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Synthesis of Controlled-Pore Silica Glass Functionalized with Quercetin and Its Application for the Separation and Preconcentration of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)

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ABSTRACT

Quercetin was anchored to controlled-pore silica glass (CPSG). The chemical bonding of quercetin based on CPSG (QCPSG) was characterized by elemental analysis, infrared reflectance analysis, ultraviolet spectroscopy, and solid state ^{13}C-nuclear magnetic resonance (NMR), in comparison with the monomer phase prepared from quercetin and aminopropyltrihydroxysilane. Controlled-pore silica glass, used as

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support for quercetin or aminopropyl moiety, showed obvious stability against Si dissolution at pH 8 in comparison with silica gel. Also, the involvement of the amine group in the bonding to quercetin was observed to relieve its local basisity, enabling low capacity fading (10%) after 40 loading/elution cycles. The QCPSG also was used for the separation and preconcentration of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) prior to their determination by inductively coupled plasma-mass spectrometry (ICP-MS). The optimum pH range for the separation of these metal ions is 7.5–8.5 at 30 min stirring time, giving an efficiency of 98.1%, 94.4%, 95.9%, 90.7%, and 87.9%, respectively, in the presence of sodium acetate. The sorption capacity of QCPSG for these metal ions is in the range of 0.24–0.46 mmol g^{-1} indicating a 1 : 2 quercetin/metal chelation for all metal ions except for Mn(II), as a 1 : 1 ratio is suggested. The QCPSG was used for the separation and preconcentration of the investigated metal ions in some water samples, using ICP-MS for determination (relative standard deviation, RSD 1.74–6.10%). The method also was applied for the determination of these metal ions in granite ores and certified samples, and the results are in good agreement with the reported values, which indicates that the method is accurate.

Key Words: Controlled-pore silica glass; Quercetin; Separation; Preconcentration; Heavy metal ions.

1. INTRODUCTION

Recently, the determination of heavy metals became one of the important quality measurements, as man cannot safely deal with the surrounding environment without affirmative information about the level of different hazards that are attributed to the harmful effects caused by the accumulation of heavy metals in human tissues, through daily contact with the polluted environment.[1]

The determination of heavy metal ions is restricted by two difficulties: (i) the very low concentration of heavy metal ions, which may be lower than the detection limit of many traditional analytical techniques; (ii) the interfering effects of the matrix. To overcome these difficulties, preconcentration and separation are prerequisite to determination. Among the different techniques used for the separation and preconcentration, chelating ion exchanger is preferred due to the low risk of contamination, the use of environmentally safe reagents, and simple methodology.[2]

Unlike conventional ion-exchange resins, few chelating ion-exchange resins are commercially available. Synthetic procedures generally are tedious, time consuming, and irreproducible. Many organic polymer-based chelating

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resins suffer from a slow rate of metal-ion uptake. Batch equilibration requires a time range from 30 min to several hours.[3,4] This severely restricts flow rates in preconcentration procedures. The lack of mechanical stability at high pressure precludes the use of most polymer-based chelating agents in chromatographic systems, where high pressure is often required.[5] In addition, many organic polymer resins are hydrophobic, although ion exchangers should be wettable to guarantee the best contact with the mobile phase, which is often an aqueous solution. Swelling and shrinking of organic polymers are troublesome in both preconcentration and separation applications. An additional problem of degradation, due to microbial action, may arise as in the case of using cellulose and cellulose derivatives.

Silica has been adopted as a support for the chelating substrate because it possesses good mechanical and thermal stability and is less susceptible to swelling, shrinking, and microbial and radiation decay.[6] However, silica has two disadvantages: (1) it is amenable to hydrolysis at pH higher than 10; therefore, the working range is restricted to a lower pH; (2) it has a small surface area, which yields lower capacity. To enlarge the surface area, either silica gel or controlled-pore silica glass (CPSG) is used, as recently indicated.[7–10] Controlled-pore silica glass is preferred over traditional silica gel, especially in processes that require a fast flow rate or high pressure, because the flow rates with CPSG are linear with pressure. The mechanical strength of CPSG provides reproducible results with constant column parameters. CPSG is a glass structure and is immune to biological degradation. This matrix is compatible with almost all organic solvents and concentric acids (except hydrofluoric acid). As a solid support, CPSG eliminates many of the problems experienced with gels. Moreover, CPSG is remarkably less hydrolysable than silica gel.

Although, quercetin (H_5R) is known to be one of the most effective chelating reagents for spectrophotometric and extraction-spectrophotometric determination of many metal ions,[11–16] little attention was given to its immobilization on different supports to be used as a chelating ion exchanger.[17,18] Although, Zaporozhets et al.[17] could immobilize quercetin on silica gel by physical adsorption from an acetone–hexane mixture, its maximum capacity was obviously very low (9.4×10^{-6} mol g^{-1}).

As the separation selectivity for trace elements analysis by inductively coupled plasma-mass spectrometry (ICP-MS) does not matter, while the efficiency in separation from matrices is much more important, because ICP-MS itself has high elemental selectivity. The aim of the current work is to chemically immobilize quercetin on CPSG (QCPSG), to be used as a solid phase extractant for Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions as a preliminary step for the determination by ICP-MS. Also, our aim is to optimize the separation conditions of these metal ions in the submicrogram level from natural waters by using QCPSG, to be determined by ICP-MS.

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2. EXPERIMENTAL

2.1. Materials and Reagents

All reagents used were of analytical grade (A.R.) from Fluka (Buchs, Switzerland), Aldrich (Chicago, USA), or Merck (Darmstadt, Germany). All solutions were prepared by using Milli-Q water or deionized water. Metal standard solutions (1000 mg L^{-1}) were obtained from Merck, and intermediate standard solutions were prepared by appropriate dilution. Granite samples were kindly supplied from Prof. Dr. I.M.M. Kenawy, Mansoura University, Egypt. Certified sample "A" is a multielement standard solution from Merck, with number OC254877; whereas certified sample "B" is steel scraps with number 2/899, which were comparatively analyzed by BAM Berlin, Max-Planck Institut für Eisenforschung, Dusseldorf and Staatl. Materialprüfungsamt Nordhein, Westfalen, Dortmund. Both certified samples were kindly supplied by Laboratory of Chemical Analytical Services, Physikalisch-Technische Bundesanstalt, Braunschweig, Germany.

2.2. Apparatus

2.2.1. Inductively Coupled Plasma-Mass Spectrometry

Analysis of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) was performed by a Finnigan Element 2 inductively coupled plasma-Quadrupole mass spectrometer (Bremen, Germany) with Faraday detector (1 M to 600 Mcps) and secondary electron multiplier (10 cps to 2 Mcps) Galileo. The m/z spectral lines 55, 59, 58, 63, and 68 were used to detect the investigated metal ions, respectively. The limits of detection (LOD) for routine analysis of these metal ions by ICP-MS were 0.0001, 0.001, 0.016, 0.0001, and 0.001 ng mL^{-1}, and operation ranges were 0.05–100, 0.05–100, 0.05–100, 0.1–100, and 0.2–100 ng mL^{-1}, respectively.

2.2.2. Inductively Coupled Plasma-Optical Emission Spectrometry

Analysis of Si was performed by a SPECTRO CIROS CCD inductively coupled plasma-optical emission spectrometer (ICP-OES) (Kleve, Germany). 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. The LOD value was 0.1 μg mL^{-1}, and the operation range was 0.1–50 μg mL^{-1}.

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2.2.3. Infrared Spectra

Infrared reflectance spectra were recorded on a Bruker IFS 48 Fourier transform infrared (FTIR) spectrometer using a gold ball as reference. The IR absorption spectra were recorded by using a Mattson 5000 FTIR spectrometer for a sample of 2–3 mg diluted with 300 mg KBr as a tablet pressed under $10\,t\,cm^{-2}$.

2.2.4. Electronic Spectra

Ultra violet (UV) absorption spectrometric measurements were performed by using a Shimadzu 190, UV-visible spectrophotometer, and a 1 cm-cell quartz crystal was used for spectrophotometric measurements. The sample (the ion exchanger and its complexes with the investigated metal ions) was introduced as slurry with nujol on a Whatmann filter paper strip by using another one wetted with nujol as a blank.

2.2.5. Solid State ^{13}C-Nuclear Magnetic Resonance

Solid State ^{13}C-nuclear magnetic resonance (NMR) measurement was performed by using a BRUKER DMX 400 spectrometer operating at 100.5 MHz. The 7-mm probe was used with Magic Angle Spinning (MAS) frequencies of 4.5 kHz. The cross polarization time was 4 msec, the repetition time was 2 sec and 2700 up to 4500 scans were acquired. High-power proton decoupling was applied during data acquisition.

2.2.6. Thermogravimetric Measurement

An automatic recording thermobalance type (951 DuPont instrument) was used in this study. Samples were subjected to heat, using a rate of heating $10^{\circ}C\,min^{-1}$ from room temperature to 750°C in air.

2.2.7. Elemental Microanalysis

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

2.2.8. Adjustment of pH and pH-Metric Titration

The pH of each sample solution was adjusted by NaOH and HNO_3 solutions to be within the range (2–11), by using an Orion pH/mV meter (model 330) and a combined Ross glass pH electrode (Orion 81-02) with an

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Orion double junction Ag–AgCl reference electrode (model 90-02) containing 10% (w/v) potassium nitrate in the outer compartment. The pH meter was calibrated on the operation state by using standard buffer solutions at 25°C. Potentiometric measurements were performed by using a Metrohm E536 potentiograph equipped with a 665 DOSIMAT (Metrohm, Herisau, Switzerland). All titrations were carried out with a rate of addition of NaOH 0.2 mL min^{-1} at 25°C.

2.3. Preparation of Controlled-Pore Silica Glass Modified With Quercetin

The synthesis of the controlled-pores silica grafted with *N*-propylamine was previously described.[8,9] In this method, H_3BO_3 was dissolved in the colloidal SiO_2 in a ratio of Si : B ≅ 1 : 6.5 to obtain borosilicate glass (BSG) then the product was milled, sieved to <75 μm, and leached with 5 M HCl to obtain CPSG. The CPSG was filtered, washed with distilled water, and dried at 90°C for 24 hr. From BET surface area measurements, CPSG is mesoporous type VI, with monolayer volume (V_m) = 47.76 $m^3 g^{-1}$, S_{BET} = 208.7 $m^2 g^{-1}$, pore volume = 0.399 $cm^3 g^{-1}$, and r = 3.825 nm.[10]

For the grafting of silica, 36 mL of γ-aminopropyltrimethoxysilane (APMS) was added to 18 g of CPSG suspended in 150 mL xylene and refluxed in a water bath at 80°C with stirring for 24 hr. The yield, 20.0 g [aminopropyl CPSG (APCPSG)], was washed with ethyl alcohol and dried at 80°C.

The synthesis of QCPSG was carried out by adding 7.5 g of APCPSG to 3 g quercetin dihydrate (Fluka), dissolved in 200 mL ethanolic solution and a minimum amount of dimethylsulfoxide (DMSO), and refluxing the mixture in a water bath for 24 hr. A brown product (7.6 g) was obtained, which was washed thoroughly with DMSO methanol and ethanol, and dried at 80°C.

The synthesis of quercetin based on silica gel (QSG) was similarly carried out by using aminopropyl silica gel (APSG) from Fluka (particle size = 35–70 μm, grafting capacity = 0.9 ± 0.1 mmol g^{-1} and pore size ≅ 9 nm), and the final weight was 9.4 g.

2.4. Monomer Phase of Ion Exchanger

For the preparation of the monomer phase of the ion exchanger, 20 mL APMS was refluxed with 200 mL distilled water for 72 hr at 80°C, then water was allowed to evaporate until dryness. There 5 g of the glassy yellowish product [γ-aminopropyltrihydroxysilane (APHS)[8,9]] was milled to a fine powder and refluxed with 12.3 g quercetin in 150 mL ethyl alcohol in a

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round-bottom flask for 3 weeks. Finally, a brown product (APHS–quercetin) was obtained. Excess quercetin was washed with methyl and ethyl alcohols in a Sohxlet condenser and dried at 80°C. The yield was then weighed to be 14.4 g and kept in a desiccator. The APHS/quercetin was observed to be insoluble in common solvents, e.g., water, alcohols, acetone, dimethyl formamide (DMF), and dimethylsulfooxide (DMSO).

2.5. Separation Technique

The given data are the average of three replicates, whereas, those of application were repeated five times and from which the statistical evaluation is performed.

2.5.1. Batch Procedure

A total of 20 mg of QCPSG was suspended with constant stirring for 30 min in 50 mL of 50 ng mL^{-1} of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) as nitrates at the desired pH value in the range 2–11. The concentrations of the investigated ions in the filtrates were determined by ICP-MS. The distribution coefficient (K_d) is determined by using the equation:

$$K_d = \frac{C_{i.ex.(\mu g\, g^{-1})}}{C_{sol(\mu g\, mL^{-1})}}\, mL\, g^{-1} \quad (1)$$

where $C_{i.ex}$ is the metal concentration in the ion exchanger (solid phase), and C_{sol} is the metal ion concentration in the solution phase.

Effect of stirring time was studied at pH = 8.0 ± 0.1 by using the same conditions applied previously, then the optimum conditions (pH = 8.0 ± 0.1, time of stirring = 30 min, and weight of QCPSG = 20 mg) were applied in all the following studies. The stability of silica phases in aqueous solution was investigated by adding 100 mg of modified silica to 200 mL of distilled water buffed by borate to pH = 8.0 ± 0.1 under continuous stirring. Aliquots of 6 mL were withdrawn with a syringe through a diaphragm membrane with pore size of a 0.20-μm type PET-20/25 from MACHEREY–NAGEL, and dissolved Si was determined by ICP-OES.

The ion exchanger capacity of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) was separately determined by adding 100 mg of QCPSG to 100 mL of 100 μg mL^{-1} of metal (M) as nitrate solution, followed by stirring for 60 min, and the pH was controlled to be 5.5 by NaOH and HNO_3 solutions. The suspension was then filtered, and the capacity was determined from the loss of metal concentration in the filtrate. The filtered M–QCPSG complexes were

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washed with deionized water, dried at 80°C, and used for the investigation of the nature of bonding.

2.5.2. Application to Water Samples

Surface water samples were collected from Nile River water from Mansoura, Damietta, Mediterranean Sea water from Ras Elbar and Port Fouad, and Red Sea water from Suez Gulf. The pH was determined, then the samples were filtered by using a sintered glass G4. The total dissolved salts were determined by evaporating 100 mL of the filtered sample at 105°C. The samples were acidified with concentrated HNO_3 acid to pH $\cong$ 2 and preserved in polyethylene vessels.

The organic matter was digested prior to the separation process. Then 0.5 g of $K_2S_2O_8$ and 5 mL of 98% (w/v) H_2SO_4 were added to 1 L of the water sample and refluxed in a closed bottle system for 30 min at 95°C. After cooling to room temperature, 100 mg of QCPSG and 100 mg acetate (as sodium salt) were added to the sample, the pH value was adjusted to 8 $\pm$ 0.1, and stirred for 30 min, then filtered. To the filtrate, another 50 mg of the ion exchanger was added and the pH value again was controlled, and the sample was stirred again for 30 min and filtered. The two residues (150 mg) were gathered, and the collected metal ions were released by 10 mL 0.5 M HNO_3, to give a concentration factor of 100-fold.

2.5.3. Application to Granite Samples

The suggested separation method was applied to the referenced granite samples.[19] A 0.5 g sample was dissolved in boiling HF and HNO_3 acids till near dryness, diluted, filtered, and completed to 100 mL. After cooling to room temperature, 100 mg of QCPSG and 100 mg acetate (as sodium salt) were added to the sample, the pH value was adjusted to 8 $\pm$ 0.1, and the separation and elution processes were continued, as previously described in water analysis, and repeated to the filtrate with another 50 mg QCPSG.

2.5.4. Application to the Certified Samples

A fresh 1000 mL of 0.1 $\mu g\,mL^{-1}$ of the investigated metal ions was prepared by subsequent dilution of certified sample A with Milli-Q water. In the case of the certified sample B, 0.1 g was dissolved in hot aqua regia prepared from ultrapure HCl/HNO_3, and the total volume was completed to 1000 mL. From this solution, 10 mL was withdrawn and diluted to 1000 mL. The separation and elution processes subsequently were performed as in granite samples.

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3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of the Quercetin-Anchored Controlled-Pore Silica Glass

Quercetin was immobilized on CPSG via the reactions given in Sch. 1. Anhydrous conditions were used for the grafting reaction, so that hydrolytic condensation of the aminopropylsiloxane is minimized, and maximum substitution of the silanol groups takes place on the surface of the porous silica. The thermogram of APCPSG (Fig. 1) shows the presence of two thermal degradation stages at 104–188°C and 373–613°C, which are attributed to loss of water content (3.3%) and to the thermal degradation of the organic content (6.8%), respectively.[9] The thermogravimetric (TG) curve of QCPSG (Fig. 1) also shows two main stages. The water loss is the first stage, and it amounts 3.12%, whereas the second step is the organic degradation, which ends at 613°C, and its amount is 8.68%. Although, elemental analysis of QCPSG (C = 5.61%, H = 0.93%, and N = 0.69%) is in agreement with the weight loss of thermogravimetric analysis (TGA) but it shows less nitrogen content than in APCPSG (C = 4.05%, H = 1.25%, and N = 1.71%) and more nitrogen content than the predicted 1 : 1 product of QCPSG. This may indicate that during reflux of APCPSG with quercetin, ~60% of the aminopropyl-trihydroxysilane substrate is hydrolyzed, and only 44% of the remaining substrate is reacted with quercetin. The low reaction yield may be attributed to the steric hindrance of the bulky quercetin molecule. Consequently, the weight loss due to quercetin is calculated to be 7.31%, and the theoretical capacity is 0.213 mmol g^{-1} of QCPSG. The IR reflectance spectrum of QCPSG shows the disappearance of bands at 3064 and 3189 cm^{-1} [assigned previously to (ν_s) and (ν_{as}) of NH_2 in the IR spectrum of APCPSG[7–9]] due to the particular involvement of this group in the reaction in addition to hydrolysis.[20]

The low organic content of QCPSG restricts its investigation by IR so that the monomer phase of QCPSG; APHS–quercetin was prepared to obtain observable IR bands. Two possibilities of reaction between quercetin and aminopropylsilica were taken into consideration: the first possibility is the formation of Schiff-base (structure 1, Scheme 1) by condensation of the amine and carbonyl groups similar to *N*-propylsalicylaldimine.[7–9] However, this is a very weak possibility, because the carbonyl group is stabilized by the hydrogen bonding to the two adjacent hydroxyl groups. As the ion exchanger showed appreciable stability against boiling with 1 M HCl in 1 : 1 ethanol/water solution, contrary to the known sensitivity of Schiffs bases toward acids, this possibility should be omitted. The second pathway was suggested to occur via the displacement of nitrogen in the propylamine substrate for pyran oxygen in quercetin.[21] The last pathway is more likely to occur in the

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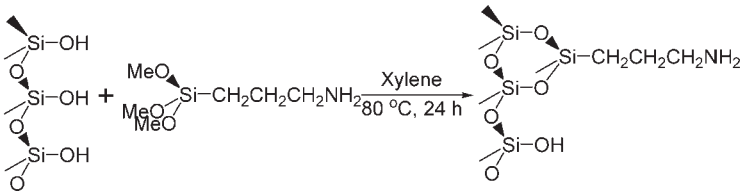
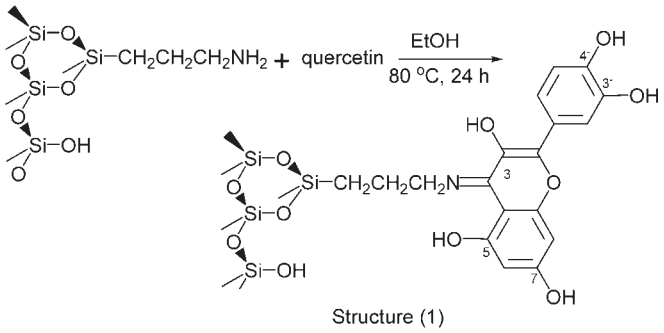
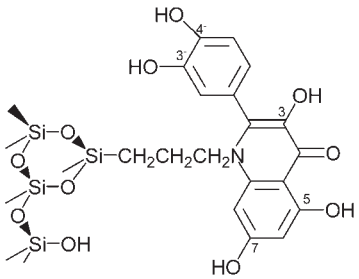


Aminopropyl controlled pore silica glass

(APCPSG)



Structure (1)



Structure (2)

quercetin anchored to APCPSG

(QCPSG)

Scheme 1. Immobilization of quercetin on CPSG.

monomer phase, as concluded from the disappearance of the (C–O–C) vibration bands in the IR reflectance spectrum of the monomer phase APHS–quercetin, which is observed at 1163 cm^{-1},[22] in that of quercetin. Solid-state ^{13}C-NMR (Fig. 2) confirmed the second possibility of the reaction via the displacement of nitrogen in the propylamine substrate for pyran oxygen in

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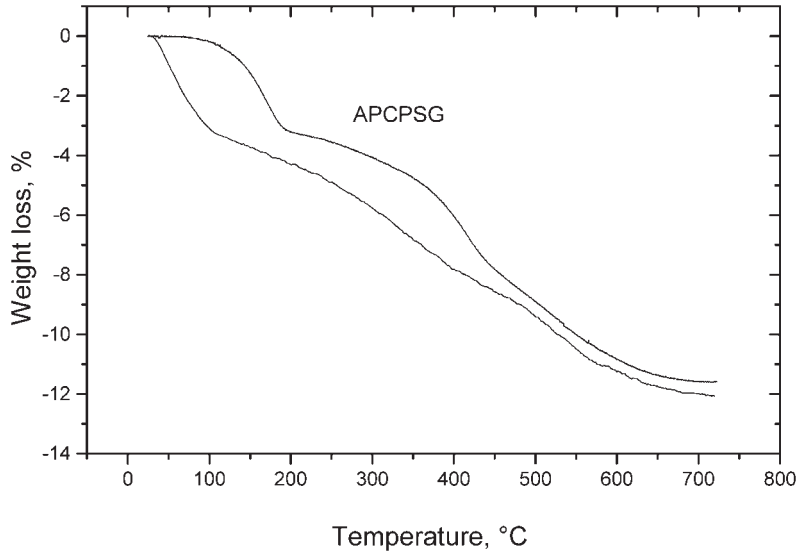

Figure 1. Thermogravimetric curves of APCPSG and QCPSG.

quercetin. The peaks of the three carbon atoms of propyl moiety were observed at 43.82, 25.84, and 9.27 ppm in APCPSG, QCPSG, and APHS–quercetin. The strongly overlapped peaks due to quercetin[23] were detected in the range of 100–200 ppm in the ^{13}C-NMR spectrum of QCPSG and more obvious in its monomer. The peak obtained at 135.39 is not observed in that of quercetin[23] and may be attributed to carbon no. 9 bonded to nitrogen[24] replacing the oxygen no. 1. The detection of the peak at 192.98 ppm confirms the presence of C═O without taking part in the reaction, which agrees with the reported values of carbonyl carbon,[24] but it is higher than the value obtained for that of quercetin (178–182 ppm[23]). This is attributed to the absence of oxygen lone pairs contribution in the delocalization of the π bonds of the molecule, whereas the lone pair of electrons of the replaced nitrogen is affected by strong hydrogen bonding to the silanol groups,[20] causing downfield of the carbonyl carbon. The broad peaks in solid-state NMR may be attributed to the presence of the organic moiety at different sites on the silica surface, causing slight change in the affecting field at each site.

Electronic spectrum of the monomer phase APHS–quercetin showed a strong absorption band at 390 nm, which represents a 20-nm red shift compared with that observed for quercetin at 370 nm.[15] This red shift

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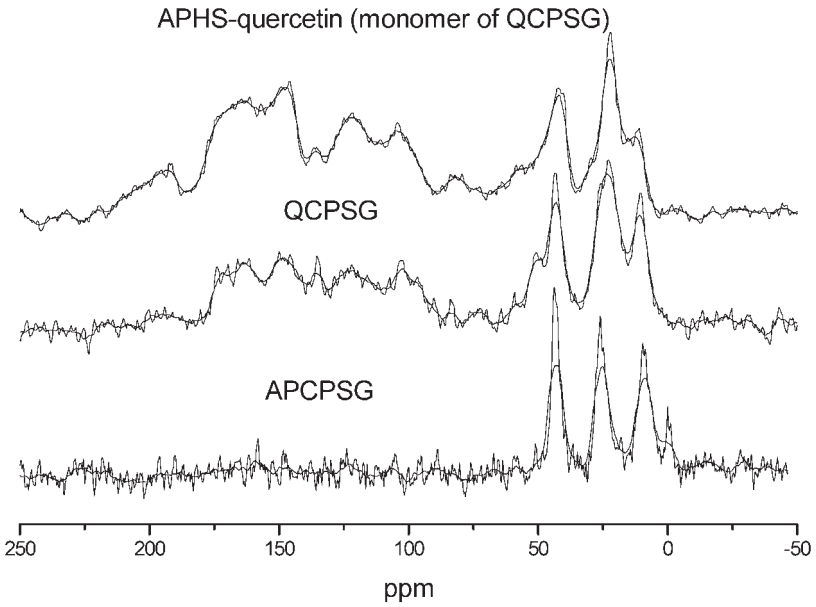

Figure 2. The ^{13}C-NMR measurement of APCPSG, QCPSG, and its monomer phase APHS–quercetin.

confirms the TGA and IR results, which may be attributed to nitrogen being less electronegative than oxygen.

3.2. Calibration and Detection Limit

The ICP-MS signals were found to be a linear function of the concentration range (0–50 ng mL^{-1}). The instrumental detection limits $(DL)_i$ of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II), based on three times the standard deviation of the blank (10 mL 0.5 M HNO_3 passed through 150 mg QCPSG after preconcentration of 1000 mL Millipore water digested for organic matter and adjusted to pH 8.0 $\pm$ 0.1 by NaOH and HNO_3) above its mean value, were 1.05, 0.17, 0.39, 7.84, and 1.11 ng mL^{-1} respectively.

The analytical detect limits (DL_a) were calculated by dividing the instrumental DLs by the preconcentration factor (100 in the case of batch separation of water samples). The DL_a, was estimated to be 10.5, 1.71, 3.92, 78.4, and 11.1 pg mL^{-1}, respectively.

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3.3. Batch Mode Separation

3.3.1. Effect of pH

Figure 3 represents the effect of pH on the separation efficiency of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) on QCPSG. At low pH, the distribution coefficients generally were low, which is attributed to the incomplete ionization of the ionogenic group of the ion exchanger. The distribution coefficient of the metal ions on QCPSG reached its maximum at pH $\cong$ 7.5–8.5 for the investigated metal ions, except for Cu(II), which showed its maximum separation at pH 6.5. Log K_d at the maximum separation efficiency was 4.11, 3.99, 4.15, 4.48, and 4.19 representing a recovery values of 83.8%, 77.3%, 84.8%, 92.3%, and 78.3% respectively. These values are lower than those obtained with salicylaldimine based on CPSG,[8] which may be attributed to the relatively better ability of imine N to donate its lone pair of electrons than oxygen, as the metal ions can be accommodated to positions 3 and 4.[11] After saturation of these positions (3 and 4), positions 3′ and 4′ could be used.

3.3.2. Kinetic Study

Figure 4 shows the Si hydrolyzed from QCPSG, in comparison with that anchored to QSG, APCPSG, and APSG, while stirring for 60 min in water buffered at an optimum pH value 8 $\pm$ 0.1. The stability of silica species may be expressed as the opposite of the hydrolysis, hence, the order of silica stability should be QCPSG > QSG > APCPSG > APSG. This indicates that silica gel generally is more easily degraded than CPSG, which may be attributed to its open structure with a larger surface area. Also, it may be observed that the anchoring of quercetin to CPSG or silica gel strongly reduces the hydrolysis of silica observed in the corresponding aminopropyl phases, indicating a neutralization effect to local basisity performed by the amino group, which catalyses the silica hydrolysis.[20] Comparing the stability of QCPSG with that of salicylaldimine-CPSG,[10] it may be observed that quercetin is more effective in reducing the hydrolysis of silica. This may be understood in view of its bulky structure hindering the attack of OH^- groups as mentioned above. In general, these results confirm the relative stability of QCPSG and indicate the possibility of studying the effect of time of stirring on the separation of the investigated metal ions by using QCPSG without a noticeable loss of the ion exchanger due to hydrolysis (wt loss = 0.45% after 60 min stirring at pH 8).

Figure 5 represents the effect of stirring time on the recovery of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) at pH = 8.0 $\pm$ 0.1 by using QCPSG. The ion exchanger shows fast kinetics of equilibration, so that 30 min of

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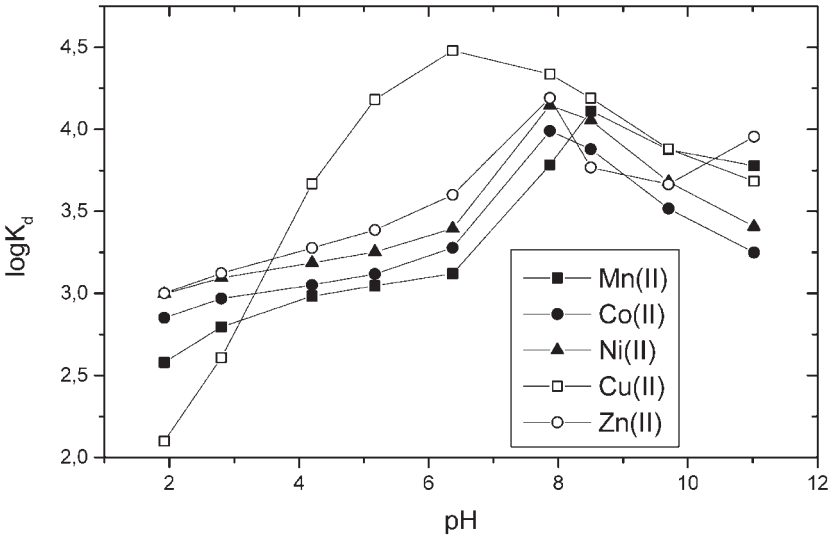

Figure 3. Effect of pH on the distribution coefficient of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) on QCPSG.

stirring was enough to reach maximum values of separation (separation efficiency = 83.8%, 75.1%, 81.9%, 86.1%, and 70.1%, respectively).

3.3.3. Effect of Some Interfering Species

The effect of interfering agents on the separation efficiency was studied for several reasons: (1) to avoid their effect during application; (2) to suggest a selective eluent as predicted from its interfering effect; (3) to study the preferred positions of different metal ion; (4) to enhance the selectivity of the ion exchanger.

No effect on the efficiency of separation of the investigated metal ions was found from the most common ions such as nitrate, sulfate, phosphate, chloride, tartarate, Na^+, K^+, Mg^{2+}, and Ca^{2+} ions (Table 1). Trace metal ions B^{3+}, Cr^{3+}, Al^{3+}, Fe^{3+}, As^{3+}, Sr^{2+}, Ag^+, Cd^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+}, and Bi^{3+}, with a concentration of 50 ng mL^{-1} do not affect the separation process. Formate, oxalate, cyanide, and citrate caused weak to strong interference, depending on the metal ion, whereas, ethylenediaminetetraacetic acid (EDTA) caused complete stripping of all metal ions. This indicates that in case of application, organic content should be digested prior to separation. An interesting phenomenon was observed in the presence of NO_2^-, S^{2-}, CO_3^{2-}, AcO^-, and NH_4^+, as the separation efficiency was found to increase. This may be attributed to the formation of a mixed ligand complex.[13] This behavior

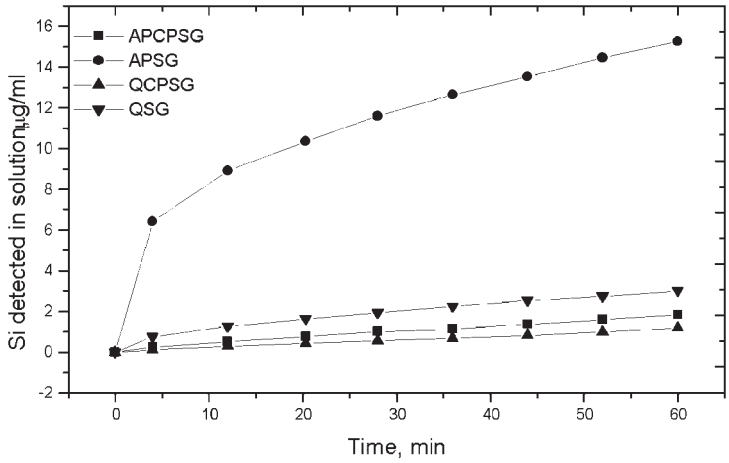

Figure 4. Dissolution of APCPSG and APSG and their corresponding condenstaion products with quercetin, QCPSG and QSG, respectively, in water buffered at pH 8. Weight = 100 mg and volume = 200 mL.

was used to enhance the separation efficiency of the metal ions on QCPSG by the addition of acetate ion.

3.3.4. Choice of Eluent and Capacity Fading During Use of Quercetin Based on Controlled-Pore Silica Glass

To choose the most effective eluent for the quantitative stripping of the retained metal ions on QCPSG after double extractions of 2.5 μg of the metal ions from 50 mL Milli-Q water (containing 100 $\mu g\,L^{-1}$ AcO^- and 3.5% NaCl), which is adjusted at pH 8.0 $\pm$ 0.1. The ions were stripped with 10 mL of 0.01–1 M HCl, HNO_3, or H_2SO_4. The results showed that all acids could offer almost quantitative elution of the metal ions from QCPSG. Subsequent elution of the metal ions was carried out with 0.5 M nitric solution. The reason of the choosing nitric acid as eluent is that it is a more acceptable matrix for ICP-MS than chloride and sulfate ions.[25]

Figure 6(a) shows a representative effect of the acid concentration (HNO_3) on the recovery. The 0.5 M HNO_3 was sufficient to obtain a recovery higher than 97%. Comparing these results with those obtained for strong chelaing agents based on different supports such as 2-pyridylazonaphthol[19] and 8-hydroxyquinoline,[26] it can be noticed that the eluting efficiency of the *N*-propylsalicylaldimine base on CPSG is much better. Obviously, too strong chelation between the ion exchanger and the metal ions is not favored due to irreversible binding.[27]

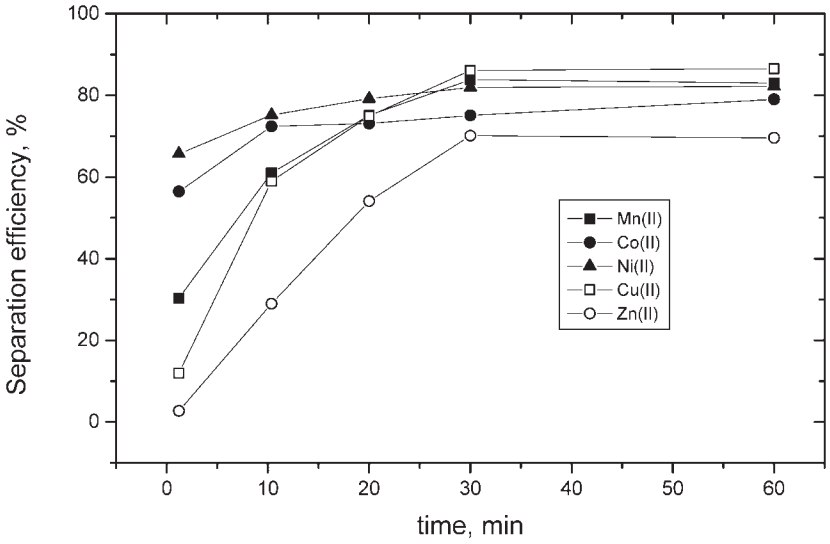

Figure 5. Effect of stirring time on the recovery of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) after separation on QCPSG at pH = 8.0 ± 0.1; 20 mg of QCPSG and 50 ng mL^{-1} of metal ion.

The use of EDTA as are eluent also was studied [Fig. 6(b)]. Although EDTA showed better stripping efficiency of the investigated metal ions, HNO_3 is a preferred matrix for measurement.

Applying the optimum conditions of separation pH = 8.0 ± 0.1 and time of stirring = 30 min for 40 cycles of loading of ions, followed by stripping with 10 mL 0.5 M HNO_3, and finally washing with 20 mL H_2O indicated a capacity fading of only 10% of the initial capacity. This indicates that QCPSG has good stability and may be reused safely without noticeable loss in capacity.

3.3.5. Nature of Bonding Between Metal Ions and Quercetin Based on Controlled-Pore Silica Glass

The IR and UV spectra of a QCPSG complex with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) could not give details about the bonding between these metal ions and quercetin due to the complex structure and low organic content. However, the effect of B(III) and Al(III) on the separation of the investigated metal ions was studied to get more information about their preferred positions. In the presence of boron, the investigated metal ions were moderately affected, especially Mn(II) at pH 8. As boron is known to be accommodated in position

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Table 1. Effect of some common ionic species on the separation efficiency (%) of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) on QCPSG at pH 8, otherwise as stated.

Species	Concentration ($mg\,L^{-1}$)	Efficiency of separation (%)				
		Mn	Co	Ni	Cu	Zn
Without	—	83.8	75.1	81.9	86.1	70.0
Cl^-	21,240	80.8	70.1	77.6	88.3	68.6
NO_2^-	200	98.7	97.6	98.8	92.4	90.8
NO_3^-	1,000	82.4	76.0	80.6	85.7	71.1
S^-	200	93.0	96.9	96.7	96.0	83.8
CO_3^-	1,000	95.7	96.8	98.0	94.2	88.4
SO_4^-	1,000	87.2	87.4	82.9	75.40	67.0
PO_4^-	1,000	78.4	72.8	73.9	79.0	65.70
Formate	200	87.9	68.1	79.2	68.5	33.3
Acetate	200	98.1	94.4	95.9	90.7	87.9
Oxalate	200	46.6	36.7	39.5	85.2	74.8
Citrate	200	14.1	16.6	11.2	78.1	46.6
Tartarate	200	89.0	71.1	81.4	71.8	67.5
EDTA	200	2.1	5.8	5.2	3.8	2.2
CN^-	200	66.0	0.6	2.7	27.7	37.2
NH_4^+	1,000	81.0	89.0	92.2	86.5	69.6
Na^+	13,761	79.3	72.8	80.9	84.6	69.8
Mg^{++}	1,000	80.1	74.5	81.4	85.1	70.2
Ca^{++}	1,000	79.8	75.8	79.5	84.5	69.2
B(III)						
pH 6	1,000	71.4	50.3	70.1	88.2	62.9
pH 8	1,000	25.5	65.3	66.3	70	55.0
Al(III)						
pH 6	1,000	0	0	0	0	0
pH 8	1,000	7.3	0	0	0	0

3′ and 4′, then the investigated metal ions should be mainly accommodated at position 3, 4, 3′, and 4′, which takes part in accommodation at high pH. Al(III) was found to prevent the separation of the investigated metal ions, indicating that it is accommodated preferably to position 3 and 4 or position 3′ and 4′. This results are in accordance with that reported earlier.[11]

Moreover, the batch capacity of QCPSG toward Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) is 0.24, 0.43, 0.42, 0.46, and 0.42 $mmol\,g^{-1}$, respectively, at pH 5.5 after stirring for 60 min. Repeating the experiment in the case of Cu(II) for 24 hr did not lead to any appreciable increase in the capacity, which means that the 1 hr time of stirring is enough to determine the maximum capacity.

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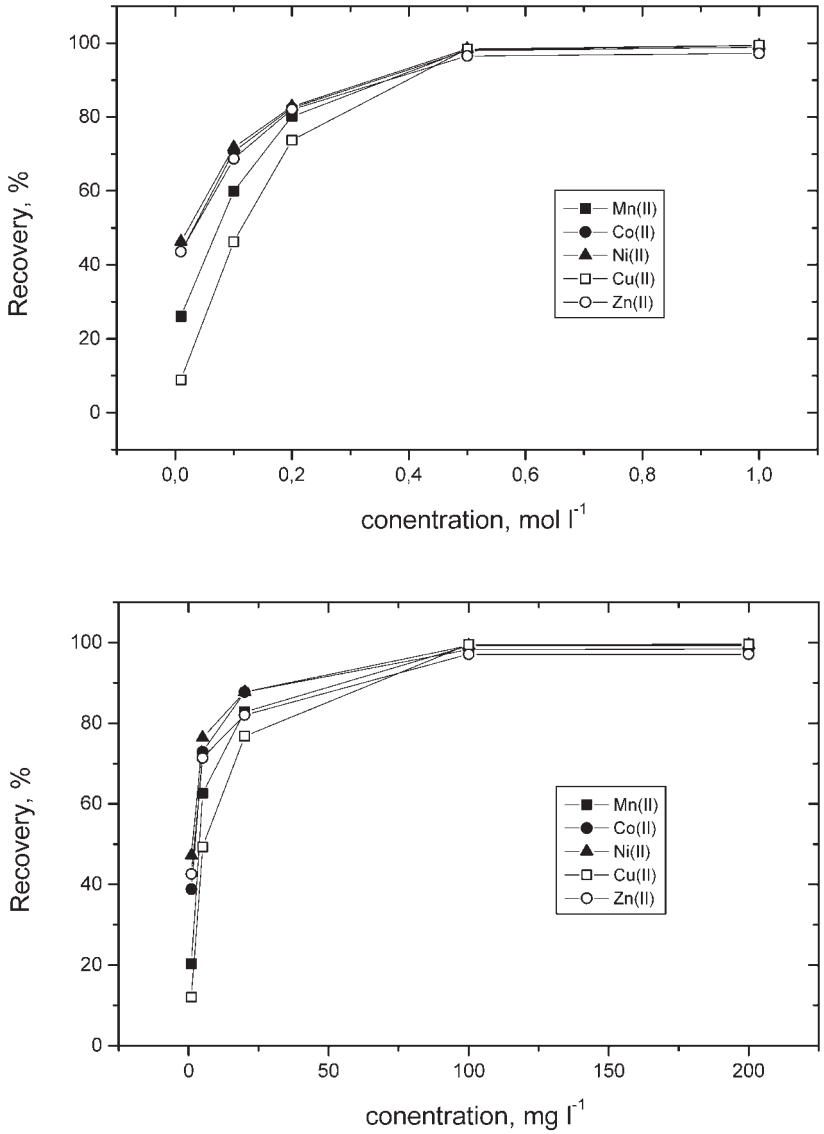

Figure 6. Effect of HNO_3 (a) and EDTA (b) concentration on the recovery of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) separated by double batches on 150 mg QCPSG at pH = 8.0 ± 0.1 and 30 min stirring time.

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This is in agreement with the kinetic study, which showed fast kinetics of equilibration. Comparing these values with the theoretical capacity, 1 : 2 quercetin/metal bonding is observed for all metal ions except for Mn, which shows equimolar bonding. The QSG experienced slightly lower capacities toward the investigated metal ions (0.21, 0.39, 0.38, 0.41, and 0.38 $mmol/g^{-1}$, respectively, at pH 5.5). This may be due to that the dissolution of the silica base in the case that silica gel is easier than CPSG, after 24 hr stirring at pH 5.5 (dissolved Si concentration was 14.6 $\mu g\,mL^{-1}$ in the case of QSG and 9.72 $\mu g\,mL^{-1}$ in the case of QCPSG).

The pH-metric titration with 0.0083 M NaOH was carried out to characterize the bonding between QCPSG and the metal ions Mn(II), Co(II), Ni(II), Cu(II), and Zn(II). A typical titration curve for the ion exchanger is shown in Fig. (7), which is in agreement with that reported earlier.[8] Two shifts could be observed, which are attributed to neutralization of the proton gained to the free propylamine below pH 6; another shift in the basic range is attributed to the phenolic groups. When the same titration was performed in the presence of the studied metal ions, the inflections on the titration curve were shifted to the right, at lower pH values. This may indicate that the organic substrate is bonded to the metal ions via position 3 and 4 and position 3′ and 4′, and the complex is neutralized by hydroxyl groups up to pH 8.

3.3.6. Analytical Application

The ion-exchange method was applied for the preconcentration and separation of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) ions in the water samples. Table 2 shows the results of the application process.

It can be concluded from the results that the concentrations of heavy metal ions in Damietta and Ras Elbar are obviously higher than that in Mansoura, Port Fouad, and Suez Gulf. This may be attributed to the anthropogenic activities and domestic wastes in the vicinity of these locations. However, the results are much lower than those reported in 1992–1996,[28,29] due to river washing with moderate to high floods in the recent few years, and the results lie within the permissible levels and are in agreement with those reported recently.[8,19,30]

The reliability of the ion exchange method was statistically examined for the analysis of Co(II), Ni(II), Cu(II), and Zn(II) ions in certified samples A and B, and granite ore samples, as shown in Table 3, in comparison with the true values. Comparison between the experimental means within the confidence margin for $P = 0.05$ and $n = 5$[31] indicates that there is good agreement between experimental and real values, and there is no significant difference between them, i.e., the method is precise.

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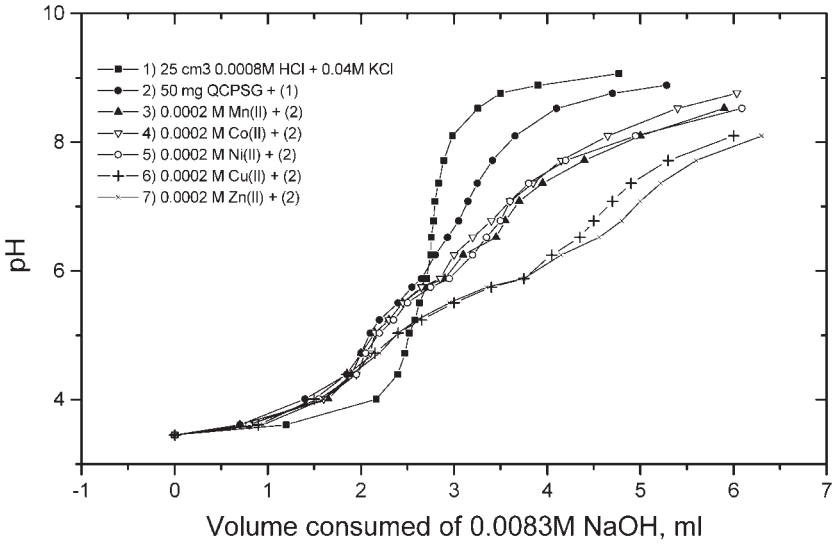

Figure 7. The pH-metric titration curves of QCPSG and its complexes with Mn(II), Co(II), Ni(II), Cu(II), and Zn(II).

4. CONCLUSION

Quercetin was successfully immobilized on controlled-pore silica, yielding good stability in an aqueous solution at pH 8 in comparison with that immobilized on silica gel or the aminopropyl silicas.

The matrix effect hampering the determination of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) by ICP-MS can be effectively removed by solid phase extraction with QCPSG. The QCPSG showed uptake capacity of 0.24, 0.43, 0.42, 0.46, and 0.42 $\mathrm{mmol/g^{-1}}$ toward Mn(II), Co(II), Ni(II), Cu(II), and Zn(II), respectively, at pH 5.5, which is slightly higher than that based on silica gel, although it possesses twice the surface area of CPSG. This is attributed to the relative stability of CPSG in comparison with silica gel. The metal ions were suggested to react with quercetin immobilized on silica, with the ratio 1 : 2 quercetin/metal, for all metal ions except for Mn(II) as 1 : 1 ratio at pH 5.5, whereas, at higher pH, the ratio 1 : 2 was adopted for all metal ions. No serious interference on the separation of these metal ions with QCPSG was detected from common ionic species except for formate, oxalate, citrate, cyanide, and EDTA. Hence, on application, the total organic matter must be digested prior to the separation process. The optimum pH range for the separation of these metal ions is 7.9–8.5 at 30 min stirring time, giving an

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Table 2. Multielements analysis of natural samples by using ICP-MS for determination of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) in $\mu g L^{-1}$ ($\cong$ppb), after preconcentration by ion exchange separation by QCPSG. Ion exchange conditions: pH = 8.0 ± 0.1, weight of QCPSG = 150 mg, stirring time = 30 min at 25°C, $\bar{X} \pm (ts/\sqrt{n})$ for n=5, where $\bar{X}$ is the average, t is the student factor and equals 2.57 for $P = 0.05$, and s is the standard deviation.

	Element						
Location	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	pH	TDS ($g L^{-1}$)
Mansoura (river water)	2.17 ± 0.099 (3.67)	0.06 ± 0.004 (6.10)	2.29 ± 0.083 (2.91)	1.61 ± 0.054 (2.68)	12.96 ± 0.478 (2.97)	7.81	0.61
Damietta bridge (brackish water)	13.83 ± 0.411 (2.39)	0.13 ± 0.004 (2.26)	3.98 ± 0.128 (2.58)	2.77 ± 0.130 (3.77)	14.18 ± 0.307 (1.74)	7.74	2.49
Ras Elbar (seawater)	3.95 ± 0.088 (1.79)	0.37 ± 0.023 (4.89)	3.11 ± 0.167 (4.32)	5.04 ± 0.169 (2.70)	20.77 ± 0.599 (2.32)	8.01	39.82
Port Fouad (seawater)	2.73 ± 0.071 (2.09)	0.08 ± 0.006 (5.29)	1.11 ± 0.050 (3.65)	2.82 ± 0.188 (5.36)	14.87 ± 0.413 (2.23)	8.15	41.27
Suez Gulf (seawater)	0.66 ± 0.032 (3.89)	0.02 ± 0.001 (4.12)	0.35 ± 0.018 (4.17)	0.48 ± 0.036 (6.03)	2.95 ± 0.134 (3.66)	8.24	43.21

Note: Values between brackets are the relative standard deviation (RSD). TDS is the total dissolved salts.

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Table 3. Analysis of certified and reported samples by using ICP-MS for determination of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) in $\mu g\,g^{-1}$, after separation by QCPSG, pH = 8.0, weight of QCPSG = 150 mg, stirring time = 30 min at 25°C.

	Element				
Location	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
Granite (1)					
Found	0.038 ± 0.003	0.199 ± 0.008	0.402 ± 0.015	0.634 ± 0.021	2.535 ± 0.094
True	ND	0.21	0.41	0.62	2.6
Granite (2)					
Found	0.02 ± 0.001	0.054 ± 0.004	0.087 ± 0.004	0.095 ± 0.004	2.723 ± 0.059
True	ND	0.06	0.08	0.09	2.8
Certified sample[a] (A)					
Found	990 ± 9.60	986 ± 6.86	1000 ± 8.83	1002 ± 12.7	995 ± 4.82
True	997 ± 10	983 ± 10	998 ± 10	1011 ± 10	989 ± 10
Certified sample[b] (B)					
Found	1.458 ± 0.016	0.085 ± 0.001	10.68 ± 0.035	0.515 ± 0.006	1.156 ± 0.007
True	1.433 ± 0.029	0.084 ± 0.005	10.63 ± 0.094	0.519 ± 0.028	—

Note: ND, not detected.
[a]Values given in $m\,g^{-1}$.
[b]Values given in percentage (w/w).

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efficiency of 98.1%, 94.4%, 95.9%, 90.7%, and 87.9%, respectively, in the presence of sodium acetate. All the metal ions can be quantitatively desorbed with 0.5 M HNO_3 or HCl. The ion exchanger QCPSG can be effectively used for the separation and preconcentration of the investigated metal ions from natural water samples. The method also was applied for the determination of these metal ions in granite ores and certified samples, and the results are in good agreement with the reported values.

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