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Solid-phase extraction of Cu, Zn, and Mn from Nile river and tap water prior to flame atomic absorption determination

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ABSTRACT

In this study, we preconcentrated Cu, Zn, and Mn from Nile river and tap water at Cairo City (Egypt) by solid-phase extraction prior to flame AAS determination. Diacetylmonoxime functionalized silica gel (DMO-SG) was used as sorbent for preconcentration/separation of metal ions. Best sorption was achieved at sample pH 6 and flow rate of 2 mL min^{-1}. Desorption was affected by a 0.3 mol L^{-1} of hydrochloric acid solution. Sorption kinetic and isotherm were found to follow the pseudo-second-order and Freundlich isotherm models, respectively. The capacity was 422, 533, and 346 μg g^{-1} for Cu, Zn, and Mn, respectively. The limit of detection (3σ) was 0.10, 0.11, and 0.12 μg L^{-1} and preconcentration factor was 100, 105, and 50, respectively. The recovery ranged between 92 and 102% and RSD % varied from 2.6 to 7.4%.

Keywords: Preconcentration; Solid-phase extraction; Metal ions; Nile river; Tap water

1. Introduction

The Nile river is the primary water resource of Egypt. The principal water treatment plants receive raw water from the Nile river. The level of heavy metals in Nile river at great Cairo ranged between 0.021 and 0.056, and 0.002 and 0.049 (mg L^{-1}) for Zn and Cu, respectively [1], and within 0.02–0.48 for Mn [2]. These heavy metals are essential and play an important role in enzymatic reactions and in the metabolism of glucose and lipids [3]. Nevertheless, at higher levels, they are highly toxic and, in some cases, carcinogenic [4]. Therefore, it is significant to determine the heavy metal content of water samples.

The direct determination by atomic absorption spectrometry (AAS) could be difficult because of complex formation and significance of the matrices, and some metals are present at low concentrations, which are near to or below the limit of detection of the instrument [5]. Therefore, a previous preconcentration and separation step of analytes from the sample is necessary.

Preconcentration can solve these problems mentioned and simplify the determination. Many techniques are available for the preconcentration/separation of trace metal ions such as solvent extraction [6], coprecipitation [7], biosorption [8], ion

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exchange [9], cloud point extraction [10], electrodeposition [11], and solid-phase extraction (SPE) [12].

SPE is an effective and attractive preconcentration technique because of its simplicity, rapidity, high preconcentration factor (PF), and adequate recovery. Many solid materials have been used as sorbents for metal ions such as polyurethane foam (PUF) [13], activated carbon [14], polymeric resins [15], alumina [16], titanium dioxide [17], and silica gel (SG) [18].

Preconcentration of Cu and Zn was performed using SG modified with 8-hydroxyquinoline [19], 1-(2-thiazolylazo)-2-naphthol-SG [20], aminothioamidoanthraquinone [21], resacetophenone [22], 2-aminothiazole [23], pyrazole-3-carbaldehyde [24], p-dimethylaminobenzaldehyde [25], 2,3-dihydroxybenzaldehyde [26], 2,4-dichlorophenoxyacetic acid [27], and diacetylmonoxime (DMO) [28]. Manganese could be preconcentrated on SG modified with N-(3-propyl)-O-phenylenediamine [29], 3-Mercaptopropyl [30], and 3-aminopropyltriethoxysilane [31]. According to the work done by Sharma et al. [28], the SG functionalized with DMO proved an efficient and recyclable organic–inorganic hybrid sorbent for the selective removal of copper from fly ash ameliorated soil samples. This study investigates the employment of DMO-SG material as SPE sorbent for preconcentration/separation of Cu, Zn, and Mn from the river and tap water prior to flame AAS determination.

2. Experimental

2.1. Instrumentation

Unicam solaar 969 MKI flame atomic absorption spectrometer (Cambridge, England) equipped with hollow-cathode lamp adjusted to current and wavelength of 10 mA, 213.9 nm for copper, 5 mA, 324.8 nm for zinc, and 12 mA, 279.5 nm for manganese. The air-acetylene fuel was flowing at 145 mL s^{-1} and flame temperature ranging at 1,900–2,100˚C were employed. The calibration lines obtained are represented by the equations: $A = 0.084\ C + 0.0055$ ($R = 0.999$), $A = 0.162\ C + 0.02$ ($R = 0.997$), and $A = 0.053\ C + 0.0078$ ($R = 0.999$) for Cu, Zn, and Mn, respectively.

Vacuum pump model AP–0IP made by Tianjin science instrument Co. (Huashuo, China) was used for propelling the solution into the packed column. The pH measurements were carried out on WTW720 pH meter (Dover, Kent, UK) equipped with a combined glass electrode. Wrist action mechanical shaker model E175 obtained from Burrel (PA, USA) was used to shake the samples. Vario automatic elemental analyzer model EL(III) was used for C, H, N, and S analysis (Hanau, Germany). The FTIR spectra were recorded in rang 400–4,000 cm^{-1} using Nicolet FTIR spectrometer model 6700 manufactured by thermo scientific Co. (Massachusetts, USA). Shimadzu TGA analyzer model Rasha-50H was employed for TGA analysis using platinum cell and nitrogen atmosphere at rate flow of 30 mL min^{-1}. Surface area measurement was made by Digi-Sorb analyzer model 2600 manufactured by Micromeritics (Norcross, USA) via single and multipoint methods using Nova software.

2.2. Chemicals and reagents

Unless otherwise stated, all reagents used were of analytical reagent grade. Laboratory glassware was cleaned by soaking in concentrated sulfuric acid, washed with double distilled water (DDW), and then kept in drying in oven. Mineral acids, including nitric, sulfuric, and hydrochloric, were of supra pure quality and used as procured from Merck (Darmstadt, Germany). SG (200–300 mesh) was purchased from Merck (Germany). Diacetyl monoxime (DMO) reagent of 99% purity was obtained from Puro Erba (Milano, Italy). Standard solutions of metal ion with concentration of 1,000 mg L^{-1} were prepared by dissolving an appropriate amount from $CuSO_4{\cdot}5H_2O$ (Adwic, El-Nasr Co., Egypt), $ZnSO_4$ (Merck), or $MnSO_4{\cdot}4H_2O$ (Adwic) in DDW, then acidified by adding about 1 mL concentrated nitric acid in order to prevent the formation of metal hydroxides, and then completed to the mark with DDW. A working solution with concentration of 10 μg mL^{-1} was freshly prepared by diluting from the standard solution.

2.3. Synthesis of DMO-SG sorbent

The DMO-SG sorbent was synthesized following the previously reported method [28].

The SG surface was activated to free the silanol OH groups and to remove any adsorbed metal ions by refluxing in 6 mol L^{-1} hydrochloric acid for 8 h. Then, it was filtered and repeatedly washed with DDW until the filtrate was neutral and then dried in an oven at 150˚C for 10 h to remove surface-adsorbed water. A 3.0 g of activated SG was placed in a 100-mL capacity quiet fitted flask, suspended in 30 mL of dried toluene, and refluxed under mechanical stirring for 2 h. Then, a 10 mL from aminopropyltrimethoxysilane (APTMS) was added dropwise and continued refluxing for 24 h. The resulted aminopropyl silica (APTMS-SG) was filtered, washed with ethanol, and dried in vacuum at room temperature.

To attach DMO, a 3.0 g from APTMS-SG was suspended in 50 mL dried toluene and 0.5 g from

DMO was added. The mixture was heated at 100°C for 6 h under vigorous stirring. After cooling, the resulted yellow-colored DMO-SG powder was filtered off, washed with dry toluene followed by methanol, and then left to dry and stored in the dark for further use.

2.4. Procedures

2.4.1. Batch procedure

The batch procedure was used to investigate optimum conditions for sorption and desorption of individual metal ions. Influence of sample pH, shaking time, and interfering by diverse ions were examined. A 10 mL model solution containing Cu(II), Zn(II), or Mn(II) each at a concentration of 2.0 μg mL^{-1} was prepared. The solution was shaken with 0.1 g of DMO-SG sorbent for 1.0 h at room temperature. After extraction of metal ions, the sorbent was filtrated through Whatman filter paper no. 1. The metal ions were desorbed from the sorbent by shaking with 10 mL of 0.3 mol L^{-1} hydrochloric acid solution. The sorbent was filtered off, and the metal ions in the filtrate were determined by a pre-standardized FAAS. Sample pH was examined in the range 3–8, and shaking time was tested at 5, 10, 15, 25, and 30 min. Sorption capacity was studied by shaking 0.1 g sorbent with 10 mL solution contains each metal ion concentration in the range 5–800 μg L^{-1}.

2.4.2. Column procedure

In column experiments, a 300 mg from DMO-SG sorbent was packed between two frits disks in polypropylene tube (5 cm length and 0.75 cm diameter). A solution containing metal ion at a concentration of 0.5 μg mL^{-1} was adjusted to pH 6.0 and percolated at a flow rate of 2.0 mL min^{-1} controlled by vacuum pump. The retained metal ions in the column were eluted with 5 mL of 0.3 mol L^{-1} hydrochloric acid and determined by FAAS. Preconcentration of metal ions was performed using solution containing varying concentrations of metal ion in the range 5.0–50 μg L^{-1} at pH 6.0. The solution was passed through the DMO-SG at a fixed flow rate of 2.0 ml min^{-1}. The sorbed metal ions were eluted, and the recovered amount was measured by FAAS.

2.5. Collection and preparation of water samples

Two water samples were subjected to analysis by the developed procedure. Tap water sample was collected from our research laboratory at the chemistry department in Ain shams University (Cairo City). River water was collected from Nile River in Cairo.

The samples were filtered to remove any suspended particulates, adjusted to pH 6.0 with a 0.01 mol L^{-1} nitric acid, and immediately analyzed by passing 100 mL sample through the column at a flow rate of 2.0 mL min^{-1}. The retained metal ions were eluted by 5 mL from 0.3 mol L^{-1} hydrochloric acid solution then measured by FAAS.

Accuracy of the method was evaluated by spiking 5.0 μg each metal ion into 100 mL water sample (4 replicates) and then percolated throughout the column under the recommended conditions.

3. Results and discussion

3.1. Characterization of DMO-SG

The IR spectra of APTMS-SG precursor and DMO-SG are compared in Fig. 1 In the spectrum of DMO-SG, a new and distinct peak appeared at 1,647 cm^{-1} and assigned for the symmetric stretching vibrations of C=N group formed via reaction between NH$_2$ groups in the precursor and C=O groups in DMO. Also, a characteristic band appeared at 1,727 cm^{-1} characteristic for C=O groups in the attached DMO ligand. The stretching vibrations of N–H in APTMS-SG and O–H in DMO were overlapped in the range of 2,927.8–3,728.8 cm^{-1} of DMO-SG. In the spectrum of APTMS-SG, an absorption band has appeared at 1,541 cm^{-1} which is characteristic of primary amino groups in aminopropyl moiety. Two new bands have appeared at 2,927.8 and 2,361.4 cm^{-1} corresponded to the typical symmetric and the asymmetric stretching vibration of –CH$_2$–. Finally, an intense band related to Si–O–Si stretching vibration was observed at 1,088.7 cm^{-1}.

Elemental analysis was carried out in order to determine C, H, and N contents in the precursor APTMS-SG and DMO-SG materials. The proportions of C, H, and N were found to be 4.1, 1.1, and 0.98%, respectively, in case of APTMS-SG and were 5.1, 1.5, and 1.3% for DMO-SG. Results showed an increase in C, H, and N content by incorporation of DMO ligand indicating the increase in organic moieties. Moreover, the nitrogen content increased by an amount of 0.32%, which confirmed the attachment of NH$_2$ group in APTMS-SG has occurred mainly via C=O group in DMO ligand rather than oxime OH. Also, the data indicated that one DMO molecule was attached to the average empirical formula of APTMS-SG as presented in Fig. 2.

Hence, the number of moles of anchored DMO could be calculated from the increased nitrogen

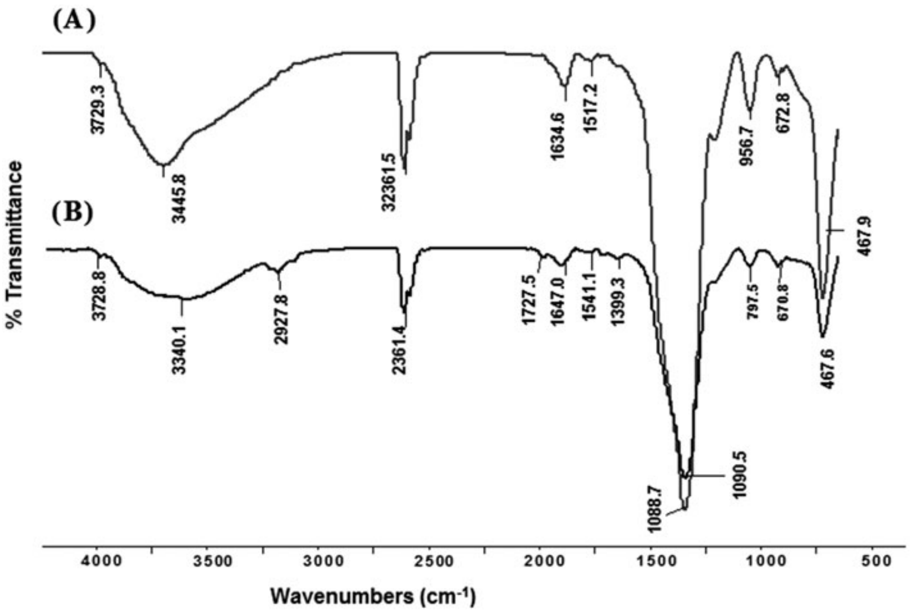

Fig. 1. FTIR spectra of the precursor APTMS-SG (A) and DMO-SG (B) materials.

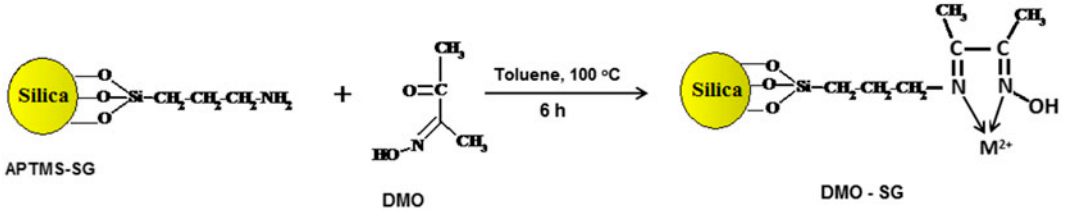

Fig. 2. Schematic diagram for the synthesis of DMO-SG from aminated SG precursor.

content since it is equivalent to the attached DMO. It was found to be 2.29 mmol g^{-1} of DMO.

Furthermore, the structure proposed for attachment of metal ions to the DMO ligand is consistent with data obtained from the IR spectrum of Cu adsorbed on DMO-SG. Results indicated no change in the broadband corresponding to OH. Thus, the site arising from the oxime, oxygen atom is not involved in complexation of metal ions. The two sites available for the complexation of metal ions are the two nitrogen atoms in a five-membered mononuclear ring as depicted in Fig. 2.

The TGA curves of the APTMS-SG and DMO-SG materials are shown in Fig. 3. The TGA for APTMS-SG showed two regions of weight loss. The first mass loss was located within a temperature range of 21–150℃. This could be due to the loss of remaining absorbed water. The second mass change was around 250–550℃ with 5.0% weight loss corresponding to the aminopropyl groups. The DMO-SG material showed also two stages of weight loss. The beginning phase was kept similar to APTMS-SG profile with mass loss of 4%. A second weight loss of 8.4% was around 220–670℃ corresponding to molecular formula of $C_7H_{13}N_2O$ equivalent to 141 g mol^{-1} which could be due to all attached organic groups including both of aminopropyl and DMO moieties.

Surface area of the sorbent was determined by the Brunauer–Emmett–Teller (BET) method of nitrogen adsorption at low temperature of 77.3 K. The maximum BET surface area was found to be 455.3 and 320.7 m^2 g^{-1} for SG and DMO-SG, respectively. The decrease in specific surface area in DMO-SG might be attributed to covalent bonding of DMO ligand, indicating part of the surface was occupied by the added groups to SG surface. Pore volume and pore diameter for DMO-SG were found to be 0.794 cm^3 g^{-1} and 56.8 Å, respectively.

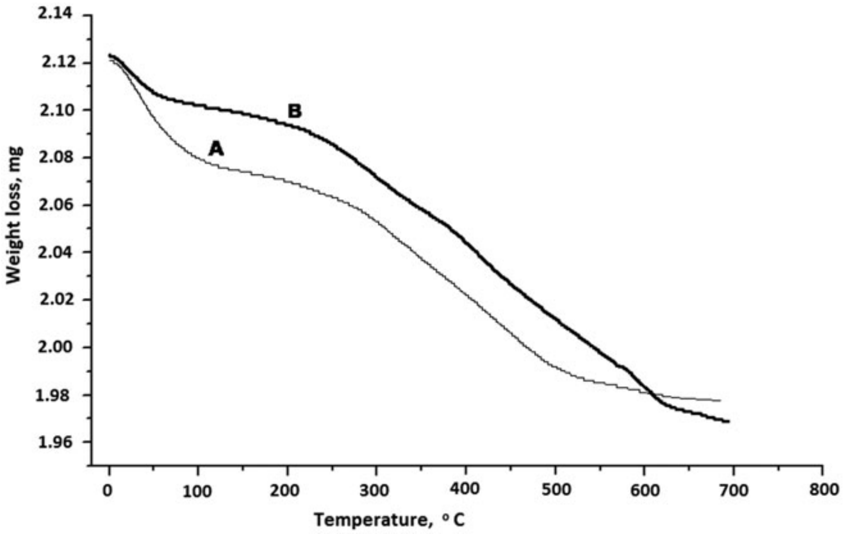

Fig. 3. TGA curves for APTMS-SG (A) and DMO-SG (B) phases.

3.2. Batch study

The sorption properties of the tested metal ions onto DMO-SG were investigated in the pH range 3–8 using 10 mL sample at a concentration of 2.0 μg mL^{-1}. Sorption of these metal ions varied significantly with pH change where it increased by raising pH from 3 to 5 and reached maximum sorption at pH 6 by a value of 90, 100, and 85% for Cu, Zn, and Mn, respectively. The cause for the increase in sorption with rising pH could be due to less protonation of the chelating groups by H^+ which enhances bonding, and thereby sorption of metal ions. At lower pH values than 3, the extent of sorption was not significant which might be attributed to partial protonation of active groups and competition of H^+ with metal ions for sorption sites on DMO-SG. At pH > 8, the sorption (%) decreased due to possible precipitation of metal hydroxides. Therefore, the pH 6.0 was selected as the optimum value for separation and preconcentration. Also, data confirmed greater affinity of sorbent to Zn^{2+} than Cu^{2+}, whereas Mn^{2+} exhibited the least sorption accessibility (Fig. 4).

The sorption kinetics of the metal ions were investigated at various shaking periods. For this purpose, a 100 mg from the sorbent was mixed with 10 mL of solution containing metal ion at a concentration of 2.0 μg mL^{-1} and pH 6.0. The samples were shaken at room temperature between 5 and 30 min, and the obtained results are presented in Fig. 5. The sorption was initially rapid and equilibration condition was attained after shaking time of 20 min for all elements. Maximum sorption followed the order $Zn^{2+} > Cu^{2+} > Mn^{2+}$ like those obtained in pH study.

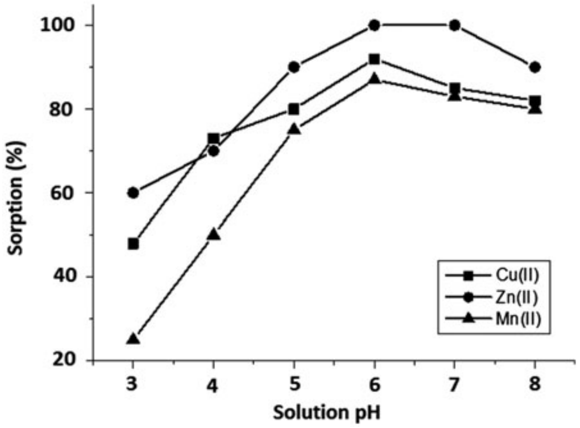

Fig. 4. Influence of solution pH on the recovery of Cu, Zn, and Mn at concentration of 2.0 μg mL^{-1}, sample volume of 10 mL, and 0.1 g of DMO-SG sorbent.

To investigate the mechanism of adsorption kinetics, three different kinetic models were tested to fit experimental data obtained. Firstly, the pseudo-first-order rate equation of Lagergren and Kungliga [32] given by Eq. (1) was applied:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{1}$$

where q_e and q_t are the amounts of metal ion adsorbed at equilibrium and at any time t (μg g^{-1}), respectively, k_1 is the first-order rate constant at the equilibrium (min^{-1}).

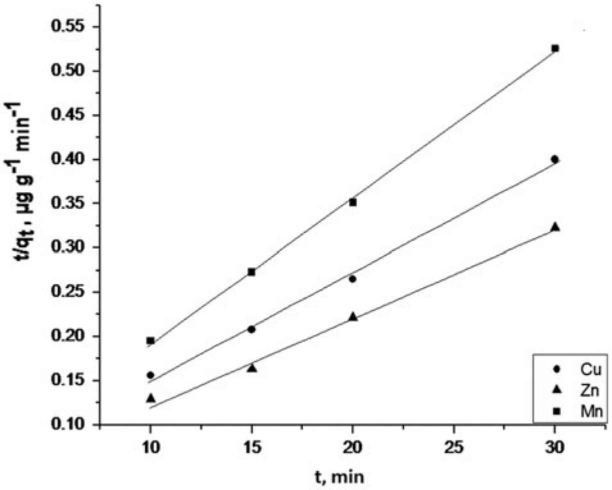

Fig. 5. Pseudo-second-order kinetic model for sorption of the studied metal ions onto DMO-SG sorbent at concentration 0.5 μg mL^{-1}, pH 6, 10 mL volume of sample, weight of sorbent 0.1 g and temperature 25°C.

Secondly, assuming that the sorption capacity is proportional to the number of active sites on DMO-SG surface, the pseudo-second-order rate equation developed by Ho and McKay [39] represented by the Eq. (2) was examined:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2}$$

where k_2 is the second-order rate constant at equilibrium with dimension of g μg^{-1} min^{-1}

Finally, the intra-particle diffusion rate [33] can be described by the Morris–Weber Eq. (3). Where k_{id} is the intra-particle diffusion constant (μg^{-1} g $min^{-1/2}$).

$$q_t = k_{id} t^{0.5} \tag{3}$$

The pseudo-second-order model has revealed good agreement between the calculated and experimental q_e values (Fig. 5). Furthermore, the obtained correlation coefficients (R^2) were comparatively higher for pseudo-second-order than pseudo-first-order or intra-particle diffusion models. Grounded on the above information, the high accuracy with pseudo-second-order kinetic model indicates that the sorption takes place mainly via chemical interactions by exchange or sharing of electron between metal ions and active websites in the immobilized ligand. Comparison of the calculated kinetic parameters is given in Table 1.

Nevertheless, the rate determining step is rather described by the intra-particle diffusion model assuming involvement of mass transfer.

Extraction isotherm for sorption of metal ions is shown in Fig. 6. Results indicated an increment in the sorbed amount with increasing concentration of metal ions and reached maximum sorption at a concentration of 25, 10, and 15 μg mL^{-1} for Cu, Zn, and Mn, respectively. Total capacity was found to be 422, 533, and 346 μg g^{-1}, respectively.

The Langmuir model is represented by Eq. (4). It is the most widely used as representative of monolayer adsorption occurring on an energetically uniform surface at which the adsorbed molecules are non interactive:

$$C_e/q_e = 1/K_L q_m + C_e/q_m \tag{4}$$

where q_e, q_m, and C_e represent the sorbed amount of metal ion at any time t (μg g^{-1}), maximum sorbed amount (μg g^{-1}), and equilibrium concentration (μg L^{-1}), respectively. Langmuir constant b is related to the affinity of sorption sites.

Freundlich model is an empirical equation used to estimate the sorption intensity of the sorbent toward the sorbate ions. It can be interpreted by a linear Eq. (5):

$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{5}$$

where K_F and n are constants which indicate the affinity of the sorbate.

The calculated constants are given in Table 2. Comparing the isotherm results revealed that the sorption of these elements to DMO-SG was well correlated to experimental data ($R > 0.989$) with the Freundlich model than Langmuir one. Freundlich constant n was found ≥1.1 which revealed good affinity of metal ions to the anchored active sites in the DMO ligand. Moreover, calculated values of maximum sorption capacity (q_m) from the Langmuir model were extremely higher than that obtained from experimental values of sorption capacity (q_{max}).

3.3. Column study

The sample flow rate can affect the retention of metal ions onto the sorbent; thus, it was investigated in the range of 0.5–5 mL min^{-1}. No effect on the sorption was observed up to 2.0 mL min^{-1}. At higher flow rates than 2.0 mL min^{-1}, the sorption was decreased due to less contact time between metal ions and sorbent. Ultimately, a sample flow rate of 2.0 mL min^{-1} was selected as the value for further experiments.

Table 1
Kinetic data obtained from pseudo-first-order and second-order models at 25˚C

		Pseudo-first order			Pseudo-second order			Intra-particle diffusion	
Metal ion	q_{exp} (μg g^{-1})	q_e (μg g^{-1})	K_1 (min^{-1})	R^2	q_e (μg g^{-1})	K_2 (μg g^{-1} min^{-1})	R^2	k_i (μg g^{-1} min$^{-1/2}$)	R^2
Cu(II)	75.4	283.1	0.308	0.996	81.4	0.006	0.998	29.1	0.905
Zn(II)	92.0	672.9	0.419	0.984	99.5	0.005	0.993	29.0	0.908
Mn(II)	57.0	80.9	0.251	0.995	60.3	0.001	0.999	10.9	0.927

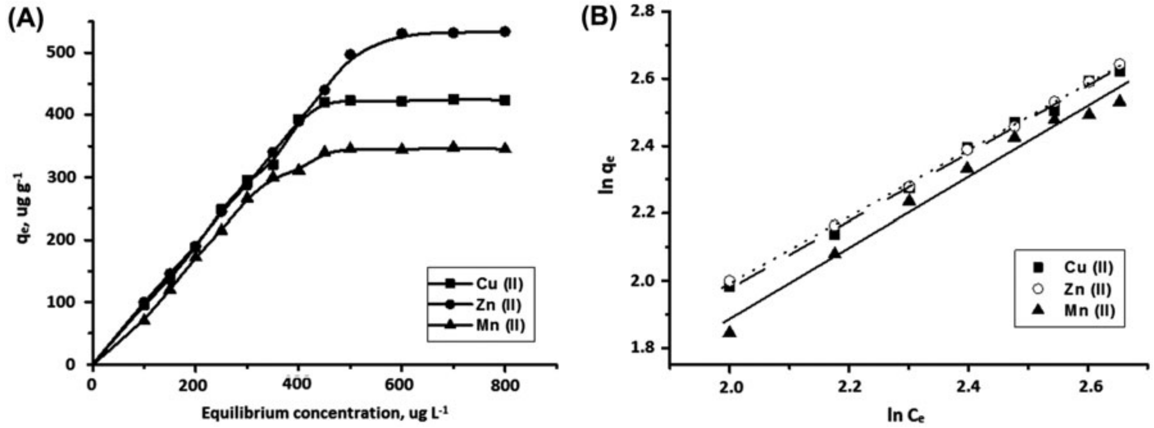

Fig. 6. Extraction isotherm (A) and Freundlich (B) model for sorption of Cu, Zn, and Mn onto DMO-SG.

Table 2
Isotherm parameters obtained from Langmuir and Freundlich models

		Langmuir parameters		Freundlich parameters		
Metal ion	$q_{max(exp)}$ (μg g^{-1})	q_{max} (μg g^{-1})	R^2	n	K (L g^{-1})	R
Cu(II)	422	893	0.974	1.6	0.98	0.998
Zn(II)	533	507	0.979	2.1	1.3	0.989
Mn(II)	346	387	0.949	1.1	0.8	0.991

Desorption of metal ions was studied by several solutions, viz. HCl, HNO_3, CH_3COONa, and $Na_2S_2O_3$. Quantitative recovery (≥95%) was achieved with hydrochloric acid at concentration of 0.3 mol L^{-1}. Other eluents resulted in a maximum recovery of 79, 60, and 49% for HNO_3, CH_3COOH, and $Na_2S_2O_3$, respectively, at a concentration of 0.10 mol L^{-1}. Therefore, a 0.3 mol L^{-1} hydrochloric acid solution was recommended as an eluent in all subsequent experiments.

Eluent volume was studied in the range 2.5–14 mL. Recovery increased as the volume increased in the range 2.5–12 mL but it became quantitative when the volume was ≥5.0 mL. Thus, a 5 mL volume of 0.3 mol L^{-1} hydrochloric acid solution was used in further experiments. Furthermore, the desorption flow rate was estimated to be 2.0 mL min^{-1}.

Preconcentration of metal ions was investigated using varying sample volumes between 100 and 1,000 ml containing a perpetual quantity of metal ion of 5.0 μg. Each sample was run through the column under the recommended sorption conditions. Quantitative recovery (>95%) was obtained up to sample volumes of 500, 550, and 250 mL with corresponding recovery of 96, 98, and 94% for Cu, Zn, and Mn, respectively. At exceeding volumes, the recovery was gradually decreased, which might be due to leaching of the bounded elements by the washing action of the sample. Therefore, sample volume was adopted not to exceed these estimated volumes for the preconcentration of analytes. The PF was calculated to be 100, 105, and 50, respectively.

3.4. Selectivity

Sorption of the studied metal ions was investigated in the presence of various foreign ions that are naturally existing or might interfere with studied metal ions such as Na^+ (10,000 mg L^{-1}), K^+ (1,000 mg L^{-1}), Ca^{2+} (100 mg L^{-1}), Mg^{2+} (100 mg L^{-1}), Fe^{3+} (0.5 mg L^{-1}), Co^{2+} (0.1 mg L^{-1}), Ni^{2+} (0.1 mg L^{-1}), Pb^{2+} (0.05 mg L^{-1}), Cl^- (1,000 mg L^{-1}), SO_4^{2-} (100 mg L^{-1}), PO_4^{3-} (50 mg L^{-1}), NO_3^- (100 mg L^{-1}), and Oxalate (50 mg L^{-1}).

For studying the matrix effect, a 20 ml aliquot of individual interfering ion solution was prepared at specified concentration above, spiked with the target metal ion at a concentration of 2.0 μg L^{-1}, and shaken for 1 h with 0.1 g sorbent. The amount extracted and remained of metal ion was determined with FAAS.

Selectivity of DMO-SG toward these metal ions could be evaluated from the determination of both distribution coefficients (K_d) as well as the separation factor (α). Good discrimination order among these elements of concentration in the μg L^{-1} range could be achieved by providing a series of K_d values. This would assist further evaluation of tendency for the metal ion sorption as well as the selectivity incorporated into DMO-SG. The distribution coefficient K_d is calculated from Eq. (6):

$$K_d = C_{ex}/C_{sol} \tag{6}$$

where C_{ex} and C_{sol} are the amount (μg g^{-1}) of extracted and remained metal ion, respectively.

Maximum K_d values in the range 720–450 were obtained for Cu(II) with Ca^{2+}, Co^{2+}, and SO_4^{2-}, followed by Zn(II) in the range 430–120 with Cl^-, Co^{2+}, Fe^{3+}, Na^+, oxalate. The lowest K_d values were obtained for Mn(II) in the range 330–75 with alkali metals Na and K. Thus, it is evident that DMO-SG attained the maximum selectivity toward Cu(II).

The separation factor (α) of any two metal ions A and B can be computed from the values of their distribution coefficients K_d (A) and Kd (B), respectively, according to Eq. (7):

$$\alpha_{(A/B)} = K_d(A)/K_d(B) \tag{7}$$

The obtained values of α as a function of added foreign ion are presented in Fig. 7. The DMO-SG sorbent showed high selectivity for Cu(II) as implied from the high values of α in the range 0.87–1.1. Lower selectivity was observed for zinc with α value in the range 0.65–0.80. Manganese attained the least selectivity where α takes the values between 0.62 and 0.70.

Finally, the developed sorbent conveyed a relevant selectivity, thus enabling successful separation of these elements from most foreign ions which might exist in real samples.

3.5. Figure of merit

Stability and potential regeneration of DMO-SG column were evaluated. Good stability in recovery after 15 repeated cycles of sorption and desorption was evaluated. Recovery was found in the range 95–97% and the corresponding RSD % varied from 3.4 to 4.7%.

Accuracy of the developed method was assessed using certified atomic absorption standard solutions (Merck). Added found test was employed to synthetic samples containing individual metal ion at a concentration of 0.5 μg mL^{-1}. The standard solution was passed through the DMO-SG column under the optimized preconcentration conditions. Quantitative recovery was obtained ranging from 95 to 97% with corresponding RSD values between 2.8 and 4.2%. Therefore, the proposed method is extensively efficient for analytical determination of these elements at low concentrations.

The DMO-SG method afforded linear analytical curves within a concentration range of 0.1–10 μgL^{-1}. The obtained regression equations are as follows: $A = 0.60175 + 0.42064$ [Cu(II), μg L^{-1}], $A = 0.96403 + 0.34014$ [Zn(II), μg L^{-1}], and $A = 0.12493 + 0.14301$ [Mn(II), μg L^{-1}] with corresponding correlation coefficient (R) of 0.982, 0.992, and 0.993, respectively. Limits of detection (LOD) and quantification (LOQ) were set based on $S/N = 3$ and $S/N = 10$, respectively, where S/N represents signal-to-noise ratio. LOD was found to be 0.10, 0.11, and 0.12 μg L^{-1}, respectively, and LOQ was found to be 0.16, 0.18, and 0.31 μg L^{-1}, respectively.

3.6. Analysis of water samples

The applicability of the proposed DMO-SG method to real samples was emphasized via determination of Cu(II), Zn(II), and Mn(II) in tap and river water samples. The obtained data are compiled in Table 3. Recovery varied from 94 to 98% for tap water and from 92 to 102% for river water. Value for RSD was found in the range 2.6–7.4% and 2.8–6.2% for tap water and river water, respectively. Evidently, the

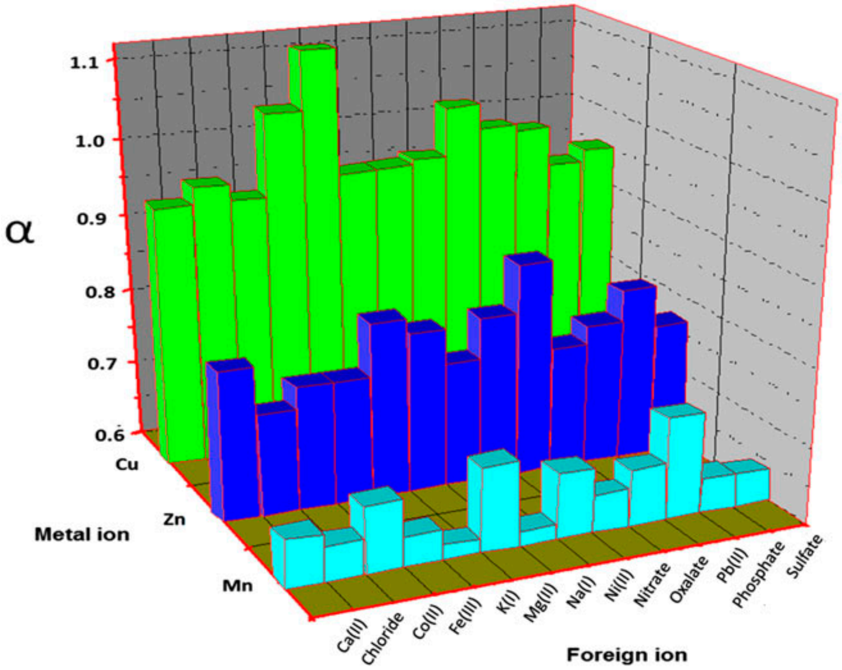

Fig. 7. Variation of separation factor (α) of Zn, Cu, and Mn on DMO-SG sorbent at pH 6.

recovery values are remarkably high confirming good selectivity of the proposed sorbent toward the studied metal ions. The obtained RSD values being less than 10% indicate that the developed method is satisfactory precise.

Therefore, the proposed method is considered reliable and accurate based on the obtained RSD as well as relative error data. This confirmed good validity of the proposed method for the preconcentration and determination of the investigated metal ions in water samples.

3.7. Comparison to other sorbents

Comparison of sorption capacity and PF of DMO-SG method with those of other modified SG sorbents is represented in Table 4. The DMO-SG showed a comparable capacity level to several reported sorbents, especially for zinc and copper data. Likewise, the PF was found corresponding to several reported methods nevertheless it is lower than some others. However, the developed procedure provides an alternative method for determination of these elements with sufficient accuracy and precision.

Table 3
Analysis of water samples (100 mL) by the developed DMO-SG procedure

Sample	Metal ion	Spike (μg)	Found (μg)[a]	Recovery (%)	RSD (%)
Tap water	Cu(II)	0.0	0.95 ± 0.06	98	6.3
		5.0	5.87 ± 1.5		2.6
	Zn(II)	0.0	7.50 ± 0.24	96	3.2
		5.0	12.30 ± 0.50		4.1
	Mn(II)	0.0	6.1 ± 0.45	94	7.4
		5.0	10.8 ± 0.6		5.6
River water	Cu(II)	0.0	3.50 ± 0.10	102	2.8
		5.0	8.60 ± 0.30		3.5
	Zn(II)	0.0	31.3 ± 1.50	92	4.8
		5.0	35.90 ± 2.20		6.2
	Mn(II)	0.0	5.50 ± 0.25	94	4.5
		5.0	10.20 ± 0.40		3.9

[a] Mean value ± standard deviation of four replicate measurements ($n = 4$).

Table 4
Comparison of sorption capacity and PF to other modified silica sorbents

	Sorption capacity (μmol g^{-1})			PF				
Immobilized ligand	Cu	Zn	Mn	Cu	Zn	Mn	RSD(%)	Refs.
DMO	5.1	8.2	6.3	100	105	50	2.6–7.4	This work
Resacetophenone	186.4	191.4	–	250	150	–	2.2–7.7	[22]
p-dimethylaminobenzaldehyde	400	560	–	125	125	–	5.0	[25]
Amidoamidoxime	16.3	–	–	20	–	–	<4	[34]
2,4,6-trimorpholino-1,3,5-triazin	–	8.1	–	–	50	–	<3	[35]
Salicylic acid	633	–	–	200	–	–	0.2–10.7	[36]
2-(3-silylpropylimino)methyl phenol	–	–	–	28.2	28.2	–	<4	[37]
1-(2-pyridylazo)-2-naphthol	–	71.5	24.2	–	50	50		[38]

4. Conclusions

The purpose of the current work is to measure the concentration of Cu, Zn, and Mn in Nile river and tap waters using SPE and flame AAS. The DMO-SG sorbent was employed for preconcentration of these elements to remove matrices and adjust the sample to the detection limit for the AAS instrument. Several preconcentration/elution cycles could be done using the same column was performed at pH 6.0 without loss of sorption capacity. The analytical figures of merit make the method a very useful tool for the reliable determination of Zn(II), Cu(II), and Mn(II) in water samples mainly with high detectability. The findings showed uniform dispersion of the legend in SG matrix, therefore improving efficiency of the proposed analytical procedure as well as doing away with noise in complex matrices.

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