2017

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Zhang Ping

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http://dx.doi.org/10.1016/j.jcis.2017.08.025

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Regular Article

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PII: S0021-9797(17)30930-X
DOI: http://dx.doi.org/10.1016/j.jcis.2017.08.025
Reference: YJCIS 22672

To appear in: Journal of Colloid and Interface Science

Received Date: 16 June 2017
Revised Date: 8 August 2017
Accepted Date: 8 August 2017


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High efficiency removal of methylene blue using SDS surface-modified ZnFe$_2$O$_4$ nanoparticles

Ping Zhang $^1$, Irene Lo $^2$, David O'Connor $^1$, Simo Pehkonen $^3$, Hefa Cheng $^4$, Deyi Hou $^1$, *

$^1$ School of Environment, Tsinghua University, Beijing 100084, China
$^2$ Department of Civil & Environmental Engineering, Hong Kong University of Science & Technology, Hong Kong, China
$^3$ Department of Environmental Science, University of Eastern Finland, Joensuu, Finland
$^4$ College of Urban and Environmental Sciences, Peking University, Beijing, China

*Corresponding author: Deyi Hou, E-mail: houdeyi@tsinghua.edu.cn

Abstract: Recent studies have shown that hazardous organic dye substances can be removed from aqueous solutions by spinel ferrite nanomaterials. We found that Sodium Dodecyl Sulfonate (SDS) surface-modified mesoporous ZnFe$_2$O$_4$ nanoparticles (10-50 nm) have a remarkably high maximum adsorptive capacity (~699.30 mg/g) for aqueous Methylene Blue (MB) removal at T of 288 K and pH of 12. Unmodified ZnFe$_2$O$_4$ nanoparticles suffer from particle agglomeration, which reduces surface area, thus reducing their adsorptive capacity. Here it is shown that when modified with SDS, the specific surface area increased by ~34%. It is also shown that the anionic SDS surfactant significantly increased the electrostatic attraction to the cationic MB compound. Moreover, it was found that adsorption of MB positively correlated with the aqueous solution’s pH, which is attributed to a stronger negative charge on the SDS-modified ZnFe$_2$O$_4$ surface at high pHs. The SDS-modified ZnFe$_2$O$_4$ adsorption of MB fitted well with the Langmuir adsorption isotherm model, and kinetic data fitted into a pseudo-second-order model. Thermodynamic parameters indicated that the adsorption was spontaneous and exothermic in nature, and physisorption dominated the adsorption of MB. The findings of this study demonstrate the potential for enhanced removal of MB contamination from aqueous solutions by SDS-modified ZnFe$_2$O$_4$ nanoparticles and, therefore, the potential for them to remove cationic organic dye from wastewater.

Keywords: Adsorption capacity; Methylene blue; SDS modification; ZnFe$_2$O$_4$ nanoparticles
1 Introduction

An estimated 17%~20% of all industrial water pollution derives from the dye industries, which together produce an astounding 9 billion tons of wastewater per year [1]. Contamination of surface and groundwater by dye substances has become a serious environmental issue with many dyes exhibiting severe biotoxicity and potential mutagenic and carcinogenic effects [2], potentially harming over 1 million people [1]. For example, Methylene Blue (MB), which is commonly applied to cotton, wood, and silk [3-5], can cause various symptoms including difficulty in breathing, nausea, and vomiting[6, 7], and can impair photosynthetic processes in aquatic ecosystems [8-10]. Furthermore, dye substances typically exhibit long term chemical stability [11-13], and their complex aromatic structure is not conducive to biological degradation [14-16]. Therefore, it is of environmental importance to develop efficient methods to remove MB from wastewater effluents.

Several physical, chemical, and biological technologies have been developed to clean-up wastewater in the dye industry [17-19]. Adsorption technologies are considered the most promising [12, 20, 21] due to their ease of operation [22], low cost [23], and removal efficiencies [24, 25]. For these reasons, various traditional adsorbents including activated carbon, inorganic materials/minerals, and biomaterials have been applied for dye removal purposes. However, these adsorbents have shown several disadvantages. In particular, they are difficult to separate from process water [26], resulting in adsorbent loss. Moreover, the typical reduction in adsorptive capacity after regeneration makes their continued use expensive [27]. This has led to a search for easily recoverable and renewable materials as alternatives.

Table 1 Comparison of adsorption capacities of MB adsorbed by various adsorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Experimental conditions</th>
<th>Dosage (g/L)</th>
<th>pH</th>
<th>Temp (K)</th>
<th>$C_0$ (mg/L)</th>
<th>$q_m$ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite/carbon nanotubes</td>
<td>0.4</td>
<td>Natural pH</td>
<td>298</td>
<td>10-30</td>
<td>48.06</td>
<td></td>
<td>[28]</td>
</tr>
<tr>
<td>Polydopamine microspheres</td>
<td>0.5</td>
<td>6.50</td>
<td>298</td>
<td>10-150</td>
<td>88.89</td>
<td></td>
<td>[10]</td>
</tr>
<tr>
<td>ZnO/ZnFe$_2$O$_4$</td>
<td>0.8</td>
<td>7</td>
<td>Ambient</td>
<td>5-100</td>
<td>37.27</td>
<td></td>
<td>[29]</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>0.3</td>
<td>9</td>
<td>Ambient</td>
<td>2-200</td>
<td>138.50</td>
<td></td>
<td>[30]</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$/MWCNT composites</td>
<td>1</td>
<td>Natural pH</td>
<td>298</td>
<td>3-15</td>
<td>11.10</td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>Mn$<em>{0.8}$Zn$</em>{0.2}$Fe$_2$O$_4$</td>
<td>0.8</td>
<td>9-10</td>
<td>Ambient</td>
<td>7.5-100</td>
<td>40.97</td>
<td></td>
<td>[32]</td>
</tr>
<tr>
<td>SDS-modified ZnFe$_2$O$_4$, NP</td>
<td>0.1</td>
<td>12</td>
<td>288</td>
<td>40-100</td>
<td>699.30</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>SDS-modified ZnFe$_2$O$_4$, NP</td>
<td>0.5</td>
<td>6.84</td>
<td>288</td>
<td>5-60</td>
<td>115.34</td>
<td></td>
<td>This work</td>
</tr>
</tbody>
</table>

a: the mass of the adsorbent contained in each volume of MB aqueous solution
b: the initial concentration of MB in the aqueous solution
c: the maximum adsorption capacity of adsorbent (calculated from the Langmuir model)
Recently, nanomaterials have become a research focus due to their large surface area and abundant active sorption sites (Table 1). Because of their magnetic properties, ZnFe$_2$O$_4$ nanomaterials have been examined as easily recoverable adsorbents. They also have other desirable properties such as low toxicity, low cost, high abundance of parent materials, and good chemical stability [33]. A number of synthesis methods have been used to prepare magnetic ZnFe$_2$O$_4$ nanoparticles, including template methods, chemical co-precipitation methods, sol–gel reactions, solvothermal methods, and microwave assisted combustion [33]. Among these, the solvothermal method is considered most promising due to its low reaction temperature, protection from further calcination, low cost, and low environmental impact [34].

Previous studies have shown that organic dye substances can be removed by spinel ferrite nanomaterials through adsorption [22], and that their adsorption capacity has a strong correlation to particle size, shape, and surface area [22, 30, 35]. However, a significant limitation for the acceptance of these materials has been that the nanoparticles in aqueous solutions tend to agglomerate. This can cause blockage of available adsorption sites. Therefore, its removal efficiency is significantly decreased to sub-optimal levels [22]. To improve its aqueous dispersibility, attempts have been made to modify or functionalize the nanoparticle surfaces with inorganic oxides [22], surfactants [36–38], amino groups [39], and polymers [22]. It was found that surfactants can best protect the nanoparticles from agglomeration while simultaneously influencing the surface charge (to anionic or cationic) [40].

The present study adopted an easy-operated and controllable method to use Sodium dodecyl sulfonate (SDS), a low-toxic and biodegradable surfactant, to modify ZnFe$_2$O$_4$ nanoparticles, rendering a highly efficient adsorbent for the removal of MB from aqueous solutions. The main objectives of this investigation were: to (i) use the solvothermal method to prepare ZnFe$_2$O$_4$ nanomaterials with small particle sizes, to surface-modify the ZnFe$_2$O$_4$ nanomaterial with SDS surfactant, and to characterize the structural, textural, and morphological properties of the prepared material, (ii) highlight the adsorption capacity of SDS modified ZnFe$_2$O$_4$ nanomaterials for aqueous MB removal, (iii) evaluate the impact of various process variables including contact time, initial pH, initial MB concentration, and temperature.

2 Experimental Materials and Methods

2.1 Chemicals and materials

Ferrous sulfate FeSO$_4$$\cdot$7H$_2$O, Zinc chloride ZnCl$_2$, Ethylene glycol (CH$_2$OH)$_2$, Ammonium Hydroxide NH$_3$$\cdot$H$_2$O, Sodium dodecyl sulfonate CH$_3$(CH$_2$)$_{11}$SO$_3$Na(SDS), methylene blue C$_{16}$H$_{18}$ClN$_3$S. All chemicals were of reagent grade.
2.2 Preparation methods

ZnFe₂O₄ was prepared by adding 0.5560 g FeSO₄·7H₂O and 0.1363 g ZnCl₂ to a 50 mL mixture of ethylene glycol and deionized water (V_{EG} : V_{H₂O}=3:2). After stirring for 10 min, 2 mL of ammonia solution was added, followed by 1h of stirring. The resulting solution was sealed into a Teflon-lined stainless-steel autoclave and kept at 453 K for 24 h. After cooling to room temperature (~293 K), the precipitate was separated by centrifugation (4000 r/min for 10 min) and then washed with deionized water and ethanol three times. Finally, the product (ZnFe₂O₄) was dried for 12 h at 333 K prior to further use.

The synthesis process of SDS-modified ZnFe₂O₄ is shown in Fig. 1. The SDS modification was undertaken by dissolving 0.1 g of SDS in 10 mL of deionized water, and then adding 0.25 g ZnFe₂O₄ to the solution, and mechanically stirring the solution for 3 h. The resulting product was separated by centrifugation (4000 r/min for 10 min) and repeatedly rinsed with deionized water to remove any residue. Finally, the product (SDS-modified ZnFe₂O₄) was dried for 12 h at 333 K.

Fig.1. Schematic illustration of the synthesis of ZnFe₂O₄ and SDS-modified ZnFe₂O₄

2.3 Characterization

Morphology and microstructures were observed using scanning electron microscopy (SEM, JSM-6360) and transmission electron microscopy (TEM, TECNAI G2). The X-ray diffraction (XRD) patterns of the samples were obtained using a Rigaku D/Max-RB diffractometer with Cu/Kα radiation (k = 0.15406 nm, 35 kV, 40 mA). Fourier transform infrared spectroscopy (FTIR, Nicolet IS10) was employed to analyze the molecular structure of the product at a resolution of 4 cm⁻¹. The Brunauer–Emmett–Teller (BET) specific surface area was determined by nitrogen adsorption–desorption measurements via an Autosorb-1 specific surface area analyser (Quantachrome Instruments, USA).
2.4 Adsorption experiments

The effects of solution pH, contact time, initial concentration and temperature on the adsorption of MB were investigated by batch adsorption. For each adsorption test, 0.01 g of adsorbent was added to 20 mL solutions at various concentrations of MB and pH values. The pH values were adjusted by 0.01 or 0.1 M HCl and NaOH solutions. The mixture was shaken for 12 h in a thermostatic shaker bath and the liquid is separated by centrifugation (4000 r/min for 5 min). The concentration of MB in the aqueous solution was determined at absorbance maxima, \( \lambda_{\text{max}} = 664 \text{ nm} \) by a UV–Vis spectrophotometer (Shimadzu UV-1800 spectrophotometer, Japan). The adsorption \( Q_e \) (mg/g) and the removal efficiency of MB was calculated using the following equations:

\[
Q_e = \frac{(C_0 - C_e)V}{m}
\]

(1)

Removal efficiency(%) = \( \frac{100(C_0 - C_e)}{C_0} \)

(2)

where \( C_0 \) (mg/L) and \( C_e \) (mg/L) are the initial and equilibrium concentrations of MB in the solution, \( V \) (L) is the total volume of the suspension, and \( m \) (g) is the mass of the adsorbent. The effect of the aqueous solution’s pH on MB adsorption onto the surface of the samples was examined. 10 mg samples of ZnFe\(_2\)O\(_4\) and SDS-modified ZnFe\(_2\)O\(_4\) were placed separately in 20 mL of 50 mg/L MB solutions at 298 K for 12 h. The effect of an adsorbent dose on MB removal was investigated by adding various masses of SDS-modified ZnFe\(_2\)O\(_4\) to 20 mL of 50 mg/L MB aqueous solutions, followed by 12 h of shaking at 298 K. The effect of contact time on the adsorption of MB to ZnFe\(_2\)O\(_4\) and SDS-modified ZnFe\(_2\)O\(_4\) was examined by batch-type studies for an initial MB concentration of 50 mg/L at 298 K. The effect of temperature on the adsorptive capacity of MB onto SDS-modified ZnFe\(_2\)O\(_4\) was also investigated. Adsorption isotherms were carried out at 288, 298, and 308 K (Fig. 1).

3 Results and discussion

3.1 Characterization of samples

The phase structure and crystallite size of the prepared ZnFe\(_2\)O\(_4\) and SDS-modified ZnFe\(_2\)O\(_4\) were characterized by XRD (Fig.2). All the characteristic reflection peaks at 2\( \theta \) = 29.86°, 35.15°, 36.77°, 42.72°, 52.98°, 56.47°, 62.25° can be ascribed to the diffraction of cubic ZnFe\(_2\)O\(_4\) crystal with the (220), (311), (222), (400), (422), (511), and (440) planes, respectively (PDF\#22-1012) [35, 41], indicating the successful preparation of the sample using the solvothermal method. The ZnFe\(_2\)O\(_4\) (311) peak showed the highest intensity, indicating that the sample’s growth was oriented along the (311) direction. No other obvious diffraction peaks were observed in the XRD patterns of the SDS-modified ZnFe\(_2\)O\(_4\) sample.
Fig. 2. XRD patterns of ZnFe$_2$O$_4$ and SDS-modified ZnFe$_2$O$_4$

The morphology, shape and size of the materials were obtained by SEM and TEM measurements. The SEM and TEM images show that the SDS-modified ZnFe$_2$O$_4$ was composed of well-dispersed and nano-sized particles (Fig. 3A, B), with diameters in the range of 10-50 nm (Fig. 3C, D). Fig. 4 shows the elemental mapping spectra of the SDS-modified ZnFe$_2$O$_4$ nanoparticles. The blue, red and green images indicate the Zn-, Fe- and O-enriched areas of the sample, respectively. It is worth noting that the elements are well dispersed in the samples and the presence of Zn, O, and Fe atoms affirms the existence of ZnFe$_2$O$_4$. 
**Fig. 3.** SEM images (A,B) and TEM images (C,D) of the SDS-modified ZnFe$_2$O$_4$
Fig. 4. The selected area (A) and the corresponding EDS mappings (B- Zn element; C- Fe element; D- O element.) of the SDS-modified ZnFe₂O₄ sample

N₂ adsorption-desorption was used to determine the specific surface area and pore size distribution. As Fig. 5A shows, the N₂ adsorption curves of unmodified ZnFe₂O₄ and SDS-modified ZnFe₂O₄ both exhibited typical type IV isotherms with an H₃-type hysteresis loop (P/P₀ > 0.4), indicating the presence of mesopores in both samples [42]. The surface area of the SDS-modified ZnFe₂O₄ sample, calculated by the standard Brunauer–Emmett–Teller (BET) method, was 55.19 m²·g⁻¹, which was ~34% greater than in the unmodified ZnFe₂O₄ (41.25 m²·g⁻¹). This indicates greater potential adsorption sites and, therefore, a greater potential adsorption capacity of the SDS-modified ZnFe₂O₄. Fig. 5B displays the pore size distribution curves, calculated by the BJH method, for unmodified ZnFe₂O₄ and SDS-modified ZnFe₂O₄ samples, which were found to be centred at 17.61 nm and 12.42 nm, respectively, again showing the mesoporous structure of the samples.
Fig. 5. The nitrogen adsorption-desorption isotherms (A) and pore size distributions (B).

Fig. 6. FTIR spectra (A) of ZnFe$_2$O$_4$ and SDS-modified ZnFe$_2$O$_4$ samples, (B) displays the FTIR spectra of MB and (c) SDS-modified ZnFe$_2$O$_4$ sample before (a) and after adsorption (b).

Fig. 6A displays the FTIR spectra of ZnFe$_2$O$_4$ and SDS-modified ZnFe$_2$O$_4$ samples in the frequency range of 400 – 4000 cm$^{-1}$. The FTIR spectrum of ZnFe$_2$O$_4$ showed strong vibrational bands in the lower frequency regions (at around 545-560 cm$^{-1}$), typical of ferrite materials and ascribable to the vibration of Fe–O in the spinel lattice [35, 43]. The absorption seen at ~3440 cm$^{-1}$ is thought to be due to the symmetric vibration of the -OH groups of the absorbed H$_2$O molecules [43]. The peak at ~1630 cm$^{-1}$ corresponds to O–H groups, again related to adsorbed H$_2$O molecules [43]. Compared with the spectra of unmodified ZnFe$_2$O$_4$, new adsorption bands for the SDS-modified ZnFe$_2$O$_4$ were located at 2910 to 2852 cm$^{-1}$, which are attributed to symmetry and asymmetry stretching vibration of the -CH$_2$- groups of the SDS. Furthermore, a peak at 1185 cm$^{-1}$ relates to asymmetry vibration of –SO$_3$ groups in the SDS. These results confirm the successful preparation of ZnFe$_2$O$_4$ and SDS-modified ZnFe$_2$O$_4$ materials. In addition, the FTIR spectra of SDS-modified ZnFe$_2$O$_4$ samples before and after adsorption with MB were recorded (Fig.6B). It can be seen in the spectra that the intensity of the peaks, located
at 2910, 2852 and 1185 cm$^{-1}$, decreased after adsorption of MB onto the SDS-modified ZnFe$_2$O$_4$ samples, indicating the involvement of the corresponding functional groups of the dye molecule in the adsorption process and the existence of electrostatic attraction between the dye molecule and the sample [44, 45].

3.2 Effects of operating conditions on MB adsorption

3.2.1 Effects of solution pH

The value of pH was found to be an important parameter affecting adsorption, with basic solutions favouring the adsorption process. As illustrated in Fig. 7, the adsorption of MB gradually increased as a function of pH for both materials. In acidic conditions, it can be explained by competition between the numerous protons (H$^+$) and cationic dye molecules for available adsorption sites. As pH increases, the electrostatic attraction between the negatively charged surface of the adsorbent and cationic MB molecules increases, resulting in increased adsorption. It is worth noting that MB adsorption by SDS-modified ZnFe$_2$O$_4$ was greater than that of unmodified ZnFe$_2$O$_4$, ascribable to the surface properties of the SDS-modified ZnFe$_2$O$_4$ nanoparticles. This shows that the anionic SDS surfactant significantly increased the nanoparticle electrostatic attraction to the cationic MB compound. This is in accordance with the results of FTIR and N$_2$ adsorption-desorption experiments. As a result, higher pH solutions and SDS modification are beneficial for MB adsorption.

![Fig. 7](image.png)

Fig. 7. Effect of initial pH on the adsorption capacity of ZnFe$_2$O$_4$ and SDS-modified ZnFe$_2$O$_4$. pH = 2.00–12.00; T = 298 K; the amount of adsorbent 0.01 g/20 mL; Initial MB concentration 50 mg/L; contact time=12 h.
3.2.2 Effect of adsorbent dose

The relation between adsorption (Qe) and removal efficiency with the adsorbent dosage (mass) is shown in Fig. 8. As the dosage of adsorbent increased from 2 to 40 mg, the specific adsorption capacity decreased from 145.85 to 22.99 mg/g. This is because as dosage increases, the amount of adsorbate per unit mass of adsorbent decreases, therefore changing the distribution equilibrium between the aqueous and solid phases. In addition, there will likely be overlapping of active adsorption sites due to adsorbent agglomeration, and less mass transfer would likely take place as the interfacial tension between the solid and aqueous phases increases with additional adsorbent mass addition [46, 47]. These factors would reduce mass transfer and thus the adsorptive capacity is decreased. On the other hand, the overall removal efficiency increased as the adsorbent dosage increased, due to the increase in the total number of available adsorption sites [46, 47].

![Graph](image)

**Fig.8.** The effect of SDS-modified ZnFe₂O₄ dose (0.002–0.04 g) on the adsorption of MB at Natural pH; temperature 298 K; initial MB concentration 50 mg/L.

3.2.3 Effect of contact time and adsorption dynamics (kinetics)

As shown in Fig. 9, the adsorption of MB initially increased rapidly with time due to the availability of numerous active adsorption sites. The rate of increase was later reduced and tended towards an asymptote, attributed to the decreasing number of available active adsorption
It can also be seen that the two materials had different adsorption capacities for MB, with the SDS-modified sample showing a much greater overall adsorption capacity.

**Fig. 9.** Effect of contact time on MB adsorption. Natural pH; temperature 298 K; amount of SDS-modified ZnFe₂O₄ 0.01 g/20 mL; initial MB concentration 50 mg/L

The adsorption kinetics of MB on the SDS-modified ZnFe₂O₄ samples were analysed using pseudo-first-order [22] and pseudo-second-order models [48]. These kinetic models can be expressed in a linear form as follows:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  
\[ \frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \]

where \( q_e \) and \( q_t \) (mg/g) are the amounts of MB adsorbed at equilibrium and at time \( t \) (min), respectively. \( k_1 \) (min⁻¹) represents the rate constant of the pseudo-first-order model and \( k_2 \) (g mg⁻¹ min⁻¹) represents the pseudo-second-order rate constant. The line plots of \( \ln(q_e - q_t) \) versus \( t \) or \( t/q_t \) against \( t \) (min) are shown in Fig. 10A and B, respectively, and the corresponding kinetic parameters are listed in Table 2. The linear relationship with a high \( R^2 \) value (0.998) between \( t/q_t \) and \( t \) indicates that the adsorption process follows the pseudo second-order model.
Fig. 10. Pseudo-first-order (A), pseudo-second-order (B), plot for the removal of MB by SDS-modified ZnFe$_2$O$_4$. Natural pH; temperature 298 K; amount of SDS-modified ZnFe$_2$O$_4$ 0.01 g/20 mL.

Table 2 Pseudo-first-order and pseudo-second-order constants and values of $R^2$ for SDS-modified ZnFe$_2$O$_4$.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>T(K)</th>
<th>$C_0$ (mg/L)</th>
<th>$Q_{e,exp}$ (mg/g)</th>
<th>$Q_{e,calc}$ (mg/g)</th>
<th>$k_1$ (min$^{-1}$)/$k_2$ (g/mg min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>298</td>
<td>50</td>
<td>75.63</td>
<td>23.34</td>
<td>0.006</td>
<td>0.539</td>
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<tr>
<td>Pseudo-second order</td>
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<td>50</td>
<td>75.63</td>
<td>73.80</td>
<td>0.00214</td>
<td>0.998</td>
</tr>
</tbody>
</table>
3.2.4 Effect of temperature and adsorption thermodynamics

The effect of temperature on the adsorptive capacity of MB onto SDS-modified ZnFe₂O₄ was investigated. Adsorption isotherms were carried out at 288, 298, and 308 K (Fig. 11). The Gibbs free energy ($\Delta G_0$), standard enthalpy ($\Delta H_0$) and the standard entropy ($\Delta S_0$) of adsorption are calculated using the equations shown in Eq. (5), (6) and (7):

\[
K_d = \frac{q_e}{C_e}
\]  
(5)

\[
\Delta G_0 = \Delta H_0 - T\Delta S_0
\]  
(6)

\[
\ln K_d = -\frac{\Delta H_0}{RT} + \frac{\Delta S_0}{R}
\]  
(7)

where $K_d$ is defined as the distribution coefficient (mL/g), $q_e$ is the amount of MB adsorbed per unit mass of adsorbent (mg/g) at equilibrium, and $C_e$ is the equilibrium concentration of MB in the solution (mg/l). $R$ is the gas constant (8.314 J/(mol·K)), $\Delta H_0$ is standard enthalpy (kJ/mol), $\Delta S_0$ is standard entropy (J/(mol·K)), $T$ is the absolute temperature (K). The thermodynamic parameters obtained from the intercept and slope of the linear plot of $\ln K_d$ vs. $1/T$ are given in Fig.11 and Table 3. The negative values of $\Delta G$ and its absolute value, which decreased with increasing temperature, indicate that the adsorption of MB on the samples was spontaneous [49]. In general, the range of free energy for physisorption lies between 0 and -20 kJ mol⁻¹, and that of chemisorption is between -80 and -400 kJ mol⁻¹ [44, 49, 50]. For the present study, the values of $\Delta G$ at the three experimental temperatures indicate a physisorption process. Moreover, the negative value of $\Delta H_0$ reflects the exothermic nature of the adsorption process, and the negative value of $\Delta S_0$ reflects reduced randomness in the solid-solution interface during the adsorption process.

![Image of graph showing lnKd vs. 1/T(K⁻¹)]
**Fig.11.** Relationship between ln $K_d$ and $1/T$ for the adsorption of MB on SDS-modified ZnFe$_2$O$_4$ at 288, 298, and 308 K. natural pH. the amount of SDS-modified ZnFe$_2$O$_4$ 0.01 g/20 mL.

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>$\Delta G_0$(kJ mol$^{-1}$)</th>
<th>$\Delta H_0$(kJ mol$^{-1}$)</th>
<th>$\Delta S_0$(J mol$^{-1}$K$^{-1}$)</th>
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<tr>
<td>288</td>
<td>-7.740</td>
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<td>298</td>
<td>-6.899</td>
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<tr>
<td>308</td>
<td>-6.059</td>
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**3.2.5 Adsorption isotherms of methylene blue (MB)**

Figure 12 depicts the adsorption of MB on the SDS-modified ZnFe$_2$O$_4$ for different initial concentrations at different initial temperatures. The equilibrium adsorption data were analysed using the Langmuir and Freundlich models [51, 52].

**Fig.12.** Adsorption isotherms of SDS-modified ZnFe$_2$O$_4$ for MB at different temperatures. Natural pH; temperature 288-308 K; the amount of SDS-modified ZnFe$_2$O$_4$ 0.01 g/20 mL; initial MB concentration 5–60 mg/L.
The Langmuir equation has been extensively applied to the analysis of monolayer sorption in the following form [51]:

\[ \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (8) \]

where \( K_L \) (L/mg) is the Langmuir constant, \( C_e \) (mg/L) is the solute equilibrium concentration, \( q_e \) (mg/g) is the amount of solution adsorbed per unit mass of the adsorbent, and \( q_m \) is the maximum adsorption capacity (mg g\(^{-1}\)). According to Eq. (8), the values of \( q_m \) and \( K_L \) can be determined from the slope and the intercept of the straight line of \( C_e/q_e \) vs \( C_e \) (Fig. 13A).

![Fig. 13. Langmuir (A) and Freundlich (B) plots for the removal of MB by SDS-modified ZnFe\(_2\)O\(_4\). Natural pH; temperature 288-308 K; amount of SDS-modified ZnFe\(_2\)O\(_4\) 0.01 g/20 mL.](image)

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_m ) (mg/g)</td>
<td>( K_L ) (L/mg)</td>
</tr>
<tr>
<td>288</td>
<td>115.34</td>
<td>0.963</td>
</tr>
<tr>
<td>298</td>
<td>89.85</td>
<td>1.029</td>
</tr>
<tr>
<td>308</td>
<td>84.60</td>
<td>1.010</td>
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</table>
The Freundlich isotherm can be used for heterogeneous surfaces and multilayer adsorption [52]:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]  

(9)

where \( K_F \) is the Freundlich constant related to the adsorption capacity, and \( 1/n \) is the adsorption intensity. The plots of \( \ln q_e \) against \( \ln C_e \) (Fig. 13B) enable the values of \( 1/n \) and \( \ln K_F \) to be obtained for Eq.(9). Table 4 summarizes the parameters \( (q_m, K_L, K_F, \text{ and } n) \) of the adsorption isotherms along with coefficient of determination \( (R^2) \) values. It is shown that the Langmuir isotherm model better fits the experimental results over the experimental range, with higher \( R^2 \) values. This may be due to the homogeneous distribution of active sites on the SDS-modified ZnFe₂O₄ surface. The \( K_F \) values (i.e., the Freundlich constants) of MB at 288, 298, and 308 K were 48.698, 37.679 and 36.467 L/g, respectively. It has previously been reported that enhanced adsorption can be related to values of \( n \) in the range 1–10 [47]. In the present work, the \( n \) values fitted within this range, suggesting favourable adsorption.

The efficiency of the adsorption can also be expressed in terms of equilibrium parameter \( R_L \), which is defined as follows [53]:

\[ R_L = \frac{1}{1 + K_L C_0} \]  

(10)

where \( C_0 \) is the initial concentration and \( K_L(L/mg) \) is the Langmuir constant. The values of \( R_L \) indicates the isotherm shapes, which can be unfavourable \((R_L \geq 1)\) or favourable \((0 \leq R_L \leq 1)\) [28, 53]. For MB adsorption on SDS-modified ZnFe₂O₄, the \( R_L \) values obtained were <1, confirming that the adsorption is a favourable process.

### 3.2.6 Performance evaluation

Finally, SDS-modified ZnFe₂O₄ samples were applied to different concentrations of MB under the determined optimal conditions. As Fig. 14 shows, the MB equilibrium adsorption increased with the increase in initial MB solution concentration. Table 1 lists the comparison of the maximum adsorption capacities \( (q_m) \) for MB of previously reported adsorbents. The SDS-modified ZnFe₂O₄ showed a remarkably high adsorption capacity of 699.30 mg/g, which is significantly greater than all other values published.
In addition, the stability of samples in aqueous solution may be important for the aimed application. As shown in Fig. 15, it was tested by reacting 50mg/L of MB with the same amount of SDS-modified ZnFe₂O₄ samples suspended in water for 0, 8, 24, 48 and 72h, separately. It’s evident that the adsorption capacities of different samples remained consistent at around 73.08mg/g, and the high stability of SDS-modified ZnFe₂O₄ NPs favor their potential application in the remediation of dye-contained water.

![Fig. 14. Adsorption isotherm of SDS-modified ZnFe₂O₄ for MB at different concentrations. pH 12; temperature 288K; the amount of SDS-modified ZnFe₂O₄ 0.002 g; V_Mb 20 mL.](image)

Table 5 Isotherm constants and values of R² for SDS-modified ZnFe₂O₄ in the optimal conditions (pH 12; temperature 288K; the amount of SDS-modified ZnFe₂O₄ 0.002 g).

<table>
<thead>
<tr>
<th>T(K)</th>
<th>Q_m (mg /g )</th>
<th>K_L (L/mg )</th>
<th>R²</th>
<th>K_F (L/g)</th>
<th>n</th>
<th>R²</th>
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<td>288</td>
<td>699.30</td>
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<td>0.987</td>
<td>144.038</td>
<td>2.669</td>
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4 Conclusions

For this work, ZnFe$_2$O$_4$ nanoparticles of sizes between 10 and 50 nm were successfully produced by the solvothermal method and modified using SDS. It was found that the SDS-modified ZnFe$_2$O$_4$ samples had a high specific surface area and mesoporous structure. Experimental results showed that the adsorption capacity of SDS-modified ZnFe$_2$O$_4$ for aqueous MB can reach up to 699.30 mg/g at 288K, pH=12. This value is greater than other adsorbent materials reported so far. This was ascribed to the strong electrostatic interactions between the negatively charged SDS-modified ZnFe$_2$O$_4$ adsorbent and the cationic MB molecules. It was also found that the level of adsorption was highly dependent on the pH of the aqueous solution. Kinetic data studies showed a good fit to a pseudo-second-order kinetic model, and the experimental equilibrium data showed that the Langmuir isotherm describes the adsorption process well. Thermodynamic analyses suggested that MB adsorption onto SDS-modified ZnFe$_2$O$_4$ nanoparticles was spontaneous and exothermic. It is expected that the
SDS-modified ZnFe$_2$O$_4$ nanoparticles will be of great interest for organic dye removal from contaminated water.

5 Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 41671316), the Thousand Talents Program of the Chinese government and Tsinghua University.

6 References


[32] X. Hou, J. Feng, X. Liu, Y. Ren, Z. Fan, M. Zhang, Magnetic and high rate adsorption properties of porous Mn(1-x)Zn(x)Fe2O4 (0 <= x <= 0.8) adsorbents, J Colloid Interface Sci 353(2) (2011) 524-9.


6.1.1 Graphical abstract