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Synthesis and characterisation of morin-functionalised silica gel for the enrichment of some precious metal ions

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Abstract

Silica gel was firstly functionalised with aminopropyltrimethoxysilane obtaining the aminopropylsilica gel (APSG). The APSG was reacted subsequently with morin yielding morin-bonded silica gel (morin-APSG). The structure was investigated and confirmed by elemental and thermogravimetric analyses, IR and ^{13}C NMR spectral studies. Morin-APSG was found to be highly stable in common organic solvents, acidic medium (<2 mol L^{-1} HCl, HNO_3) or alkaline medium up to pH 8. The separation and preconcentration of Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) from aqueous medium using morin-APSG was studied. The optimum pH values for the separation of Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) on the sorbent are 5.7, 2.2, 3.7, 3.7 and 6.8, giving rise to separation efficiencies of 43.9, 85.9, 97.7, 60.9 and 91.0%, respectively, where the activity was found to be >90% in the presence of acetate ion. The ion sorption capacity of morin-APSG towards Cu(II) at pH 5.5 was found to be 0.249 mmol g^{-1} where the sorption capacities of Ag(I) and Pd(II) were 0.087 and 0.121 mmol g^{-1} and 0.222 and 0.241 mmol g^{-1} at pH 2.2 and 5.7, respectively. This indicates a 1:1 and 1:2 morin/metal ratios at pH 2.2 and 5.7, respectively. Complete elution of the sorbed metal ions was carried out using 10 mL (0.5 mol L^{-1} HCl + 0.01 mol L^{-1} thiourea) in case of Au(III), Pd(II), Pt(II) and Rh(III) and 10 mL 0.5 mol L^{-1} HNO_3 in case of Ag(I). Morin-APSG was successfully employed in the separation and preconcentration of the investigated precious metal ions from some spiking water samples yielding 100-folds concentration factor. The relative standard deviation (R.S.D.) and the *T*-test ($|t|_1$) were calculated.

Keywords: Silica gel; Morin; Enrichment; Precious metal ions

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1. Introduction

Over the last three decades, chelating ion exchangers have acquired great attention for the fast and selective heavy metal ions separation, in spite of the tedious, time consuming and irreproducible procedures. Organic polymers (the base of chelating agents) are often hydrophobic and affected from variable swelling at different pH; radiation and microbial decay. In addition, slow rate of metal ion uptake and the lack of mechanical stability at high pressure preclude the use of most organic polymer-based chelating sorbents in chromatographic systems, particularly, at high pressure [1,2].

In contrast, silica has been adopted as a good alternating support for chelating substrate to be used as sorbent in chromatographic separation [3,4]. This is due to the availability of many silylating agents and silica phases of large specific surface area, such as silica gel (SG) and controlled-pore silica glass (CPSG) in commercial scale with constant composition. Moreover, SG is inert towards acids and organic solvents and has a high surface activity, good thermal and mechanical stability and resistance against swelling. CPSG is characterised by a relatively higher mechanical stability and lesser hydrolysability than SG [5–7].

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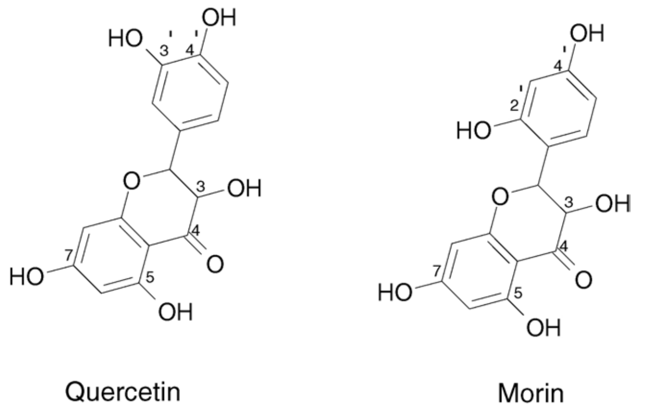


Scheme 1. Structure of quercetin and morin.

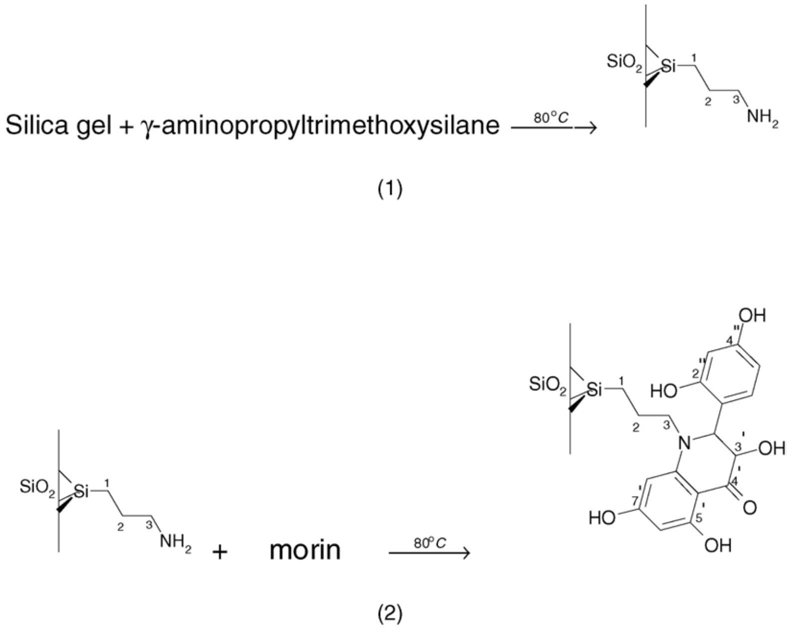
Due to these advantages of using silica, both CPSG and SG are increasingly utilized as supports for different chelating agents. Resacetophenone [8], 8-hydroxyquinoline [9], 8-quinolinol [10], bis-benzimidazoles [11], *o*-hydroxybenzene [12], dithizone [13], dithiocarbamate [14], diethyldithiocarbamate [15], *N*-propylsalicylaldimine [16–18], and quercetin [6,19–21] are typical examples.

Flavonoids (quercetin and morin are given as examples in Scheme 1) have attracted attention as effective multi-nuclei chelating reagents for extraction and spectrophotometric determination of many metal ions [20,22–28]. The metal ions bind to the 3-hydroxo/4-keto oxygen or 5-hydroxo/4-keto oxygen. The 3′- and 4′ hydroxo-group in quercetin, are also involved in chelation. Little attention was given to their immobilization on different supports [21,29,30]. Zaporozhets et al. [21] immobilized quercetin on silica gel by adsorption from acetone/hexane mixture (1:4) yielding a sorbent of a capacity of 0.035 mmol g^{-1}. Nevertheless, the sorbent was used to extract tin(IV) at pH 5.0 and the formed complex was eluted at pH 1.8–2.2. Azeredo et al. [19] determined molybdenum in apple leaves after separation on quercetin-functionalised silica gel. The sorbent showed a capacity of 0.089 mmol g^{-1} towards molybdenum. Moreover, Luo et al. [30] immobilized morin on an aminated poly(vinylchloride) with a capacity 0.417–0.762 mmol g^{-1} in the separation and preconcentration of molybdenum and tungsten. Quercetin [6] was chemically bonded to CPSG and SG and used for the separation and preconcentration of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). In the present study, a new silica gel chemically modified with morin (Scheme 2) was synthesized. The product was used for the separation and preconcentration of the precious metal ions Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) ions by batch mode followed by determination by flame atomic absorption spectrometry (FAAS).

2. Experimental

2.1. Materials and reagents

All reagents used were of analytical grade (A.R. from Fluka, Aldrich or Merck). All solutions were prepared using double distilled water. Metal standard solutions (1000 mg L^{-1}) were used as chlorides in case of Au(III), Pd(II), Pt(II) or Rh(III) and as nitrate in case of Ag(I). Hundred milligrams per litre of Ag(I) as sulphate was used in spiking of natural water samples. Proper concentrations were obtained by dilution.



Scheme 2. Immobilization of morin on silica gel.

2.2. Immobilization of morin onto amino silica gel

Silica gel (size 63–88 μm) was further homogenised by milling in a ball-mill for 2 h to a pore size <0.09 mm. Its surface area is a mesoporous type VI, monolayer volume (V_m) = 93.85 $m^3 g^{-1}$, S_{BET} = 410.1 $m^2 g^{-1}$, pore volume = 0.685 mL g^{-1} and r = 33.4 nm.

Silica gel was functionalised with aminopropyl moiety [6] to produce APSG. Its BET surface area is 203.4 $m^2 g^{-1}$ with pore volume = 0.36 mL g^{-1}.

Morin-APSG was prepared by adding 10 g of APSG to 3 g morin, dissolved in 100 mL ethanolic solution and 5 mL of dimethylsulfoxide (DMSO), and heating the mixture under reflux in a water-bath for 24 h. A brown product (10.5 g) thus formed was washed thoroughly with DMSO, and ethanol and dried at 120 °C and kept in a desiccator. Morin-APSG has BET surface area of 111.45 $m^2 g^{-1}$ and pore volume = 0.22 mL g^{-1}.

2.3. Separation technique

Ag(I) and Au(III) were studied individually where Pd(II), Pt(II) and Rh(III) were studied in combination. The given data are the average of triplicates where those of application were repeated five times from which the statistical evaluation is performed (Table 3).

For batchwise separation, 20 mg of morin-APSG was suspended with constant stirring for 30 min in 25 mL of 10 mg L^{-1} of the investigated metal ion. The desired pH value was adjusted using 0.1 mol L^{-1} NaOH, 0.1 mol L^{-1} HCl, 0.1 or mol L^{-1} HNO_3. The concentration of the investigated ions in the filtrates was determined by FAAS. The distribution coefficient (K_d) is determined using the equation:

$$K_d = \frac{C_{\text{iex}\,(\mu g\,g^{-1})}}{C_{\text{sol}\,(\mu g\,mL^{-1})}}\ \text{mL g}^{-1} \tag{1}$$

where C_{iex} and C_{sol} are the metal concentrations in solid and in solution phases.

The effect of stirring time on the separation efficiency was studied using a weight of morin-APSG 100 mg at pH 5.7 ± 0.1 and at pH 2.2 for Au(III). Sodium acetate buffer (0.2 mol L^{-1}) was used in addition to these conditions in all next studies, unless otherwise stated.

The stability of silica phases in aqueous solution was investigated by adding 100 mg of modified silica to 200 mL of distilled water buffered by acetate to pH 5.7 ± 0.1 with continuous stirring. Aliquots of 6 mL were withdrawn with a syringe through a diaphragm membrane with pore size of 0.20 μm type PET-20/25 from MACHEREY–NAGEL and the dissolved Si was determined by ICP-OES.

The ion exchanger capacity of morin-APSG towards Ag(I) and Pd(II) was determined by adding 100 mg of morin-APSG to 100 mL of metal (100 μg mL^{-1}) followed by stirring for 60 min and the pH was controlled using acetate buffer (0.2 mol L^{-1} sodium acetate) to 2.2 or 5.7, respectively. The suspension was then filtered and the capacity was determined. The capacity of the new sorbent towards Cu(II) at pH 5.5 was compared with that reported [1].

The metal–morin-APSG complexes were washed with deionised water, dried at 80 °C and to be used in the investigation of the bonding nature.

For application, a fresh 1000 mL (tap water, river Nile water) from Mansoura city, seawater from Suez Gulf and electroplating waste water samples were filtered using G4 then 100 mg of morin-APSG + 50 mg sodium fluoride were added to the samples. The samples were spiked with 100, 60 or 20 μg of the investigated metal ions as chlorides [Au(III), Pd(II), Pt(IV) and Rh(III) and as sulphate in case of Ag(I)]. The pH value was adjusted to 5.7 and 2.2 and stirred for 10 min then filtered. To the filtrate, another 100 mg of the sorbent was added and the pH value was again controlled. The sample was stirred again for 10 min and filtered. The two residues (200 mg) were gathered and the collected metal ions were released by 10 mL 0.5 mol L^{-1} HCl/0.01 mol L^{-1} thiourea in case of Au(III), Pd(II), Pt(II) and Rh(III) and 10 mL 0.5 mol L^{-1} HNO_3 in case of Ag(I), to give a concentration factor of 100-folds.

2.4. Apparatus

Analyses of Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) were performed by Perkin-Elmer (A Analyst, 100) 238 using the recommended parameters.

Analysis of Si was performed by a SPECTRO CIROS CCD inductively coupled plasma-optical emission spectrometer. The emission lines at 212.412, 251.612 and 288.158 nm were used to detect Si whereas the Ar lines at 404, 442 and 430.01 nm were used to observe the stability of the generated plasma.

Infrared spectra were recorded on a Mattson 5000 FTIR spectrometer.

Solid state ^{13}C NMR measurement was performed using a BRUKER DMX 400 spectrometer operating at 100.5 MHz. The 7 mm probe was used with MAS frequencies of 4.5 kHz. The cross polarization time was 4 ms, the repetition time 2 s and 2700 up to 4500 scans have been acquired. High power proton decoupling was applied during data acquisition.

Thermogravimetric analysis was performed using an automatic recording thermobalance type (951 DuPont instrument) was used in this study. Samples were subjected to heat using a rate of heating 10 °C min^{-1} from room temperature to 800 °C in N_2.

An automatic VARIO EL ELEMENTAR instrument was used to determine the percentage of C, H and N.

The pH-metric measurements were performed using a Metrohm E536 potentiograph equipped with a 665 DOSIMAT (Metrohm, Herisau, Switzerland). All titrations were carried out with rate of addition (0.2 mL min^{-1}) of NaOH at 25 °C.

3. Results and discussion

3.1. Synthesis and characterisation of morin-APSG

Morin was immobilized on silica gel via the reactions given in Scheme 1. Anhydrous conditions were used for the functionalisation of silica gel so that hydrolytic condensation of aminopropyltrimethoxysilane is minimised and maximum substitution of the silanol groups takes place on the surface of silica gel [31]. The thermogram of APSG shows three thermal degradation stages at 25–105, 201–267 and 337–613 °C. The first is attributed to the loss of adsorbed water (4.19%) where the second (0.89%) and the third stages (6.21%) may be attributed to the thermal degradation of the organic part attached to the two energetically different silanol groups with surface population of 13 and 87%, respectively. The presence of two types of silanol groups on the silica gel was reported previously in comparable population, 15–19 and 85–81%, respectively [32,33]. The weight loss attributed to the organic part is in good agreement with the results of elemental analysis (C = 4.36 and N = 1.71%) which predict a weight loss of 7.05% giving rise to a grafting capacity of 1.21 mmol g^{-1}.

The TG curve of morin-APSG shows three main stages. The water loss occurs at 88.3 °C(4.0%), where the second and third steps represent the organic degradation which ends at 808 °C (10.14%). Although, the elemental analysis of morin-APSG (C = 7.02 and N = 1.24%) is close to the weight loss of TGA but it shows less nitrogen content (0.065) than in APSG and more nitrogen/carbon ratio (0.18) than in the predicted 1:1 product of morin-APSG. This may be due to part of aminopropyltrihydroxysilane substrate is hydrolysed and the remaining part partly reacts with morin. The low reaction yield may be attributed to the steric hindrance of the bulky morin molecule. Consequently, the weight loss due to morin is calculated from elemental analysis to be only 10.33% enabling a theoretical capacity of 0.152 mmol g^{-1} of morin-APSG.

IR absorption spectrum of APSG shows the appearance of bands at 462, 800, 1000–1250, 1640, 2865 and 2940 cm^{-1}, due to δ(Si–O–Si), ν_s(Si–O–Si), longitudinal SiO_2 lattice vibration, δ(H_2O), ν_s(CH_2) and ν_{as}(CH_2), respectively. The bands due to aminopropyl group appear at 3274 and 3360 cm^{-1} assigned to ν_s and ν_{as}(NH_2) [15–17].

Comparing the IR spectrum of the morin-APSG with that of APSG, the bands at 3274 and 3360 cm^{-1} disappear with the appearance of new bands at 1380, 1448, 2865 and 2940 cm^{-1} assigned to ν(C–OH), ν(CNC), ν_s(CH_2) and ν_{as}(CH_2) [34]. Consequently, the bonding of morin to the aminopropyl group is suggested to occur via the displacement of nitrogen in the propylamine substrate for pyran oxygen in morin [35].

Solid state ^{13}C NMR (Fig. 1), confirmed the suggested mode of bonding between morin and APSG. The propyl carbon atoms have peaks at 43.82, 25.84 and 9.27 ppm in APSG and morin-APSG. The strongly overlapped peaks due to morin [36] were detected in the range of 100–200 ppm in the ^{13}C NMR spectrum of morin-APSG. The appearance of a peak at 173.2 ppm confirms the C=O without taking part in the reaction which agrees with the reported values of carbonyl group of morin (178–182 ppm [36,37]). The broad peaks in ^{13}C NMR spectrum may be attributed to the presence of the organic moiety at different sites on the silica surface.

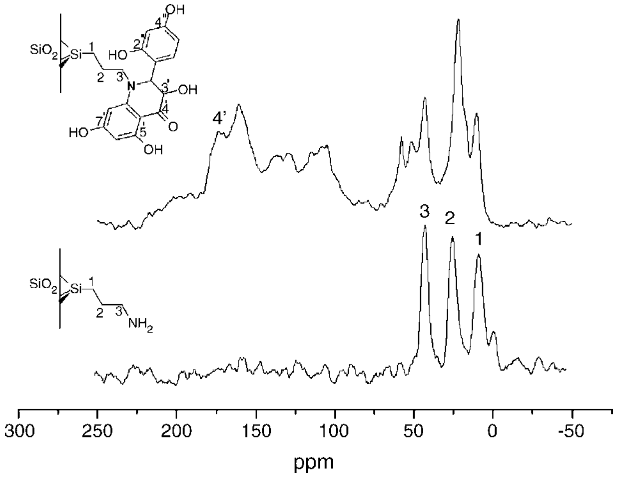


Fig. 1. ^{13}C NMR measurement of APSG (bottom) and morin-APSG (top).

Morin-APSG has high chemical stability towards some organic solvents, such as methanol, ethanol, acetone, diethylether, DMSO, DMF, toluene, xylene and kerosene as well as concentrated acids (HCl, H_2SO_4 or HNO_3) up to 2 mol L^{-1}. This is concluded from its elemental analysis after soaking for 24 h, washing with distilled water and drying at 80 °C for 6 h.

Fig. 2 shows the amount of hydrolysed Si in both morin-APSG and APSG after stirring for 60 min in acetate buffer at pH 8 ± 0.1. The stability of silica was improved by capturing the active amino group, which represents local basisity on the silica surface and consequently enhancing its hydrolysis [31]. Comparing the stability of morin-APSG with that of aminopropyl, salicylaldimine, or quercetin immobilized silica gel at different pH values (Table 1), one can observe that morin is more effective in reducing the hydrolysis of aminopropy-

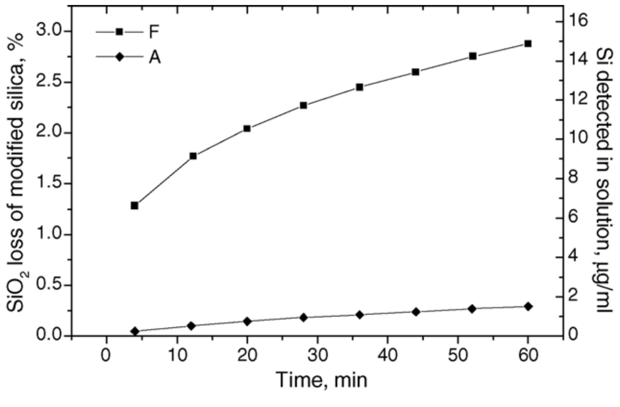


Fig. 2. Dissolution of APSG and morin-APSG in water buffered at pH 8. Weight = 100 mg and volume = 200 mL.

Table 1
Hydrolysis of some modified silica gel phases at different pH values

Modified silica	Abbreviation	Hydrolysed silica (%)	pH	Reference
Aminopropylsilica gel	APSG	2.88	8 ± 0.1	This work
Morin immobilized on silica gel	Morin-APSG	0.63	8 ± 0.1	This work
Morin immobilized on silica gel	Morin-APSG	0.29	5.7 ± 0.1	This work
Quercetin immobilized on silica gel	QSG	1.19	8 ± 0.1	[9]
Salicylaldiminesilica gel	SSG	0.74	9 ± 0.1	[10]

lsilica. This may be explained in view of its bulky structure, hindering the attack of OH^- on the surface of silica which causes its hydrolysis [31]. In general, these results confirm the relative stability of morin-APSG especially at low pH values and indicate the possibility of studying the separation of the investigated metal ions using morin-APSG up to pH 8 without noticeable loss of the sorbent due to hydrolysis (weight loss = 0.29% after 60 min stirring at pH 5.7).

The sorption capacity morin-APSG was measured to estimate how large the quantity of modified silica would be needed for quantitative recovery of an interesting metal ion from aqueous solution. The capacity of morin-APSG was found to be 0.095 mmol H^+ g^{-1} as concluded from pH-metric titration. The capacity towards Cu(II) at pH 5.5 was 0.249 mmol g^{-1}. Comparing this value with that expected from thermal and elemental analysis, it can be concluded that the sorbent reacts with Cu(II) in 1:2 (morin:copper) ratio. The capacity value is higher than previously reported for quercetin or morin immobilized on silica gel [21,29,30]. On the other hand, the capacity of morin-APSG towards Ag(I) and Pd(II) at pH 2.2 was 0.087 and 0.12 mmol g^{-1} whereas at pH 5.5 it raised to 0.22 and 0.24 mmol g^{-1}, respectively. These results indicate that at lower pH, morin-APSG reacts with the metal ions in 1:1 ratio whereas at pH 5.5, it can accommodate two metal ions in two different sites. According to the IR spectra of Ag(I) and Pd(II) morin-APSG complexes at these pH values, it may be concluded that morin is bonded to Ag(I) through pyran nitrogen and phenolic O attached at C_2'' while Pd is bonded via C=O and O attached to C_3' at pH 2.2. At pH 5.5, another Pd(II) can be bonded to another active site of morin. The band at 1380 cm^{-1}, assigned to ν(C–OH), in the IR spectra of Ag(I) and Pd(II) complexes at pH 2.2 disappear at pH 5.5. The capacity towards Ag(I) and Pd(II) is higher than the reported values using amidinothioureido–silica gel 0.096 and 141 mmol g^{-1}, respectively [38]. Moreover, the capacity towards Pd(II) was apparently higher than found using dimethylglyoxime–silica gel 0.038 mmol g^{-1} [39].

3.2. Calibration and detection limit

The FAAS response was found linear in the concentration range 0–10 μg mL^{-1} for the tested metal ions. The detection limits, based on three times the standard deviation (3σ), were found equal to 0.086, 0.41, 0.21, 2.33 and 0.37 μg mL^{-1} for Ag(I), Au(III), Pd(II), Pt(II) and Rh(III), respectively. Considering the theoretical preconcentration factor of 100 after preconcentration by morin-APSG, the detection limits of the proposed method for Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) were 0.86, 4.12, 2.09, 23.3 and 3.74 ng mL^{-1}, respectively.

3.3. Batch mode separation

Fig. 3 represents the effect of pH on the separation efficiency of Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) on morin-APSG. At low pH, the distribution coefficients were generally low for the investigated metal ions except for Au(III), which is attributed to the incomplete ionisation of the ionogenic group of the ion exchanger. The $\log K_d$ values of Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) ions on morin-APSG reached its maximum values (2.99, 3.88, 4.73, 3.29 and 4.10) at pH 5.7, 2.2, 3.7, 3.7 and 6.8, respectively. These correspond to separation efficiencies of 43.9, 85.9, 97.7, 60.9 and 91.0%, respectively, of the initial concentration of the investigated metal ions. This indicates that selectivity of morin-APSG towards the metal ions have the order: Pd(II) > Rh(III) > Au(III) > Pt(II) > Ag(I). The presence of adsorption maxima of metal ions on morin-APSG in acidic region is an advantage to enable their extraction with minimum interference from common metal ions.

Fig. 4 represents the effect of stirring time on the recovery of Ag(I), Pd(II), Pt(II) and Rh(III) at pH 5.7 ± 0.1 and Au(III) at pH 2.2, using morin-APSG. The ion exchanger shows fast kinetics of equilibration so that 10 min of stirring was enough to reach maximum values of separation.

The most effective eluent for the quantitative stripping of the retained metal ions on 2 mg × 100 mg morin-APSG after twice extractions of 50.0 μg of the metal ions from 1000 mL distilled water adjusted at pH 5.7 ± 0.1 (except

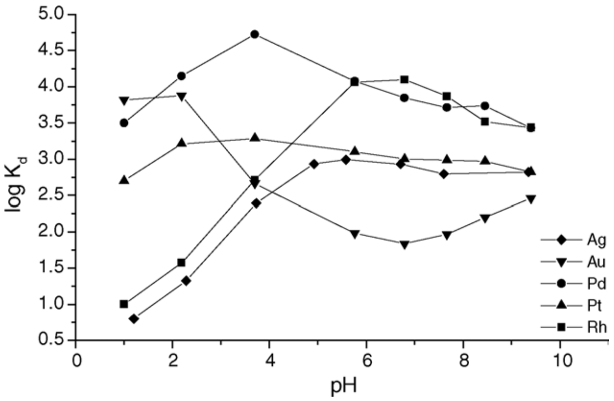


Fig. 3. Effect of pH on the distribution coefficient of Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) on morin-APSG.

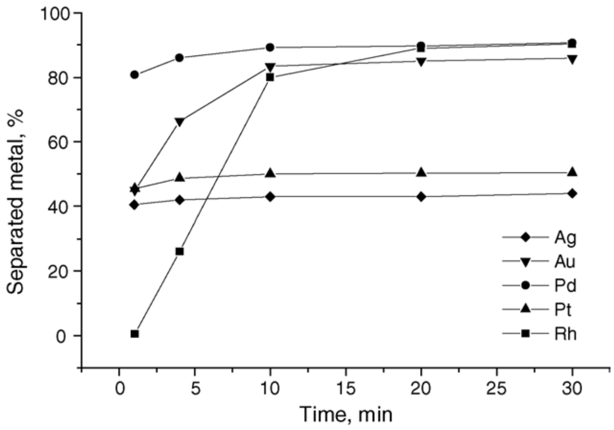


Fig. 4. Effect of stirring time on the separation efficiency of 10 mg L^{-1} Ag(I), Pd(II), Pt(II) and Rh(III) at pH 5.7 and 10 mg L^{-1} Au(III) at pH 2.2 after separation on 20 mg morin-APSG.

for Au(III), as the solution was separately adjusted at pH 2.2). The ions were stripped with 10 mL of 0.01–2 mol L^{-1} HCl + 0.01 mol L^{-1} thiourea in case of Au(III), Pd(II), Pt(II) and Rh(III) or 0.01–2 mol L^{-1} HNO_3 in case of Ag(I). The results show that 0.5 mol L^{-1} HCl + 0.01 mol L^{-1} thiourea could offer a good eluent for the quantitative elution of all metal ions except Ag(I) in which the eluent is 0.5 mol L^{-1} HNO_3.

The efficiency of separation of the investigated metal ions was not affected in the presence of nitrate, sulphate, phosphate, chloride, Na^+, K^+, Zn^{2+}, Cu^{2+}, Mg^{2+} and Ca^{2+} ions (Table 2). Al^{3+} and Fe^{3+} show strong competition with Ag^+ and Rh^{3+} and can be overcome by adding fluoride. Trace ions (B^{3+}, Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, As^{3+}, Sr^{2+}, Cd^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+} and Bi^{3+}) with concentration of 10 mg L^{-1} do not affect the separation process. EDTA, thiourea, oxalate, and citrate show weak and/or strong interferences depending on the metal ions. In application, the organic part must be digested prior to separation. The separation efficiency was found to increase for the investigated metal ion especially Ag(I) and Rh(III) in the presence of carbonate and acetate. This may be attributed to the formation of mixed ligand complex [6,24]. Therefore, 0.2 mol L^{-1} acetate buffer is chosen in the next studies depending on this interesting phenomenon which was also reported elsewhere [6,7].

Applying the optimum conditions of pH and time of stirring (10 min) for 50 cycles of ions loading followed by stripping and washing with 20 mL H_2O, the capacity decreases by 7.7% of the initial capacity towards Cu(II) in case of the metal ions Ag(I), Pd(II), Pt(II) and Rh(III) whereas in case of Au(III) the capacity fading is lower (5.2%). This may be attributed to that that silica hydrolysis decreases with decreasing the applied pH [31]. However, both capacity fading values are low which indicates that morin-APSG has a relative stability and may be reused safely without noticeable loss in capacity.

Environmental water samples were used in this investigation after spiking with the investigated metal ions (absence or presence) for their separation and/or preconcentration similar to the literature [40–43].

Table 2
Effect of some common ionic species on the separation efficiency (%) of 1 L 100 ng^{-1} mL Ag(I), Au(III), Pd(II), Pt(II) or Rh(III) on morin-APSG followed by elution with 10 mL 0.5 mol L^{-1} HCl/0.01 mol L^{-1} thiourea in case of Au(III), Pd(II), Pt(II) and Rh(III) and 10 ml 0.5 mol L^{-1} HNO_3 in case of Ag(I)

Interfering species	Concentration (mg L^{-1})	Efficiency of separation (%)				
		Ag^+	Au^{3+}	Pd^{2+}	Pt^{2+}	Rh^{3+}
Without	–	43.0	85.0	89.7	50.2	88.9
Cl^-	21240	–	86.1	90.2	51.0	89.2
$NO_3{}^-$	1000	43.0	–	–	–	–
S^{2-}	200	52.8	91.9	93.2	88.9	95.1
$CO_3{}^{2-}$	1000	88.6	97.1	98.8	97.1	98.1
$SO_4{}^{2-}$	1000	49.1	88.3	97.0	72.9	90.0
$PO_4{}^{3-}$	1000	67.3	89.4	94.6	87.1	89.8
Acetate	200	92.8	97.8	99.7	98.2	98.7
Oxalate	200	34.3	64.1	72.7	30.9	61.7
Citrate	200	25.4	55.8	49.6	30.5	58.5
EDTA	200	22.3	40.6	77.8	39.7	44.4
Thiourea	200	15.8	28.9	49.7	41.3	41.4
$NH_4{}^+$	1000	32.1	78.9	69.4	26.8	19.7
Na^+	13761	43.1	84.7	88.8	51.9	89.7
K^+	1000	43.9	85.9	89.9	49.8	87.9
Mg^{2+}	1000	43.1	85.2	89.0	51.4	89.8
Ca^{2+}	1000	42.8	84.5	89.3	50.8	90.1
Zn^{2+}	1000	43.2	85.7	90.1	50.2	89.6
Cu^{2+}	1000	42.2	83.8	89.7	49.8	88.2
Al^{3+}	100	10.1	72.7	79.9	42.7	78.9
Fe^{3+}	100	28.2	77.3	83.6	23.3	64.8
$Al^{3+} + F^-$	100	45.5	84.7	89.9	52.0	88.5
$Fe^{3+} + F^-$	100	44.5	85.2	88.8	51.1	89.4

Table 3

Statistical evaluation for the data obtained on the determination of the analytes in 1 L of spiked water samples by FAAS after separation and preconcentration to final volume of 10 mL with solid phase extraction on morin-APSG and elution with 0.5 mol L^{-1} HCl/0.01 mol L^{-1} thiourea in case of Au(III), Pd(II), Pt(II) and Rh(III) and 10 mL 0.5 mol L^{-1} HNO_3 in case of Ag(I)

Spike (μg)	Ag(I) (μg L^{-1})		Au(III) (μg L^{-1})		Pd(II) (μg L^{-1})		Pt(II) (μg L^{-1})		Rh(III) (μg L^{-1})	
	$\overline{X} \pm \frac{ts}{\sqrt{n}}$	$\lvert t\rvert_1$	$\overline{X} \pm \frac{ts}{\sqrt{n}}$	$\lvert t\rvert_1$	$\overline{X} \pm \frac{ts}{\sqrt{n}}$	$\lvert t\rvert_1$	$\overline{X} \pm \frac{ts}{\sqrt{n}}$	$\lvert t\rvert_1$	$\overline{X} \pm \frac{ts}{\sqrt{n}}$	$\lvert t\rvert_1$
Tap water										
–	BDL	–	BDL	–	BDL	–	BDL	–	BDL	
20	19.8 ± 0.49 (2.01)	1.12	20.0 ± 0.39 (1.55)	0	19.8 ± 0.33 (1.35)	1.67	BDL	–	19.7 ± 0.43 (1.74)	1.96
60	60.1 ± 1.32 (1.76)	0.21	59.8 ± 1.47 (1.98)	0.38	60.0 ± 0.73 (0.98)	0	59.8 ± 1.39 (1.87)	0.40	59.9 ± 0.65 (0.87)	0.43
100	99.9 ± 1.50 (1.21)	0.18	99.7 ± 1.29 (1.04)	0.65	99.8 ± 1.52 (1.23)	0.36	99.9 ± 1.60 (1.29)	0.17	99.7 ± 2.32 (1.87)	0.36
River Nile water										
–	BDL	–	BDL	–	BDL	–	BDL	–	BDL	–
20	20.3 ± 0.51 (2.00)	1.71	19.9 ± 0.42 (1.69)	0.66	19.8 ± 0.49 (2.01)	1.12	BDL	–	19.8 ± 0.44 (1.78)	1.27
60	60.0 ± 1.04 (1.39)	0.03	59.9 ± 0.98 (1.32)	0.28	59.9 ± 1.28 (1.72)	0.22	60.1 ± 1.19 (1.59)	0.23	59.8 ± 0.73 (0.98)	0.76
100	100.2 ± 1.15 (0.92)	0.51	100 ± 1.47 (1.18)	0	99.9 ± 1.61 (1.30)	0.17	99.8 ± 1.72 (1.39)	0.32	100.1 ± 1.52 (1.22)	0.18
Seawater										
–	BDL	–	BDL	–	BDL	–	BDL	–	BDL	-
20	20.22 ± 0.50 (1.97)	1.23	19.9 ± 0.49 (1.99)	0.56	20.1 ± 0.50 (2.00)	0.56	BDL	–	20.1 ± 0.50 (1.99)	0.56
60	60.12 ± 1.48 (1.98)	0.22	59.7 ± 1.18 (1.59)	0.71	59.9 ± 0.96 (1.29)	0.29	59.7 ± 1.39 (1.88)	0.60	60.0 ± 0.91 (1.22)	0
100	99.9 ± 1.52 (1.22)	0.15	99.8 ± 2.47 (1.99)	0.23	99.7 ± 1.09 (0.87)	0.77	99.9 ± 0.81 (0.65)	0.34	99.8 ± 2.26 (1.82)	0.25
Wastewater										
–	1.41 ± 0.03 (1.96)	–	BDL	–	BDL	–	BDL	–	BDL	–
20	21.1 ± 0.39 (1.50)	7.84	19.9 ± 0.49 (1.99)	0.56	19.9 ± 0.47 (1.91)	0.59	BDL	–	19.8 ± 0.39 (1.59)	1.42
60	61.3 ± 1.29 (1.69)	2.83	59.9 ± 1.28 (1.72)	0.22	59.9 ± 1.41 (1.89)	0.20	59.9 ± 1.16 (1.56)	0.24	59.9 ± 1.40 (1.88)	0.20
100	101.5 ± 2.39 (1.89)	1.76	99.9 ± 1.38 (1.11)	0.20	99.7 ± 1.26 (1.02)	0.66	99.7 ± 1.48 (1.19)	0.57	99.8 ± 1.23 (0.99)	0.45

Values between brackets are the relative standard deviation (R.S.D.). $\overline{X}$ is the average for five replicates, t is the student factor and equals 2.78 for $P = 0.05$ and s is the standard deviation.

Table 4
Comparison of important characteristics of some sorbents used for the separation and preconcentration of the studied metal ions

Support	Functional group	Mode of bonding	Capacity mmol g^{-1}	Studied metals	LOD ng mL^{-1}	Eluent	Detection technique	Analysed sample	CF	Reference
Silica gel	Amine	Chemical	0.17	Ag	Ag(I) 4	2 mol L^{-1} HCl	GFAAS	Spiked seawater	40	[45]
Silica gel	Isodiphenyl-thiourea	Chemical	–	Pd, Pt	Pd(II) 4.7, Pt (II) 69	TU	FAAS	Geological samples	–	[46]
Silica gel	*N*-Allyl-*N*′-propylthiourea	Chemical	–	Pd	Pd(II) 0.05	TU in HCl	FAAS	Cu–Ni ore	100	[47]
Silica gel	Amidinothio-ureido	Chemical	0.096 Ag, 0.277 Au, 0.141 Pd	Ag, Au, P	Ag(I) 1.1, Au(III) 13, Pd(II) 17	5% TU	FAAS	Ni alloy, anode slime, $CoCl_2$ solution		[38]
Silica gel	Dimethyl-glyoxime	Physical	0.038 Pd	Pd	Pd(II) 1.2, 0.4	1 mol L^{-1} HCl in acetone	FAAS GFAAS	Street dust, anode slime	75 25	[39]
Silica gel	TU	Chemical	24.5 Ag, 50.9 Au, 30.3 Pd[a]	Ag, Au, Pd	Ag(I) 1.3, Au(III) 14, Pd(II) 21	5% TU	FAAS	Ni alloy, anode slime $CoCl_2$ solution		[48]
Silica gel	TU	Chemical	0.182 Pt	Pt	Pt(II) 60	10% TU	FAAS	Ni alloy, anode slime, $CoCl_2$ solution		[49]
Silica gel	2-Mercapto-benzothiazole	Chemical	0.343 Ag[a]	Ag	not determined	0.005 mol L^{-1} sodium thiosulphate	FAAS	Lake water	300	[50]
Silica gel	Morin	Chemical	0.22 Ag, 0.249 Cu, 0.24 Pd	Ag, Au, Pd, Pt, Rh	Ag(I) 0.86, Au(III) 4.12, Pd(II) 2.09, Pt(II) 23.3, Rh(II) 3.74	0.5 mol L^{-1} HCl (HNO_3 in case of Ag(I)) + 0.01 mol L^{-1}	FAAS	Spiked water samples	100	This work
Polymath-acrylic ester	Dithizone	Physical	0.16 Pt	Pd, Pt	Pd(II) 0.2[b], Pt(II) 1[b]	Concentrated nitric acid or TU	GFAAS	Spiked soil	–	[51]
Cross-linked chitsan	Amine	Chemical	–	Au, Pt, Pd	not determined	1 mol L^{-1} HCl, 0.05 mol L^{-1} TU	ICP-MS	Concentrated HCl	–	[52]
Surfactant-coated alumina	2-Mercapto-benzothiazole	Physical	–	Ag	not determined	0.2 mol L^{-1} TU at pH 6.5	FAAS	–	100	[53]
Chelating resin YPA4	Mercapto	Chemical	67.2 Au, 64.8 Pd, 27.6 Pt[a]	Au, Pd, Pt	Au(III) 0.075, Pd(II) 0.060, Pt(II) 0.217	–	ETV-ICP-AES	Geological and auto catalyst reference material	100	[54]
Calcium alginate beads	Yeast *Saccharomyces cerevisiae*	Physical	0.014 Pd[a]	Pd	Pd(II) 7[b]	0.3 mol L^{-1} TU in 0.25 mol L^{-1} HC1	GFAAS	Road dust	–	[55]

CF, concentration factor; TU, thiourea.

[a] mg g^{-1}.

[b] ng g^{-1}.

The procedures proposed for the separation of Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) using morin-APSG were applied for spiked tap water and river Nile water from Mansoura city, seawater from Suez Gulf and electroplating waste water samples. Fluoride was added to mask Fe(III) and Al(III). The procedure was followed by elution of the collected metal ions by 10 mL of the suitable eluent and determined by FAAS. The results in Table 3, indicate that an agreement between the amount of the spiked and detected by the proposed method. The reliability of the procedure was statistically examined using the null hypothesis of $|t|_1$ for $P = 0.05$ and $n = 10$. It was found that $|t|_1 = 0 - 1.98$ which is less than the tabulated value ($|t|_1 = 2.31$) [44].In the determination of Ag(I) in wastewater, the value is 1.41 ng mL^{-1} due to the presence of natural background which indicates that the method is not precise.

3.4. Comparison with other metal ion sorbents

The sorption capacity of morin-APSG, limits of detection (LOD) of Ag(I), Au(III), Pd(II), Pt(II) and Rh(III) and the attained concentration factor were compared with those of other important matrices used for the separation and preconcentration of the investigated metal ions (Table 4). Morin-APSG exhibits better than or comparable capacity and LOD's values to a large number of the metal–matrix combination. Only, mercapto-functionalised chelating resin YPA4 showed appreciaby higher capacity towards Au(III), Pd(II) and Pt(II) and lower LOD's. However, morin-APSG has the advantage of its ability to be recycled according to the proposed method in addition to the availability of the detection technique. Also, it is important to refer to the reversibility of the sorption process as the organic substrate (morin) is not a too strong ligand which enables the recovery of the metal ions at mild elution conditions (0.5 mol L^{-1} HCl or $\mathrm{HNO_3}$ + 0.01 mol L^{-1}). The physical adsorption functionalisation generally shows low capacities of the sorbents in comparison with the chemical functionalisation. Unfortunately, there were no data on the stability of these matrices to enable further comparison. The above data revealed that the proposed method is simple, sensitive and reliable for: (i) the lower tendency of the sorbent to hydrolysis which can be used over 50 cycles; (ii) the high preconcentration factor (100); (iii) the low detection limit for separation; and (iv) its antifungal activity.

4. Conclusion

Morin could be chemically immobilized on silica gel yielding a sorbent of high capacity and good stability against hydrolysis in comparison with those reported. Morin substrate was found to capture one metal ion per molecule of morin at pH 2.2 and two metal ions at pH 5.7. Morin-APSG was used effectively to separate the investigated metal ions with relative selectivity: Pd(II) > Rh(III) > Au(III) > Pt(II) > Ag(I). The separation efficiency was enhanced using acetate buffer which forms a mixed ligand complex. No interferences could be observed from common ions except EDTA, thiourea, oxalic and citric acids which can be eliminated by digestion before separation. Fe(III) and Al(III) masked by fluoride. The method was applied for the determination of the investigated metal ions in spiked natural water samples and found accurate and precise.

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