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Solid Phase Extraction and Determination of Ultra Trace Amounts of Copper using Activated Carbon Modified by *N,N′*-Bis(Salicylidene)-1,2-Phenylenediamine

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Abstract: N,N′-bis(salicylidene)-1,2-phenylenediamine(salophen) modified activated carbon was prepared and used as an effective sorbent for solid phase extraction of Cu(II) ions from aqueous solutions. The salophen modified activated carbon showed a high sorption affinity for Cu(II). In this method a column mode was used for preconcentration of copper(II) in the pH range 3.5–6.5. The retained copper was eluted with 0.1 mol l^{-1} EDTA and determined by atomic absorption spectrometry. The calibration graph was linear over the copper concentration in the range 0.05–1.5 μg ml^{-1}. Five replicate determination of 0.4 μg ml^{-1} of copper(II) gave a mean absorbance of 0.385 with a relative standard deviation of 1.35%. The detection limit was 0.0133 μg ml^{-1}. The interference of a large number of anions and cations has been studied and the optimized conditions developed were utilized for determination of copper in various real samples.

Keywords: Solid phase extraction, copper, salophen, modified activated carbon, Schiff base

INTRODUCTION

Due to the vital importance of copper in industry (1) and in many biological systems (2, 3), the development of new methods for selective

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separation, preconcentration, purification, and determination of copper in sub-micro levels in different material, medicinal, and environmental samples is of continuing interest. Thus the determination of trace amount of copper from different matrices is of great importance. Flame and graphite furnace atomic absorption spectrometry (4, 5) and spectrophotometric methods (6, 7) are among the most widely methods used for the copper determination, but their sensitivity usually is insufficient for monitoring the low copper concentration in environmental sample. Consequently, a preconcentration and matrix elimination steps is usually required.

Solid phase extraction (SPE) or solid-liquid extraction has come to the forefront compared to the other preconcentration techniques due to the following advantages. These include higher enrichment factors, absence of emulsion, safety with respect to hazardous samples, minimal costs due to low consumption of reagents, and flexibility and easier incorporation into automated analytical techniques (8–10). In recent years various SPE procedures have been developed for the enrichment of the trace amount of copper(II). A number of solid sorbents such as cellulose (11), sephalex A-25 anion exchanger (12), chitosan (13), polystyrene (14), amberlite XAD-2 resin (15), octadecyl silica membrane disks (16), ion exchanger (17), chromosorb-105 resin (18), silica gel modified with Schiff bases (19), naphthalene (20), have been reported for the enrichment of copper(II) from dilute solutions prior to determination by a variety of analytical techniques. Despite the latest progress in the development of polymeric material for the removal of ions from solution, the use of some of them sometimes restricted by their limited stability in some application, low sorptive, selectivity, etc. In view of high retention capacity, ready availability, ease of elution, high chemical stability, thermal stability and applicability to enrich trace amount of inorganic, activated carbon (AC) was chosen as a SPE supported/sorbent in the present study. However, activated carbon alone does not adsorb inorganics selectively and quantitatively at trace and ultra trace levels (21, 9). On the other hand, for the enrichment of metal ions, it is necessary to use modified activated carbon (9, 22, 23). To our best knowledge there are a fewer SPE procedures for preconcentration and selective removal of copper ions using modified activated carbon (24–26). We reported here the preparation of salophen modified activated carbon and its application for preconcentration and determination of copper(II) at trace levels using a column operation mode. The cost of this adsorbent is much less than the chelating resin and EDTA was used that, is a good eluent from the point of ecology and toxicology and can be used in determination of copper in real samples. The proposed method is very suitable in comparison with recent reports (27–31) in view of preconcentration factor, cost and can be used for determination of copper in ng ml^{-1} level.

EXPERIMENTAL

Reagent and Materials

A stock solution of copper(II) (1000 μg ml^{-1}) was prepared by dissolving exactly 0.05 g of copper powder in 5 ml nitric acid and dilute with distilled water in a 500 ml flask. The working solutions of copper were prepared by diluting of the stock solution. Activated carbon was purchased from Merck company and used as the support in preparation of the adsorbent for copper. Sodium acetate-acetic acid (pH = 5, 0.02 mol l^{-1}) was used to maintain the pH. Nitric acid, chloroform, hydrochloric acid, ethylenediaminetetracetic acid (EDTA) and other reagents (Merck) were also of analytical reagent grade. Distilled water was used throughout.

Apparatus

A Shimadzu model AA-670 atomic absorption spectrometer was used for copper determination, (parameters are shown in Table 1). A Hanna pH meter model 302 was used for adjusting the pH of sample solutions. The vacant standard disposable syringe barrel and their fitted disk (20 μm poly propylene) were used as column.

Synthesis of N,N′-Bis(Salicylidene)1,2-Phenylenediamine

To an ethanol solution (10 ml) containing 2.70 g of 1,2-phenylenediamine, salicylaldehyde (5.20 ml) was added drop wise. After refluxing the mixture for 10 h, an orange solid was produced, filtered, and recrystalized twice in ethanol (32). The chemical structure of the salophen is shown in Fig. 1.

Table 1. Atomic absorption spectrophotometer parameters

Instrument condition				
Copper HCL[a]	Current(mA)	Slit (nm)	Wavelength (nm)	Mode
	3	0.5	324.8	(BGC)[b]
Flame condition				
Flame	Fuel flow	Oxidant flow	Burner (cm)	H (mm)
Air-C_2H_2	1.8	8	10	6

[a] Hollow cathode lamp.

[b] Back ground correction.

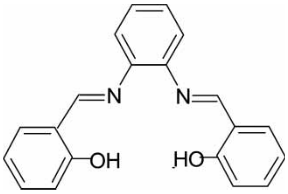

Figure 1. Chemical structure of the N,N′-bis(salicylidene)1,2′-phenylenediamine (Salophen)

Preparation of Salophen Modified Activated Carbon

0.9 gr of activated carbon was added to 10 ml of chloroform solution containing 0.1 g of salophen and the resulting mixture was stirred for 10 h and was allowed to settle at room temperature. Then the solid phase (modified activated carbon) was dried in an oven at 70°C. Then it was stored in an amber colored bottle.

General Procedure

The syringe barrel cartridge was packed with 50 mg of 10% salophen modified activated carbon. It was conditioned by passing 5 ml of a 0.02 mol l^{-1} acetate buffer ($pH = 5.0$). An aliquot sample solution containing 1.25–37.5 μg copper was transferred to a 25 ml calibrated flask, and then 2.5 ml 0.2 mol l^{-1} of acetate buffer ($pH = 5.0$) was added and dilute to 25 ml. The resulted solution was passed through the column with flow rate of 3.5 ml min^{-1}. After that the copper was stripped from the sorbent with 1 ml of 0.1 mol l^{-1} EDTA. The copper content of resulting solution was measured by atomic absorption spectroscopy.

RESULT AND DISCUSSION

Our pervious spectrophotometric investigation of complexation of salophen with some divalent ions revealed that salophen form stable 1:1 complexes with Cu^{2+}, Co^{2+}, and Ni^{2+}. Their stability constants varied in order $Cu^{2+} > Co^{2+} > Ni^{2+}$ in different non aqueous solvents such as DMSO, MeOH, and their binary mixtures. Thus, considering the observed stability trend we decided to use salophen as a suitable modifier for selective preconcentration and determination of copper ions on the activated carbon (AC). Some preliminary experiments were undertaken in order to investigate the quantitative extraction of copper ions by AC in the absence and presence of salophen. The solid phase extraction of 10 μg of copper in 25 ml of solution at $pH = 5.0$ with AC and salophen modified AC was investigated. The salophen (10%) modified AC gave quantitative enrichment while AC alone gave an enrichment of 39% of copper.

Choice of Eluent

In order to choose the proper eluent for the retained Cu^{2+} ions, after the extraction of 10 μg of copper from 25 ml water by the modified activated carbon, the copper ions were stripped with 3 ml of 0.2 mol l^{-1} of different eluents (Table 2). From the results given in Table 2 it is obvious that the complete stripping was taking place with nitric acid, sulfuric acid, and EDTA. Desorption of copper from the surface of the adsorbent may be taking place as a complex of Cu^{2+}-salophen or may be due to decomposition of salophen in the presence of acid (33) and releasing of copper when nitric and sulfuric acids were used as stripping solution, while EDTA only stripped the copper ions from the modified AC and the column can be used for at least ten subsequent experiments. Thus EDTA was chosen as the eluent in this work. The effects of concentration and volume of EDTA on desorption of copper ions were tested. The concentration greater than 0.1 mol l^{-1} has no change on desorption of copper ions (Fig. 2a). As it is seen from Fig. 2b the quantitative elution of copper from the sorbent was carried out by 1 ml of 0.1 mol l^{-1} EDTA that was selected for subsequent uses.

Effect of Amount of Salophen and Adsorbent

The concentration of salophen in AC was varied from 2–33%. As it is seen from Fig. 2c a minimum of 5% salophen in AC was need for quantitative preconcentration of copper(II). So 10% salophen modified AC was chosen as SPE in subsequent studied. Also the effect of amount of salophen modified AC on the extraction of copper was examined in the range 10–70 mg. The results (Fig. 2d) indicate the quantitative recoveries of copper(II) in the range of 30–70 mg. Hence, 50 mg of 10% salophen modified AC was used in subsequent studies.

Effect of pH

The extraction of copper from the sample solution on the surface of modified AC is accompanied by the releasing of protons of salophen into the sample

Table 2. Percent recovery of copper(II) from modified AC using different stripping reagent

Stripping reagent (0.2 mol l^{-1})	% Recovery
HCl	94.5
HNO_3	99.9
H_2SO_4	100
EDTA	99.9
ThioUrea	83
Cupferron	50

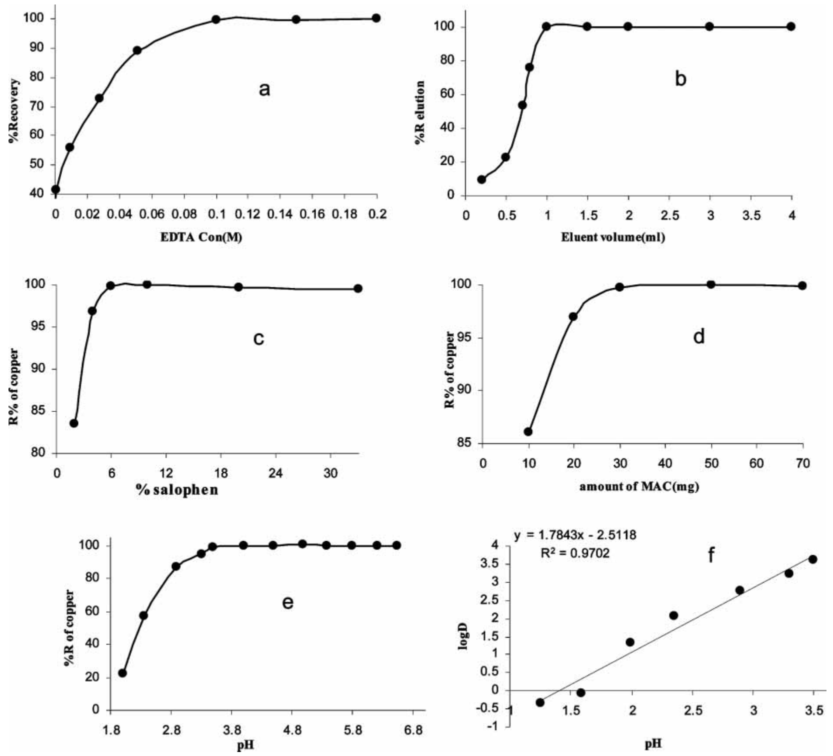

Figure 2. The effect of various parameters on the recovery of 10 μg of copper: a; EDTA concentration, b; volume of eluent, c; amount of salophen on modified AC, d; amount of 10% salophen modified AC, e; pH, f; distribution ratio as function of the pH.

solution. The pH, therefore, will be a very important factor in the adsorption and elution of copper ions. In other word, the separation of metal ions by chelation with conjugate bases of weak acid groups (such as salophen) is pH dependence. The pH will determine the values of the conditional stability constants of the metal complexes on the surface of sorbent (34). Due to the presence of two hydroxyl group on salophen structure, it is expected that the extent of its complexation is sensitive to pH (35). Thus the effect of pH on the extraction of copper ion was investigated. The pH of 25 ml of solution containing of 10 μg copper was varied from 1.5–6.5 using appropriate buffer solution. The result is shown in Fig. 2e. As is seen the percent of recovery of copper ion increased with increasing pH of the solution until a pH of 3.5 is reached. The quantitative extraction of copper ion occurs at a pH range 3.5–6.5. Higher pH values were not tested because of the possibility of the hydrolysis of copper ion in the solution. Therefore, the pH 5.0 was chosen in the subsequent uses.

The plot of log D versus pH gave straight line with slope near 2 (Fig. 2f), indicating that the adsorption of 1 mol copper released 2 mol of hydrogen ions.

$$(\mathrm{Cu}^{2+})_{\mathrm{aq}} + (\mathrm{H_2R})_{\mathrm{s}} \longleftrightarrow (\mathrm{RCu})_{\mathrm{s}} + (2\mathrm{H}^{+})_{\mathrm{aq}}$$

$$\mathrm{K_{ex}} = [\mathrm{RCu}]_{\mathrm{s}}[\mathrm{H}^{+}]^{2}_{\mathrm{aq}}/[\mathrm{Cu}^{2+}]_{\mathrm{aq}}[\mathrm{H_2R}]_{\mathrm{s}} \quad \text{and} \quad \mathrm{D} = [\mathrm{RCu}]_{\mathrm{s}}/[\mathrm{Cu}^{2+}]_{\mathrm{aq}}$$

Hence:

$$\log \mathrm{D} = \log \mathrm{K_{ex}} + \log[\mathrm{H_2R}]_{\mathrm{s}} + 2\,\mathrm{pH}$$

Where H_2R represents the chelating sorbent and D is the distribution ratio of copper between solid phase and the aqueous phase. The indices ‘s’ and ‘aq’ denote the solid and aqueous phases, respectively.

The Effect of Flow Rate

The effect of flow rate in the range of 1 to 6.0 ml min^{-1} on the extraction of copper(II) of sample solution onto SPE and elution of enriched copper(II) were studied. As it is seen from Table 3 up to a preconcentration flow rate 3.5 ml min^{-1} and an elution flow rate of 0.5 ml min^{-1}, quantitative recoveries of copper were obtained. Thus 3.5 ml min^{-1} flow rate was chosen for preconcentration and 0.5 ml min^{-1} for elution of copper was chosen.

Preconcentration and Capacity Factor

To assess the suitability of a SPE system, the preconcentration factor is the most important characteristic. Thus the effect of volume of sample solution in the range of 25–300 ml was investigated. Quantitative preconcentration and elution of copper(II) was obtained at aqueous phase volume up to 250 ml. Under these optimal conditions the enrichment factor of 250 was obtained. For determination of capacity factor of modified AC, 25 ml solution containing 500 μg of copper passed through the 0.05 g of 10% salophen modified AC followed 2 ml EDTA 0.1 M. Then the resultant elution sample was diluted to 25 ml and analyzed by AAS. The maximum capacity of the cartridge was 26.98 mg g^{-1}.

Table 3. Effect of flow rate on extraction efficiency of 10 μg copper

Flow rate (ml min^{-1})	0.5	1.0	2.0	3.0	4.0	5.0	6.0
%R of preconcentration	>99.9	>99.9	>99.9	>99.9	89	72	53
%R of stripping	>99.9	>99.9	85	75	—	—	—

Adsorption Kinetics

The kinetic of the sorption of copper ions onto salophen modified AC was investigated in the range of 0.75–20 min agitation time between sorbent (50 mg) and copper ion (20 μg). The amount of copper ions loaded onto modified AC was determined by general procedure described above. The kinetics of copper(II) adsorption on modified AC follows the first order rate expression given by Lagergren (36, 37):

$$\mathrm{Log}\ (q_e - q_t) = \mathrm{Log}\ q_e - k_{ad} \cdot t/2.303$$

Where q_t and q_e are the amounts of copper adsorbed (mg g^{-1} of modified AC) at time, t (min) and equilibrium time (30 min) respectively and K_{ad} is the rate constant of adsorption. The Lagergren equation was tested by plotting log ($q_e - q_t$) versus time (t). In the initial stage up to 20 min, the plot shown in Fig. 3a appears to be linear and the slope gives a value for the overall rate constant $K_{ad} = 0.231$ lit min^{-1}.

Adsorption Isotherms

The adsorption of copper ions onto salophen modified activated carbon as adsorbent from an aqueous solution was studied by the two most frequently

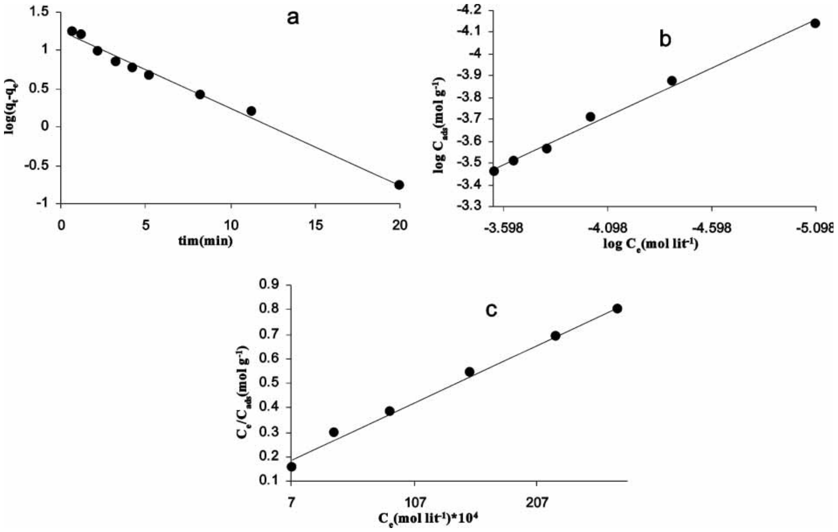

Figure 3. a; Lagergren plot for the adsorption of 2.0 μg ml^{-1} Cu(II), pH = 5.0, b; Frundlich plot for the adsorption of (0.31–12.5) × 10^{-4} mol l^{-1} Cu(II), pH = 5.0, equilibrium time = 60 min, adsorbent dose: 300 mg per 100 ml, c; Langmuir plot for the adsorption of (0.31–12.5) × 10^{-4} mol l^{-1} Cu(II), pH = 5.0, equilibrium time = 60 min, adsorbent dose: 300 mg per 100 ml.

used models for dilute solution (38, 39). The Freundlich isotherm (38), most widely used for the description of adsorption in aqueous systems, usually by fits the experimental data over a wide range of concentration. The Freundlich equation is given by:

$$\log C_{ads} = \log K_F + 1/n \log C_e$$

Where C_{ad} represent the amount of solute adsorbed per unit weight of adsorbent ($\mathrm{mol\,g^{-1}}$), C_e is the concentration of adsorbate in solution at equilibrium conditions ($\mathrm{mol\,l^{-1}}$) and K_F and $1/n$ are the adsorption capacity and adsorption affinity, respectively.

The Langmuir model (39) generally recognized for monolayer chemisorptions and energetically equivalent all sites is written in the form:

$$C_e/C_{ads} = 1/K_L\,b + C_e/K_L$$

Where C_{ads} and C_e have the same definition as previously presented for the Freundlich isotherm, K_L is the amount of solute adsorbed per unit weight of adsorbent required for monolayer coverage of surface, also called monolayer capacity and b is equilibrium constant related to the heat of adsorption.

The plot of log C_{ads} vs. log C_e is shown in Fig. 3b, which facilitates to determine the Freundlich constants $1/n$ and K_F from the slope and intercept of the plot. The numerical value of adsorption capacity (K_F) and n are $0.434\ \mathrm{mmol\,g^{-1}}$ and 2.23, respectively. The numerical value $1 < n < 10$ indicates a favorable adsorption of copper onto salophen modified activated carbon (38). The correlation coefficient for the Freundlich plot was found to be 0.9917.

For testing the curve fit of the Langmuir model to experimental data involves plotting of C_e/C_{ads} against C_e as shown in Fig. 3c. The model parameters K_L and b obtained from the slope and intercept of the plot are $27.82\ \mathrm{mg\,g^{-1}}$ and $0.214\ \mathrm{lit\,mg^{-1}}$, respectively. The value of K_L corresponded to the monolayer coverage and independent of temperature, while the sorption coefficient (b) is related to the enthalpy of adsorption and should vary with temperature. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor, or equilibrium parameter, R_l, which is defined by $R_l = 1/(1 + bC_0)$, where b is a Langmuir constant and C_0 is the initial concentration of Cu(II) (40). R_l values observed between 0.0 and 1 (Table 4) indicate favorable adsorption of Cu(II) onto 10% salophen MAC.

Effect of Divers Ions

In order to investigate the selective separation and determination of Cu^{2+} ion from its binary mixtures with diverse ions, an aliquot aqueous solution containing 10 μg of copper and mg amounts of other ions was taken and recommended procedure was followed. The results are summarized in

Table 4. Equilibrium parameter, R_1

Initial Cu(II) conc. (mg l^{-1})	R_1 value
2	0.70
5	0.48
10	0.32
15	0.24
20	0.19
25	0.16

Table 5. The results clearly indicate that 10 μg of copper ions in the binary mixtures are retained almost quantitatively by the salophen modified activated carbon. Thus, there is no interference in the presence of many cations and anions.

Calibration Curve

The calibration curve shows that Beer's law is obeyed in the concentration range of 0.05–1.5 μg ml^{-1} of Cu(II) in the measured solution. The

Table 5. Effect of divers ion on extraction efficiency of 10 μg of Cu(II) at pH = 5

Divers ions	Taken amount (mg)	%Recovery of copper
Li^+	5.0	99.7
Na^+	5.0	98
Ca^{2+}	5.0	99
Mg^{2+}	3.5	96.9
Mn^{2+}	3.5	100
Ni^{2+}	1.5	95.8
Co^{2+}	1.5	94
Pb^{2+}	2.0	92.8
Cd^{2+}	2.5	95.4
Ag^+	3.0	100
Fe^{3+}	3.0	97.9
Cr^{3+}	3.0	98.8
SO_4^{2-}	5	101
CO_3^{2-}	3	99.4
Cl^-	5	98.5
F^-	1.5	100.2
Br^-	1.5	100.3
$HCit^{3-}$	0.1	94.3
Na_2Y	2.2[a]	97.1

[a] μg.

linear regression equation obtained was: $A = 0.391\ C^{-1}_{Cu(\mu g.ml)} + 0.008$, ($r = 0.999$). The relative standard deviation at a concentration level of 0.4 $\mu g\ ml^{-1}$ of Cu(II) ($n = 5$) was 1.35%. The LOD of Cu(II) obtained from $C_{LOD} = K_b S_b m^{-1}$ (41) for a numerical factor of $K_b = 3$ is 0.0133 $\mu g\ ml^{-1}$, S_b is the standard deviation of blank measurement ($n = 10$), K_b is confidence factor (is most often chosen to be 2 or 3) and m is the slope of calibration curve at a particular concentrations.

Application

In order to assess to applicability of the method to real samples, it was applied to the separation and recovery of copper ions from different water, synthetic, drug, and tea samples. The tea sample solutions were prepared according to

Table 6. Recovery of copper from real samples

Sample	Found in real sample[a]	Found after added (5 μg)[b]	%R	RSD[c]	Found after added (10 μg)[b]	%R	RSD[c]
Paveh river	—	4.9	98	1.3	9.8	98.0	0.8
Tagh Bostan spring	—	5.0	100	0.3	9.9	99.0	1.02
Persian Gulf	1.1 μg	6.3	98	2.2	11.4	98.0	2.05
Synthetic Sample[d]	4.6 μg	9.3	94	2.9	14.5	99.0	2.59

[a] The sample volume is 25 ml.

[b] Standard addition method was used.

[c] $n = 5$

[d] Containing [Na^+ (2.5 mg), K^+ (2.5 mg), Pb^{2+} (1.0 mg), Cr^{3+} (1.0 mg), and Cu^{2+}(5.0 μg)].

Table 7. Determination of copper in tea and drug samples

Sample	Added (μg)	Found
Iranian black tea	—	0.3 (μg/50 mg)
	1	1.25
Indian black tea	—	0.71
	1	1.65
Sanatogen tablet[a]	—	1.99

[a] containing 2 mg per tablet.

the reported paper (42), 0.0030 g sample of Sanatogen tablet (taken from ten powdered tablets) was completely dissolved in 2 ml nitric acid on a water bath, and the mixture was cooled and filtered through filter paper (Watman No.1). the filtered mixture was diluted to 50 ml after adjustment of pH (pH = 5.0) with distilled water in a calibrated flask. The results are summarized in Tables 6–7.

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