Fe$_3$O$_4$-CS-L: a magnetic core-shell nano adsorbent for highly efficient methyl orange adsorption

Shuangzhen Guo, Jian Zhang, Xianlong Li, Fan Zhang and Xixi Zhu

ABSTRACT

A novel core-shell bio-adsorbent was fabricated by using biological materials for removing methyl orange (MO) from aqueous solution. The structure characteristics results of scanning electron microscopy (SEM), Fourier transform infrared spectrometry (FT-IR), thermo-gravimetric analysis (TGA), vibrating sample magnetometer (VSM), and Brunauer–Emmett–Teller (BET) shows that Fe$_3$O$_4$-CS-L has been successfully prepared. The effects of contact time, pH, temperature and initial concentration were explored. The results suggested pH was a negligible factor in adsorption progress. Kinetic studies showed that the experiment data followed pseudo-second-order model. Boyd mode suggested that external mass transfer showed a rather weak rate control for MO adsorption onto Fe$_3$O$_4$-CS-L. Equilibrium studies showed that isotherm data were the best described by Langmuir model. The maximum adsorption capacity of MO estimated to be 338.98 mg/g at 298 K. Moreover, the adsorption capacity of Fe$_3$O$_4$-CS-L can keep about 74% in the fifth adsorption–regeneration cycle. Thus, the Fe$_3$O$_4$-CS-L could be a kind of promising material for removing MO from wastewater.

Key words | adsorption, bio-adsorbent, L-arginine and chitosan, methyl orange

INTRODUCTION

In recent years, water pollution has caught social and academic attention. Dye and heavy metals pollution are the two most common pollution scenarios in water pollution. More than 7 × 10$^4$ tones commercial dyes are produced per year for coloring product (Sen et al. 2010). Among them, the consumption of dyes are more than 10,000 t/year in the textile industry and over 100 t/year of dyes is discharged into environment (Yagub et al. 2012). It is very difficult to degradation for most of dyes, due to complex composition, stable chemical properties and high chemical oxygen consumption. Hence, the treatment of dye wastewater are attracted more and more attention.

Various of techniques have been used to deal with dye wastewater such as membrane filtration (Alventosa et al. 2012), aerobic or anaerobic treatment (Hosseini et al. 2011), electrochemical treatment (Körbahti et al. 2011), coagulation–floculation (García et al. 2008) and adsorption methods (Tang et al. 2013; Zhang et al. 2014). Among of them, more and more attention is given to adsorption because of its cost-effective and easy to operate. Conventionally, inorganic nanoparticle (Muthukumaran et al. 2016; Wang et al. 2016), zeolites (Faki et al. 2008), bentonite (Weng & Pan 2007; Lian et al. 2009) and active carbon (Jiang et al. 2015) were reported to deal with dye wastewater. As one coin has two sides, these adsorbents also have their own shortcomings, such as separation inconvenience, high cost of raw materials and low adsorption capacity. Hence, it is the design aim of adsorbent which own the advantages of high adsorption capacity, low cost of raw materials and facile separation.

Chitosan, as a biopolymer, can be extracted from chitin and has abundant sources (Wu et al. 2016). Due to abundant amino groups and hydroxy groups, which were located on the carbon skeleton of chitosan, chitosan have potential for removing dye from wastewater by adsorption method. Recently, magnetic adsorbents have been widely used to remove dyes and heavy metals from aqueous solution, because it can enhance the separation rate (Asfaram et al. 2015; Habila et al. 2016). Chitosan was often used to combine with magnetic materials to prepare magnetic core-shell nanoparticles which consist of an iron oxide core and chitosan shell. Li has investigated that 3-chloro-2-hydroxypropyl trimethyl ammonium modified chitosan magnetic composite was used to remove methyl orange...
(MO) from aqueous solution (Li et al. 2016). Elwakeel also discussed magnetic chitosan for the removal of reactive black 5 from wastewater (Elwakeel 2009). However, chitosan is not stable and soluble in acidic solution and its ability to adsorb dye is still insufficient, which limits its future application in the treatment of dye wastewater. In modifying the chitosan shells by chemical modification, it not only can solve the instability and acid resistance, but also can achieve a specific function, such as large adsorption capacity and bioseparation (Reddy & Lee 2015). Various dyes could be adsorbed by some specific interactions such as hydrogen bond and electrostatic attraction (Sakkayawong et al. 2005). Various functional groups could be flexibly grafted onto chitosan for effective adsorption of dyes (Li et al. 2016). L-arginine with amino groups and carboxyl groups has good water solubility. It could improve stability and adsorption capacity of chitosan, if chitosan was modified by L-arginine (Arash et al. 2016).

In this paper, a novel magnetic core-shell adsorbent was prepared by grafting chitosan and L-arginine on the surface of Fe3O4. This magnetic adsorbent was developed for the adsorption of MO from aqueous solution. Combining functionalities of magnetism and biopolymer, magnetic core-shell chitosan nanoparticles show fast separation properties and high adsorption capacity.

**MATERIALS AND METHODS**

**Materials**

Potassium iodide, FeSO4·7H2O, L-arginine, sodium hydroxide, sodium thiosulfate, acetone, NaOH, HNO3 and ethanol were purchased from Sinopharm Chemical Reagents Corp. (Shanghai, China). Chitosan, glutaraldehyde and epoxy chloropropane were Aladdin products (Shanghai, China). In this study, the water is deionized water and all reagents were of analytical grade.

**Synthesis of magnetic composite**

Fe3O4 is prepared by traditional hydrothermal synthesis method (Guo et al. 2017).

Chitosan (1.0 g) was dissolved in acetic solution (3%, 100 mL), then Fe3O4 (1.0 g) were added in the chitosan solution. Glutaraldehyde (8.0 mL) was dropwise added into the mixed solution under stirring at 333 K for 2 h (Fan et al. 2012). The residues were washed with deionized water and ethanol until pH was about 7. Afterward, the residues were dissolved in acetone (100 mL) and stirred to form a suspension. Epichlorohydrin (5.0 mL) was added dropwise to suspensions. This suspension was stirred for 24 h at 303 K (Kuang et al. 2013).

L-arginine (6.0 g) was dissolved in dimethyl formamide (50 mL) and then slowly dropped into the reaction, K2CO3 (3.0 g) which have roasted under high temperature and KI (0.05 g) were added in solution and the mixture was reflux at 338 K for 12 h. The residues were washed with distilled water, ethanol and acetone in turn. The residue was dried at 333 K under vacuum condition. The structure diagram of Fe3O4-CS-L is shown in Figure 1.

**Characterization**

X-ray powder diffraction (XRD) results were obtained on Rigaku IV (Rigaku, Japan). Scanning electron microscope (SEM) images were obtained on IGMA (Carl Zeiss, Germany). The hysteresis loops were tested by a vibrating sample magnetometer (LDJ 9600, USA). Fourier transform infrared (FT-IR) spectra were gained by infrared spectrometer (Thermo Nicolet 380, USA). The thermogravimetric analysis (TGA) result was obtained by thermogravimetric analyzer (SDTA851, Swit). The concentration of MO was determined with double beam ultraviolet (UV)–vis spectrophotometer (TU-1901, China).

**Batch adsorption experiments**

Batch adsorption experiments were shocked on water bath equipment (Bote Ltd, China) with a shock speed of 629

Figure 1 | The structure diagram of Fe3O4-CS-L.
300 rpm, Fe₃O₄-CS-L (0.1 g) was added in 100 mL different concentrations of MO solution. NaOH(0.1 mol/L) or HNO₃(0.1 mol/L) solution was used to adjust the pH of the aqueous solutions. The adsorption capacity of Fe₃O₄-CS-L at any time and equilibrium are calculated according to the formula:

\[ q_t = \frac{(C_0 - C_t) \cdot V}{W} \]  

(1)

\[ q_e = \frac{(C_0 - C_e) \cdot V}{W} \]  

(2)

The removal percentage (%) was calculated as follows:

\[ \eta = \frac{C_0 - C_e}{C_0} \times 100\% \]  

(3)

where \( C_0 \) (mg/L), \( C_t \) (mg/L) and \( C_e \) (mg/L) represent the initial MO concentration, at time \( t \) and the equilibrium time, respectively; \( V \) on behalf of the volume of the MO solution (mL) and \( W \) is the amount of adsorbent (mg).

**RESULTS AND DISCUSSION**

**Characteristics of the prepared Fe₃O₄-CS-L**

Figure 2 shows the microtopography of Fe₃O₄ and Fe₃O₄-CS-L. From Figure 2, we found that Fe₃O₄ and Fe₃O₄-CS-L showed irregular polyhedron morphologies. Moreover, the radius of Fe₃O₄-CS-L was larger than that of Fe₃O₄. The agglomeration of Fe₃O₄ was more serious than Fe₃O₄-CS-L.

Figure 3 shows FT-IR spectra of Fe₃O₄, Fe₃O₄-CS and Fe₃O₄-CS-L. As for Fe₃O₄, Fe₃O₄-CS and Fe₃O₄-CS-L, the absorption peak in 568 cm⁻¹ appears which related to Fe-O stretching vibrations. As for magnetic chitosan, a broad weak absorption peak in the range of 2,600–3,300 cm⁻¹ appears which corresponds to N-H and O-H stretching vibrations, the new peaks at 2,030 cm⁻¹ are ascribed to the ammonium salt feature peaks, the peaks at 1,210–1,010 cm⁻¹ are related to the C-O and C-N stretching vibrations. It proved that chitosan has been grafted on surface of magnetic Fe₃O₄ with the help of glutaraldehyde. When L-arginine is grafted on magnetic chitosan, a new band at 1,750 cm⁻¹ and 1,690–1,640 cm⁻¹ due to C = O and C = N stretching vibration in L-arginine. In addition, the obviously strengthened peak at 1,073 cm⁻¹ in Fe₃O₄-CS-L, which is related to the reaction between acyl chloride (in Fe₃O₄-CS) and amino (in L-arginine). The FT-IR spectra results proved that Fe₃O₄-CS-L has been prepared successfully.
Thermogravimetric results of Fe$_3$O$_4$, Fe$_3$O$_4$-CS and Fe$_3$O$_4$-CS-L are shown in Figure 4. From Figure 4, it can be found that there were two decomposed quantities of 3.67% from 55°C to 122°C, and of 3.27% from 601°C to 708°C in magnetic Fe$_3$O$_4$ thermogravimetric curve, corresponding to adsorbed water and to condensation of the iron oxide hydroxyl. For Fe$_3$O$_4$-CS, there is an additional mass loss step of 44.1% from 135°C to 715°C attributed to the chitosan grafted on surface of magnetic Fe$_3$O$_4$. As for Fe$_3$O$_4$-CS-L, it showed four decomposed quantities of 4.15% from 55°C to 120°C, of 31.46% from 122°C to 352°C, of 7.19% from 352°C to 419°C, and of 15% from 419°C to 516°C, which are related to adsorbed water, amino, carboxyl and hydroxyl in chitosan carbon skeleton thermal decomposition. The TGA results showed that the grafted chitosan and L-arginine were calculated to be approximately 58.41% for the total mass of Fe$_3$O$_4$-CS-L.

Figure S1 (available with the online version of this paper) shows Brunauer–Emmett–Teller (BET) results of Fe$_3$O$_4$-CS-L. Adsorption measurements were performed under the same conditions, followed by desorption measurements. According to International Union of Pure and Applied Chemistry (IUPAC) classification, the isotherm is a type III and the BET surface area is 3.63 m$^2$/g.

The magnetization of Fe$_3$O$_4$ and Fe$_3$O$_4$-CS-L were investigated with a vibrating sample magnetometer (VSM). From Figure S2 (available online), the saturation magnetization (M$_s$) value of Fe$_3$O$_4$ and Fe$_3$O$_4$-CS-L were 57.6 and 14.1 emu/g, respectively. Although magnetization strength decreased after grafting chitosan and L-arginine, it could be concluded that the separation of Fe$_3$O$_4$-CS-L in aqueous solution could be controlled by electromagnet with convertible magnetic field.

### Adsorption experiments

#### Effect of initial MO concentration

Figure 5 shows the effect of initial MO concentration on adsorption capacity. As shown in Figure 5, the equilibrium adsorption capacity increases while the removal efficiencies drop rapidly with increases of initial MO concentrations from 100 mg/L to 500 mg/L. At range of 500–700 mg/L, the equilibrium adsorption capacity keeps in a stable value (240 mg/g). This is due to the fact that the functional groups which were located on the surface of Fe$_3$O$_4$-CS-L tend to saturate with increases of MO concentrations and it reached saturation at a concentration of 500 mg/L. So, the equilibrium adsorption capacity remains constant in the range of 500–700 mg/L. Thus, the optimal MO concentration was confirmed at 500 mg/L for the following experiments.

#### Effect of pH

As we all know, there are two main structures of MO at different pH values. It is present as a quinone type at a lower pH (under acidic conditions), while it is rearranged into azo structure at a higher pH (Zhu et al. 2010). The rearrangement of MO is shown below:

![MO structure rearrangement](image)

The adsorption capacity was certainly influenced by the change of structure of MO, so it is essential to explore the effect of pH changes on adsorption capacity. Figure 6 shows the adsorption capacity as a function of pH.

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**Figure 4** Thermogravimetric curve of magnetic Fe$_3$O$_4$, Fe$_3$O$_4$-CS and Fe$_3$O$_4$-CS-L.

**Figure 5** Effect of initial concentration of MO on adsorption removal efficiency and adsorption capacity (Experiment condition: pH = 3, T = 298 K, contact time is 50 min).
shows that the change of adsorption capacity was investigated at varying pH values 2–11. As shown in Figure 6, the adsorption capacity increased from 231 mg/g to 252 mg/g with increases of pH from 2 to 3. The maximum value of adsorption capacity was reached at pH = 3, and the adsorption capacity decreases at range of 3–11.

The dissociation constant of MO is 3.46, it means the structure of MO is presented as quinone at the pH < 3.0, the two main active sites of quinone structure are sulfanyl and amino groups. The –S=O group can be served as the electron pair acceptor and form regular hydrogen bonding with the amino group (–NH₂) of Fe₃O₄-CS-L surface, while the –NH group can be served as the electron pair donor and form regular hydrogen bonding with the carboxyl group (–COOH) in Fe₃O₄-CS-L composite. The hydrogen bonding between MO and Fe₃O₄-CS-L may result in the presence of large adsorption capacity at lower pH. With increases of pH from 3 to 11, the adsorption capacities of MO drop gradually. When the pH is increased, quinone structure of MO is gradually transformed into its azo structure. Azo structure of MO only has one reaction site –S=O can form regular hydrogen bonding and the hydrogen bonding between MO and Fe₃O₄-CS-L is reduced, which leads to the decrease of adsorption capacity (Liu et al. 2015). In addition, there is competition repulsion existence between MO anions and OH⁻, which lead to the decrease in MO adsorption (Subbaiah & Kim 2016).

**Effects of contact time and temperature**

Contact time and temperature are two of the most important factors which can affect adsorption progress. As shown in Figure 7, the effect of temperature and contact time on adsorption MO. From Figure 7, we can find that the adsorption capacity is increasing with increases of contact time within 50 min and then the adsorption capacity keep a stable value beyond 50 min. In addition, the adsorption capacity is increasing with increases of temperature from 298 K to 313 K, it also proved that the adsorption progress is endothermic in nature. According to the above results, 50 min was considered to equilibrium time in batch adsorption experiments. There is no significant change of adsorption capacity from 298 K to 313 K, so the temperature is determined as 298 K in the following experiment.

**Adsorption kinetic**

The mechanism of adsorption progress can be investigated by fitting kinetic model. Considerable research efforts have been devoted to three kinetic models (pseudo-first-order kinetic model, pseudo-second-order kinetic model and intraparticle diffusion model) to describe adsorption progress mechanism.

The equation of pseudo-first-order model and pseudo-second-order are represented as follows:

\[
\log\left(\frac{q_e}{q_t}\right) = \log\frac{q_e}{K_1t} + \frac{1}{2.303}
\]

\[
\frac{t}{q_t} = \frac{1}{K_2(q_e)^2} + \frac{t}{q_e}
\]

where \(q_t\) and \(q_e\) (mg/g) are the adsorption capacity for MO adsorbed at any time \(t\) and at equilibrium time. \(K_1\) (min⁻¹) is...
the rate constant of the pseudo-first-order and $K_2$ (min$^{-1}$) is
the rate constant of the pseudo-second-order. $t$ is contact
time. The data of the fitted models by use of these equations
are shown in Table 1 and Figure S3 (available online).

The $R^2$ values of the pseudo-second-order model are
higher than the pseudo-first-order model. In others word,
the pseudo-second-order model is more suitable for describing
the adsorption behavior of MO on Fe$_3$O$_4$-CS-L,
indicating the sort of adsorption is chemical adsorption.

As we all know, the adsorption process can be divided into
two stages: (1) MO was moved from the bulk solution to the
surface of adsorbent; (2) adsorb onto an active site. Intraparti-
tle diffusion model was often used to describe the contribution
of intraparticle diffusion to rate control step. The intraparticle
diffusion model can be described as follows:

$$ q_t = K_i t^{0.5} + C $$  \hspace{1cm} (6)

where $C$ is a constant and $K_i$ is the rate constant. The data of
the fitted models by using of these equations are shown in
Table 2 and Figure S4 (available online). It is obvious that
the $q_t - t^{0.5}$ polts can be divided into three distinct regions.
The external mass transfer is related to the first linear portion.
The intraparticle diffusion is related to the second linear por-
tion. The adsorption–desorption equilibrium is related to the
third linear portion. It is important to highlight that the time
of intraparticle diffusion is decreasing with increases of temper-
perature, indicating temperature would influence the diffusion
rate in intraparticle diffusion stage. Table 2 data show that
the second linear portion does not get through the origin point
from 293 to 308 K, meaning that intraparticle diffusion
is not the only rate-limiting step.

Boyd mode was used to distinguish the rate control step
in adsorption between intraparticle diffusion and mass
transfer. Boyd mode can be described as follows:

$$ B_t = -\ln\left(1 - \frac{q_t}{q_m}\right) = 0.4977 $$  \hspace{1cm} (7)

where $q_t$ and $q_m$ are the adsorption capacity of MO adsorbed
on the adsorbent (mg/g) at any time $t$ (min) and at equili-
trum time (min), respectively. As shown in Figure S5
(available online), the fitted linear (298–313 K) do not pass
through the origin point, confirming the existence of exter-
al mass transfer in the whole adsorption process. What is
more, it is clear that there are two parts in the fitting line,
implying that external mass transfer shows a rather weak
rate control for MO adsorption onto Fe$_3$O$_4$-CS-L materials
(Ma et al. 2012).

### Adsorption isotherms

Adsorption isotherms can be expressed as functional
equations which describes the amount of metal ions
adsorbed per unit mass of the adsorbent and the concen-
tration of metal ions in bulk solution under equilibrium
conditions. The three most common adsorption isotherm
for describing solid–liquid sorption systems are Langmuir,
Freundlich and Temkin isotherms The equation for the
Langmuir (8), Freundlich (9) and Temkin (10) isotherm
are as follows:

$$ \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} $$  \hspace{1cm} (8)

$$ \log q_e = \log K_F + \frac{\log C_e}{n} $$  \hspace{1cm} (9)

$$ q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e $$  \hspace{1cm} (10)

where $C_e$ and $q_e$ are the equilibrium concentration of the
metal ions (mg/L) and the adsorption capacity (mg/g),
respectively. The maximum adsorption capacity of

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**Table 1** Dynamic parameters for the adsorption of MO onto Fe$_3$O$_4$-CS-L

<table>
<thead>
<tr>
<th>$T(K)$</th>
<th>$K_1$</th>
<th>$q_m$</th>
<th>$R^2$</th>
<th>$K_2$</th>
<th>$q_m$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.075</td>
<td>219.28</td>
<td>0.991</td>
<td>$3.60 \times 10^{-4}$</td>
<td>292.40</td>
<td>0.9991</td>
</tr>
<tr>
<td>303</td>
<td>0.081</td>
<td>233.35</td>
<td>0.988</td>
<td>$3.66 \times 10^{-4}$</td>
<td>297.62</td>
<td>0.9992</td>
</tr>
<tr>
<td>308</td>
<td>0.092</td>
<td>259.42</td>
<td>0.971</td>
<td>$3.74 \times 10^{-4}$</td>
<td>302.11</td>
<td>0.9990</td>
</tr>
<tr>
<td>313</td>
<td>0.097</td>
<td>272.27</td>
<td>0.966</td>
<td>$3.94 \times 10^{-4}$</td>
<td>302.75</td>
<td>0.9991</td>
</tr>
</tbody>
</table>

**Table 2** Parameters of the Intraparticle diffusion model for the adsorption of MO onto Fe$_3$O$_4$-CS-L

<table>
<thead>
<tr>
<th>First linear portion</th>
<th>Second linear portion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T(K)$</td>
<td>$K_d1$</td>
</tr>
<tr>
<td>298</td>
<td>58.923</td>
</tr>
<tr>
<td>303</td>
<td>61.543</td>
</tr>
<tr>
<td>308</td>
<td>60.776</td>
</tr>
<tr>
<td>313</td>
<td>60.512</td>
</tr>
</tbody>
</table>
adsorbents (mg/g) and the adsorption constant (L/mg) in Langmuir mode are represented by \( q_m \) and \( K_L \). \( K_F \) is related to the adsorption capacity. \( n \) is the Freundlich constants which positive relate to the adsorption strength. \( b \) and \( A \) are the constant related to the adsorption heat (J/mol) and isothermal adsorption constant of Temkin, respectively. \( T \) is the temperature (K). \( R \) is the ideal gas constant (8.314 J/mol K).

The fitted data for MO adsorption on Fe₃O₄-CS-L were obtained as shown in Figure S6 (available online) and Table 3. As shown in Table 3, \( R^2 \) of Langmuir isotherm is greater than the Freundlich and Temkin model, it means that the Langmuir isotherm model is more suitable for the adsorption process. In other words, the adsorption process is a single adsorption and active sites evenly distributed on the surface of Fe₃O₄-CS-L.

In Langmuir mode, the degree of appropriate of adsorbent towards MO is predicted from the values of separation factor constant (\( R_L \)), which is shown as follows:

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

where \( K_L \) is the Langmuir isotherm constant (L/mg). \( C_0 \) is the initial MO concentration (mg/L). The value of \( R_L \) shows that the adsorption MO on Fe₃O₄-CS-L is favorable (0 < \( R_L < 1 \)) or irreversible (\( R_L = 0 \)), linear (\( R_L = 1 \)), unfavorable (\( R_L > 1 \)) (Ren et al. 2015). As shown in Table 3, the values of \( R_L \) were between 0.3 and 0.7, suggesting favorable adsorption of the MO on Fe₃O₄-CS-L.

Possible adsorption mechanism of MO by Fe₃O₄-CS-L

Figure 8 shows the conceptual model for the MO removal mechanism by Fe₃O₄-CS-L. MO is represented as the quinone structure in the solution when the pH is lower than 3.46. The secondary amino groups and sulfanyl on the surface of the quinone structure of MO can form hydrogen bonds with the carboxyl and amino groups on the surface of Fe₃O₄-CS-L, respectively. In addition, the electrostatic force is a factor that cannot be ignored in the adsorption process. There is electrostatic repulsion that exists between \( N^+ \) group in quinone type structure of MO and \( -NH\tilde{3} \) group of Fe₃O₄-CS-L surface. With increasing the value of pH, the quinone structure of MO was gradually transformed into azo structure, the hydrogen bond between \( -NH \) and \( -COOH \) becomes gradually weakened and the electrostatic repulsion between \( N^+ \) group in quinone type structure of MO and \( -NH\tilde{3} \) group of Fe₃O₄-CS-L surface also become gradually weakened. As shown in Figure 8, the adsorption capacity gradually decreased with the increase of pH value, suggesting that the influence of hydrogen bond is much larger than electrostatic interaction on MO adsorption process. What is more, the Van der Waals force enhances as the unit surface charge density increase, which suppress the adsorption capacity of MO in Fe₃O₄-CS-L.

Removal of MO in real wastewater samples

The adsorption progress was often influenced by various kinds of factors such as ion strength and coexistence organic molecules. In order to confirm the adsorption capacity of Fe₃O₄-CS-L under real conditions, removal of MO in real wastewater samples were investigated. The sample of wastewater was obtained from Ruibei printing and dyeing mill (Jiangsu, China). Nylon membrane (0.45 μm) was used to removal contamination particles of samples. Table 4 shows the main components of the sample. Figure S7 (available online) shows that the effect of contact time on MO adsorption under real conditions. From Figure S7, it can be found that the adsorption equilibrium contact time was 60 min, which was larger than the adsorption time in the simulated solution. Moreover, the adsorption capacity of Fe₃O₄-CS-L is 145 mg/g, which is reduced by 23% comparing to the adsorption capacity in

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Table 3 | Langmuir, Freundlich and Temkin isotherm model parameters for MO adsorption on Fe₃O₄-CS-L

<table>
<thead>
<tr>
<th>T(K)</th>
<th>( q_m )</th>
<th>( K_L )</th>
<th>( R_L )</th>
<th>( R^2 )</th>
<th>( K_F )</th>
<th>( n )</th>
<th>( R^2 )</th>
<th>( A )</th>
<th>( b )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>338.98</td>
<td>0.0031</td>
<td>0.315–0.762</td>
<td>0.997</td>
<td>6.668</td>
<td>1.816</td>
<td>0.979</td>
<td>0.026</td>
<td>31.09</td>
<td>0.994</td>
</tr>
<tr>
<td>303</td>
<td>353.36</td>
<td>0.0030</td>
<td>0.323–0.769</td>
<td>0.999</td>
<td>6.486</td>
<td>1.790</td>
<td>0.977</td>
<td>0.025</td>
<td>30.53</td>
<td>0.992</td>
</tr>
<tr>
<td>308</td>
<td>363.64</td>
<td>0.0029</td>
<td>0.330–0.775</td>
<td>0.997</td>
<td>6.389</td>
<td>1.772</td>
<td>0.982</td>
<td>0.025</td>
<td>30.25</td>
<td>0.991</td>
</tr>
<tr>
<td>313</td>
<td>374.53</td>
<td>0.0027</td>
<td>0.346–0.787</td>
<td>0.998</td>
<td>6.310</td>
<td>1.757</td>
<td>0.980</td>
<td>0.024</td>
<td>29.99</td>
<td>0.995</td>
</tr>
</tbody>
</table>

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the simulated solution at pH = 8.3. It can be explained that there are a variety of co-existing ions present in the actual wastewater. Azo structure of MO could be combined with organic groups by hydrogen bonding, resulting in a larger molecular structure and increased resistance to diffusion. In addition, azo structure with negative charged can interact with the coexistence of cations by electrostatic attraction, thereby reducing the interaction with Fe$_3$O$_4$-CS-L, which also results in slower adsorption rates and lower adsorption capacity. Moreover, the coexistence of cations can also interact with the functional groups on Fe$_3$O$_4$-CS-L, resulting in a decrease in hydrogen bonding between Fe$_3$O$_4$-CS-L and MO. This also leads to a decrease in adsorption capacity.

**Regeneration of Fe$_3$O$_4$-CS-L**

It is a very important feature for adsorbent in industrial applications. Figure S8 (available online) shows desorption and reusability studies of Fe$_3$O$_4$-CS-L in 1 mol/L HNO$_3$. The adsorption capacity of Fe$_3$O$_4$-CS-L can keep about 74% in the fifth adsorption-regeneration cycle, suggesting that this material has the prospect of industrial applications.

**Comparison with other adsorbents**

Table 5 shows the maximum adsorption capacities of different types of adsorbent. It was found that the adsorption capacity of Fe$_3$O$_4$-CS-L was greater than other adsorbent...
for MO adsorption, suggesting that Fe₃O₄-CS-L can be used as an efficient adsorbent of MO.

CONCLUSION

In summary, a novel magnetic bio-adsorbent was prepared by use of chitosan and L-arginine. The SEM and FT-IR results show that chitosan and L-arginine have been grafted on surface of magnetic Fe₃O₄ and TGA results future confirms that chitosan and L-arginine account for 58.4% of total mass. pH plays an important role in adsorption progress and the optimum pH for adsorption is 3. The adsorption capacity of Fe₃O₄-CS-L has reached saturated at a concentration of 500 mg/L. Kinetic studies show that the experiment data can be better described by pseudo-second-order model, not pseudo-second-order model. Boyd mode shows that external mass transfer shows a rather weak rate control for MO adsorption onto Fe₃O₄-CS-L. Equilibrium studies show that isotherm data were best described by Langmuir model. The maximum adsorption capacity of MO estimated to be 338.98 mg/g at 298 K and pH 3.0. The adsorption capacity of Fe₃O₄-CS-L can keep about 74% in the fifth adsorption-regeneration cycle, indicating that it has potential for industrial applications.

REFERENCES

Habila, M. A., Al Otheman, Z. A., El-Toni, A. M. & Yaghoobia, F. 2016 Synthesis and application of Fe₃O₄@SiO₂@TiO₂ for photocatalytic decomposition of organic matrix simultaneously with magnetic solid phase extraction of heavy metals prior to ICP-MS analysis. Talanta 154, 539–547.

Table 5 | Comparison of MO adsorption capacity among different adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>qₑ₀ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Fe₂O₃/2C nanocomposite</td>
<td>42.34</td>
<td>Istratie et al. (2016)</td>
</tr>
<tr>
<td>Mesoporous NiO microspheres</td>
<td>137.00</td>
<td>Jia et al. (2014)</td>
</tr>
<tr>
<td>CuO/NaA zeolite</td>
<td>79.49</td>
<td>Mekatel et al. (2019)</td>
</tr>
<tr>
<td>Activated carbon/NiFe₂O₄</td>
<td>182.82</td>
<td>Jiang et al. (2015)</td>
</tr>
<tr>
<td>Chitosan biomass</td>
<td>29.00</td>
<td>Allouche et al. (2015)</td>
</tr>
<tr>
<td>Maghemite/chitosan nanocomposite films</td>
<td>29.41</td>
<td>Jiang et al. (2012)</td>
</tr>
<tr>
<td>Immobilized PANI/glass</td>
<td>93.0</td>
<td>Haitham et al. (2015)</td>
</tr>
<tr>
<td>Activated clay</td>
<td>16.78</td>
<td>Ma et al. (2015)</td>
</tr>
<tr>
<td>Fe₃O₄-CS-L</td>
<td>338.98</td>
<td>In this work</td>
</tr>
</tbody>
</table>

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