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Research Article

# Amino Acid Ionic Liquid Coated Magnetic Core $Fe_3O_4$@$SiO_2$ Nanoparticles Coupled with UV Spectrophotometry for the Separation /Analysis Congo Red

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## Abstract

Congo red has strong tinting strength, low price that it was used in meat dyeing. Amino acid ionic liquids (AAILs) containing amino acid cations or anions are synthesized from natural amino acids, which has the characteristics of low toxicity. Nowadays, $Fe_3O_4$@$SiO_2$@AAIL composites has seemly not been reported for the separation/analysis of congo red. In this work, $Fe_3O_4$@$SiO_2$@AAIL nanoparticles were used as magnetic solid phase adsorbents in combination with UV spectrophotometry for separation of congo red.

## Keywords

Congo Red, Amino Acid Ionic Liquids (AAILs), Solid Phase Extraction, UV Spectrophotometry

## 1. Introduction

Congo red (diphenyl-4,4'-(azo-2-)2-1-amino naphthalene-4-sodium sulfonate, CR) is a kind of benzidine anionic dyes. It is commonly used as biological stain and chemical indicator. CR is not edible pigment which is not allowed to add into food because it has good stability and cannot be biodegradable which causes serious harm to aquatic organisms and food web [1]. CR causes also the human body dyspnea, emesis, diarrhea and nausea and its metabolites benzidine has toxic and carcinogenic to the human body [2]. CR is used in the textile, printing and dyeing, paper, rubber and plastics industry, the use of congo red staining process needs to consume large amounts of water, so it polluted water [3]. At the same time, congo red has strong tinting strength, low price that it was used in meat dyeing. Therefore, it is very important to establish an accurate and sensitive method for separation of congo red in drinking water and beverages.

UV-vis spectrophotometry was used in literatures for CR determination in high concentration of CR [4]. However, direct determination is difficult owing to low concentration of CR in samples. Therefore, it is necessary to develop a more accurate procedure for separation/preconcenrtation of CR in trace amounts. The separation/preconcenrtation methods of CR mainly include adsorption [5], electrochemical oxidation [6], biological degradation [7], photodegradation [8].

Commonly used separation/enrichment techniques include liquid-liquid extraction [9] and solid-phase extraction [10].

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Magnetic solid phase extraction (MSPE) is a kind of magnetic or magnetizable material as absorbent matrix solid-phase extraction technique, which has the advantages of easy separation, short extraction time and less organic solvent consumption [11]. MSPE extractants are mainly $Fe_3O_4$ nanoparticles modified by specific functional groups to achieve selectivity, affinity and extraction ability to target analytes [12]. Many functional materials have been used to modify $Fe_3O_4$, such as $SiO_2$ [13], β-cyclodextrin [14]. Magnetic material modified by ionic liquid has been successfully used for analysis of bovine serum albumin [15] and cephalosporin antibiotics [16].

Amino acid The ionic liquid is a novel hydrophilic ionic liquid functionalized with amino acid, with stronger polarity and better biocompatibility. Studies have shown that amino acid ionic liquids have a good ability to capture metal ions. Therefore, the amino acid ionic liquid and salt formed by the double water relative to the metal ions have a good extraction capacity.

Amino acid ionic liquids (AAILs) containing amino acid cations or anions are synthesized from natural amino acids, which has the characteristics of low toxicity, good biocompatibility and good biodegradability [17]. Nowadays, $Fe_3O_4$@$SiO_2$@AAIL composites has seemly not been reported for the separation/analysis of congo red.

In this work, $Fe_3O_4$@$SiO_2$@AAIL nanoparticles were used as magnetic solid phase adsorbents in combination with UV spectrophotometry for separation of congo red, and the factors affecting the extraction and elution conditions were studied. The method has been satisfactorily applied to separate congo red in real samples.

# 2. Experimental

## 2.1. Equipment and Reagents

FTIR spectra were measured with a Bruker Tensor 27 spectrometer (Bruker Company, Germany) UV-1780 Vis-spectrophotometer (Shimadzu Corporation, Japan).

All chemicals and reagents were at least of analytical grade unless otherwise stated. $FeCl_3$, $FeSO_4$ ·$7H_2O$, PEG, tetraethyl orthosilicate (TEOS), Ammonia, anhydrous ethanol, tetraethyl orthosilicate, isopropanol, N-hydroxysuccinimide(NHS), 1-ethyl- (3-dimethylaminopropyl) phthalimide acetate (EDC), N, N-dimethylformamide (DMF), Hydrazine hydrate 85%, 3-aminopropyltriethoxysilane (APTES), Alanine, methyl imidazole, bromo-n-hexane, congo red standard solution, glacial acetic acid, (the above reagents are produced by Sinopharm Group Chemical Reagent Co., Ltd.).

## 2.2. Preparation of $Fe_3O_4$@$SiO_2$ @AAIL

Amino acid ionic liquid AAIL ($Fe_3O_4$@$SiO_2$@AAIL) synthesis was carried out according to previous studies [18].

Firstly, $Fe_3O_4$NPs were prepared by the conventional co-precipitation method [19, 20]. Secondly, $Fe_3O_4$@$SiO_2$@AAIL was prepared according to the literature method [21, 22], the ultrasonic coating method was used to synthesize the $Fe_3O_4$@$SiO_2$@AAIL composite. 0.1g of ready-prepared AAIL were dissolved in 10mL methanol, then 0.1g $Fe_3O_4$@$SiO_2$ material was added was added into aqueous mixtures for further reaction. Putting the whole reaction device into ultrasonic bath, and ultrasonication for 2h intermittently. $Fe_3O_4$@$SiO_2$@AAIL composite was washed with methanol 3 times, then dried in vacuum.

## 2.3. Extraction Procedure

In the MPSE procedure, $Fe_3O_4$@SiO2@AAIL was applied to the extraction of congo red,40.0 mL of the working solution or aqueous sample and 0.10 g of $Fe_3O_4$@$SiO_2$@AAIL nanoparticles 0.5mL of congo red standard solution (20μg $mL^{-1}$) were added into the 10 ml centrifuge tube. The mixture was shaken for 15 min at room temperature. Afterwards, the magnetic adsorbent was separated from the suspension by an external magnet. congo red was analyzed using UV-Vis-spectrophotometer.

## 2.4. Sample Preparation

1.0 mL of the beverages samples were weighed in a small beaker. The distilled water was added to the liquid at 60 ℃ ultrasonically shaked for 30 min and then filtrated. The solution was poured in 250 mL flask.1.0 mL city water sample was transferred into a100 mL volumetric flask. The sample solution was put in dark at 4 ℃ for 12 h.

# 3. Results and Discussion

## 3.1. Characterization of $Fe_3O_4$@$SiO_2$@ AAIL

The morphology of the as-prepared $Fe_3O_4$@$SiO_2$@ AAIL NPs was characterized by FT-IR, SEM and XRD.

### 3.1.1. The Characterization of FTIR

The FTIR spectra of $Fe_3O_4$ (curve a) $Fe_3O_4$@$SiO_2$ and (curve b)$Fe_3O_4$@$SiO_2$@AAIL were shown in Figure 1. Fe-O bonds produce a peak at about 750 $m^{-1}$. The peak at 1100 $cm^{-1}$ is generated by the Si-O bond stretching vibration. In the amino acid ionic liquid the N-H stretching vibration peak was at 1630$cm^{-1}$. It is proved that $Fe_3O_4$ has been successfully modified by $SiO_2$ and AAIL.

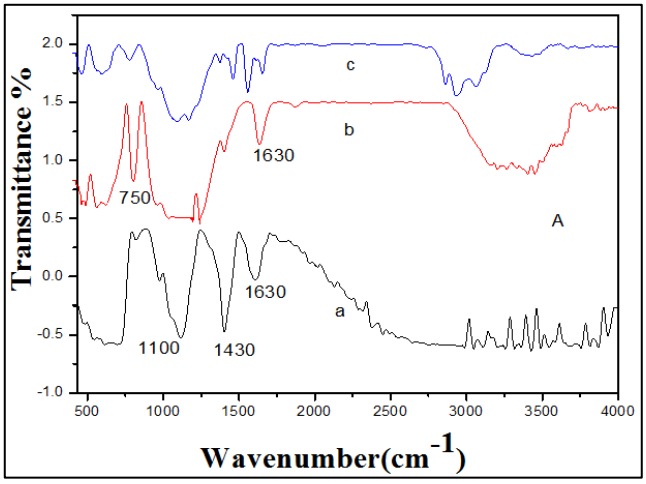


***Figure 1.*** *Infrared spectrum: $Fe_3O_4$ (a) $Fe_3O_4$@ $SiO_2$ (b) $Fe_3O_4$@$SiO_2$@ AAIL(c).*

### 3.1.2. The Characterization of SEM

As shown in Figure 2, it can be seen that the spherical shape of $Fe_3O_4$, and the surface of $Fe_3O_4$@$SiO_2$@AAIL is relatively rough, which can be considered to be modified by ionic liquid, which makes the surface of nanometer material changed. This indicates that $Fe_3O_4$@$SiO_2$@AAIL have been successfully synthesized.

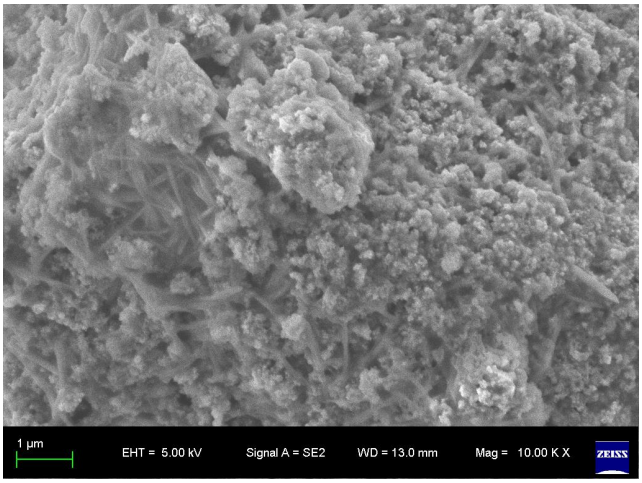


***Figure 2.*** *The image of SEM: $Fe_3O_4$@$SiO_2$@ AAIL.*

### 3.1.3. Characterization by XRD

Figure 3. Illustrated the XRD spectra of the $Fe_3O_4$ (A), $Fe_3O_4$@$SiO_2$(B)and $Fe_3O_4$@$SiO_2$@AAIL(C). The five clear peaks were appeared at 2 θ of 29.3 °, 36.4 °, 43.3 °, 57.3 °, and 63.5. The XRD spectra of $Fe_3O_4$@$SiO_2$@ AAIL was same to $Fe_3O_4$ and $Fe_3O_4$@$SiO_2$, which proved that the crystal shape of $Fe_3O_4$ particles was not altered through modifying of $Fe_3O_4$@$SiO_2$@AAIL.

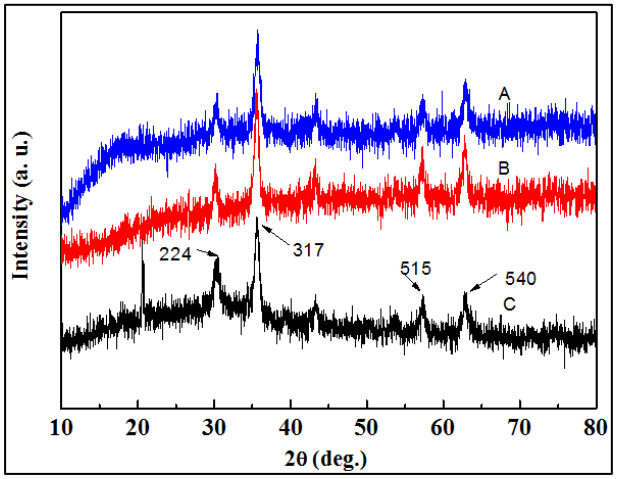


***Figure 3.*** *XRD spectra of the $Fe_3O_4$ (A), $Fe_3O_4$@$SiO_2$(B)and $Fe_3O_4$@$SiO_2$@AAIL(C).*

## 3.2. Adsorption Process

### 3.2.1. The Effect of pH

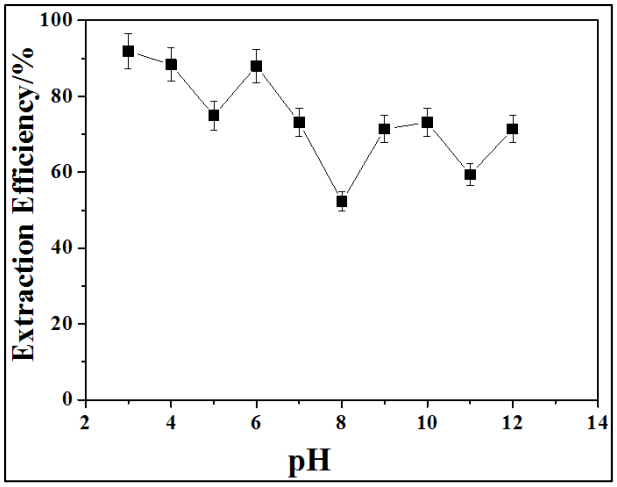


***Figure 4.*** *Effect of pH on extraction efficiency ($c_{c0}$=4.0 μg $mL^{-1}$).*

Different pH (pH = 3.0~12.0) had a significant effect on the extraction of target analytes. As shown in Figure 4, when the pH value of the solution is 3.0~12.0, the extraction rate of congo red was higher (93.0%) at 3.0 pH and then it was gradually decreasing and increasing in the range of pH 4.0~12.0. In contrast, at pH> 3.0, congo red is predominantly in the form of ions in solution. So congo red in acidic form is more easily extraction [23]. Therefore, the best solution for the sample pH is 3.0.

### 3.2.2. Effect of Amount of Adsorbent

Fixed congo red concentration of 20.0μg $mL^{-1}$, $Fe_3O_4$@$SiO_2$@AAIL nanoparticles from 0.05~3.0g. Results as shown in Figure 5, the extraction efficiency of $Fe_3O_4$@

$SiO_2$@ AAIL nanoparticles on congo red was the highest at 0.25g, reaching 91.0%, then it decreased. In this work, the amount of adsorbent ($Fe_3O_4$@$SiO_2$@ AAIL) nanoparticles is 0.25g.

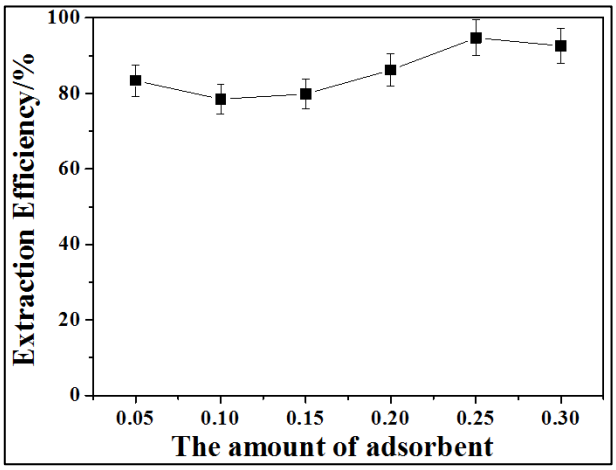


***Figure 5.*** *Effect of amount of adsorbent on extraction efficiency ($c_{c0}$=4.0 μg $mL^{-1}$).*

### 3.2.3. The Effect of Temperature

The extraction efficiency of $Fe_3O_4$@$SiO_2$@AAIL on congo red was studied at 0.0-50.0 ℃. The temperature has little effect on the extraction efficiency, and the extraction rate is kept above 90.0%. Therefore, this experiment is selected at room temperature.

### 3.2.4. The Effect of Extraction Time

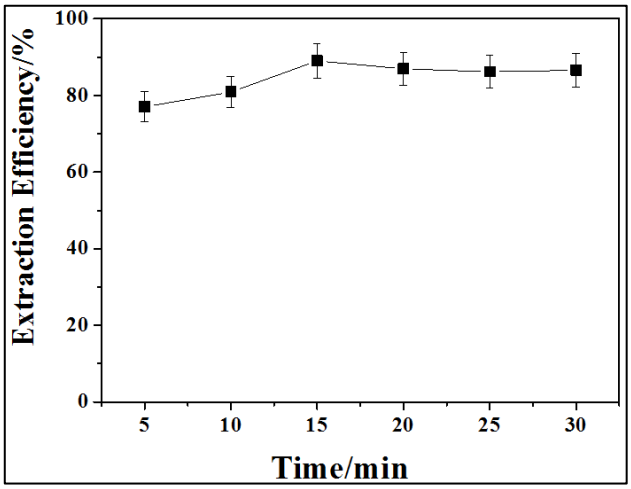


***Figure 6.*** *Effect of adsorption time on extraction efficiency ($c_{c0}$=4.0 μg $mL^{-1}$).*

The adsorption kinetic of $Fe_3O_4$@ $SiO_2$@AAIL on congo red at pH=3.0 at room temperature was studied. As shown in Figure 6, the extraction efficiency is more than 92.0% in 15 min with time (5-30 min) and remains stable. The extraction process takes some time to achieve the extraction equilibrium in order to obtain higher extraction rate. Therefore, the extraction time chosen in this experiment is 15min.

### 3.2.5. Effect of Ionic Strength

The effect of ionic strength on congo red was investigated using 5-30% (w/v) sodium chloride as the electrolyte model, as shown in Figure 7. In the 25% of NaCl solution, the extraction efficiency of congo red was the highest. $Na^+$ competes with $[C_6ALA]^+$ for the $Fe_3O_4$@$SiO_2$ matrix [17], leading to a decrease in the extraction efficiency after that, so this experiment was done at 25% of NaCl solution.

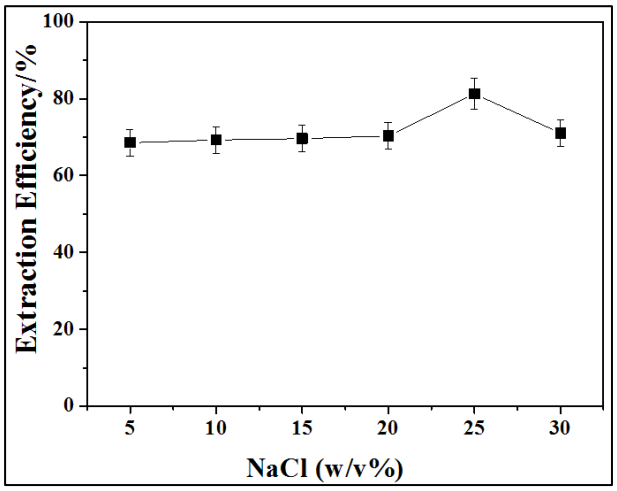


***Figure 7.*** *Effect of ionic strength on extraction efficiency ($c_{c0}$=4.0 μg $mL^{-1}$).*

## 3.3. Adsorption Capacity

To study the adsorption capacity of $Fe_3O_4$@$SiO_2$@AAILs on congo red ($q_e$, mg $g^{-1}$), the maximum amount of congo red extracted by 1.0 g $Fe_3O_4$@$SiO_2$@AAIL can be calculated by the following formula [24]:

$$\Delta H_T^0$$

Where $C_o$ represents the concentration of congo red before extraction, $C_e$ represents the concentration of congo red in the extraction equilibrium (μg $mL^{-1}$), and V is the volume of the solution (mL). In this study, the adsorption capacity of $Fe_3O_4$@$SiO_2$@ AAIL for congo red was achieved by changing the concentration of congo red during the extraction process. The results are shown in Figure 8. The results showed that the adsorption capacity of $Fe_3O_4$@$SiO_2$@ AAIL was 90.0 mg $g^{-1}$ when the concentration of congo red reached 70 mg $mL^{-1}$.

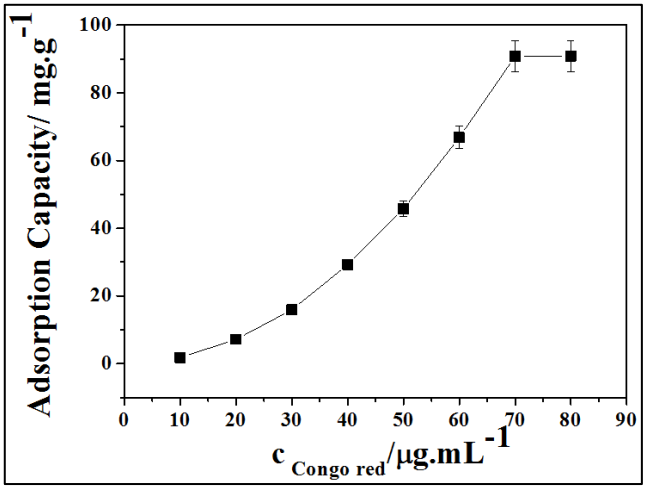


*Figure 8. Adsorption capacity.*

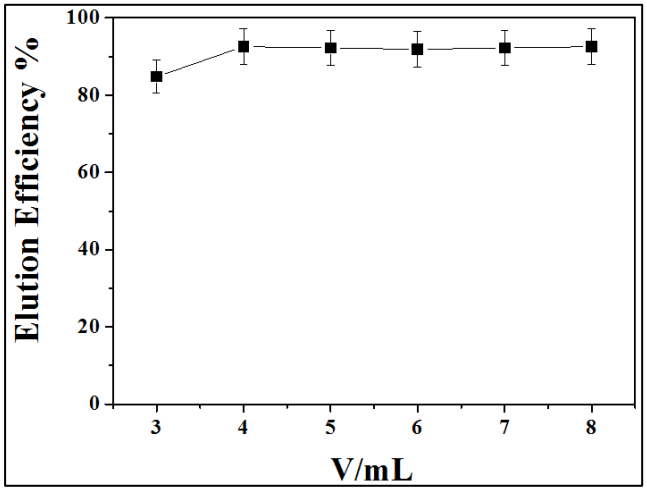


*Figure 10. Effect of elution volume on the elution efficiency.*

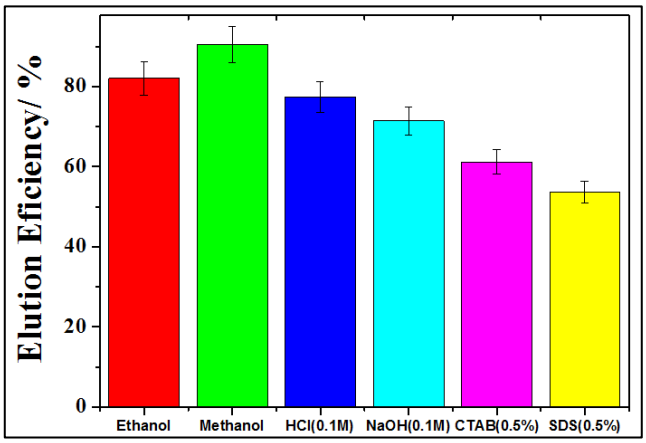


*Figure 9. Effect of different dissolvent on elution efficiency.*

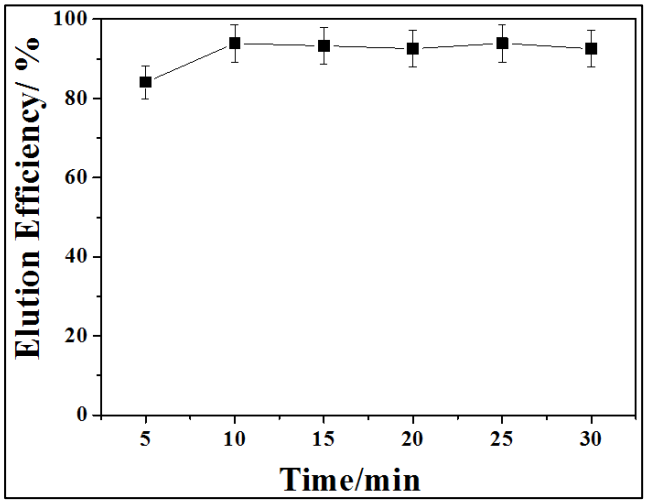


*Figure 11. Effect of elution time on elution efficiency.*

## 3.4. Elution Process

### 3.4.1. Eluent Selection

Various eluents were studied in this work, their elution efficiency was ordered as follow: Methanol > ethanol > HCl (0.1 mol.$L^{-1}$) > NaOH (0.1 mol.$L^{-1}$) > cetyltrimethyl ammonium bromide (CTAB) > sodium dodecyl sulfonate (SDS) >. So methanol was selected. (Figure 9).

### 3.4.2. The Effect of Eluent Volume

The eluent volume was studied in the range of 3.0-8.0 mL, as shown in Figure 10, and the elution efficiency increased from 3.0 to 4.0ml and then remains static approximately 93.0%. Therefore, the optimal elution volume was 4.00 mL so the volume 4.0 mL of methanol was selected for the eluent.

### 3.4.3. The Effect of Elution Time

The elution of $Fe_3O_4$@$SiO_2$@AAIL extracted with congo red was carried out as shown in Figure 11. As the elution time increased (5-30 min), the elution process completed within 10 min, the elution efficiency of 93.0% or more, and remained stable within 30 min, so the best elution time is 10min.

### 3.4.4. The Effect of Elution Temperature

The effects of elution temperature on the elution efficiency of congo red (5.0-50.0 ℃) were studied. As shown in Figure 12, the elution rate increases with the rise of elution temperature, and the elution efficiency was the highest at 50.0 ℃, reaching 88.0%. So the experiment selected 50.0 ℃ as a best elution temperature.

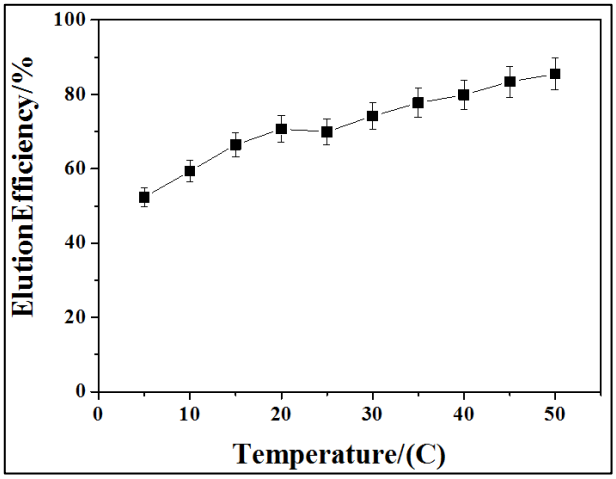


*Figure 12. Effect of elution temperature on elution efficiency.*

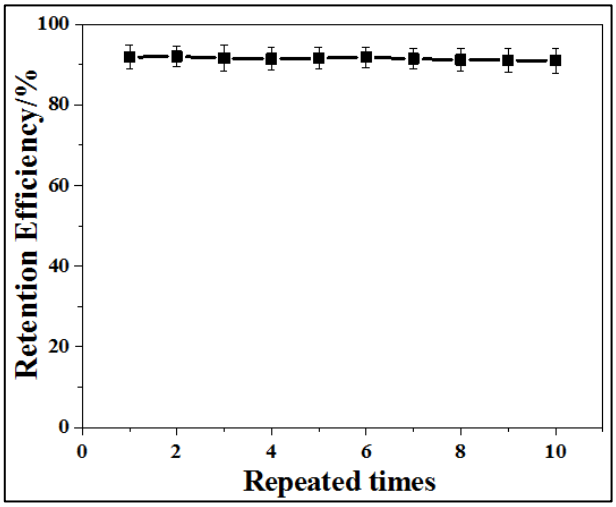


*Figure 13. Effect of reuse of $Fe_3O_4$@$SiO_2$@ AAIL in extraction and elution.*

### 3.5. The Repeated Times of $Fe_3O_4$@$SiO_2$@AAIL

In order to investigate the recycling use of $Fe_3O_4$@$SiO_2$@AAIL, each MSPE use 4.0mL methanol, and then re-used in the MSPE process, the experimental results shown in Figure 13. The results clearly show that the adsorption capacity of the adsorbent did not decrease significantly after 10 times of repeated use with no loss of the sorption capacity occurred after ten times of recycling. These results indicated that the self-assembly did not influence the stability of the $Fe_3O_4$@$SiO_2$@ AAIL material MNPs for reusability.

### 3.6. Interference Experiment

The effect of interfering substance on the extraction of congo red (c=1.0 μg $mL^{-1}$) was studied. The allowable error range was ≤±5%. The effect of interferents which food samples may contain on separation of CR in the availability of interferents was investigated. The limit of tolerance for different interferents were found as follow, $SO_4^{2-}$, $NO_3^-$ was 500, Citrate was 250, $Br^-$, glucose was 100, $Zn^{2+}$, $Cu^{2+}$ was 50, Bright yellow, sunset yellow, Rhodamine B was 20 and for Allura red, safranin T, was 10. The results showed that most of the foreign material in samples had no interference in CR separation.

### 3.7. Analytical Performance

This method introduced wide linear range of 15-350ng/$mL^{-1}$, the correlation coefficient was 0.9991, the equations of calibration graph was A (absorbance) = 0.04+0.13c (μg $mL^{-1}$), the detection limit was 0.37 ng/$mL^{-1}$(RSD = 5.1%).

## 4. Sample Analysis

This method was introduced to separate the amount of Congo red in certain types of beverage and city water. To further verify for the viability of the method, recovery experiments were carried out for the spiked samples ranged from 97.1 % to 102.2 %, the results were satisfactory for congo red separation (Table 1).

*Table 1. The recorvies of congo red in samples.*

| Sample | Added (μg $mL^{-1}$) | Found (μg $mL^{-1}$) | Recovery (%) | RSD intra-day (%) | RSD inter-day (%) |
|---|---|---|---|---|---|
| City water | 0.00 | 0.77 | — | 2.8 | 3.0 |
| | 0.51 | 1.25 | 97.1 | 3.8 | 7.9 |
| | 2.00 | 2.79 | 102.2 | 2.6 | 8.6 |
| | 3.00 | 3.72 | 98.6 | 2.9 | 4.9 |
| Beverage | 0.00 | 1.3 | — | 2.2 | 9.2 |
| | 0.51 | 1.82 | 101.8 | 5.1 | 9.1 |
| | 2.00 | 3.27 | 98.3 | 4.5 | 7.4 |

| Sample | Added (μg mL$^{-1}$) | Found (μg mL$^{-1}$) | Recovery (%) | RSD intra-day (%) | RSD inter-day (%) |
|---|---|---|---|---|---|
| | 3.00 | 4.23 | 97.4 | 4.3 | 6.5 |

## 5. Discussion on Adsorption Mechanism of $Fe_3O_4$@$SiO_2$ @AAIL

*Adsorption kinetic model*

The adsorption mechanism can be discussed by using the adsorption kinetic model to explore the extraction mechanism. The general adsorption kinetic model has a first-order kinetic model, a second-order kinetic model and a Weber-Morris model [25]. Among them, the second-order kinetic model is a chemical adsorption model, which is mainly through the extraction agent and analyte between the chemical force, including: electrostatic force, intermolecular force, hydrogen bonds, hydrophobic effects [26]. The second-order adsorption kinetic model is fitted and the formula is as follows [27]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

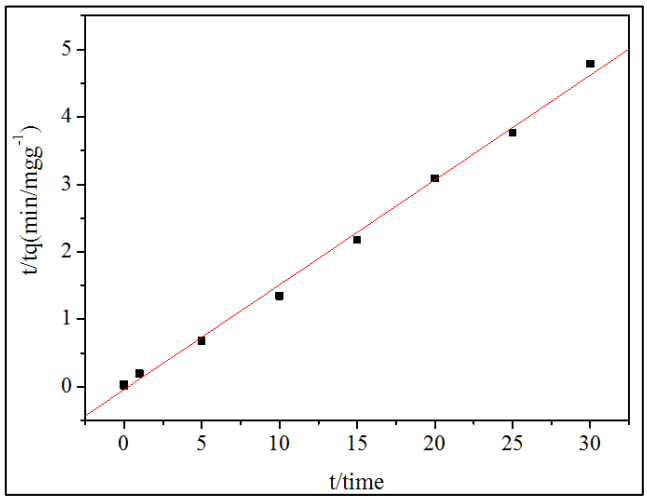


***Figure 14.*** *Adsorption kinetic model.*

Where $q_e$ is the adsorption amount of the analyte at the time of adsorption equilibrium, and $q_t$ is the adsorption amount of the analyte at time t adsorption. Usually by $t/q_t$ on t mapping, linear regression and fitting to get the corresponding kinetic parameters, if the fitting equation shows that the adsorption process in line with the secondary adsorption dynamic model. In this study, $Fe_3O_4$@$SiO_2$@AAIL adsorption of CR, with this method to fit (Figure 14). The results show that the linear relationship is good, $R^2$=0.9997, indicating that the adsorption process is in accordance with the secondary adsorption dynamic model. The adsorption process is a chemical adsorption process. It can be seen that the interaction between the ionic liquid and the congo red on the surface of the extractant is mainly hydrophobic. The method has good extraction effect on congo red, and can obtain higher extraction rate and shorter extraction time.

## 6. Conclusion

In this paper, $Fe_3O_4$@$SiO_2$@AAIL, a magnetic solid phase extraction material, was synthesized and analyzed in combination with UV spectrophotometry. In this method, the extraction of congo red was successfully enriched by the advantages of simple operation, separation and analysis time and high extraction efficiency. The method is simple, safe, rapid and stable, and the result of sample separation is satisfactory.

## Conflicts of Interest

The authors declare no conflicts of interest.

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