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Adsorption behaviors of Congo red onto Fe₂O₃/Fe₃O₄ heterogeneous nanoparticles prepared via an alcohol-assisted combustion process

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Abstract

Magnetic Fe₂O₃/Fe₃O₄ heterogeneous nanoparticles were prepared through an alcohol-assisted combustion process. The composition, morphology and magnetic properties of the nanomaterials were characterized by XRD, TEM and VSM techniques. The magnetic Fe₂O₃/Fe₃O₄ heterogeneous nanomaterials were soft magnetic nanoparticles with a saturation magnetization of 38.6 emu g⁻¹ and an average particle size of approximate 29 nm. The adsorption behavior of Congo red (CR) onto Fe₂O₃/Fe₃O₄ heterogeneous nanoparticles was examined by UV-visible absorption spectroscopy, and the data for the kinetics and the isotherm of CR adsorption onto Fe₂O₃/Fe₃O₄ heterogeneous nanoparticles were in good agreement with the pseudo-second-order model and Langmuir model, respectively, which suggested that the adsorption mechanism of CR onto Fe₂O₃/Fe₃O₄ heterogeneous nanoparticles was the chemical and monolayer adsorption. Moreover, the influence of pH on the adsorption process was investigated, and when pH was equal to and less than 7, there would be larger adsorbances.

1. Introduction

At this stage, water pollution has become a major problem that must be solved, and dyes play a very disadvantageous role in the source of sewage [1–3]. Dyes are widely applied in biomedicine [4–7], textile [8, 9], agriculture [10, 11] and so on, but a large number of wastewater containing dyes are discharged into the environment due to the imperfect wastewater treatment process. However, dye wastewater contains high content of organic pollutants, complex components, and so on. Many of these dyes have biotoxicity, anti-photodegradation, anti-oxidation, most of them are carcinogenic, teratogenic, mutagenic organic compounds, some of them are even difficult to biodegrade, and even though some of them are degraded, the degradation products are toxic, thus causing extremely serious harm to human beings and the environment [12, 13]. Therefore, it is imperative to remove dyes from sewage. Among them, Congo red (CR) is a typical benzidine azo dye with strong toxicity and carcinogenic effect, and the structure of CR is displayed in figure 1. In the process of production and utilization, CR has a high loss rate, and it is easy to enter water, causing great harm to the surroundings [14, 15]. The traditional sewage treatment methods, such as electrochemical degradation [16], bio-treatment [17], catalysis [18] and photodegradation [19, 20], are usually complex and their effects are frequently not ideal. At present, the adsorption method is considered to be a simple, efficient and non-secondary pollution method [21].

The adsorbent is the key factor to determine the adsorption efficiency. There are many substances that can be used as adsorbents [22, 23]. Magnetic ferrite nanomaterials have been paid more and more attention because of their strong adsorption and surface separation ability. In particular, superparamagnetic Fe₃O₄ nanoparticles are usually applied as adsorbents due to their small size and large specific surface area [24, 25]. In addition, superparamagnetic Fe₃O₄ nanoparticles do not contain toxic metals, and their magnetic advantage is favorable for recycling, making them more environmentally friendly. However, the magnetic Fe₃O₄ nanoparticles with
high saturation magnetization are easy to agglomerate, which leads to the decrease of adsorption capacity and brings inconvenience to its application. To solve this problem, the magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles with appropriate magnetic properties are selected as the adsorbent to remove CR [26, 27]. As for the nanomaterials, many researchers have proposed a variety of fabrication methods, such as one-pot coprecipitation method [28], hydrothermal/solvothermal process [29], electrochemical strategy [30], and etc. But these methods usually require high equipment and experimental conditions. However, the alcohol-assisted combustion process is a controllable and simple process, which has lower requirements for equipment and only includes the dissolution in absolute alcohol and combustion-calcination process, so its production cycle is short.

Therefore, in this project, magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles were fabricated via the alcohol-assisted combustion process and were applied to adsorb CR, and the mechanism of the adsorption process was explored.

2. Experimental

2.1. Chemicals

The iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O) of analytical grade and Congo red (C$_{32}$H$_{22}$N$_6$Na$_2$O$_6$S$_2$) were purchased from Shanghai Zhanyun Chemical Co., Ltd. Absolute alcohol with a purity of 99.7% or more was procured from Sinopharm Chemical Reagent Co., Ltd.

2.2. Fabrication and characterization of magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles

The alcohol-assisted combustion process was applied to fabricate the magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles. 10.46 g Fe(NO$_3$)$_3$·9H$_2$O was placed in absolute alcohol and stirred with a magnetic agitator for 2–4 h to dissolve and a uniform solution was obtained. Then this solution was transferred into a crucible and ignited to burn off, and then naturally cooled to the environment temperature. The intermediate product was placed in the programmed temperature-controlled furnace together with the crucible. In the furnace, the temperature was raised at the rate of 3 °C min$^{-1}$, and the sample was calcined at various temperatures for 2 h. When the calcination process was over, the sample was taken out and ground to obtain the final product.

The morphology and particle size of the prepared nanomaterials could be captured by TEM. The compositions of the productions were detected by X-ray diffraction (XRD) under Cu-Kα irradiation at 2θ angle ranging from 20° to 80°. The VSM could be applied to measure the hysteresis loops of Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanomaterials, and the magnetic properties of the samples could be obtained via analyzing the curve.

2.3. Adsorption experiments

To investigate the adsorption kinetics process of CR onto magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanomaterials, 16 time points were selected for observation. The specific experiments were as follows. Five parts of 20 mg nanoparticles were dispersed in 4 ml centrifuge tubes containing 100–500 mg l$^{-1}$ CR solutions, and the pH of the solutions was adjusted by 1 M hydrochloric acid and sodium hydroxide solutions, respectively. After 5 min of ultrasound, the obtained suspensions were placed on the revolver for mixing and adsorption for 0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 110, 130, 150, 180 min. Then, the absorbances of supernatants were measured with UV at 500 nm, and the adsorbance at each time point was calculated according to Formula (1).
Where, $C_0$ was the initial CR concentration (mg/L), $V$ was the volume of CR solution, $C$ was the surplus CR concentration after time $t$ (mg/L), and $m$ was the mass of Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles (g).

The research of adsorption isotherm helps to reveal the mechanism of adsorption process. Therefore, CR solutions with different concentrations (50, 100, 150, 200, 300, 400, 450, 500, 550, 600 mg ml$^{-1}$) were placed in 4 ml centrifuge tubes at room temperature and were in contact with 20 mg of magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles. After 5 min of ultrasound, the adsorption process continued for 2 h on the revolver. When the time passed by, the adsorption reached the equilibrium state under the current concentration. After adsorption, the UV was employed to measure the supernatants, and the adsorbances were calculated. The data for the adsorption isotherms and the adsorption kinetics of CR onto Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles could be obtained, and then the adsorption mechanism of the adsorption process could be acquired.

### 3. Results and discussion

#### 3.1. Characterization of Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles

Figure 2 showed the characterization of magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles. From TEM image (figure 2(a)), it could be directly observed that the heterogeneous nanomaterials were spherical nanoparticles with an average size of about 29 nm, and the edges of the heterogeneous nanoparticles were clearly visible. The phase compositions of the fabricated nanoparticles could be obtained by comparing the XRD patterns of the samples with the standard PDF card patterns (figure 2(b)). It could be seen that almost all the peaks corresponded to Fe$_2$O$_3$ standard PDF (JCPDS No.33-0664), indicating the presence of Fe$_2$O$_3$ in the phase of the nanoparticles. Meanwhile, the peaks at 30.1° and 43.4° were consistent with Fe$_3$O$_4$ standard PDF (JCPDS No.03-0863), indicating the existence of Fe$_3$O$_4$ in the object phase. The peaks at 35.4° and 56.7° were slightly stronger than those on the standard PDF cards of Fe$_2$O$_3$, which further proved the existence of Fe$_3$O$_4$ phase. The above characterization results confirmed the successful preparation of the designed heterogeneous nanoparticles. VSM was a magnetic measuring instrument with high sensitivity and wide application, and the hysteresis loop diagram (figure 2(c)) of the sample could be obtained by VSM, which displayed that the saturation magnetization of the magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles was 38.6 emu g$^{-1}$. And the

\[
q_t = \frac{V(C_0 - C)}{m}
\]
The coercivity and remanence of the materials were very small, indicating that the Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles were soft magnetic materials.

The XRD patterns of magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles prepared under various conditions were shown in figure 3. Figure 3(A) revealed the XRD patterns of magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles calcined at 400 °C for 2 h with absolute alcohol of 20–35 ml, and obviously, the diffraction peaks for the heterogeneous nanoparticles became more and more higher, which suggested that the crystallinity degree of the heterogeneous nanoparticles became more and more larger, that is, the average particle size became larger. While, figure 3(B) displayed the XRD patterns of the heterogeneous nanoparticles calcined at various calcination temperatures for 2 h with 20 ml absolute alcohol, and it could be seen that with the increase of the calcination temperature, the crystallinity degree of the heterogeneous nanoparticles also increased, and similarly, the average particle size became larger with the increase of the calcination temperature. Therefore, for larger adsorbance, Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles calcined at 400 °C for 2 h with absolute alcohol of 20 ml were selected to remove CR from solutions.

Figure 3. XRD patterns of magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles calcined at various calcination temperatures (B) for 2 h with different volumes of absolute alcohol (A).

Figure 4. Photograph of the CR solution at 200 mg ml$^{-1}$ (a); suspension of the magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles mixed with 200 mg ml$^{-1}$ CR (b); nanoparticles adsorbed CR (200 mg ml$^{-1}$) and then attracted by magnet (c).

3.2. Adsorption of CR onto Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles

The adsorption of CR onto Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles was shown in figure 4. Figure 4(a) depicted the photograph of CR solution at 200 mg l$^{-1}$, figure 4(b) revealed suspension of the heterogeneous nanoparticles mixed with 200 mg l$^{-1}$ CR, and figure 4(c) showed the heterogeneous nanoparticles adsorbed CR (200 mg l$^{-1}$) and then attracted by magnet. The color of the dye solution in figures 4(a) and (c) changed significantly from red to transparent, indicating that the materials had a larger adsorption capacity for CR, that is, the magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles could adsorb and remove CR from water. As shown in figures 4(b) and (c), when an external magnetic field was added, the heterogeneous nanoparticles in the solution could be completely attracted and aggregated by the magnet. The above phenomena demonstrated that magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles which had adsorbed CR could easily separate CR under an external magnetic field.
The adsorption time and the initial CR concentration were the two main variables affecting the adsorption process. To reveal the influence law of these two factors, a series of adsorption experiments were carried out. Figure 5 showed the adsorption rate curves of CR adsorbed by 10 mg materials at various initial CR concentrations. Obviously, the adsorbance of CR onto the heterogeneous nanoparticles multiplied apparently with the increase of the initial CR concentration. As the initial concentration of CR solution was 100 mg l\(^{-1}\), the maximum adsorbance of CR onto the heterogeneous nanoparticles was only 17.6 mg g\(^{-1}\). However, when the initial CR concentration was up to 500 mg l\(^{-1}\), the maximum adsorbance reached 57.9 mg g\(^{-1}\), which increased more than three times. The reason for this phenomenon was not complicated. When the CR concentration was low, the dispersion of CR was extensive, and the nanomaterials could not contact with CR completely, which lead to the limitation of adsorption. When the initial concentration of CR increased, there were a lot of CR molecules around the nanoparticles and the adsorption rate was significantly accelerated. The results showed that the equilibrium adsorbance (\(q_e\)) reached the maximum when the contact time reached 2 h. The higher the concentration was, the greater the slope of the curve was, and the faster the adsorption rate was. When the adsorption time was further increased, the slope of the curve was almost zero, the adsorption rate was very low, and the adsorbance was no longer increased. This is due to the step-by-step occupation of CR molecules on the surface of the magnetic Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heterogeneous nanoparticles. First, due to hydration, the CR molecules were diffused from the current position in the solution to the surface of the liquid film formed on the adsorbent surface. Then the CR molecules overcame the resistance of the liquid film and passed through the liquid film to the adsorbent surface. Finally, the CR molecules were adsorbed on the active sites of the nanoparticles’ surface. Therefore, when the adsorption time was short, the nanoparticles could be exposed to a higher concentration of dye, which would be conducive to the adsorption process. With the extension of adsorption time, the adsorption amount of dye in solution decreased, the adsorption sites of nanoparticles were occupied gradually, and the adsorption rate decreased.

### 3.2.1. Adsorption kinetics

The adsorption kinetics could reflect various influencing factors of the adsorption process and the adsorption rate, which was helpful to reveal the mechanism of the adsorption process. Adsorption kinetic models include the pseudo-first-order kinetics, the pseudo-second-order kinetics and the intraparticle diffusion models, which were often employed to fit the adsorption data at different concentrations and explain the adsorption mechanism. The pseudo-first-order kinetics model was widely applied in liquid-phase adsorption, which assumed that the key step affecting the adsorption rate was the diffusion process. The pseudo-second-order adsorption kinetics model assumed that the rate of adsorption depended on the chemisorption mechanism, so the interaction between adsorbent and adsorbate determined the adsorption rate. The intraparticle diffusion model, i.e. the Webber-Morris Model, held that the adsorption rate was related to how the adsorbate entered the adsorbent. The diffusion in the inner pore of the adsorbent controlled the adsorption rate. The corresponding models were represented by the following equations [31–33]:

\[
\ln (q_e - q_t) = \ln q_e - k_1 t
\]
Where, $q_e$ and $q_t$ (mg/g) represented the mass of CR absorbed at the equilibrium status and the stated time. $k_1$ (min$^{-1}$), $k_2$ (min$^{-1}$), and $k_i$ (mg · g$^{-1}$ · min$^{-1}$) were expressed as the adsorption rate constants of the three models. $C_i$ was related to the boundary layer thickness. If internal diffusion occurred, $q_t$ would be linear to $t^{1/2}$, and the internal diffusion would be the only process to limit the adsorption rate. At the same time, there might be multiple mechanisms involved.

Figure 6 showed the fitting of three adsorption kinetics curves to the adsorption data at different initial concentrations of CR. The corresponding parameters were revealed in table 1. At all concentrations, the adjusted squared correlation coefficients (Adj. R-Square) of the pseudo-second-order adsorption kinetics curves of CR adsorption onto Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles were the largest, and they were greater than 0.98.

$$
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} 
$$

(3)

$$
q_t = C_i + k_i t^{\frac{1}{2}} 
$$

(4)
Therefore, the adsorption rate of CR on the magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles was related to the chemisorption mechanism. Electron transfer and electron sharing were involved in the adsorption process.

Figure 7 showed the relation curves between $t/q_t$ and $t$ in CR solution adsorbed by magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles at different concentrations of 100 mg l$^{-1}$, 200 mg l$^{-1}$, 300 mg l$^{-1}$, 400 mg l$^{-1}$, and 500 mg l$^{-1}$.

Table 1. Fitting kinetics parameters of adsorption of CR in aqueous solution onto magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles at room temperature.

| CR concentration (mg l$^{-1}$) | Pseudo-first-order model |  |  |  |  |  |
|-------------------------------|--------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                               | Parameter                | 100             | 200             | 300             | 400             | 500             |
| Pseudo-first-order model      | $q_e$ (mg g$^{-1}$)       | 17.4757         | 31.5178         | 38.9600         | 46.9564         | 51.4846         |
|                               | $k_1$                     | 0.1132          | 0.0807          | 0.0643          | 0.0754          | 0.0658          |
|                               | Adj. R-Square             | 0.8647          | 0.9541          | 0.9493          | 0.9179          | 0.9502          |

|                               | Pseudo-second-order model |  |  |  |  |  |
|                               | $q_e$ (mg g$^{-1}$)       | 18.8653         | 34.8930         | 43.6516         | 51.9306         | 56.4850         |
|                               | $k_2$                     | 0.0100          | 0.0034          | 0.0021          | 0.0022          | 0.0017          |
|                               | Adj. R-Square             | 0.9851          | 0.9948          | 0.9955          | 0.9921          | 0.9932          |

|                               | Intraparticle diffusion model |  |  |  |  |  |
|                               | $x_i$                      | 11.4594         | 16.7715         | 17.7824         | 24.3345         | 27.3005         |
|                               | $k_i$                      | 0.6339          | 1.4973          | 2.0881          | 2.2762          | 2.1095          |
|                               | Adj. R-Square             | 0.7166          | 0.7249          | 0.7894          | 0.7823          | 0.7359          |

Therefore, the adsorption rate of CR on the magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles was related to the chemisorption mechanism. Electron transfer and electron sharing were involved in the adsorption process.

Figure 7 showed the relation curves between $t/q_t$ and $t$ in CR solution at different concentrations adsorbed by magnetic Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles. It could be seen that there was a good linear relationship between independent variables and dependent variables at five different initial concentrations, indicating that the adsorption process followed the pseudo-second-order adsorption kinetics, and the adsorption process belonged to the chemisorption mechanism determined by adsorbent and adsorbate. Moreover, the slope of the fitting line was inversely proportional to the equilibrium adsorption capacity. With the increase of the initial CR concentration, the slope difference between the two adjacent lines decreased, indicating that the equilibrium adsorption amount approached to the maximum adsorption amount. According to the adsorption data, compared with literatures [34–38], as shown in table 3 the adsorption equilibrium time of CR onto Fe$_2$O$_3$/Fe$_3$O$_4$ heterogeneous nanoparticles was shorter, or the adsorbance of CR...
onto the heterogeneous nanoparticles was larger, therefore, the Fe₂O₃/Fe₃O₄ heterogeneous nanoparticles had advantages in the dye removal.

3.2.2. Adsorption isotherm
To further explore the adsorption behaviors, the interrelation of adsorbance and the CR concentration in solution was investigated. 10 groups of dyes with different concentrations were adsorbed by 10 mg nanoparticles, and two adsorption isotherm models were commonly applied to fit the adsorption data: Langmuir and Freundlich isotherm models. Langmuir isotherm assumed there was a monomolecular layer adsorption without interaction between the adsorbed molecules, the adsorbent surface had uniform physical and chemical properties, and only one adsorption site could bind to one adsorptive molecule. When the adsorption sites reached saturation, the adsorbance of the adsorbent no longer increased, and the adsorption process reached a dynamic equilibrium state. So, the Langmuir model was usually explained as the monolayer chemisorption process. The mathematical expression equation was expressed as an equation (5).

\[
q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}
\]

(5)

Freundlich isotherm was different from the Langmuir model. It believed that the distribution of adsorption sites on the adsorbent surface was not uniform, and it described heterogeneous systems and reversible adsorption, which were independent of monolayer structure, and occurred simultaneously with the monolayer and multi-layer adsorption. Therefore, the Freundlich model was usually applied to explain the physical adsorption process on the surface. The Freundlich adsorption isotherm expression was the following equation (6).

\[
q_e = q_{\text{max}} K_F C_e^{\frac{1}{n}}
\]

(6)

Where, \( q_e \) (mg/g) was the mass of CR adsorbed by the heterogeneous nanoparticles, \( C_e \) (mg/L) was the CR equilibrium concentration in solution, \( q_{\text{max}} \) (mg/g) was the maximum adsorbance, and \( K_L \) (L/mg) and \( K_F \) [(mg/g)(L/mg)\(^{1/3}\)] were the constants of Langmuir and Freundlich models. \( K_F \) decreased with the increase of temperature. The value of \( 1/n \) was between 0 and 1 and it was a dimensionless parameter that reflected the surface.
Table 3. The adsorptivities of CR onto various adsorbents.

| Adsorbents                              | $q_e$ mg g$^{-1}$ | Adsorption equilibrium time min | Initial CR concentration mg l$^{-1}$ | Reference |
|-----------------------------------------|-------------------|---------------------------------|--------------------------------------|-----------|
| water-treated pineapple peel            | 80.6              | 150                             | 300                                  | [34]      |
| Magnetic Ni$_{0.3}$Mg$_{0.3}$Zn$_{0.4}$Fe$_2$O$_4$ Nanoparticles | 36.5              | 60                              | 100                                  | [35]      |
| MgO/graphene oxide nanocomposite        | 191.2             | 10                              | 700                                  | [36]      |
| C/MnCuAl double layered oxides nansadorbent | 317.5             | 180                             | 250                                  | [37]      |
| Montmorillonite                         | 8.4               | 40                              | 50                                   | [38]      |
heterogeneity or adsorption strength. This value represented the influence of the concentration on the adsorbance. When \( \frac{1}{n} \) was less than 0.5, it was easy to adsorb; but when \( \frac{1}{n} \) was greater than 2, it was difficult to adsorb [39–41].

The fitting results were revealed in figure 8, and the corresponding parameters were exhibited in the table 2. Obviously, the experimental data were more consistent with the Langmuir adsorption isothermal model. The Adj. R-Square of Langmuir isotherm was 0.9949, while the Adj. R-Square of the Freundlich model was only 0.9348, indicating that the Langmuir model could well explain the adsorption. According to the assumption of the Langmuir model, the adsorption of CR onto Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heterogeneous nanoparticles was uniform, in which all adsorption sites were the same and were equivalent in energy, so the specific surface area of magnetic Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heterogeneous nanoparticles was a key factor to the adsorption performance of CR.

3.2.3. Effects of pH and FTIR on adsorption

Figure 9(a) illustrated the pH had a significant effect on the adsorption of CR onto the heterogeneous nanoparticles. When the pH changed from acidic to alkaline, the adsorbance of CR onto the heterogeneous nanoparticles decreased by about 10 times. The reason was that there were far more hydrogen bond receptors than hydrogen bond donors on the CR molecule. In acidic condition, Ph value had little effect on the adsorption experiment. And when in alkaline environment, since the hydrogen bond receptors in the CR molecule tended to bind to the hydroxyl group in the solution, and because the surface of the heterogeneous nanoparticles was positive, the adsorption sites of the material were more likely to be occupied by negatively charged hydroxyl ions [42, 43]. Therefore, the adsorption effect of dye on the material was greatly reduced. In this way, the change of pH value could effectively adjust adsorption and desorption, which was beneficial to the application of Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heterogeneous nanoparticles in the field of adsorption.

The infrared spectra of bare Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heterogeneous nanoparticles, CR, the heterogeneous nanoparticles after absorbing CR and the heterogeneous nanoparticles desorbed after washing with alkali liquor were displayed in figure 9(b). The peaks located at 551 cm\(^{-1}\) and 451 cm\(^{-1}\) were the vibration peaks of Fe–O bond. The peaks at 642 cm\(^{-1}\) and 1055 cm\(^{-1}\) belonged to the characteristic peaks of the sulfonic acid group. And the peaks at 1180 cm\(^{-1}\), 1585 cm\(^{-1}\), and 3465 cm\(^{-1}\) belonged to the peaks of C–N, N = N, N–H bonds on the CR molecule, respectively. According to the curve of the Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heterogeneous nanoparticles after absorbing CR, both characteristic peaks of ferrite and CR in the infrared spectra could be clearly seen, which indicated that the heterogeneous nanoparticles did have adsorption effect on CR. Besides, it could be seen from the desorption curve that the characteristic peak of CR on the magnetic Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heterogeneous nanoparticles completely disappeared after washing with alkali liquor, which illustrated that the heterogeneous nanoparticles could be recovered through alkali liquor treatment.

4. Conclusions

(1) Magnetic Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heterogeneous nanoparticles were successfully prepared by the alcohol-assisted combustion approach. Fe\(_2\)O\(_3\)/Fe\(_3\)O\(_4\) heterogeneous nanoparticles were prepared at 400 °C for 2 h with 20 ml absolute alcohol. And their average particle size was about 29 nm, and saturation magnetization was 38.6 emu g\(^{-1}\).
(2) The adsorption process of CR onto the heterogeneous nanoparticles could accord well with the pseudo-second-order kinetics model and Langmuir isotherm, which indicated that the adsorption mechanism of CR onto the heterogeneous nanoparticles was monolayer.

(3) When the pH value was equal to and less than 7, the adsorbance of CR onto magnetic Fe$_3$O$_4$/Fe$_2$O$_4$ heterogeneous nanoparticles remained large, and when the pH value was more than 7, the adsorbance would decrease rapidly. Combined with the FTIR analysis, the heterogeneous nanoparticles could be recycled through changes in pH and the calcination.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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