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Synthesis of magnetic nanoparticles for analytical applications

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A simple method based on magnetically assisted chemical separation has been developed for analytical purposes. In this method, morin-modified magnetic nanoparticles were used for the selective extraction and preconcentration of copper ions from aqueous solutions. The influence of different parameters, such as the presence of the morin extractant, the amount of morin extractant loaded on the nanoparticles, the pH, adsorption time and the type and minimum amount of eluent required for elution of the copper from the magnetic nanoparticles, were evaluated. The detection limit of the proposed method followed by ICP–OES was found to be $1.3 \mu\text{g L}^{-1}$ and a dynamic linear range of $10\text{--}200 \mu\text{g L}^{-1}$ was obtained. The relative standard deviation was less than 5%. The method was applied to the recovery and determination of copper in real samples.

Keywords: copper (II); magnetic nanoparticles; morin; separation; environmental application

1. Introduction

Copper is an environmental pollutant, which has been tested and assessed over the past years from both the toxicological and human health viewpoints [1]. While a small quantity of copper is essential for normal physiological processes, copper in excess of the recommended dosage may pose a threat to human health. The maximum tolerable daily intake for copper is 0.5 mg kg^{-1} body weight [2]. The development of new methods for quantifying trace metals is required but may be challenging. In some common procedures for the determination of low concentrations of heavy metals a preconcentration step is required before performing the analysis. Traditional separation and preconcentration methods for metal ions include liquid–liquid extraction, coprecipitation, ion exchange, etc. These methods often require large amounts of high-purity organic solvents, some of which are harmful to health and may cause environmental problems [3].

The magnetically assisted chemical separation (MACS) method, which uses nano- or micron-sized particles, is suitable for this purpose. It combines the selectivity and efficient separation offered by chemical extraction with the magnetic recovery of the extractant for the selective separation of metal ions [4,5], radionuclides and transuranic elements [6,7] and organic compounds [8]. Furthermore, this method can be applied in the fields of liquid waste treatment [9].

In the MACS method, there are two ways of binding metal ions onto particle surfaces. One method is based on the simple physical adsorption of chelators or metal ions on the

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particle surfaces. The other is based on the covalent immobilisation of complex metal ions on the particle surfaces. After being suspended in the solution sample, the metal ions that are now bound to the magnetic nanoparticles are easily separated through the applicability of an external magnetic field. A variety of magnetic particles (uncoated) that are available from commercial vendors were evaluated for stability towards acid hydrolysis and radiolysis [10].

Using magnetic nanoparticles for separation and preconcentration in analytical chemistry may result in the development of a new methodology that is faster, simpler and more precise than existing methodologies. The greatest advantage of this method is that the desired materials can be separated from solution by a simple and compact process producing less secondary wastes. Other advantages are: the large active surface area for a given mass of particles, the ability to process solutions that contains suspended solids [11], the avoidance of channelling effects that are common in packed beds and the ability to immobilise the target particles at a specific location in a column by the application of an external magnetic field [12].

In this work, the magnetic nanoparticles were first modified with an extractant, morin, by simple physical adsorption. The morin-coated magnetic nanoparticles were then used for the selective separation of copper from aqueous solutions. The effect of different parameters, for example, the amount of morin extractant loaded on the nanoparticles, the pH, the adsorption time, the type and minimum amount of eluent required for the elution of the copper from the magnetic nanoparticles, the breakthrough volume and the detection limits have been studied.

2. Experimental

2.1 Materials

Morin (3, 5, 7, 2', 4'-pentahydroxyflavone), dichloromethane and dimethylsulphoxide (DMSO) were obtained from Merck (Darmstadt, Germany). All acids used were of the highest purity available from Merck and were used as received. Reagent grade FeCl_2 , FeCl_3 and nitrate or chloride salts of other cations (all from Merck) were of the highest purity available and were used without any further purification. A copper stock solution was required by dissolving the proper amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in doubly distilled water in a 10 mL flask. Dilute solutions were prepared by an appropriate dilution of the stock solution in doubly distilled water.

2.2 Apparatus

Metal ion concentrations were analysed by simultaneous inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian Vista-Pro, Australia) coupled to a Vgroove nebuliser and equipped with a charge coupled device (CCD). The ICP instrument settings are shown in Table 1. The pH was determined with a model 630 Metrohm pH meter with combined glass-calomel electrode.

2.3 Preparation of morin-bound iron oxide magnetic nanoparticles

Iron oxide nanoparticles were prepared by the co-precipitation of Fe(II) and Fe(III) ions through the addition of ammonia solution and by treating under hydrothermal conditions.

Table 1. ICP-OES instrument conditions.

Plasma	Argon
RF generator power (kW)	1.5
Plasma gas flow rate (L min^{-1})	15.0
Auxiliary gas flow rate (L min^{-1})	1.5
Frequency of RF generator (MHz)	40.0
Observation height (mm)	8.0
Nebuliser pressure (kPa)	240

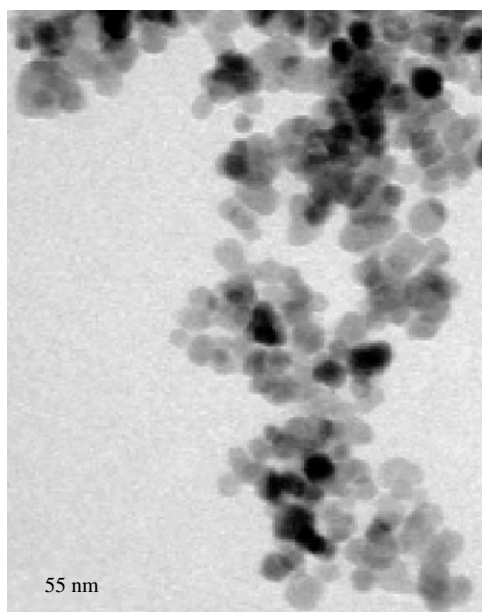


Figure 1. TEM image of the magnetic nanoparticle.

The ferric and ferrous chlorides (mole ratio 2 : 1) were dissolved in water at a 0.3 M total iron concentration. Chemical precipitation was achieved at 25°C under vigorous stirring by the addition of NH_4OH solution (29.6%). During the reaction process, the pH was maintained at approximately 10.5. The precipitate was heated and maintained at 80°C for 30 min, and was then washed several times with deionised water and ethanol. Finally, the precipitate was dried in a vacuum oven at 70°C. The representative TEM image of Fe_3O_4 nanoparticles is shown in Figure 1 from which it can be seen that the most of the particles are quasi-spherical with an average diameter of 15 nm.

For the binding of the morin to the particle surface, an appropriate amount of dried nanoparticles was poured into a Teflon beaker to which a morin–ethanol solution was added. The mixture was gently stirred by a Teflon rod and the solvent was slowly evaporated. The modified particles were then heated at 90°C for 2 h to completely remove the residual solvent and then they are dispersed in 50 mL solution containing 25 μg copper ions.

2.4 Adsorption and desorption studies

The adsorption of copper from aqueous solutions was investigated in batch experiments. Adsorptions were performed in test tubes containing 25 μg copper ions in 50 mL deionised water. The pH was adjusted to 4.5 by drop-wise addition of 1 M sodium hydroxide (NaOH) and 1 M hydrochloric acid (HCl). Five milligrams of modified particles were added to the solutions. Thereafter, the mixture was shaken for an appropriate time to completely extract the copper ions from the solution. Finally, the test tubes were placed in a magnetic rack, where a permanent magnet was used to aggregate the particles on one side of the test tube. The amount of copper adsorbed was estimated from the concentration change of the copper in solution after adsorption by ICP-OES analysis at 324.8 nm. The instrument response was checked periodically with known copper standard solutions. Three replicate extractions and measurements were performed for each aqueous solution. The percent extraction of copper was calculated from the following equation:

$$\text{Extraction \%} = (C_A - C_B/C_A) \times 100,$$

where C_A and C_B are the concentration of the copper ions in the solution before and after extraction.

The adsorbed copper was desorbed by contacting the extractant particles with 10 mL of CH_2Cl_2 -DMSO (1:1, v/v). After mixing for several minutes and removing the nanoparticles, 10 mL of HNO_3 (0.5 M) were added to the organic solvents and, the concentration of copper in the aqueous phase was measured to estimate the amount of copper desorbed.

3. Results and discussion

Some preliminary experiments were carried out in order to investigate quantitative retention of the copper ions by the magnetic nanoparticles in the absence and presence of morin in solution.

3.1 Effect of pH

The effect of pH on the extraction of copper ions from water samples was studied in the pH range of 1–6. The pH of the solution was adjusted to the required value by the addition of 1 M NaOH and 1 M HCl. Results showed that the percent extraction was nearly constant and quantitative in the pH range of 4–6. At the pH values below 4, however, when the pH of the sample was lower than 4, the functional groups of morin remain protonated, thereby reducing affinities at lower pH values. Magnetic nanoparticles was relatively stable (leachate <5 wt% of total Fe) in matrices ranging from 0.5 M acid solution to a strong alkaline solution (2 M NaOH) [13]. Therefore, pH of 4.5 was chosen as the optimum pH for extraction (Figure 2).

3.2 Effect of amount of extractant

In order to investigate the optimum amount of extractant required for the extraction of the copper, the amount of extractant loaded on the magnet particles was varied from 0 to 5% (extractant-nanoparticles, w/w). The results are illustrated in Figure 3.

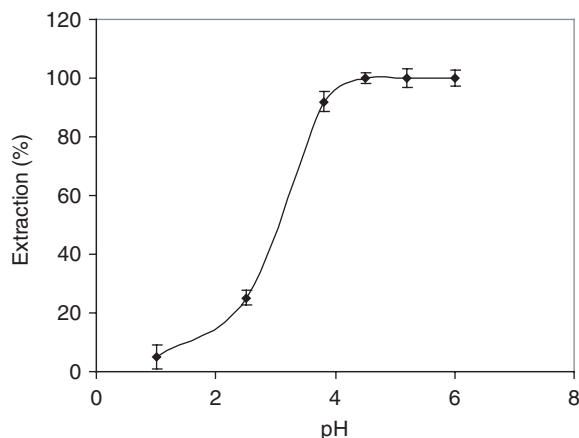


Figure 2. Effect of pH on the extraction efficiency of copper ions.

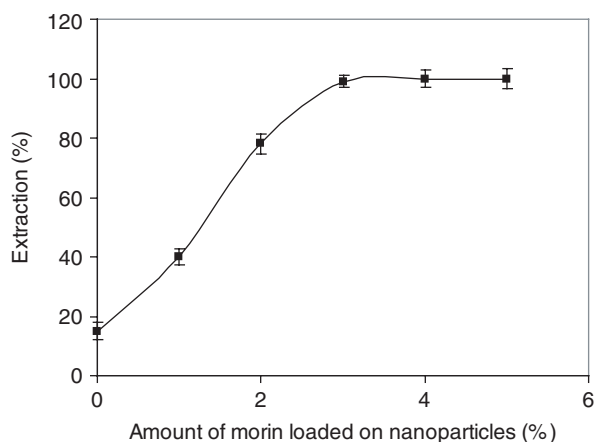


Figure 3. Effect of amount of morin used for modifying of nanoparticles on extraction efficiency.

Magnetic nanoparticles were loaded with morin to approximately 5% in line with previous literature studies [11]. Also, when particles were loaded with concentrations of morin exceeding 5% some nanoparticles became hydrophobic and floated on the surface of the solution. The extraction was found to be quantitative when nanoparticles were loaded with more than 3% morin. Hence, subsequent extraction experiments were carried out with nanoparticles coated to 5% morin by mass, to achieve maximum extraction capacity.

3.3 Effect of mass of nanoparticles

The effect of the mass of nanoparticles used for the quantitative extraction of copper is shown in Figure 4. The addition of various amounts of nanoparticles (from 1 mg to 8 mg) was investigated. When the mass of nanoparticles used was greater than 4 mg,

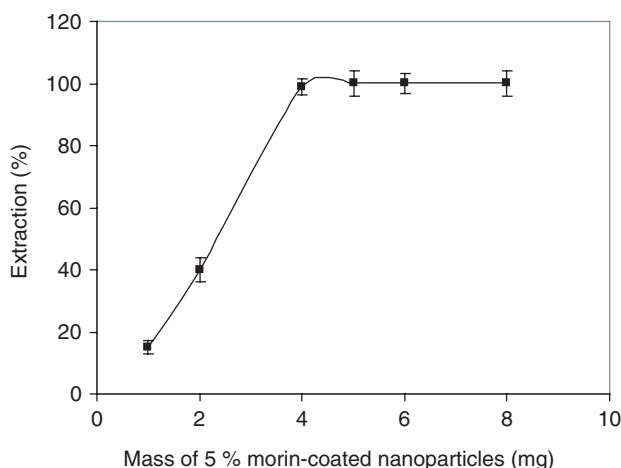


Figure 4. Effect of amount of modified nanoparticles (5%) on extraction efficiency of copper ions.

Table 2. Effect of type and amount of eluent on desorption efficiency.

Eluent	Volume (mL)	Recovery (%)
HNO ₃ 0.5 M	10.0	9.0
HNO ₃ 1 M	10.0	15.5
CH ₃ OH	10.0	20.6
CH ₃ OH:HNO ₃	10.0	27.8
CH ₃ OH-CH ₃ COOH (2:1)	15.0	46.3
CH ₃ OH-CH ₃ COOH (1:2)	15.0	73.2
CH ₂ Cl ₂ -DMSO (1:1)	10	100

the percent recovery was greater than 99%. As the mass of nanoparticles increased, the amount of morin extractant increases, thereby increasing the percent copper recovery. Subsequent experiments were carried out with 5 mg modified nanoparticles.

3.4 Choice of eluent

Several stripping solutions were tested as eluents for extracted copper ions. From the data given in Table 2, it is obvious that 10 mL of a 1:1 (v/v) mixture of CH₂Cl₂-DMSO can ensure quantitative elution of the copper ions from the nanoparticles.

3.5 Optimal time for adsorption and desorption

In order to investigate the effect of shaking time on the extraction efficiency, extraction experiments were carried out at 2, 5, 10, 15 and 20 min time intervals. Results showed that extraction is quantitative and very fast in all cases. Thus, the mixtures were been agitated for 10 min to reach equilibrium in the subsequent experiments. The desorption equilibrium of copper ions was achieved within about 20 min.

3.6 Analytical performance

The break-through volume of the solution sample was tested by dissolving 25 µg of copper and 5 mg of modified nanoparticles in 25, 50, 100, 250, 500 and 1000 mL water and a recommended procedure was followed. The copper ion recoveries were 100, 100, 100, 100, 97.5 and 94%, respectively. From these results, it can be concluded that a 1000 mL is a suitable sample volume because with higher sample volumes the recovery decreased.

The adsorption data were analysed according to the linear form of the Langmuir isotherm as follow [14]:

$$\frac{C_e}{q} = \frac{1}{Kq_m} + \frac{C_e}{q_m},$$

where q is the adsorption capacity (mg g^{-1}) based on the dry weight of nanoparticles, C_e is the equilibrium concentration (mg L^{-1}) in solution, q_m is the maximum adsorption capacity (mg g^{-1}) and K is the Langmuir adsorption equilibrium constant (L mg^{-1}). The plot of C_e/q versus C_e at various temperatures yielded straight lines, revealing that the adsorption of copper ions on magnetic nanoparticles obeys the Langmuir adsorption isotherm. From the isotherm, the values of q_m and K might be estimated as 22.1 mg g^{-1} and 0.0162 L mg^{-1} , respectively. The maximum adsorption capacity based on the weight of morin was 421 mg g^{-1} . This might be reasonably referred to the high specific surface area because the bound morin might be spread on the surface of Fe_3O_4 nanoparticles, leading to almost chelation sites available.

Under the optimum conditions described, the calibration curve was linear over the concentration range of $10\text{--}200 \text{ }\mu\text{g L}^{-1}$. The least square equation at the above dynamic linear range was as follows:

$$A = 0.0048 C(\mu\text{g L}^{-1}) - 0.0077 \quad (r^2 = 0.998).$$

The limit of detection (LOD) of the proposed method for the determination of copper was studied under the optimal experimental conditions. The LOD was obtained from $C_{\text{LOD}} = 3(S_d)_{\text{blank}}/m$ was $1.3 \text{ }\mu\text{g L}^{-1}$.

All the statistical calculations are based on the average of triplicate readings for each standard solution in the given range.

In order to investigate the selective separation and determination of the copper ion from its binary mixtures with diverse metal ions, an aliquot of aqueous solution (50 mL) containing 25 µg copper and milligram amounts of other cations was used and the recommended procedure was followed. The results are summarised in Table 3. The results show that the copper recovery was almost quantitative in the presence of milligrams of diverse ions. Since the chloride, nitrate and sulphate salts were employed in this study without any interference, their respective anions pose no possibility of interference.

In order to assess the applicability of the method to real samples with different matrices, it was applied to the extraction and separation of copper ions from 50 mL of three different samples.

Table 4 shows the extraction of spiked copper ions from 50 mL of different samples. As seen, the results of three analyses of each sample show that the copper recovery was almost quantitative.

Table 3. Extraction of copper from binary mixture.^a

Foreign ion	Amount used (mg)	Recovery of copper (%)
Li ⁺	12.5	100.0
Na ⁺	12.5	100.0
K ⁺	12.5	100.0
Mg ²⁺	12.5	100.0
Ca ²⁺	12.5	100.0
Sr ²⁺	12.5	100.0
Ba ²⁺	12.5	100.0
Mn ²⁺	0.5	95.0
Zn ²⁺	0.5	96.4
Fe ³⁺	0.5	94.2
Pb ²⁺	0.5	97.2

Note: ^aAmount of copper used is 25 µg.

Table 4. Recovery of 5 µg copper added to 50 mL of samples.

Sample	Spiked amount (µg L ⁻¹)	Copper found (µg L ⁻¹)	Recovery (%)	RSD ^a (%)
Tap water	20	19.9	99.5	1.5
Chahnemah water	20	19.7	98.5	2.5
Copinox ^b	—	30.60	—	4.5
Copinox	20.0	50.4	99	5

Note: ^aRelative standard deviation.

^bCopinox capsules are used for the prevention of congenital swayback in lambs by the treatment of ewes.

4. Conclusion

In this work, magnetic nanoparticles were synthesised. The surface modification of the magnetic nanoparticles through the use of morin was achieved easily. As the diameter of the particle decreases to the nanometer scale, ample external surface area becomes available for surface modifications, thereby raising the rate of reaction. Magnetic nanoparticles can be quickly and easily recovered in the presence of external magnetic fields for reuse. Also, internal diffusion limitations can be avoided, because all of the available surface area of the magnetic nanoparticles is external.

A magnetic nanoadsorbent was fabricated by covalent binding of morin on magnetic nanoparticles. Magnetic nanoparticles have great applications in the fields of high density data storage, ferro-fluids, magnetic resonance imaging, wastewater treatment, bioseparation, and biomedicine. In this work, copper was chosen to study the feasibility of the MACS method as a simple, effective procedure for the separation and preconcentration of metal ions in aqueous solution. It was revealed that morin-modified magnetic nanoparticles were capable of separating and preconcentrating copper from solution quantitatively without pre-filtration of samples. The selectivity relies on the modification of particles with morin. The adsorption of copper increases with an increase in the solution pH, and the amounts of extractant and nanoparticles used. The adsorbed copper could be desorbed using the CH₂Cl₂-DMSO solution. By making use of this principle, it would be possible to develop a general, simple procedure for recovery and analyses of metals.

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