of Fe₃O₄@C for methylene blue and methyl orange was about 50% and 70%, respectively. Gong et al. [19] presented a facile method to synthesize tiny Au satellites decorated Fe₃O₄@APF core-shell nanoparticles. The Fe₃O₄@APF@Au NPs possessed excellent catalytic activity as well as efficient reusability for the reduction of organic dyes. Yao et al. [20] prepared activated carbons with the surface decorated with Fe₃C/Fe₃O₄ nanosheets using a biomass tofu as the precursor. The dye adsorption capacity of this activated carbon was enhanced by five times. Li et al. [21] composed the aminated hollow magnetic nanospheres with oxidized mesoporous carbon to gain a good adsorption capacity for methylene blue at mild conditions. The results demonstrated that the adsorption was affected by the initial concentration, ionic strength, and temperature. Also the adsorption was well fitted with the Freundlich model and the pseudo-second-order model.

Lignin is the second most abundant biomass material on earth. It is estimated that global lignin production by the pulp and paper industry exceeds 50 million tons annually [22]. Among natural biomass materials, lignin has a higher carbon content and is a good carbon source [23]. As a result, carbon materials derived from lignin can be used as supercapacitors [24, 25] or sensors [26]. But up to now, most of lignin is used as an energy source via combustion; only a small percentage is modified for commercial application [27]. This low efficiency, low-value added usage of lignin is a major wastage and not conducive to sustainability. There have been few reports in the literature on the preparation of magnetic carbon nanomaterials using lignin as a precursor.

In this study, we reported the synthesis of magnetic lignin-based carbon nanoparticles and their adsorption characterization for methyl orange. In the preparation process, lignin was first coated onto the surface of iron oxide via precipitation to create a lignin-iron oxide complex. The complex was then calcined at high temperature to produce magnetic carbon nanoparticles. The nanoparticles were subsequently used in the removal of methyl orange from aqueous solution. This study would provide a new way to prepare magnetic carbon materials as well as increasing the added value of lignin, allowing for a more effective utilization of a major natural resource.

2. Experiments
2.1. Synthesis of lignin-coated iron oxide (LCIO)

5.4 g of ferric chloride hexahydrate and 3.5 g of ferrous sulfate heptahydrate were dissolved in 100 mL of deionized water and then transferred to a four-necked flask. Under vigorous stirring, 30 mL of 10 wt% ammonia was slowly added drop-wise to the solution as the temperature was increased gradually to 90°C. The color of the solution immediately changed from orange to black. During the reaction, the pH value of the solution was maintained at approximately 10. The precipitate was then aged at 90°C for 1.5 h. 3.0 g of lignin was dissolved in deionized water to make a 20 wt% lignin solution at pH=12, then added drop-wise into the reaction system after which 10 mL of 10 wt% ammonia was added to the system. The mixture was then incubated with stirring at 90 °C for 2.0 h. When the reaction was completed, the magnetic composite particles were separated with a permanent magnet and washed twice with ethanol. The final lignin-coated iron oxide (LCIO) was dried under a vacuum at 60 °C and kept for further use.

2.2. Carbonization of LCIO

Under a N₂ atmosphere, LCIO was carbonized in a tube furnace at 500°C for 3.0 h. The final residue was cooled down and ground to obtain magnetic lignin-based carbon nanoparticles (MLBCN). After dissolving the lignin in a certain weight of MLBCN by alkali dissolution, the residual Fe₃O₄ was dried and weighed. The content of carbon in the MLBCN was calculated through the weight lost method. Under the optimal process, the content of carbon in MLBCN was calculated to be 20wt%.

1.3. Characterization of MLBCN

MLBCN were characterized using different techniques in order to characterize its physical properties. FT-IR spectra were recorded using a Nexus spectrometer (Thermo Nicolet Corp., USA). The dried nanoparticles were embedded in KBr pellets to a concentration of approximately 1 mg/100 mg. A scanning region of 400~4000 cm⁻¹ was recorded, with a resolution of 4 cm⁻¹ and 16 scans. XRD analysis using Cu Kα radiation (λ = 1.54178 Å) was carried out on a X-ray diffractometer (XD-3A, Shimadzu, Japan) with Bragg–Brentano geometry for 2θ values in a range of 20~70°. N₂ gas adsorption and desorption analysis was carried out using BET analyzer (ASAP2020, Micromeritics Corp., USA) at constant temperature (-196°C). The dry samples were
pretreated for 2 h at 200°C under N₂ atmosphere to remove any surface water or gas. The surface area of samples was calculated using the BET method. Morphological analysis was done using SEM (S-4800, Hitachi, Japan). The particle size and zeta potential was measured using a Zetasizer Nano S analyzer (Malven Instruments Co. Ltd., UK). Raman spectra were determined on a Raman spectrometer (inVia Reflex, Renishaw Co. Ltd., UK). The magnetic properties of the MLBCN were determined using VSM (7410 series, Lakeshore Inc., US) at room temperature.

1.4. Adsorption of methyl orange

20 mg of MLBCN were added to an aqueous solution of methyl orange, and then oscillated in a water bath to allow for adsorption. After the adsorption was completed, the particles were magnetically separated from the solution using an external magnetic field for 5 min, after which the supernatant was removed. The methyl orange concentration of the supernatant was measured using a UV spectrophotometer (UV-1780, Shimadzu Co. Ltd., Japan) at a wavelength of 463 nm (which produces maximum UV absorption for methyl orange).

3. Results and discussion

3.1. Physical and chemical properties of MLBCN

The FT-IR spectra of MLBCN and LCIO are shown in Fig.1(a). In LCIO, the bands near 3425 cm⁻¹ are due to O-H stretching vibration and the bands near 3070 cm⁻¹ are due to asymmetrical C-H stretching vibration. The peaks at 1425 and 1608 cm⁻¹ are due to the skeletal vibration of the aromatic ring [28]. The peaks at 1268 and 1336 cm⁻¹ are due to the stretching vibration of aromatic groups. The peak at 1720 cm⁻¹ is due to the stretching vibration of carbonyl group. That at 560 cm⁻¹ is the characteristic adsorption peak for Fe₃O₄. The spectra demonstrate the formation of lignin-coated iron oxide nanoparticles. The nanoparticle structure in MLBCM was much more uniform than in LCIO. After carbonization most of the aromatic groups disappeared in MLBCM, but the Fe₃O₄ structure was retained as well as some O-H groups and C-C bonds, showing that certain functional groups could be maintained after carbonization at an appropriate temperature.

The XRD pattern of MLBCN revealed five characteristic peaks, as shown in Fig.1(b). The peaks with 2θ at 30.4°, 35.6°, 43.3°, 57.3°, and 62.8° were assigned to (220), (311), (400), (511), and (440) Bragg reflection respectively, which indexes to a Fe₃O₄ cubic spinel structure [29]. This
pattern indicates that MLBCN nanoparticles contain ultra-fine crystallite magnetite. In LCIO, similar diffraction peaks were found, but the intensity was lower than those in MLBCN. Two other peaks with 2θ at 22.3° and 32.9° were found in LCIO, which were assigned to (012), (104) reflection of FeO, illustrating that FeO was converted to FeO crystal through carbonization. The XRD patterns indicate that the FeO crystallite structure is rather uniform after carbonization, which enhances magnetic properties.

Fig.1(c) shows the N2 adsorption desorption isotherms of LCIO and MLBCN. They belong to the IV isotherms with H3 hysteresis loop [30], for they both rise rapidly in higher P/P0 and the adsorption hysteresis loops are generated, indicating that there are rich mesoporous in the structure of MLBCN [31, 32]. It can be concluded that the specific surface area of LCIO is 32.1 m²/g, and that of MLBCN is 82.8 m²/g, further showing carbonization benefits the formation of pores in MLBCN, resulting in the increase of the specific surface area. From Fig.1(d), it can be easily seen the average pore size in MLBCN is 12.0 nm, which belongs to mesoporous.
In the Raman spectroscopy of MLBCN (as shown in Fig.2a), The most prominent feature is that the $G$ band appearing at 1585 cm$^{-1}$ is Raman active for sp$^2$ carbon networks. The $D$ band appeared at 1355 cm$^{-1}$ is known as the disorder-induced character of graphite in porous carbon. The $I_D/I_G$ value shows the carbon in MLBCN is partly graphitized and mainly exists in the form of amorphous carbon with abundant pore structure [33].

The SEM images of MLBCN are shown in Fig.2(b) and Fig.2(c), demonstrating that MLBCN has a rough surface and large surface area. The irregular surface enhances the adsorption capacity. From the SEM images, it can also be seen that the particle size distribution of MLBCN is relatively uniform and narrow, with an average diameter of 76.6 nm, as shown in the DLS analysis (Fig.2(d)).

Fig.2(e) shows the zeta potential of MLBCN. It is obvious that the zeta potential increases as the decrease of pH, with a zero potential point at pH6.0. When pH<6.0, the zeta potential increases rapidly, indicating the functional groups and the surface of MLBCN are easy to be protonized. On the contrary, the zeta potential decreases under basic conditions, reflecting that the ferric ions can easily attract OH$^-$ in the alkaline solution.

The VSM analysis of MLBCN was carried out to determine the magnetic field strength (Fig. 2(f)). The results indicate that the LS-CCM is magnetically soft [34]. The saturation magnetization of the particles was 15.3 emu/g.
Fig. 2. Surface character and magnetism of MLBCN. (a) Raman spectrum, (b)(c) SEM, (d) DLS, (e) zeta potential, (f) VSM.

3.2. The application in the adsorption for methyl orange

3.2.1. Effect of initial concentration of methyl orange on the adsorption

Dye wastewater is one of the most difficult degradation resistant industrial wastewaters, and is also a main source of environmental pollution. Methyl orange is a dye used in the manufacture of textiles. It has an azo configuration and a quinoid configuration in the aqueous solution, which is common configuration in dye molecules. Methyl orange exhibits typical dye configurations, making it a model substance to study the adsorption behavior of MLBCN in dye wastewater treatment. Using the protocol from our previous study, 20 mg of MLBCN was placed in 20 mL of methyl orange solution with varying concentrations (20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 120 mg/L, 140 mg/L, 160 mg/L and 180 mg/L, respectively), with a final pH of 5.0. The solutions were oscillated in a 20°C water bath for 160 min. The percent adsorption and the adsorption capacity for methyl orange were measured against a standard curve and the results are shown in Fig. 3.

![Adsorption isotherm](image)

**Fig. 3.** The adsorption isotherm of methyl orange on MLBCN \( (T=20{\degree}C, \text{pH}=5.0) \).

With increasing methyl orange concentrations, adsorption capacity increased from an initial
16.8 mg/g to final of 98.9 mg/g indicating that adsorption capacity is proportional to methyl orange concentrations at first, for the reason that as the concentration of methyl orange increased, the probability of collision between the adsorption sites on the surface of MLBCN and methyl orange also increased. At the end, the adsorption capacity eventually reached a horizontal level, with increasing methyl orange concentrations no longer leading to increased adsorption capacity for the adsorption sites have been occupied.

At the same time, the percent adsorption of methyl orange basically decreased as the increasing of concentration, from 90.7% to 55.0%. Within the concentration range of 20-40 mg/L, the percent adsorption of methyl orange was much higher than other concentrations, indicating that in lower concentration (20-40 mg/L), the removal of methyl orange by MLBCN was more complete.

Generally, the adsorption isotherm model can be described by either the Langmuir equation or the Freundlich equation [35, 36].

The Langmuir equation can be expressed as

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m}$$  \hspace{1cm} (1)

where $q_e$ is the adsorption capacity of MLBCN at the adsorption equilibrium (mg/g); $q_m$ is the maximum adsorption capacity of MLBCN (mg/g); $C_e$ is the concentration of methyl orange in solution at equilibrium (mg/L); $b$ is the Langmuir adsorption equilibrium constant (L/mg).

The Langmuir equation assumes that the surface of the adsorbent is uniform, and any single adsorption site can only adsorb only one ion (or molecule). The adsorption performance of all adsorption sites is assumed to be the same, so the Langmuir equation describes a monolayer adsorption model. When the adsorption site on the surface of an adsorbent reaches a saturation state, the adsorption capacity is at a maximum, and there is no longer transfer of adsorbed ions (or molecules) at that time.

The Freundlich equation is given by

$$\ln q_e = \ln C_e / n + \ln k_f$$  \hspace{1cm} (2)

where $k_f$ is the constant related to the adsorption capacity; $1/n$ is the empirical constant, reflecting the heterogeneity of the adsorption reaction.

The Freundlich equation assumes that the surface of the adsorbent is heterogeneous and the
adsorption is not limited by the formation of monolayer. It is often used to describe reversible adsorption within different systems.

The equilibrium data is linearly fitted using either the Langmuir equation or the Freundlich equation, with the results shown in Fig. 4 and Table 1.

![Fig. 4](image-url)

**Fig. 4.** Line of best fit of adsorption isotherm by (a) Langmuir equation, (b) Freundlich equation.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Isotherm parameters obtained by fitting with the Langmuir and Freundlich models</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbate</td>
<td>Langmuir model</td>
</tr>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>113.0</td>
</tr>
</tbody>
</table>

Based on the intercept and slope of the line of best fit in Fig. 4(a), it can be calculated that $q_m$ for the adsorption for methyl orange is 113.0 mg/g and $b=0.0997$. The coefficient of determination ($R^2$) is 0.9970. It is known that the constant $b$ in the Langmuir equation is an important index for measuring the stability between the adsorbent and the adsorbate. The relationship between the constant $b$ and the Hall separation factor ($R_L$) is as follows:

$$R_L = 1/(1 + b \cdot C_m)$$

where $C_m$ is the maximum initial concentration of methyl orange (mg/L); $R_L$ is the separation constant (dimensionless) and an important factor for measuring the extent of the adsorption reaction. The value of $R_L$ suggests that: $R_L > 1$, unfavorable to adsorption; $R_L < 0$, unfavorable to adsorption;
In this work, it can be determined that $R_L=0.0528$ ($0<R_L<1$), which means the conditions are favorable to adsorption, showing as a monolayer adsorption.

In Fig. 4(b), with linear fitting by using the Freundlich model, it can be determined that $n=2.0665$ and $k_F=15.873$. $R^2$ is 0.9539. Based on the results, the adsorption process of methyl orange onto MLBCN is described better by the Langmuir adsorption isotherm model.

### 3.2.2. Comparison with other published absorbents

In order to compare between the present researches with some adsorbent used for methyl orange removal, a list of previous published works was shown in Table 2. From this table, the adsorption capacity of MLBCN obviously was superior to or comparative to the other published adsorbent. Moreover, the fabrication process of MLBCN is much easier; also the raw material is from the byproduct of paper and pulp industrial. Base on the above results, MLBCN is green adsorbent with good performance for the methyl orange removal, which is of great significance to the environmental protection and resource recycling.

### Table 2

Comparison of the adsorption capacity for methyl orange by other published adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Preparing method</th>
<th>Adsorption capacity (mg/g)</th>
<th>Experimental conditions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>hexagonal shaped nanoporous carbon</td>
<td>template, calcination</td>
<td>18.8</td>
<td>25°C</td>
<td>[37]</td>
</tr>
<tr>
<td>modified ultrafine coal powder</td>
<td>pulverized, acid wash</td>
<td>18.52</td>
<td>30°C, pH=11</td>
<td>[38]</td>
</tr>
<tr>
<td>biochar adsorbent derived from chicken manure</td>
<td>pyrolysis</td>
<td>39.37</td>
<td>25°C</td>
<td>[39]</td>
</tr>
<tr>
<td>graphene oxide</td>
<td>commercial product</td>
<td>16.83</td>
<td>25°C, pH=3</td>
<td>[40]</td>
</tr>
<tr>
<td>chitosan/organic rectorite composite</td>
<td>template, intercalating</td>
<td>5.56</td>
<td>25°C, pH=3</td>
<td>[41]</td>
</tr>
<tr>
<td>mesostructured silicas with large accessible disordered pores</td>
<td>self-assembly, hydrothermal recrystallization</td>
<td>37.13</td>
<td>25°C, pH=4</td>
<td>[42]</td>
</tr>
<tr>
<td>polyacrylonitrile-coated kapok hollow</td>
<td>surfactant-assisted,</td>
<td>34.72</td>
<td>pH=5</td>
<td>[43]</td>
</tr>
</tbody>
</table>
3.2.3. Effect of temperature on the adsorption

It is well known that temperature plays an important role in affecting the adsorption. The effect of temperature on the adsorption kinetics of MLBCN for methyl orange was investigated in this paper. 20 mg of MLBCN was placed in 20 mL methyl orange solution at a concentration of 120 mg/L with a final pH of 5.0. The solution was then oscillated for 160 min in a water bath at various temperatures (20°C, 25°C, 30°C, 35°C, and 40°C). The results are shown in Fig. 5(a).

From Fig. 5(a), it can be seen that the adsorption capacity of MLBCN for methyl orange decreases as the temperature increases. When the temperature increases from 20°C to 40°C, the
adsorption capacity significantly decreases from 77.3 to 59.8 mg/g, showing that the nature of the adsorption is exothermic.

Generally, the thermodynamics parameters can be obtained by the Van’t Hoff equation [49]. The variation of free energy (\(\Delta G^0\)) of the adsorption process is described by Eq.(6)-(7).

\[
\Delta G^0 = -RT \ln \left( \frac{C_A}{C_e} \right) \tag{6}
\]

\[
\ln \left( \frac{C_A}{C_e} \right) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{7}
\]

where \(\Delta G^0\) is the variation of the Gibbs free energy (J/mol); \(C_A\) is the concentration of adsorbed methyl orange at adsorption equilibrium (mg/L); \(C_e\) is the concentration of methyl orange remaining in solution (mg/L); \(T\), temperature (K); \(R\) is the gas constant, 8.314. \(\Delta H^0\) and \(\Delta S^0\) are the enthalpy change (kJ/mol) and entropy change (J/mol·K), respectively. \(\Delta H^0\) and \(\Delta S^0\) can be calculated using the line of best fit for the plot of \(\ln \left( \frac{C_A}{C_e} \right)\) vs. \(\frac{1}{T}\), which is shown in Fig.5(b).

According to the slope and intercept of the line of best fit in Fig.5(b), the thermodynamics parameters was listed in Table 3.

**Table 3**

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>(\Delta H^0)/kJ/mol</th>
<th>(\Delta S^0)/J/mol·K</th>
<th>(R^2)</th>
<th>(\Delta G^0)/J/mol</th>
<th>20°C</th>
<th>25°C</th>
<th>30°C</th>
<th>35°C</th>
<th>40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>-24.43</td>
<td>-78.18</td>
<td>0.9765</td>
<td>-1511.5</td>
<td>-1120.6</td>
<td>-729.7</td>
<td>-338.8</td>
<td>52.1</td>
<td></td>
</tr>
</tbody>
</table>

From \(\Delta H^0\) and \(\Delta S^0\), it can be seen that the adsorption is an exothermic, entropy reduction process. As the temperature increases, the value of \(\Delta G^0\) changes gradually from negative to positive, showing that the adsorption turns from spontaneous to non-spontaneous at the same time. When the temperature is below 35°C, the adsorption is spontaneous, thus MLBCN can be used better at ambient temperature.
3.2.4. **Effect of pH on the adsorption**

pH can affect the performance of adsorbent to much degree. The effect of pH on the adsorption capacity of MLBCN was explored. As described previously, 20 mg of MLBCN was placed in 20 mL of 120 mg/L methyl orange solution at different final measured pH (1.1, 2.2, 3.1, 4.0, 5.0, 6.0, 6.9, and 8.1) and agitated at 20°C for 160 min. The percent adsorption and adsorption capacity were then determined with the results shown in Fig.6.

![Fig.6](image)

**Fig.6.** The adsorption behavior as a function of pH ($T=20^\circ C$, initial concentration=120 mg/L, contact time=160 min)

From Fig.6, it can be obviously seen that MLBCN showed better adsorption for methyl orange under acidic conditions. As can be seen in Fig.2(e), the surface of MLBCN is positively charged under acidic conditions, resulting in increase of the electrostatic attraction to the sulfo groups of methyl orange. When pH<4.0, the zeta potential of MLBCN increases slowly, the adsorption capacity shows minor increases as well, confirming that the electrostatic attraction plays important roles in the methyl orange adsorption. Under near neutral conditions, although the surface of MLBCN is negatively charged, still had a larger adsorption capacity for methyl orange, indicating there is pi-pi effect between the methyl orange molecules and the MLBCN surface, which also contributed to the adsorption. Based on the results, from the aspect of easy operation, methyl orange can be absorbed by MLBCN under milder conditions (pH 5.0-7.0), though the adsorption capacity is larger under acidic conditions.

3.2.5. **Adsorption kinetics model**

20 mg of MLBCN was placed in 20 mL methyl orange solution at a concentration of 120 mg/L with a pH of 5.0. The solutions were then oscillated in a 20°C water bath for varying times. The
The effect of contact time on the adsorption for methyl orange was studied. The results are shown in Fig.7.

![Graph](image)

**Fig.7.** The adsorption kinetics of methyl orange on MLBCN ($T=20\,^\circ C$, $pH=5.0$, initial concentration=120 mg/L).

From Fig.7, it can be seen that as the adsorption time increased, both the percent adsorption and adsorption capacity of MLBCN for methyl orange gradually increased.

Within 90 min, methyl orange was rapidly adsorbed onto the surface of MLBCN. The percent adsorption and the adsorption capacity of methyl orange on the adsorbent increased sharply during this initial stage. At the moment of 90 min, the percent adsorption was 57.2%, and the adsorption capacity 68.6 mg/g. Then the adsorption slowed down, for the driving force between the solution and the solid phase gradually decreased. At 140 min, the percent adsorption and capacity were 62.6% and 74.1 mg/g, respectively. At the stage of 140-280 min, the percent adsorption of methyl orange only increased from 62.6% to 64.1%, and the adsorption capacity from 74.1 mg/g to 76.9 mg/g. It can be concluded that the surface of the adsorbent have been basically occupied by the methyl orange molecules at 140 min, meaning the dynamic equilibrium for the adsorption have been reached at about 140-170 min.

The kinetics of this adsorption case can be described either as pseudo-first-order or pseudo-second-order [50].

A pseudo-first-order reaction is expressed as

$$\ln(q_e-q_t) = \ln q_e - k_1t$$

where $k_1$ is the pseudo-first-order rate constant ($\text{min}^{-1}$); $q_e$ is the adsorption capacity of methyl
orange at equilibrium (mg/g); \( q_t \) is the adsorption capacity of methyl orange at \( t \) min (mg/g).

A pseudo-second-order reaction is expressed as

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

(5)

where \( k_2 \) was the Pseudo-second-order rate constant (g/(mg·min)).

The linear regression for the plot of \( \ln(q_e - q_t) \) vs. \( t \) and \( \frac{t}{q_t} \) vs. \( t \) is shown below.

![Graphs showing line of best fit for (a) pseudo-first-order model and (b) pseudo-second-order model.](image)

**Fig.8.** The line of best fit of adsorption kinetics using (a) pseudo-first-order model, (b) pseudo-second-order model.

The kinetics parameters were calculated from the lines of best fit, as shown in Table 4.

**Table 4**

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>( q_{e\text{exp}} ) (mg/g)</th>
<th>pseudo-first-order model</th>
<th>pseudo-second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_{e\text{cal}} ) (mg/g)</td>
<td>( R^2 )</td>
<td>( k_2 ) (min(^{-1}))</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>77.2</td>
<td>57.8</td>
<td>0.9397</td>
</tr>
</tbody>
</table>

Though the value of \( R^2 \) for the line of best fit using the pseudo-first-order kinetic equation is 0.9397, the theoretically calculated equilibrium adsorption capacity (\( q_{e\text{cal}} \)) and the experimentally measured adsorption capacity (\( q_{e\text{exp}} \)) are quite different, indicating the adsorption of methyl orange by MLBCN doesn’t conform to pseudo-first-order kinetics. In Fig.8(b), the value of \( R^2 \) for the line of best fit is 0.9992, showing that the relation of \( \frac{t}{q_t} \) vs. \( t \) is linear basically. The theoretically
calculated equilibrium adsorption capacity \((q_{\text{ecal}})\) of 81.6 mg/g is close to the experimentally measured one \((q_{\text{exp}}, 77.2 \text{ mg/g})\), indicating that the adsorption kinetics can be described as pseudo-second-order well. Thus it can be concluded that chemisorption is the rate controlling step for the adsorption of methyl orange onto the surface of MLBCN.

3.2.6. Regeneration of recycled MLBCN

After adsorption, MLBCN was separated in an external magnetic field (Fig.9), then soaked overnight in 50 mL 95% ethanol solution, and washed with 100 mL deionized water three times. The regenerated MLBCN was reemployed in the adsorption for methyl orange. In Fig.13, it can be seen that MLBCN retained good adsorption capacity even after 4 cycles of regeneration, with an adsorption capacity of about 69.0 mg/g for methyl orange (89.3% of the initial capacity), showing that a majority of adsorption sites on the surface could be renewed after regeneration. The results illustrates that MLBCN can be a sustainable absorbent.

4. Conclusion

In this paper, MLBCN was prepared by precipitation and carbonization strategy, and its application as a methyl orange adsorbent was investigated. FTIR, XRD, Raman spectra, BET, SEM, DLS and VSM were conducted to determine the structure, morphology and magnetism of MLBCN. The adsorption isotherm for methyl orange fit the Langmuir model, demonstrating a monolayer adsorption process with a maximum adsorption capacity of 113.0 mg/g. The adsorption kinetics
conformed to pseudo-second-order, indicating chemisorption would be the rate controlling step.

The study of the adsorption thermodynamics illustrated the adsorption was an exothermic, entropy reduction process. When the temperature was below 35°C, the adsorption was spontaneous, thus the adsorption for methyl orange could be performed at ambient temperature. Acidic conditions favored the adsorption, but MLBCN could also be easily used under near neutral conditions. In addition, MLBCN was easily regenerated. This study demonstrates that MLBCN is a promising sustainable absorbent which can be applied in the removal of industrial dyes from waste effluent.

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