Effective sorptive removal of five cationic dyes from aqueous solutions by using magnetic multi-walled carbon nanotubes

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ABSTRACT

The excellent properties of micro-nano materials and structures have attracted extensive attention especially in wastewater treatment. Based on this, magnetic multi-walled carbon nanotubes (MMWCNTs) have been prepared and used for the sorptive removal of five typical cationic dyes from aqueous solutions in the present study. Effects of several operational and environmental factors were investigated carefully, including initial pH values, common ions, contact time and temperature. The kinetics processes were well fitted by the pseudo-second-order kinetic model. The maximum adsorption capacities on MMWCNTs at 298.15 K for malachite green oxalate, auramine O, neutral red, crystal violet and rhodamine B were 442.2, 295.2, 183.4, 165.3 and 143.0 mg g⁻¹, respectively. Differences in the size, structure and properties of these dyes led to the difference of adsorption amounts. ΔG⁰ were all negative within the temperature range tested, which meant the adsorption processes were spontaneous nature. Moreover, the adsorption processes of targeted dyes, except auramine O, were exothermic and entropy decreasing. The regeneration studies indicated that the MMWCNTs showed high reusability and the removal efficiencies can be achieved above 75% after four consecutive cycles. For the adsorption mechanism, electrostatic interaction, hydrogen bonds, π-π interaction together with hydrophobic interaction, could coexist during the adsorption process.

Key words: adsorption, adsorption mechanism, cationic dyes, magnetic carbon nanotubes, reusability

HIGHLIGHTS

- MMWCNTs were applied to the adsorption of five cationic dyes from aqueous solutions.
- Various environmental factors were investigated during the adsorption process.
- The MMWCNTs have high adsorption capacity for all five cationic dyes.
- The MMWCNTs showed high reusability after several consecutive cycles.

1. INTRODUCTION

Industries based on textile, paper, plastic, leather, and cosmetics continuously discharge several contaminants into the environment, in which the major pollutants are organic dyes (Hou et al. 2019). Additionally, it has been reported that cationic dyes, commonly used in the printing and dyeing industries, are more harmful than other kinds of dyes (Singh et al. 2011; Ibrahim et al. 2021). Most of the cationic dyes, such as methylene blue (MB), malachite green oxalate (MG), auramine O (AO), neutral red (NR), crystal violet (CV), and rhodamine B (Rhb) are relatively stable and have large molecular structures composed of hydroxyl, amino, conjugated aromatic rings and other active groups (Wei et al. 2020; Xiao et al. 2020a), which render dyes high toxicity and poor biodegradability after discharged into water bodies (Hou et al. 2020). Large amounts of organic dyes dissolved in water decrease the transparency and lessen the penetration of sunlight in water bodies (Nagpal & Kakkar 2020). This causes severe pollution and thereby poses a great threat to aquatic plants and animals. The sustainable means for the treatment of organic dyes have been in high demand, while it is still great challenge to find effective ways to treat with them.

Many techniques have been developed and employed, such as various chemical methods including electrochemical processes (de Moura et al. 2016; He et al. 2016), advanced oxidation processes (Gayathri et al. 2017; Alcocer et al. 2018), and various physical treatment methods including coagulation/flocculation (de Camargo Lima Beluci et al. 2019; Song...
et al. 2019), membrane filtration (Han et al. 2017; Zhu et al. 2017), adsorption (Hadi et al. 2016; Li et al. 2017; Hong et al. 2018; Li et al. 2020) and biological treatment methods (Hosseini Koupaei et al. 2013). Among these technologies, the adsorption is a promising technique due to the advantages of low cost, no secondary pollution, environmental friendliness, less energy consumption and excellent performance (Ahmed et al. 2019; Hu et al. 2019). For example, Huang et al. (2019) synthesized magnetic graphene oxide modified zeolite for the removal of MB with the maximum adsorption amount of 97.3 mg g⁻¹ at 318 K and the removal efficiency of MB could still reach about 76.9% after five reuse cycles. Yao et al. (2020) prepared an activated wakame biochar material, which exhibited high adsorption capacities for various cationic dyes including MB, RhB and MG. Thus, the adsorption method has significant advantages for the removal of dyes from wastewater.

While the merit of adsorption method is being discussed intensively, the choice of adsorbent has become a top priority. In fact, many high-efficiency materials have been developed for the sorptive removal of cationic dyes from wastewater. Adsorbents, such as nanomaterials based on metal-organic framework (Oveisi et al. 2018), graphene oxide hydrogels (Narula & Rao 2019), zeolites (Xue et al. 2019), activated carbon (Xiao et al. 2020b), and functionalized graphene (Liu et al. 2015), have been widely reported in the literature. In particular, carbon nanotubes (CNTs), as a kind of carbon-based nanomaterials, have been suggested as promising adsorbents for the treatment of wastewater. The application originates from their extraordinary surface chemistry performance and unique structures, that is, high surface area, small size, a large amount of oxygen-containing functionalities on the surface and hollow layered structures (Jun et al. 2018). Compared to traditional materials, nanostructure adsorbents have exhibited much higher adsorption efficiency and faster adsorption rate in the treatment of wastewater. These characteristics render nano-adsorbents favorable for the sorptive removal of various organic compounds and heavy metal from wastewater (Shirmardi et al. 2015; Hosseinzadeh et al. 2018; Yi et al. 2020; Zhao et al. 2021).

Unfortunately, it is not easy to intercept them from wastewater after the adsorption due to their tiny size, and the characteristic prone to outflow usually causes unexpected loss of nano-adsorbents and secondary pollution in their actual application. Therefore, it is desirable to develop high-quality nano-adsorbents, which can also be easily and conveniently separated from water. Magnetic separation technique has provided an optional method for the solid-liquid separation of nanoadsorbents. The combination of CNTs with magnetic nanoparticles can produce new adsorbents, namely magnetic carbon nanotubes (MCNTs). MCNTs are superparamagnetic, which can be easily separated from water by employing a magnetic field while preserve no residual magnetism after the magnetic field is removed (Duman et al. 2016). Therefore, MCNTs have great magnetic response and high adsorption capacity, which facilitate their separation, adsorption and regeneration after the adsorption (Santhosh et al. 2016).

Nowadays, most of studies focus on the properties of adsorbents prepared and the adsorption of various dyes on them, and high adsorption performances have been achieved (Jawad et al. 2021; Wang et al. 2021b). Nevertheless, few studies have been focused on the varieties of adsorbate to investigate the difference in adsorption performance caused by their different structures. For example, the hydrophilicity and steric hindrance between the adsorbent and the positive charge center (C⁺ or N⁺) of cationic dyes could lead to the adsorption affinity or force difference (Liu et al. 2020). Furthermore, adsorption sites have an unequal affinity to dyes with different molecular structures or sizes, which leads to the difference in the adsorption amounts. In our previous study (Song et al. 2021), the effect of the diameter of magnetic multi-walled carbon nanotubes (MMWCNTs) on the adsorption performance of MB has been investigated, and it was concluded that the adsorption capacities decreased with increasing diameters. In this study, MMWCNTs with the optimum performance were subsequently applied to remove other five typical cationic dyes, including MG, AO, NR, CV, and RhB, to check their adsorption performance, and the effect of dye structures on the adsorption performance was investigated.

2. MATERIALS AND METHOD

2.1. Chemicals

Five cationic dyes, including MG, NR, CV, RhB and AO, were purchased from J&K Scientific Ltd and used without further purification. The molecular structures and properties of these five dyes have been shown in Table 1. Chemicals applied in the present study were all analytical grade without further treatment and deionized water was used in all experiments.

2.2. Synthesis and characterizations of MMWCNTs

MMWCNTs were prepared by the same method reported in our previous study (Song et al. 2021). In addition, magnetic nanoparticles (MNPs) were also synthesized without adding MWCNTs and used as a comparison (Text SI). The MMWCNTs were characterized by using Transmission electron microscope (TEM), Fourier transform infrared spectrometer (FTIR), X-ray
diffraction (XRD), BET surface area analysis and Vibrating sample magnetometer (VSM). The corresponding characterization results were summarized in Text S II.

2.3. Batch adsorption experiments

Batch adsorption experiments for these five dyes were conducted in duplicate to investigate their adsorption behaviors on the MMWCNTs. More details of the batch adsorption experiments have been presented in Text S III. Subsequently, the adsorption performance was evaluated based on the dye concentrations changed before and after the adsorption. The removal efficiency ($R_{%}$) and equilibrium adsorption capacity ($q_e$) of dyes could be calculated according to Equations (1) and (2), respectively.

$$R_{%} = \frac{C_0 - C_t}{C_0} \times 100\%$$

(1)

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

(2)

where $C_0$ and $C_t$ (mg L$^{-1}$) are concentrations of dyes at time 0 and $t$, respectively, $C_e$ (mg L$^{-1}$) is the concentration of dye at equilibrium, $V$ (L) is the volume of the solution, and $m$ (mg) is the weight of the MMWCNTs used.

Table 1 | Names, properties and molecular structures of five cationic dyes studied

<table>
<thead>
<tr>
<th>Dyes</th>
<th>CAS No.</th>
<th>M.W.$^*$</th>
<th>Molecular size (nm)</th>
<th>$\lambda_{max}$ (nm)</th>
<th>Molecular formula</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malachite Green oxalate (MG)</td>
<td>2437–29-8</td>
<td>418.5</td>
<td>$1.47 \times 1.16 \times 0.60$</td>
<td>616</td>
<td>C$<em>{25}$H$</em>{26}$N$<em>{2}$O$</em>{4}$</td>
<td><img src="image" alt="Structure of Malachite Green oxalate" /></td>
</tr>
<tr>
<td>Auramine O (AO)</td>
<td>2465-27-2</td>
<td>303.8</td>
<td>$1.23 \times 0.58 \times 0.33$</td>
<td>430</td>
<td>C$<em>{17}$H$</em>{22}$ClN$_{3}$</td>
<td><img src="image" alt="Structure of Auramine O" /></td>
</tr>
<tr>
<td>Neutral Red (NR)</td>
<td>553-24-2</td>
<td>288.8</td>
<td>$1.22 \times 0.49 \times 0.23$</td>
<td>527</td>
<td>C$<em>{15}$H$</em>{17}$ClN$_{4}$</td>
<td><img src="image" alt="Structure of Neutral Red" /></td>
</tr>
<tr>
<td>Crystal Violet (CV)</td>
<td>548-62-9</td>
<td>408.0</td>
<td>$1.41 \times 1.21 \times 0.18$</td>
<td>588</td>
<td>C$<em>{25}$H$</em>{30}$ClN$_{3}$</td>
<td><img src="image" alt="Structure of Crystal Violet" /></td>
</tr>
<tr>
<td>Rhodamine B (RhB)</td>
<td>81-88-9</td>
<td>479.0</td>
<td>$1.59 \times 1.18 \times 0.56$</td>
<td>554</td>
<td>C$<em>{28}$H$</em>{31}$ClN$<em>{2}$O$</em>{3}$</td>
<td><img src="image" alt="Structure of Rhodamine B" /></td>
</tr>
</tbody>
</table>

*Molecular Weight (g mol$^{-1}$).

$^*$Maximum absorption wavelength (nm).
2.4. Reusability experiments

To verify the reuse performance of MMWCNTs, the adsorption-desorption experiments were conducted under the same conditions. Briefly, 15 mg MMWCNTs were dispersed in 30 mL dye solutions (60 mg L\(^{-1}\)). After shaking for 6 h, the MMWCNTs were separated from the aqueous solutions with an external magnet, which were then regenerated with 0.1 M HCl and ethanol (V: V = 1: 1). Subsequently, the adsorption and desorption efficiencies were calculated, respectively. The whole process was carried out four cycles under the same condition.

3. RESULT AND DISCUSSION

3.1. Comparison of the adsorption performance of MNPs, MWCNTs and MMWCNTs

To compare the adsorption performance of MNPs, MWCNTs and MMWCNTs, the adsorption efficiencies for five dyes were conducted, respectively. All of the adsorption procedures were carried out under identical conditions (t = 6 h, m = 15 mg, V = 30 mL, T = 298.15 K). As shown in Figure 1, the adsorption performance of MMWCNTs was slightly lower than that of MWCNTs, but greatly higher than that of MNPs. The reason is that MNPs loaded on the surface of MMWCNTs occupy the adsorption sites and block the pore (Zhang et al. 2019), which consequently decreases the adsorption performance. However, the loading of MNPs on MWCNTs could be beneficial taking the efficient magnetic separation property endowed by these MNPs into consideration. From the magnetic hysteresis loop of the MMWCNTs (Figure S1), it can be seen that the MMWCNTs are superparamagnetic, and the saturation magnetization of the MMWCNTs is approximately 28.8 emu g\(^{-1}\). From Video S1, it can be seen that the MMWCNTs can be quickly separated from the solutions within seconds under the presence of a magnet.

3.2. Effect of pH and common ions

The influences of pH values and several common ions on the adsorption performance were subsequently analyzed. The adsorption of four dyes, MG, AO, CV and RhB, on MMWCNTs were tested over a wide pH range from 4.0 to 10.0. However, the adsorption process of NR was investigated in a relative narrow pH range from 4.0 to 7.0 as precipitates would be formed under alkaline conditions (Guo et al. 2019). As illustrated in Figure 2, the adsorption amounts for MG (Figure 2(a)), AO (Figure 2(b)) and CV (Figure 2(c)) gradually increased with increasing pH values from 4.0 to 10.0. Similarly, the adsorption amounts of NR also increased from 4.0 to 7.0 (Figure 2(d)). According to Figure 2(f), the zeta potentials of the MMWCNTs decreased with increasing pH values, which was attributed to the gradual deprotonation of surface functional groups, including carboxyl and hydroxyl groups on MMWCNTs. The increased amounts of negative charged sites could benefit the
electrostatic attraction with cationic dyes under increased pH values, thus the adsorption amounts of dyes gradually increased.

However, the adsorption behavior of RhB was found to be an exception (Figure 2(e)). It is known that the RhB molecule possesses amphoteric characteristics due to the presence of both the amino group (-NHR2) and the carboxyl group (-COOH), thus the charge stage of RhB is largely dependent on the pH value (Li et al. 2010). The pKa value of the aromatic carboxyl group on the RhB molecule is about 3.7 (Wang et al. 2014). When the pH value was higher than 3.7, carboxyl groups got ionized and zwitterions of RhB were formed (Li et al. 2010; Rao et al. 2020). With increasing pH values, electrostatic attraction with the positive $N^+$ site and electrostatic repulsion with negatively charged carboxyl groups were both increased. As a result, the adsorption performance of RhB was almost unaffected in a wide pH range as shown in Figure 2(e).

Common ions, such as Na$^+$, Ca$^{2+}$ and Al$^{3+}$, could also affect the adsorption of dyes on MMWCNTs. As shown in Figure 3, the presence of Ca$^{2+}$ and Al$^{3+}$ in solutions obviously inhibited the sorptive removal of five dyes, while the effect of Na$^+$ was unobvious. The effect of Al$^{3+}$ was greater than that of Ca$^{2+}$. It may be attributed to the fact that Al$^{3+}$ had higher valence states and more surface charges compared with Ca$^{2+}$, thus the adsorption amounts would be significantly decreased. As for Na$^+$, the negative shielding effect of monovalent cation for the negatively charged groups on MMWCNTs exhibited weaker effect than di/tri-valent cations (Moharrami & Motamedi 2020). Therefore, Na$^+$ had a little effect for the adsorption process.

### 3.3. Adsorption kinetics

The effect of different contact time for the dye adsorption on MMWCNTs was investigated and shown in Figure 4. It was clearly seen that the adsorption amounts increased rapidly in the first 60 min. Then the adsorption amounts increased gradually until equilibrium was obtained. The equilibrium times for these dyes were found to be from 180 to 300 min. The rapidly adsorption process at the initial period originated from the presence of abundant adsorption sites on the surface of MMWCNTs, which improved the surface accessibility and utilization. Subsequently, dye molecules went through a sluggish adsorption rate to equilibrium through the deeper internal pores, where they suffered much greater mass transfer resistance.

The pseudo-first-order kinetic model (Figure 4(b)), the pseudo-second-order kinetic model (Figure 4(c)) and the intra-particle diffusion model (Figure 4(d)) were used to fit the adsorption kinetic process (Text SIV), which evaluated the mass transfer of five dyes on MMWCNTs. The kinetic parameters fitted were summarized in Table 2. The calculated results
demonstrated that the adsorption kinetic process with these five dyes followed the pseudo-second-order kinetic model well with higher coefficient of determination ($R^2$) and the calculated theoretical $q_{e,\text{cal}}$ values were closer to corresponding experimental $q_{e,\text{exp}}$ values. Furthermore, the intra-particle diffusion model was also applied (Makrygianni et al. 2021) to investigate the staged adsorption process. As shown in Figure 4(d) and Table 2, the adsorption of five dyes on MMWCNTs can be regarded as a two-step process. The rapid increase in the first step was the adsorption stage on the outer surface because it was an instantaneous diffusion stage. The second step was the gradual adsorption stage, in which the rate was controlled by the intra-particle diffusion process. However, it can be observed that the straight line between $q_t$ and $t^{1/2}$ was not basically linear from the origin. Thus the adsorption rate was jointly controlled by the two stages and the intra-particle diffusion was not the only rate-limiting step (Gupta & Singh 2018). Compared with the slope of the first step, the slope of the second step was lower. This might be related with the reduction in the active sites on the MMWCNTs, which extended the diffusion time of dye molecules.

### 3.4. Adsorption isotherms

Langmuir, Freundlich and Langmuir-Freundlich models were used to analyze the isotherm data of five dyes on MMWCNTs (Text S IV). The Langmuir isotherm model was further analyzed with the dimensionless constant, separation factor $R_L$ (also called equilibrium parameter), which was defined as Equation (3).

$$R_L = \frac{1}{1 + K_L C_0}$$

where $C_0$ is the initial concentration of dyes. The $R_L$ demonstrates the nature of the isotherm, which either can be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$), respectively (Huang et al. 2017).

The obtained figures and parameters for these five dyes were shown in Figure 5 and listed in Table 3. It can be seen that $R^2$ values of three models were almost close to 1. $R^2$ values for the Langmuir-Freundlich model were higher (>0.941) than those of other two models, indicating that the adsorption occurred by the monolayer adsorption mechanism and the adsorption of...
these five dyes on MMWCNTs was attributed to a heterogeneity distribution of dye molecules on various adsorption sites (Yan et al. 2017; He et al. 2019). It can be seen from Table 3 that $R_L$ values were in the range of 0.004 to 0.050, demonstrating that the adsorption was favorable and there were strong affinities between dyes and MMWCNTs (Tran et al. 2017; Zhao et al.)
The maximum adsorption capacity for five cationic dyes on MMWCNTs was found to be 442.2 mg g\(^{-1}\) for MG dye, which was obtained from the Langmuir model. While for AO, NR, CV and RhB, the maximum adsorption capacities were 295.2, 183.4, 165.3 and 143.0 mg g\(^{-1}\), respectively. Obviously, the MMWCNTs had adequate adsorption capacity for these five cationic dyes. However, the difference in the adsorption capacity indeed existed and it was necessary to analyze the difference.

It has been reported previously that the carbon-doped boron nitride material with negatively charge can selectively adsorb protonated dyes from dye wastewater (Wang et al. 2021a). As known as well, AO and NR are cationic dyes and the positive charges come from the bound H\(^+\) with the N atom in AO and NR molecular structure. MG is an oxalate dye, and its positive charge comes from protons (Table 1). As the MMWCNT possess negative charge as indicated from the Zeta potentials (Figure 2(f)), the MMWCNT could have high affinity to these protonated dyes of AO, NR and MG, which is highly consistent with the obtained experimental results. According to our previous study (Song et al. 2021), the MMWCNT prepared was a mesoporous material. Dye molecules with smaller sizes could hardly be adsorbed because smaller dye could not only easily enter but also easily leave pores of the MMWCNT, while larger dye could enter and bind closer to the micropores (Ge & Liu 2017).

![Figure 5](image-url) Adsorption isotherms of five dyes on MMWCNTs fitted by Langmuir model, Freundlich model and Langmuir-Freundlich model for MG (a), AO (b), NR (c), CV (d) and RhB (e).

### Table 3 | Isotherm model parameters of five dyes on MMWCNTs

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
<th>Langmuir-Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_m) (mg g(^{-1}))</td>
<td>(K_L) (L mg(^{-1}))</td>
<td>(R_L)</td>
</tr>
<tr>
<td>MG</td>
<td>442.2</td>
<td>0.439</td>
<td>0.005–0.022</td>
</tr>
<tr>
<td>AO</td>
<td>295.2</td>
<td>0.378</td>
<td>0.009–0.050</td>
</tr>
<tr>
<td>NR</td>
<td>183.4</td>
<td>0.572</td>
<td>0.009–0.028</td>
</tr>
<tr>
<td>CV</td>
<td>165.3</td>
<td>2.219</td>
<td>0.004–0.011</td>
</tr>
<tr>
<td>RhB</td>
<td>143.0</td>
<td>2.812</td>
<td>0.004–0.018</td>
</tr>
</tbody>
</table>
Therefore, the adsorption capacity of these three dyes decreased in the order of MG > AO > NR, which was in accordance with the order of decreasing molecular size.

For CV and RhB dye, the positive charge of CV is distributed in its organic skeleton, which is not a protonated dye (Guo et al. 2019). Thus this might give rise to the lower adsorption capacity of CV. As for RhB, which is also not a protonated dye, both cationic and zwitterionic RhB could exist and dimers could be formed at high concentrations in a neutral solution (Alig et al. 2007). Due to the larger molecular size of RhB dye, it was hard to be adsorbed on the surface or pores after more larger dimers formed. The lower adsorption capacity of RhB might attribute to the lower adsorption of RhB dimers on MMWCNTs.

### 3.5. Adsorption thermodynamics

The adsorption thermodynamics of five dyes on MMWCNTs were further investigated to analyze the adsorption mechanisms. Three thermodynamic parameters, including the Gibbs free energy change ($\Delta G^0$), enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$), were calculated (Text S IV) and the results were shown in Table 4.

It can be seen that, for these five dyes, values of $\Delta G^0$ were all negative within the temperature range tested, which meant the adsorption process was a spontaneous process. In addition, the absolute values of these $\Delta G^0$ were all less than 20.00 kJ mol$^{-1}$, indicating that the adsorption of these dyes on MMWCNTs was mainly the physical adsorption (Djebri et al. 2016). The obtained $\Delta H^0$ values, except for AO dye, were negative, which confirmed the exothermic adsorption process. Likewise, the absolute values of these $\Delta H^0$ ranged from 6.969 to 64.29 kJ mol$^{-1}$, which were lower than 84.00 kJ mol$^{-1}$, also suggesting the physisorption process (Benhouria et al. 2015; Lin et al. 2020). $\Delta S^0$ values of MG, NR, CV and RhB, were all negative in the range of $-41.00$ to $-177.5$ J (mol k)$^{-1}$, indicating the decreased randomness at the solid/solution interface during the adsorption process (Benhouria et al. 2015).

For AO, the positive $\Delta H^0$ indicated that the adsorption of AO on MMWCNTs was an endothermic process. It was noticed that the endothermic nature of the adsorption process of AO is different from other dyes, which might be explained by the phenomenon of hydration in water solutions. In general, AO cations must be firstly stripped out of their hydration shell (at least partially) which required energy input, and then they can travel through the solutions to reach the adsorption sites and be adsorbed (Bahgat et al. 2012). If the dehydration energy of AO exceeds the attractive force of AO on MMWCNTs, the endothermic process will occur through the overall energy balance. The positive $\Delta S^0$ value might be attributed the fact that the water molecules desorbed from MMWCNTs were much more than AO molecules adsorbed on MMWCNTs (Li et al. 2015). Thus, the adsorption process showed an entropy increasing nature and caused the increased randomness at the solid-liquid interface (Konicki et al. 2017).

<table>
<thead>
<tr>
<th>Dyes</th>
<th>$T$ (K)</th>
<th>$\ln K_d$</th>
<th>$\Delta G^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^0$ (J [mol k]$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>MG</td>
<td>298.15</td>
<td>3.696</td>
<td>$-9.162$</td>
<td>$-17.03$</td>
<td>$-26.19$</td>
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<tr>
<td></td>
<td>308.15</td>
<td>3.543</td>
<td>$-9.078$</td>
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</tr>
<tr>
<td></td>
<td>318.15</td>
<td>3.262</td>
<td>$-8.631$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR</td>
<td>298.15</td>
<td>2.342</td>
<td>$-5.804$</td>
<td>$-23.28$</td>
<td>$-58.06$</td>
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<tr>
<td></td>
<td>308.15</td>
<td>2.243</td>
<td>$-5.748$</td>
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<td></td>
<td>318.15</td>
<td>1.747</td>
<td>$-4.620$</td>
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<tr>
<td></td>
<td>308.15</td>
<td>2.995</td>
<td>$-7.667$</td>
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<td></td>
<td>318.15</td>
<td>2.814</td>
<td>$-7.444$</td>
<td></td>
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<tr>
<td>RhB</td>
<td>298.15</td>
<td>4.477</td>
<td>$-11.10$</td>
<td>$-64.29$</td>
<td>$-177.5$</td>
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<tr>
<td></td>
<td>308.15</td>
<td>3.963</td>
<td>$-10.15$</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>318.15</td>
<td>2.839</td>
<td>$-7.512$</td>
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<tr>
<td>AO</td>
<td>298.15</td>
<td>3.013</td>
<td>$-7.468$</td>
<td>$6.969$</td>
<td>$48.48$</td>
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<td>$-8.008$</td>
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<td></td>
<td>318.15</td>
<td>3.189</td>
<td>$-8.436$</td>
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</table>
3.6. Regeneration performance

Reusability is a crucial factor to evaluate the commercial suitability of an adsorbent. From Figure 6, it can be seen that the adsorption amounts of AO on regenerated MMWCNTs did not decrease obviously even after four cycles. Similarly, the adsorption equilibrium almost reached within 360 min, indicating that the regenerated MMWCNTs has good reusability and fast adsorption rate. In addition, the adsorption and desorption efficiencies of these five dyes were exhibited in Figure S2. It can be seen that the adsorption efficiency gradually decreased with increasing number of regenerations. However, the removal efficiency can still exceed 75% for all of these five dyes. This may be due to the incomplete desorption of dyes from the MMWCNT. The desorption efficiency slightly fluctuated with increasing desorption times. However, the desorption efficiency maintained at a high level (>74%) when the 0.1 M HCl and ethanol were used as the desorbents to regenerate the MMWCNTs. Overall, the as-prepared MMWCNTs possess useful properties, such as good adsorption ability, easy regeneration, excellent reusability and high stability, suggesting that the MMWCNTs could be a kind of potential adsorbent for the removal of cationic dyes.

3.7. Adsorption mechanism

To analyze the adsorption mechanism of these cationic dyes on MMWCNTs prepared, FTIR spectra of MMWCNTs before and after the adsorption were measured and shown in Figure 7 and Figure S3. For MMWCNTs, characteristic peaks at ~3,156 cm\(^{-1}\), ~1,715 cm\(^{-1}\) and ~1,384 cm\(^{-1}\) were attributed to the stretching vibration of O-H, C=O and C-H bonds on MMWCNTs, respectively (Duman et al. 2019; Cemin et al. 2021). Absorption peak at ~812 cm\(^{-1}\) was ascribed to the C-O stretching (Jin et al. 2020). Strong peaks around 558 cm\(^{-1}\) and 628 cm\(^{-1}\) corresponded to the Fe-O bond in the Fe\(_3\)O\(_4\) spinel structure (Deng et al. 2019). After the adsorption of AO, the spectrum of MMWCNTs was slightly different from the original one (Figure 7). The strength of bonds located at ~1,300 to ~1,700 cm\(^{-1}\) decreased obviously, suggesting that both C-H and C=O bonds were involved in the adsorption process of AO, and the same results were observed in Figure S3. In addition, the characteristic peak of the C=C bond shifted from ~1,598 cm\(^{-1}\) to ~1,589 cm\(^{-1}\). It can be seen that there was a similar shift in the position of the peak for other dyes (Figure S3). This suggested that the \(\pi-\pi\) interaction had a certain contribution to the adsorption process (Dai et al. 2018). Importantly, a new peak at ~1,006 cm\(^{-1}\) appeared after the AO adsorption, which was assigned to the stretching vibration of C-N bond suggesting the presence of AO on MMWCNTs.

The plausible adsorption mechanisms of five dyes on MMWCNTs were analyzed based on the results of previous studies (Meng et al. 2015; Gao et al. 2019; Cai et al. 2020; Huan et al. 2020; Saxena et al. 2020) and this study. There could be four
types of interactions between dyes and MMWCNTs, namely electrostatic interaction, hydrogen bonds, π–π interaction and hydrophobic interaction (Dai et al. 2018).

A schematic diagram of possible adsorption mechanism was shown in Figure 8. Firstly, MMWCNTs possessed carboxyl functional groups, which acquired negative charge at pH > 4. The dyes investigated in this study normally possessed positively charged groups, whether it was distributed in its organic skeleton or the positively charged proton connected to the N atom. Thus, the electrostatic interaction was expected to be the main driving force, which had been confirmed by previous studies (Cai et al. 2020). Besides the electrostatic interactions, the interactions such as hydrogen bonds and the π–π interactions between dye molecules and MMWCNTs could also play important roles in the adsorption process (Gao et al. 2019). Hydrogen bonding could be formed between the hydrogen of -COOH and -OH groups on the surface of MMWCNTs and nitrogen in the dye molecules (Huan et al. 2020). As for the π–π interactions, the carbon atoms of MWCNTs are primarily sp² hybridized and have multiple π-bonds between the unpaired p orbital electrons, which thus generates freely moving π-electrons (Meng et al. 2015). The aromatic ring structure all existed in these five dyes which contained π electron and conjugated planes. Therefore, π–π interactions could also be formed and performed important role during the adsorption process. Furthermore, hydrophobic interaction between MMWCNTs and dyes could also exist as there are hydrophobic structures in both MMWCNTs and dyes studied.

4. CONCLUSIONS

The MMWCNTs prepared in the present study possessed good adsorption performance for five cationic dyes with different molecular structures. The adsorption amounts for MG, AO, CV and NR gradually increased with increasing pH values, while the adsorption performance of RhB was almost unaffected in a wide pH range. Several common ions, such as Na⁺, Ca²⁺ and Al³⁺, in solutions inhibited the sorptive removal of these five dyes on MMWCNTs. The adsorption kinetics processes were all accorded with the pseudo-second-order kinetic model. The maximum adsorption capacity of MG on the MMWCNTs was measured to be 442.2 mg g⁻¹, and the MMWCNTs preferred to adsorb protonated dyes. The reusability experiments revealed that the dyes removal efficiency by the MMWCNTs could still achieve above 75% after four cycles, suggesting that the MMWCNTs could be a kind of potential adsorbent for the removal of cationic dyes. For the adsorption mechanism, electrostatic interaction, hydrogen bonds, π–π interaction together with hydrophobic interaction, could coexisted to promote the adsorption process.
Figure 8 | The possible adsorption mechanism of cationic dye onto the MMWCNTs.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT
All relevant data are included in the paper or its Supplementary Information.

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