Flame atomic absorption spectrometry combined with surface-modified magnetic mesoporous silica microspheres by polyethyleneimine for enrichment, isolation and determination of Cu\(^{2+}\) in preserved eggs after high-temperature digestion

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ABSTRACT
A new efficient magnetic solid-phase extractant based on a surface-modified magnetic mesoporous silica microsphere referred as MMSM-PEI was synthesised and used for the enrichment and isolation of copper ions (Cu\(^{2+}\)) in preserved eggs. The physicochemical properties and morphology of MMSM-PEI were characterized by X-ray diffraction (XRD) spectroscopy, Fourier transform infrared spectroscopy (FT-IR), vibration sample magnetometry (VSM), scanning electron microscopy (SEM) and thermogravimetric analyses (TGA). The concentrations of trace Cu\(^{2+}\) in the preserved egg were determined by flame atomic absorption spectroscopy (FAAS). The effects of important parameters were examined. The most suitable pH values and temperature for adsorbing Cu\(^{2+}\) were 6.5 and 25°C, respectively. According to the determination of Cu\(^{2+}\) in egg white, egg yolk and the outer coating mixture (TOCM) of preserved eggs, the spiked recovery and RSD were 94.1–103.8% and 0.96–4.35%, respectively. The limit of detection (LOD) and the limit of quantitation (LOQ) were 0.14 mg/kg and 0.46 mg/kg, respectively. The developed method improved the sensitivity and accuracy of FAAS for the determination of Cu\(^{2+}\) and it could be applied to the determination of trace Cu\(^{2+}\) in real samples.

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Introduction
Preserved eggs, also known as Pidan, changed eggs, ash-wrapped eggs and century eggs, are a traditional Chinese egg product. They are deeply appreciated by people due to their unique taste and flavor. Preserved eggs are usually made from fresh duck eggs wrapped with a mixture of black tea, plant ash, alkaline substances, loess, metal ions and water in a certain ratio and pickled at room temperature for 4–6 weeks (Su and Lin 1993; Ji et al. 2013). The egg white becomes a dark brown transparent gelatinous substance, the egg yolk is a dark green solid, and the whole preserved egg has a strong smell of sulphur and ammonia after pickling (Eiser et al. 2009). The egg white of some preserved eggs has lots of geometric crystals like Songhua (Zhao et al. 2014). Therefore, preserved eggs with such crystals are often called Songhua eggs. Lead oxide is involved in the traditional manufacturing process of preserved eggs, although lead is a toxic heavy metal. The traditional manufacturing process will result in the accumulation of lead in preserved eggs. Long-term consumption by consumers will damage the nervous system, hematopoietic organs, kidneys and immune system (Xu et al. 2014) due to the accumulation of lead in the human body. Therefore, researchers have conducted a lot of studies on lead-free processes in which copper, zinc and iron compounds are used as a processing aid instead of lead oxide in the manufacture of preserved eggs (Ganasen and Benjakul 2011). Cu\(^{2+}\) forms insoluble compounds with H\(_2\)S produced by protein degradation under strong alkaline conditions, which can plug the
eggshell and membrane pores, meshes and corrosion holes generated from the alkali processing. At present, copper sulphate has been extensively used in the manufacturing of preserved eggs to regulate the infiltration of the alkali, which aims to prevent excessive alkali from damaging eggs during post-pickling (Zhao et al., 2016). Additionally, the decomposition of sulphur-containing proteins under strong alkaline conditions to produce $\text{S}_2^-$, which forms sulphide with metal ions ($\text{Cu}^{2+}$, $\text{Fe}^{2+}$, $\text{Fe}^{3+}$, $\text{Zn}^{2+}$, $\text{Pb}^{2+}$) can affect the colour of egg white and egg yolk (Viguier and Hulme, 2006). As a result, $\text{Cu}^{2+}$ is involved in producing the unique flavour, taste and colour formation of preserved eggs. It is inevitable that there is copper intake when eating preserved eggs. However, there is no feasible guide on how to consume preserved eggs within an acceptable range of human health, which is related to the lack of unified standardization of the manufacturing preserved egg processes. Copper is an essential microelement for the human body. It is also a component of many important human enzymes, such as tyrosinase, lysine oxidase and superoxide dismutase (Wondracek et al., 2016). However, it becomes toxic at high concentrations, leading to various health problems, especially injury to the liver, bone and central nervous system (Gaggelli et al., 2006). The limit of daily $\text{Cu}^{2+}$ uptake though vegetables, adopted from FAO-WHO, is 2.0–3.0 mg/day for adults (FAO/OMS, 2013), and the Tolerable Upper Intake Level has been set at 10 mg/day (Gaggelli et al., 2006). Thus, the determination of copper content in preserved eggs can provide a guide for the healthy consumption of preserved eggs and a reference point for the improvement of the preserved eggs pickling process.

FAAS occupies a major role in trace analysis due to its high sensitivity, strong anti-interference ability, high precision, good selectivity, simple operation and rapid measurement (Majeed et al., 2019). However, high interference of other matrix components and low metal ion concentrations will prevent the direct use of this analytical method in real samples. The above disadvantages can be effectively avoided by conducting a sample pre-treatment step before the final determination. The sample pre-treatment step eliminates other matrix interferences and enriches the target metal ions, which improves the accuracy of the determination. Common sample pre-treatment techniques include chemical separation, chromatographic separation, solvent extraction, and solid-phase extraction (SPE). Solid-phase micro-extraction (SPME) and dispersive micro solid-phase extraction (DMSPE) derived from SPE are commonly used for the enrichment and separation of heavy metal ions (Janik et al., 2018). The choice of an appropriate solid-phase sorbent is very important for the sample pre-treatment step. This requires the sorbent to have a series of characteristics such as inert base material, abundant adsorption active sites, rapid separation and uniform particle size distribution, etc. The content of the target in the pre-treated sample is close to that of the real sample to ensure the reliability of the determination.

Mesoporous silica microspheres (MSM) have received increasing attention in several scientific and technical fields due to their unique features including large surface area, good mechanical stability, low toxicity and capability of interacting with atoms, ions and molecules on their surfaces and along with their porous networks (Nicola et al., 2020; Narayan et al., 2021). Consequently, MSM has been widely used in catalysis, drug delivery and separation. In addition, the core-shell structure formed by introducing the $\text{Fe}_3\text{O}_4$ magnetic core into the spherical MSM structure makes the base material magnetically responsive. As a result, it can be separated by an external magnetic field instead of filtration or centrifugation steps.

Polyethyleneimine (PEI) is a water-soluble polymer that contains three types of amino groups: primary, secondary and tertiary (Aljarrah et al., 2020). The multiple amino structures of PEI make it highly adhesive and adsorptive and can chelate with heavy metal ions, thus separating a variety of heavy metals such as uranium, chromium, cadmium and copper from an aqueous medium (Larraza et al., 2012; Sarri et al., 2013; Ning et al., 2014; Ying et al., 2014; Snoussi et al., 2016). The sorbent (MMSM-PEI) prepared by grafting PEI onto the base material of magnetic MSM (MMSM) not only has magnetic responsiveness and the multiple amino structures of
PEI, but also has excellent dispersibility in water. This provides operability for the enrichment and separation of copper in the aqueous solution.

In this work, we synthesized a magnetic solid-phase extractant to enrich and separate Cu$^{2+}$, and combined it with FAAS to determine the content of Cu$^{2+}$ in preserved eggs. Magnetic SPE, MMSM-PEI, could be separated from the sample matrix by an external magnetic field, which simplified the separation process and saved analysis time. Furthermore, batch adsorption experiments were carried out to study the effects of pH, temperature and initial concentration. Adsorption kinetic models (pseudo-first order and pseudo-second order) and adsorption isotherm models (Langmuir and Freundlich) were used to fit the experimental data. The developed method was used to successfully determine Cu$^{2+}$ in preserved eggs of two kinds of manufacturing methods with copper sulphate in TOCM and without that in TOCM.

**Materials and methods**

**Materials and reagents**

Ferrous chloride (FeCl$_2$.4H$_2$O), ferric chloride (FeCl$_3$.6H$_2$O), sodium hydroxide (NaOH), hexadecyl trimethyl ammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), APTES and PEI were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Copper sulphate anhydrous (CuSO$_4$) was purchased from Guangzhou Guanghua Sci-Tech Co., Ltd. Succinic anhydride (SA) was purchased from Sinopharm Chemical Reagent Co., Ltd. Triethylamine was purchased from Tianjin Guangfu Fine Chemical Research Institute. All reagents were used as received without further treatment in this experiment.

**Synthesis of Fe$_3$O$_4$ nanoparticles and MMSM**

Fe$_3$O$_4$ nanoparticles were synthesized by a co-precipitation method following the procedure reported in previous work (Xiong et al. 2020). Briefly speaking, FeCl$_2$.4H$_2$O (11.2 mmol) and FeCl$_3$.6H$_2$O (22.4 mmol) were dissolved in deionized water (300 mL) in a three-necked round-bottomed flask (500 mL) and sonicated for 20 min. The solution was continuously stirred and ammonia (26%, v/v) added dropwise until the pH of the solution reached 11. During 30 min of vigorous mechanical stirring in an oil bath at 80 °C in a nitrogen atmosphere, black precipitates gradually formed. The black precipitates were separated by an external magnetic field and washed with deionized water until the water became neutral. Next, the products were dried overnight in a vacuum at 50 °C.

MMSM was synthesised by a classical method (Neamani et al. 2020). Fe$_3$O$_4$ nanoparticles (500 mg) and CTAB (1.0 g) were dissolved in deionized water (300 mL). Then, the solution was ultrasonically mixed for 20 min. TEOS (3.5 mL) and NaOH (280 mg) were added to the mixed solution. The mixture was mechanically stirred for 2 h at 80 °C under a nitrogen atmosphere. The obtained product was separated by an external magnetic field and washed with deionized water and ethanol in turn until the pH of the eluent became neutral. The product was calcined at 550 °C for 6 h to remove any remaining CTAB.

**Synthesis of MMSM-NH$_2$ and MMSM-COOH**

MMSM (500 mg) and APTES (1.5 mL) were added to anhydrous ethanol (60 mL). The solution was ultrasonically dispersed for 20 min. Next, the solution was deoxygenated with nitrogen for 20 min and mechanically stirred for 12 h at 40 °C. After the reaction was completed, the remaining solids were separated by an external magnetic field and washed four times with methanol to remove the residual reagent, then the obtained reddish-brown solid powder (MMSM-NH$_2$) was dried in a vacuum at 50 °C.

The experimental method was improved according to previous literature (Wen et al. 2020). MMSM-NH$_2$ (300 mg) obtained from the previous step and SA (300 mg) were added to anhydrous toluene (80 mL) and ultrasound for 10 min in a water bath to dissolve SA fully. Standing solution and adding triethylamine to it. For 24 h at 40 °C in a nitrogen atmosphere, the mixture was gently mechanically stirred. The product was separated by an external magnetic field and washed four times with methanol. Finally, the product referred to as MMSM-COOH was obtained after vacuum drying.
**Synthesis of MMSM-PEI**

PEI (1.0 g) and MMSM-COOH (200 mg) were dissolved in DMF (80 mL). The mixture was added to a three-necked round-bottomed flask (250 mL) after thorough stirring. Consequently, the mixture was mechanically stirred for 36 h at 40°C. The final product was also separated by an external magnetic field and washed thoroughly with methanol and deionized water. The separated product referred to as MMSM-PEI was dried in an oven at 50°C for 12 h.

**Adsorption experiments**

To study the influence of various factors on the experimental process of Cu\(^{2+}\) adsorption. Initial concentration, pH, solution temperature and adsorption time were verified in the following experiments. The equilibrium adsorption experiments were carried out by dissolving 10 mg sorbent in 20 mL of the Cu\(^{2+}\) solution at a pH of 6.5 and a temperature of 25°C. An aliquot of 2.0 mL was taken at specified time intervals during the experiment. Two millilitres of sample solution was diluted five times with deionized water each time. The effect of solution pH on the Cu\(^{2+}\) adsorption process was studied over a range of 3–9 and the solution pH was adjusted by adding HCl (0.2 M) and NaOH (0.2 M) solution. Three temperatures (25°C, 35°C and 45°C) were investigated. To study the effect of different initial concentrations of Cu\(^{2+}\), different concentrations of Cu\(^{2+}\) solution prepared with anhydrous CuSO\(_4\) were added into 10 mg sorbent respectively, while keeping other conditions the same (pH 6.5, 25°C, 40 min). All the adsorption processes were carried out in an air bath with a constant temperature oscillator with an oscillation intensity of 200 rpm/min. The parameters of all studies in the adsorption experiment were listed in Supplemental material Table S1.

The adsorption capacity was calculated using the Equation (1).

\[ q_e = \frac{C_0 - C_e}{W} \times V \]  

where \( q_e \) (mg/g) represents the equilibrium capacity; \( C_0 \) (mg/L) represented the Cu\(^{2+}\) initial concentration and \( C_e \) (mg/L) represented the adsorption equilibrium Cu\(^{2+}\) concentration; \( V \) (L) represented the volume of Cu\(^{2+}\) solution and \( W \) (g) is the dry weight of the sorbent.

The removal efficiency of Cu\(^{2+}\) from the solution was calculated according to Equation (2).

\[ \text{Removal efficiency} \% = \frac{C_0 - C_e}{C_0} \times 100 \]  

An experiment on the reusability of sorbents was studied as follows: sorbent (10 mg) was added to a 20 mL Cu\(^{2+}\) (25 mg/L) solution. After reaching adsorption equilibrium, the sorbent was separated by an external magnet. Then, 5 mL of HNO\(_3\) (1.0 M) was added for ultrasonic desorption for 20 min. The above operation was cycled five times.

**Pre-treatment of samples**

1.0 g each of egg white, egg yolk and TOCM were taken from preserved eggs purchased from the market and dried after digestion at 550°C for 6 h (Majeed et al. 2019). The residual ash was dissolved in 2 mL of concentrated HNO\(_3\) and then diluted to 50 mL with deionized water. The diluted solution was filtered and the pH was adjusted to 6.5 for later use. Sorbent (MMSM-PEI) was added to 20 mL of diluted solution and an external magnetic field was used to separate sorbent from the solution. The sorbent was desorbed ultrasonically by 5 mL of 1 M nitric acid (HNO\(_3\)). The desorption solution was determined by FAAS.

**FAAS determination conditions**

Cu\(^{2+}\) was determined by FAAS. A copper hollow cathode lamp was selected and the characteristic spectral line was set at 324.7 nm, and Cu was atomized by a gas-acetylene flame. A single sample was determined three times in parallel, each determination time was 5 s.

**Instrument**

The instruments used in this work were as follows: TENSOR27 Fourier transform infrared spectrometer (Bruker, Germany); BrukerD8 X-ray diffractometer (Bruker, Germany); BPZ-6033 vacuum drying box (Shanghai Yiheng Technology...
Co., Ltd); SX2-A-10 muffle furnace (Shanghai Experimental Instrument Co., Ltd); HJ-5 multi-functional constant temperature agitator (Changzhou Yuexin Instrument Manufacturing Co., Ltd); ZD-85 air bath thermostatic oscillator (Changzhou JTLIANGYOU Instrument Co., Ltd); PE PinAAcle900T flame atomic absorption spectrometry; TGA 4000 Thermogravimetric analyzer (PerkinElmer, USA); Nova NanoSEM 450 scanning electron microscope (FEI, USA).

**Results and discussion**

**Characterisation of MMSM-PEI**

FT-IR analysis was carried out for Fe\(_3\)O\(_4\), MMSM, MMSM-NH\(_2\), MMSM-COOH and MMSM-PEI. The results of the FT-IR spectrum were shown in Figure 1. The peak appearing at 3400 cm\(^{-1}\) and 1628 cm\(^{-1}\) was the stretching and bending vibration absorption peak of –OH on the surface of Fe\(_3\)O\(_4\) particles, respectively (Orooji et al. 2020). The stretching vibration peak of C=O in the carboxyl group appears at 1718 cm\(^{-1}\), which indicated that the carboxyl group was successfully introduced into MMSM-COOH. The peak at 1561 cm\(^{-1}\) was attributed to N-H bending vibration of the amide group. The deformation vibration of –OH in the carboxyl group was at 1402 cm\(^{-1}\). The absorption peak at 1080 cm\(^{-1}\) was the asymmetric stretching vibration of the Si-O-Si group, and the absorption peaks at 460 cm\(^{-1}\) and 804 cm\(^{-1}\) were the stretching vibrations of the Si-O group, which indicated the formation of silica coating on the surface of Fe\(_3\)O\(_4\). The peaks appearing at 636 cm\(^{-1}\) and 557 cm\(^{-1}\) were the bending vibration of Fe-O in Fe\(_3\)O\(_4\) (Zhang et al. 2012). It showed the presence of magnetic nanoparticles in the structure.

The XRD patterns of the synthesized Fe\(_3\)O\(_4\), MMSM, MMSM-NH\(_2\), MMSM-COOH and MMSM-PEI were shown in Supplemental material Fig. S1. From this figure, it clearly showed the major diffraction peaks identified at 30.34\(^{\circ}\), 35.67\(^{\circ}\), 43.31\(^{\circ}\), 53.61\(^{\circ}\), 57.31\(^{\circ}\) and 62.82\(^{\circ}\) corresponded to the cubic structure of Fe\(_3\)O\(_4\) and were associated with the crystal face index of Fe\(_3\)O\(_4\) 220, 311, 400, 422, 511 and 440 planes (Xie et al. 2019). The result showed silica coating on the surface of Fe\(_3\)O\(_4\) and surface functionalization didn’t change its crystal structure. Furthermore, from a to e, the intensity of its diffraction peak had a decreasing trend at the diffraction peak of 35.67\(^{\circ}\). This might be related to a series of surface modifications of Fe\(_3\)O\(_4\), and the formed composite coating hindered the expression of Fe\(_3\)O\(_4\) peak signals.

SEM images of the Fe\(_3\)O\(_4\) and MMSM-PEI were shown in Figure 2. It could be observed from Figure 2(a) that the Fe\(_3\)O\(_4\) nanoparticles prepared by the chemical coprecipitation method had a uniform particle size distribution and a regular sphere, and the average particle size of

![Figure 1. FT-IR spectra of Fe\(_3\)O\(_4\) (a), MMSM (b), MMSM-NH\(_2\) (c), MMSM-COOH (d) and MMSM-PEI (e).](image-url)
Fe₃O₄ was approximately 15 nm. It could be observed from Figure 2(b) that the average particle size of MMSM-PEI was about 300 nm which was compared with a single Fe₃O₄ nanoparticle and the morphology of MMSM-PEI was close to spherical. Its increase in particle size was attributed to a series of surface modifications of Fe₃O₄ nanoparticles.

TGA analyses of MMSM-PEI and MMSM-NH₂ were listed in Figure 3. The results showed that the weight of both samples decreased slightly below 100°C, which corresponded to the loss of gas mass absorbed by the sample surface. According to the TGA curve of MMSM-PEI, there was an obvious weight loss of about 2.47% from 115°C to 210°C (DTG peak at 182°C), which corresponded to the moisture volatilization in the pores and interior of MMSM-PEI. There was a weight loss of about 8.73% from 210°C to 409°C (DTG peak at 366°C), indicating that the cleavage of the amide bond and the degradation and evaporation of the carboxyl and the amine group. There was also a weight loss of about 7.78% from 409°C to 654°C (DTG peak at 474°C), which corresponded to the thermal decomposition of PEI. According to the TGA curve of MMSM-NH₂, the weight loss was about 1.31% from 210°C to 409°C, which corresponded to the degradation and evaporation of the amine group. By comparing the curve of weight losses of MMSM-NH₂ and MMSM-PEI, the results showed that the amount of PEI coating on the surface was approximately 7.78%. Strategies of carboxylation and grafting PEI onto the MMSM-NH₂ surface were successful.

Figure 4 showed the hysteresis loops of MMSM-PEI and Fe₃O₄, respectively. The VSM plot showed that there was no hysteresis in the
magnetization. The remanence and coercive force were not detected, which suggested that the two samples synthesized were superparamagnetic (Wang et al. 2010). The saturation magnetization of Fe₃O₄ was 67.72 emu/g and it was 41.32 emu/g for MMSM-PEI. Compared with Fe₃O₄, the saturation magnetization of MMSM-PEI decreased because of the inclusion of mesoporous silica in Fe₃O₄ and subsequent surface modification, which could be attributed to the shielding effect of the inclusion shell (Aljarrah et al. 2018). In experimental operation, MMSM-PEI could still be separated from aqueous solutions by an external magnetic field in less than one minute.

**Adsorption study**

**Effect of pH**

The pH of the Cu²⁺ solution was a vital factor in the adsorption process. As shown in Fig. 5, it was found that the adsorption capacity and removal efficiency of MMSM-PEI increased gradually in the range of pH 3 to 8, and decreased slightly when pH continued to increase to 9. The adsorption capacity was 2.23 mg/g and the removal efficiency of Cu²⁺ was 4.46% at pH 3. When the solution pH increased to 8, the adsorption capacity reached up to 47.91 mg/g and the removal efficiency of Cu²⁺ was up to 95.82%. At low pH values, the amino group of PEI and the amine part of amide grafted on the surface of MMSM-PEI were highly protonated in solution, which resulted in the existence of electrical repulsion between the amino group and Cu²⁺ and hindered the adsorption process. With the increase of pH, the degree of amino protonation decreased, and the chelation ability of Cu²⁺ on the surface of MMSM-PEI increased. The adsorption capacity was affected by both pore structure and coordination ability when pH > 6. The alkaline environment was favorable for the formation of chelation between Cu²⁺ and -NH₂ on the surface of MMSM-PEI. However, Cu²⁺ in an
aqueous solution began to precipitate as Cu(OH)$_2$ when pH $> 7$. Therefore, considering the adsorption capacity of MMSM-PEI and the presence of copper in an aqueous solution in ionic form, the Cu$^{2+}$ solution (pH 6.5) was selected for the adsorption study in the later experiments.

**Effect of adsorption time**

The effect of adsorption time on the adsorption process of Cu$^{2+}$ by MMSM-PEI was shown in Figure 6(a). The amount of Cu$^{2+}$ adsorbed by four kinds of sorbent (MMSM-PEI, MMSM-COOH, MMSM-NH$_2$ and MMSM) increased with the growth over time. In the first 10 min, the adsorption capacity changed greatly. The adsorption capacity tended to be stable at 40 min. Therefore, it could be considered that the adsorption of Cu$^{2+}$ on MMSM-PEI reached equilibrium at 40 min. The adsorption capacities of MMSM-PEI, MMSM-COOH, MMSM-NH$_2$ and MMSM were 39.20, 21.51, 23.23 and 18.03 mg/g, respectively. The adsorption capacity of MMSM for Cu$^{2+}$ could be attributed to the interaction of Si-OH on the surface of MMSM with Cu$^{2+}$ and the physical adsorption of Cu$^{2+}$ by the surface mesoporous structure. MMSM-NH$_2$ had a higher adsorption capacity than MMSM due to the stronger interaction of -NH$_2$ with Cu$^{2+}$ on its surface. The surface of MMSM-NH$_2$ was a single-chain amino group, while the surface of MMSM-PEI was a dense polymer network structure with dendritic branching of three types of amino groups. Therefore, compared with MMSM-NH$_2$, MMSM-PEI had a higher adsorption capacity for Cu$^{2+}$. The adsorption capacity of MMSM-COOH was lower than that of MMSM-NH$_2$, which might be attributed to -COOH on the surface was not completely dissociated to -COO$^-$ at pH 6.5.

**Sorbent type**

The adsorption performance of MMSM-PEI was verified by adsorption experiments. As shown in Figure 6(a), MMSM, MMSM-NH$_2$, MMSM-COOH and MMSM-PEI were used as sorbents,
with MMSM-PEI having the highest adsorption capacity. We attributed the better adsorption performance of MMSM-PEI to the following major factors: 1, the large specific surface area and mesoporous structure of MMSM; 2, the multiple active sites of -NH₂, -COOH, and -CONH- functional groups formed after functionalization; 3, the PEI polymerization network structure on the surface of MMSM-PEI.

**Effect of temperature**
To study the influence of temperature, the adsorption capacity of sorbent at 25, 35 and 45°C was verified respectively. The result was shown in Figure 6(b). The adsorption capacity decreased as the temperature increased from 25°C to 35°C; as the temperature continued to increase to 45°C, the adsorption capacity remained almost unchanged. It indicated that the adsorption process was exothermic, the thermal motion of the molecules was enhanced by the increase in temperature, which might hinder the chelation of the polymer surface amino groups with Cu²⁺. Therefore, adsorption experiments were set up at 25°C in the process of studying the adsorption kinetics. This temperature-dependent behavior was consistent with the reported literature (Gao et al. 2009; Liu et al. 2017); it was found that most nitrogen-based sorbent materials show exothermic adsorption behaviour.

**Effect of initial concentration**
Figure 6(c) showed the effect of initial Cu²⁺ concentration on the adsorption capacity of MMSM-PEI. It can be found that the adsorption capacity increased from 13.60 mg/g to 207.10 mg/g as the initial concentration was increased from 10 mg/L to 300 mg/L. This result indicated that the initial Cu²⁺ concentration had an important influence on the adsorption process and a higher initial concentration was more favorable to the adsorption process of MMSM-PEI. With the increase in initial Cu²⁺ concentration, the increasing trend of adsorption capacity decreased gradually. It may be due to the fact that at low Cu²⁺ concentrations, the MMSM-PEI surface had not yet reached saturation, while the adsorption capacity increased with increasing Cu²⁺ concentrations because of the gradual occupation of adsorption sites. However, the adsorption capacity increased at a relatively slow rate with the increase of the initial Cu²⁺ concentration compared with low Cu²⁺ concentrations due to the presence of a limited number of active sites on the MMSM-PEI surface.

**Adsorption kinetics study**
To study the rate-controlling step and adsorption mechanism in the physicochemical process. Two kinetic models including pseudo-first-order equation (Equation (3)) and pseudo-second-order equation (Equation (4)) were used to fit experimental data, and their linear formulas were expressed as follows:

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

where \( q_e \) (mg/g) was the adsorption capacity of Cu²⁺ at equilibrium; \( q_t \) was the capacity of sorbent on Cu²⁺ at time \( t \) (min); \( k_1 \) (min⁻¹) and \( k_2 \) (g·mg⁻¹·min⁻¹) were the rate constants of pseudo-first-order and pseudo-second-order adsorption kinetics, respectively. Figure 7(a,b) showed the fitting curves of the two adsorption kinetic models. The parameters involved in the two adsorption kinetic models were listed in Table 1. It was found that the value of the correlation coefficient \( R^2 \) of pseudo-first order was 0.8629 and the \( k_1 \) was 0.1017 min⁻¹. The \( q_e \) calculated from this equation was 13.00 mg/g. It can be observed that the value of correlation coefficient \( R^2 \) of pseudo-second-order was 0.9993 and the \( k_2 \) was 0.01628 g·mg⁻¹·min⁻¹. The \( q_e \) calculated from this equation was 40.29 mg/g. Compared with the pseudo-first order, the \( q_e \) calculated by the pseudo-second-order was closer to \( q_e \) (39.20 mg/g) obtained by the adsorption experiment. It indicated that the pseudo-second-order adsorption kinetics fitted the data better than the pseudo-first-order adsorption kinetics.

**Adsorption isotherm study**
In order to determine the parameters related to Cu²⁺ adsorption, Langmuir (Equation (5)) and Freundlich (Equation (6)) adsorption isotherm models were introduced to fit experimental data linearly. The general forms of the Langmuir and
Freundlich isotherm models can be expressed as follows:

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

(5)

\[
\log q_e = \log k_f + \frac{1}{n} \log C_e
\]  

(6)

where \( q_{\text{max}} \) (mg/g) was the maximum adsorption capacity of \( Cu^{2+} \) on MMSM-PEI; \( b \) (L/mg) was the Langmuir adsorption constant related to the adsorption energy. In Freundlich model, \( k_f \) and \( n \) represented the adsorption capacity and adsorption intensity (Feng et al. 2009; Parida et al. 2011), respectively. The linear fitting curves of the two models to the experimental data were shown in Figure 7(c,d), and the corresponding parameters were listed in Table 2. According to the Langmuir model, the maximum absorption capacity of MMSM-PEI to \( Cu^{2+} \) was 274.35 mg/g. Combining with the experimental data and the data fitted by the two models, the results showed that the Langmuir model can better describe the adsorption process, and further indicated that the adsorption of \( Cu^{2+} \) by MMSM-PEI was monolayer adsorption.

Table 1. Kinetic model parameters.

| Parameter                  | MMSM-PEI | MMSM |
|---------------------------|----------|------|
| Pseudo-first-order        |          |      |
| \( R^2 \)                 | 0.863    | 0.766|
| \( k_1 \) min\(^{-1} \)  | 0.102    | 0.086|
| \( q_e \) (calculated), mg/g | 13.00    | 5.25 |
| Pseudo-second-order       |          |      |
| \( R^2 \)                 | 0.999    | 0.999|
| \( k_2 \) g mg\(^{-1}\) min\(^{-1} \) | 0.016    | 0.082|
| \( q_e \) (calculated), mg/g | 40.29    | 18.08|
| \( q_e \) (measured), mg/g | 39.20    | 18.03|

Table 2. Langmuir and Freundlich isotherm model parameters for MMSM-PEI.

| Parameter                  | Langmuir | Freundlich |
|---------------------------|----------|------------|
| \( R^2 \)                 | 0.950    | 0.910      |
| \( q_{\text{max}} \) (calculated), mg/g | 274.35   | 11.75      |
| \( b \)                   | 0.022    | 1.74       |

Table 3. Interference studies of some commonly interfering ions in the determination of \( Cu^{2+} \) (2.0 mg/L).

| Interferent | Add as | Concentration (mg/L) | Recovery% | RSD (n = 3) |
|-------------|--------|-----------------------|-----------|-------------|
| Na\(^+\)    | NaCl   | 200                   | 95.7      | 3.22        |
| K\(^+\)     | KCl    | 200                   | 95.3      | 4.51        |
| Mg\(^{2+}\) | MgSO\(_4\) | 100               | 94.7      | 4.65        |
| Ca\(^{2+}\) | CaCl\(_2\) | 100              | 96.1      | 4.97        |
| Fe\(^{3+}\) | FeCl\(_2\) | 20               | 93.3      | 3.55        |
| Zn\(^{2+}\) | ZnCl\(_2\) | 20               | 94.0      | 4.03        |
| Pb\(^{2+}\) | Pb(NO\(_3\))\(_2\) | 20          | 93.7      | 4.77        |
Effect of amount of sorbent
In order to ensure the economical use of the sorbent and the maximum adsorption efficiency, different amount of sorbent (5, 10, 25 and 50 mg) was taken. Different amount of sorbent was added into 20 mL of 200 µg/L Cu^{2+} standard solution. The result indicated that the larger amount of sorbent could improve adsorption efficiency. However, the adsorption efficiency changes at 10, 25 and 50 mg of sorbent tended to be fixed (Figure S2). Hence, 10 mg was chosen as the optimal amount of sorbent for future experiments.

Effect of eluent on the desorption of Cu^{2+}
The elution conditions including desorption reagent and concentration were investigated systematically. A series of different volume and concentration of acidic eluent solutions such as HCl, HNO₃ and H₂SO₄ were used to elute Cu^{2+} from this sorbent. In the first series of experiment, 0.1 M HNO₃, 0.1 M HCl, 0.1 M H₂SO₄, 0.5 M HCl and a mixture of 0.1 M HCl + 0.1 M H₂SO₄ (the volume of eluent solution was 5 mL), were tested on the MMSM-PEI. Among all of acidic eluent solutions, 0.1 M HNO₃ showed highest elution efficiency (Figure S3a). In the second set of experiments, different concentration and volume of HNO₃ were taken. The result indicated that the elution efficiency of Cu^{2+} loaded on the MMSM-PEI enhanced with increasing HNO₃ concentration (Figure S3b). Comparing the volume of 5 mL and 10 mL, the elution efficiency was almost the same. However, an elution volume of 5 mL could provide better enrichment compared to 10 mL. Thus, 5 mL of 1.0 M HNO₃ was optimized as the efficient eluting agent.

Regeneration study
To evaluate the reusability of MMSM-PEI, the sorbent loaded the Cu^{2+} was ultrasonically desorbed with 5 mL of HNO₃ (1.0 M) for 20 min, and the adsorption and desorption process was repeated five times. The first adsorption capacity was 39.2 mg/g. The fifth adsorption capacity was 35.3 mg/g which accounted for 90.0% of the first time (Fig. S4a). It showed that MMSM-PEI had good reusability and can still maintain high adsorption capacity after repeated use. The application of the sorbent in preserved eggs after repeated use was further explored, and the recoveries were determined. 10 mg of the recycled sorbent and a standard solution containing a known amount of Cu^{2+} were added to the sample solution. After the adsorption-desorption process, it was determined by FAAS. The measurement was repeated three times and the average value was taken. The change of recoveries was shown in Figure S4b.

Interference studies
The influence of Pb^{2+}, Zn^{2+}, Fe^{2+}, Ca^{2+}, Mg^{2+}, K+ and Na+ in the proposed method was studied. Considering their occurrence in real samples, 10 mg of MMSM-PEI was taken and a binary mixture was formed by adding interfering substances to 20 mL of 2.0 mg/L Cu^{2+} standard solution. The potential interfering factors were studied to evaluate the applicability of the method. As shown in Table 3. It could be seen that the presence of Pb^{2+}, Fe^{2+}, Zn^{2+}, Ca^{2+}, Mg^{2+}, K+ or Na+ had a slight influence on the adsorption capacity of MMSM-PEI for Cu^{2+}, which might be attributed to the surface functional groups on MMSM-PEI had stronger chelation capability with Cu^{2+} than with interfering metal ions. Furthermore, the possible explanation for the decline of Cu^{2+} sorption capacity of MMSM-PEI might be that the increase of ionic strength resulted in the decrease of the activity of Cu^{2+}, and the K+, Na+, Ca^{2+}, Fe^{2+}, Zn^{2+}, Pb^{2+} or Mg^{2+} also had a competition with Cu^{2+} for the active sites on MMSM-PEI. Ca^{2+}, Pb^{2+}, Fe^{2+}, Zn^{2+} and Mg^{2+}, as multivalent metal ions, were more competitive than K+ and Na+ when chelated to the active sites. Thus, the degree of interference was relatively high with K+ or Na+.

Ionic strength
The ionic strength of the aqueous solutions had a critical role in the extraction of analytes on the SPE sorbent. In order to check the effect of ionic strength on the signal/noise ratio of Cu^{2+}, different concentrations of NaCl were tested in the range of 0–1.0% (w/v). The results (Figure S5) indicated that NaCl had approximately no effect on the Signal/Noise ratio of Cu²⁺ from 0 to 0.8% (w/v), which could be conclude that this sorbent
Method validation

After optimizing the experimental conditions, the concentration of Cu\(^{2+}\) was the horizontal coordinate, the absorption value was the vertical coordinate, and the concentration of Cu\(^{2+}\) had a good linearity in the range of 0.46 - 15 mg/kg. The linear regression equation was y = 0.086x + 0.0443 (R\(^2\) = 0.997). The LOD and LOQ, which are indicators of the sensitivity of the analytical method, were calculated to be 0.14 mg/kg and 0.46 mg/kg, respectively. Although the LOD and LOQ involved in the developed method were not as good as other methods, the adsorption capacity was higher than most of the sorbents listed in Table 4.

Application to real samples

In order to determine the practicability of the method, the concentrations of trace Cu\(^{2+}\) in egg white, egg yolk and TOCM of preserved eggs were determined. Cu\(^{2+}\) could not be directly determined by FAAS after digestion due to insufficient sensitivity. Magnetic SPE was helpful for trace determination and matrix effect elimination. The developed method was used for pre-concentration of Cu\(^{2+}\), and then the standard addition experiment was performed by adding a known amount of Cu\(^{2+}\) analyte. As shown in Table 5, the results showed that the recoveries of Cu\(^{2+}\) with different concentrations were in the range of 94.1–103.8%, and the RSD was 0.96–4.35% (n = 3). Through the comparison of the results, it could be found that the Cu\(^{2+}\) content of preserved eggs made without copper sulphate was significantly lower than that with copper sulfate according to the content of Cu\(^{2+}\) in the respective TOCM. It was also observed that the addition of copper sulfate would lead to enrichment of Cu\(^{2+}\) in preserved eggs compared to the manufacturing process without the addition of copper sulphate. Moreover, the difference in Cu\(^{2+}\) content in preserved eggs might also be related to other factors, such as differences in duck feeding methods, different pickling processes and the environmental impact of different areas, etc.

Conclusions

In this work, we synthesized an efficient magnetic solid-phase extractant for enrichment and isolation of Cu\(^{2+}\), which combined with FAAS to quantitatively determine Cu\(^{2+}\) in real samples. After optimizing the adsorption conditions, pH

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**Table 4.** Comparison of the analytical parameters obtained by the proposed method with other related methods in the determination of Cu\(^{2+}\) by FAAS.

| Adsorbent       | Detection mode | Adsorption capacities of Cu\(^{2+}\) (mg/g) | LOD (mg/kg) | LOQ (mg/kg) | Samples               | Reference                        |
|-----------------|----------------|---------------------------------------------|-------------|-------------|-----------------------|----------------------------------|
| SCP             |                | –                                           | 2.75        | –           | Vinegars              | Saei-Dehkordi et al, 2012        |
| Fe\(_3\)O\(_4\)/CD/AC/SA | UV-vis        | 0.11                                       | 0.38        | –           | Corn, wheat and white beanflours | Santos et al, 2017 |
|                 | spectrophotometry | 10.1                                       | –           | –           | Water                 | Yadav et al, 2021                |
| Fe\(_3\)O\(_4\)@PDA | FAAS          | 0.66 μg/kg                                  | 2.25 μg/kg  | –           | Organic baby food, muesli, macaroni, honey and milk | Yavuz et al, 2018 |
| F-MWCNTs        | FAAS          | 118.4                                       | –           | 0.46 mg/kg  | Preserved eggs        | Gupta et al, 2017                |
| MMMS-PEI        | FAAS          | 274.3                                       | 0.14 mg/kg  | 0.46 mg/kg  | Preserved eggs        | This work                        |

**Table 5.** FAAS determination of Cu\(^{2+}\) in preserved eggs after preconcentration with MMMS-PEI.

| Samples | Added (ug/g) | Found (ug/g) | Recovery% | RSD (n = 3) |
|---------|-------------|--------------|-----------|-------------|
| 1       | Egg white   | 0            | 9.77      | 95.6        | 1.21       |
|         |             | 10           | 18.91     | 95.6        | 1.43       |
|         |             | 20           | 28.87     | 97.3        | 2.19       |
|         | Egg yolk    | 0            | 5.81      | –           | 0.96       |
|         |             | 10           | 15.52     | 98.2        | 1.37       |
|         |             | 20           | 25.40     | 98.4        | 3.09       |
| 2       | TOCM        | 0            | 410.93    | –           | 0.63       |
|         | Egg white   | 0            | 7.09      | –           | 1.32       |
|         |             | 10           | 16.35     | 95.7        | 3.65       |
|         |             | 20           | 26.28     | 97          | 2.68       |
|         | Egg yolk    | 0            | 18.87     | –           | 2.29       |
|         |             | 10           | 28.09     | 97.3        | 2.12       |
|         |             | 20           | 36.58     | 94.1        | 4.35       |
| 3       | TOCM        | 0            | 455.93    | –           | 1.45       |
|         | Egg white   | 0            | 1.95      | –           | 3.31       |
|         |             | 10           | 12.41     | 103.8       | 2.16       |
|         |             | 20           | 21.65     | 98.6        | 3.07       |
|         | Egg yolk    | 0            | 1.66      | –           | 3.60       |
|         |             | 10           | 11.32     | 97.1        | 1.86       |
|         |             | 20           | 20.97     | 95.5        | 3.45       |
|         | TOCM        | 0            | 5.64      | –           | 1.62       |
|         |             | 10           | 15.79     | 100.9       | 1.16       |
|         |             | 20           | 26.17     | 102.1       | 2.39       |

*a*No preconcentration, direct determination by FAAS.
6.5 and an adsorption temperature of 25°C were determined as the most suitable adsorption conditions. The experimental data fitted well with the pseudo-second-order model ($R^2 = 0.999$). Additionally, Langmuir isotherm ($R^2 = 0.990$) was found to fit the experimental data better than that of Freundlich, which indicated that the adsorption was monolayer surface adsorption, and the calculated maximum adsorption capacity was 274.35 mg/g according to Langmuir isotherm equation. The sorbent was separated from water by an external magnetic field and showed excellent stability in the five-cycle adsorption/desorption experiments (the fifth adsorption capacity reached 90.0%), which indicated the possibility of reuse. The method was used to pre-concentrate trace Cu$^{2+}$ in preserved eggs and then combined with FAAS for quantitative determination. The determination results of preserved eggs showed that the recovery was 94.1 - 103.8%, and the RSD was 0.96 - 4.35. The performance of the developed method was validated with good linearity in the range of 0.46 - 15 mg/kg (the correlation coefficient $R^2 = 0.997$), LOD = 0.14 mg/kg and LOQ = 0.46 mg/kg. Additionally, the addition of copper sulfate to TOCM inevitably led to enrichment of Cu$^{2+}$ of egg white and yolk in preserved eggs. This work provided a feasible strategy for enrichment, separation and determination of Cu$^{2+}$ in real samples, and provided a guide for people to eat preserved eggs healthily.

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**Disclosure statement**

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