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Preconcentration and separation of some heavy metal ions by solid-phase extraction using silica modified with zirconium phosphate

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An analytical method was developed for the separation and preconcentration of Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} from surface water samples collected from ten locations at Suez Gulf, using silica gel chemically modified with zirconium (IV) phosphate. The effects of pH value, time of stirring, concentration of eluting acids and some common ionic species on the separation and preconcentration of the investigated metal ions in synthetic aqueous solutions were firstly studied. The results indicate that the optimum conditions for separation are pH = 5.0- 5.5 and time of stirring = 30 min. HNO_3 is better eluent for the investigated metal ions than HCl hence 2M HNO_3 was used as an eluent. Citrate and EDTA severely affect on the recovery of the metal ions therefore the water samples were previously oxidized to digest organic matter prior to the application process.

Key words: Separation, preconcentration, modified silica, metals, water.

INTRODUCTION

Metals differ from other toxic substances in that they are neither created nor destroyed by human. The pollution levels of the aquatic environmental by heavy metals can be estimated by analyzing water, sediment and marine organisms after a prerequisite separation and/or precon-centration step (Hamed et al., 2006). In recent years, solvent extraction and coprecipitation have been increasingly replaced by solid phase extraction (SPE). It has been extensively studied for different analytical application (Hamed, 2006). Advantages of silica as a base for chelating agents to be used as an ion sorbent, over the organic polymers, are its good mechanical and thermal stability, and it is less susceptible to swelling, shrinking and microbial and radiation decay (Lashein, 2005). The use of chelating agents, immobilized on silica, is a promising route for its efficiency and selectivity of extraction. 8-Quiolinol immobilized on silica gel (Obata et al., 1993). 3-(trimethoxysilyl)-1-ropanethiol modified silica gel (Köklü et al., 1995) and diethylenetriamine with

salicylaldehyde and naphthaldehyde immobilized on silica gel (Soliman et al., 2001) were used to separate trace amounts of heavy metal ions from their parent solutions. It was found that the efficiency of the separa-tion depends on the concentration of the metal ion, the nature of the extractant and its surface area, temperature and the stability of the formed chelate. Synthesis of chemically-modified porous silica with Zirconium phosphate as chelating agent (denoted SZP) was described in material and methods. The nature of bonding of IE with some metal ions was investigated by elemental analysis, infrared spectra and thermal analysis (Lopez et al., 1996). According to the importance of metals to the aquatic environs, it may be divided into three groups i) light metals such as sodium, potassium and calcium which are normally mobile cations in aqueous solution; ii) transitional metals such as iron, copper, cobalt and manganese which may be toxic in high concentrations and iii) heavy metals and metalloids such as mercury, lead, cadmium, tin, selenium and arsenic which are generally not required for metabolic activities and are toxic to the cell at quite low concentrations (Abou-El-Sherbini et al., 2003b).

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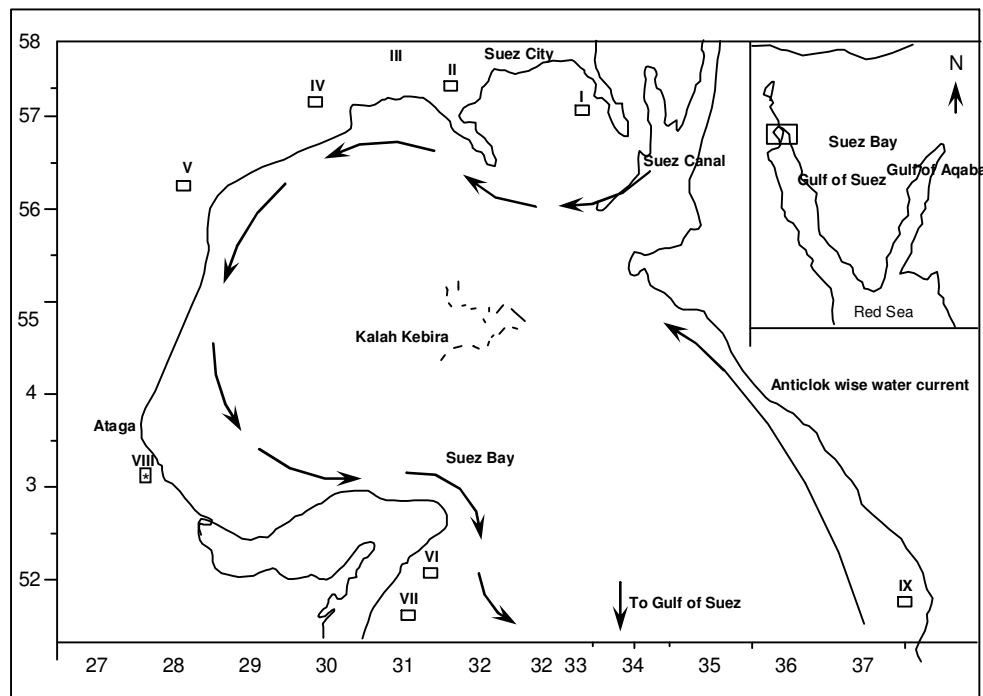
Figure 1. I) Summer Balas Hotel beach. II) Zaitiya. III) El-Kabanon beach. IV) Power Planned Station. V) National Institute of Oceanography and Fisheries (NIOF). VI) Ain Sokhna. VII) Sand Beach.   VIII) North of the Adabyia Harbour. IX) Uyun Mousa. X) Ras Sudr

Due to the interest of water quality, many studies had been performed on the water sources to estimate the levels of heavy metals periodically (Fifield and Haines 2000). The factors controlling and influencing the metal uptake capacity such as pH of solution and stirring time were determined to discuss the performance towards extraction of Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} (Hamed, 2004). As continuation, the present paper is aimed to study the uptake behavior of SZP towards Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} to suggest the optimum conditions for the separation, preconcentration and determination of these metal ions in aquatic environs.

MATERIALS AND METHODS

Area of study

The Suez Gulf extends for about 250 km South-Southeast from the Suez port in the north (lat. 29° 56') to Shadwan island in South (latutude 27° 36'). The width of the Gulf varies between 20 and 40 km, and its depth, throughout its axis is fairly constant with a mean of 45 m (El-Sabh and Beltagy, 1983) Depth increases abruptly to about 250 m, at its mouth (Meshal, 1970).

Sampling stations

Samples were collected from ten stations along the northern part of the Gulf of Suez (Suez Bay) (Figure 1). Station (1): Summer Palace Hotel beach (west of Port Tawific Harbour), Station (2): El-Zeitiya, Station (3): El-Kabanon beach. Station (4): Suez Thermal Power

Station beach. Station (5): Beach of National Institute of Oceanography and Fisheries. Station (6): El-Sukhna. Station (7): Sand Beach. Station (8): North of the Adabyia Harbour, Station (9): Aeon Musa and Station (10): Ras Sudr.

Experimental

Synthesis

The ion sorbent (SZP) was prepared as follow: $56.4 \ cm^3$ of water glass (sodium silicate, 36%) was diluted to one liter with double distilled water (DDW), and neutralized by adding HCl acid drop with drop with vigorous stirring to pH=1. The formed gel was crushed and aged for 1 day. Then, the gel was washed with DDW to remove the formed NaCl and excess acid by decantation till pH > 5 then 0.09, 1.0, 2.0 or 4.0 g $ZrOCl_2.8H_2O$ (Merck) dissolved in minimum amount of DDW was thoroughly mixed. Then the mixture was dried in a water bath to get xero gel which was further dried at 200°C for 2 h then, the sample was cooled and 100 ml H_2O was added. Then 0.03, 0.37, 0.74 or 1.49 cm^3 H_3PO_4 (98%) was added, respectively. The samples were stirred for 60 min, dried at 120°C and annealed at 150, 300 or 400°C for 5 h.

Optimum conditions of the ion sorbent (SZP)

A 0.02 g of SZP was added to 25 cm^3 of 10 µg/cm^3 of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+} (as nitrate) and the pH values of the solutions were adjusted in the range 5-5.5 using 2M NaOH and 0.1M HNO_3 was used instead. Then the solutions were stirred at constant rate for 30 min., filtered and the concentrations of the investigated ions in the filtrates were determined by AAS. After adjusting the pH of the solution at 5.0-5.5 to give maximum K_d
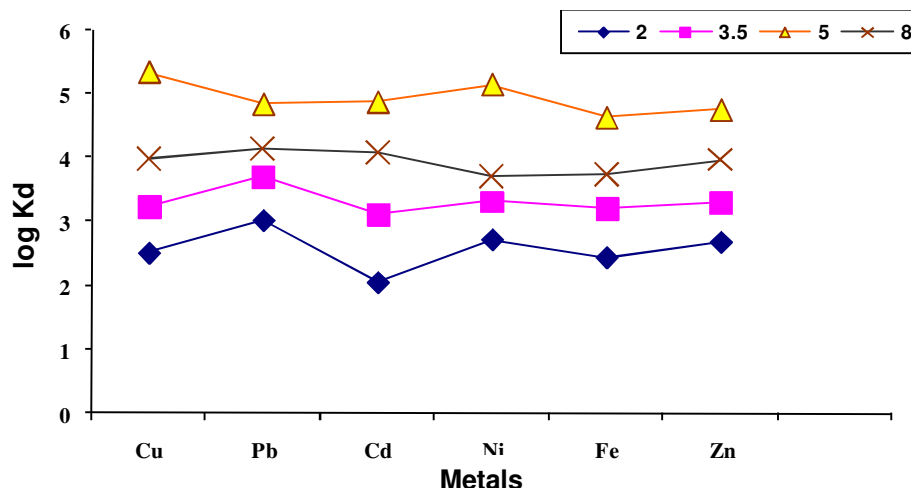
Figure 2. Effect of pH on the logarithmic values of distribution coefficient; log K_d of the preconcentration of heavy metal ions on the modified silica gel as ion sorbent.

stirring time and effect of weight of ion sorbent was studied to obtain optimum time of stirring and weight of ion sorbent for preconcentration and separation of the investigated metal ions. Then these optimum conditions (pH= 5.0-5.5, time of stirring= 30 min., and weight of SZP= 100mg) were applied during the study of the interfering effects of the different foreign ions on the efficiency of separation and the effect of concentration of the eluent acids (10 cm^3 of HCl or HNO$_3$) on the recovery. The distribution coefficient (K_d) is determined using the equation: (Helfferich, 1962; Korkisch, 1969).

$$K_d = C_{iex\,(mg/g)}/C_{sol\,(mg/cm3)} \qquad cm^3/g \qquad (1)$$

Where C_{iex} is the metal concentration in the ion sorbent (solid phase) and C_{sol} is the metal ion concentration in the solution phase. For the capacity determination, 100mg of the ion sorbent was added to 100 cm^3 of 100 μg/cm^3 of Cu and stirred for 24 h, at pH 5.0-5.5. The decrease in the metal concentration was determined by AAS and accordingly the capacity is calculated by the equation: 63.55

$$Capacity= \frac{(100 - C_{sol}(\frac{\mu g}{cm^3}))/63.55}{} \qquad (2)$$

Where C_{sol} is the concentration of the solution after extraction.

Application

100 mg of ion sorbent was added to 10 dm^3 of the sample and the pH value was adjusted to 5.0 - 5.5 and stirred for 30 min then the sample was filtered. To the filtrate another 50 mg of the ion sorbent was added and pH value was again controlled. The sample was stirred again for 30 min. and filtered. Both residue were gathered and the collected metal ions were released by 10 cm^3 2 M HNO$_3$ to give a concentration factor of 100 fold.

Equipment

The absorption measurements were made with a Perkin Elmer

model A-Analyst 100, equipped with hollow cathode lamps for copper, zinc, lead, cadmium, nickel and iron, portable digital Orion pH meter, model 230A, was used and also IR spectrum model (Perkin Elmer, 1430) was used for the identification of prepared compound.

RESULTS AND DISCUSSION

Optimization of separation conditions of some metal ions, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+}

Best stability against hydrolysis and capacity towards Cu^{2+} (1.09 mmole/g) was found for ion sorbent SZP functionalized with 1.0 g ZrOCl$_2$.8H$_2$O, 0.37 cm^3 H$_3$PO$_4$ and annealed at 400°C. Hence, the optimum conditions of separation of Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} were studied on SZP synthesized at these conditions.

Effect of pH

Figure 2 represents the effect of pH on the uptake behavior of Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} on SZP. The distribution coefficient of these metals on SZP increases with pH and reaches a maximum value at pH = 5.0 - 5.5. The decrease in the distribution coefficient at pH>7 is attributed to the hydrolysis of the silica based ion sorbents (Hamed et al., 2006). The order of decreasing the efficiency of separation at the pH 5.0 - 5.5 is arranged as follows: Cu^{2+} > Ni^{2+} > Cd^{2+} > Pb^{2+} > Zn^{2+} > Fe^{3+}.

Effect of stirring time

Effect of stirring time 1 to 60 min on the separation efficiency of the investigated heavy metal ions was studied at pH 5.0 - 5.5. It was found that the recovery
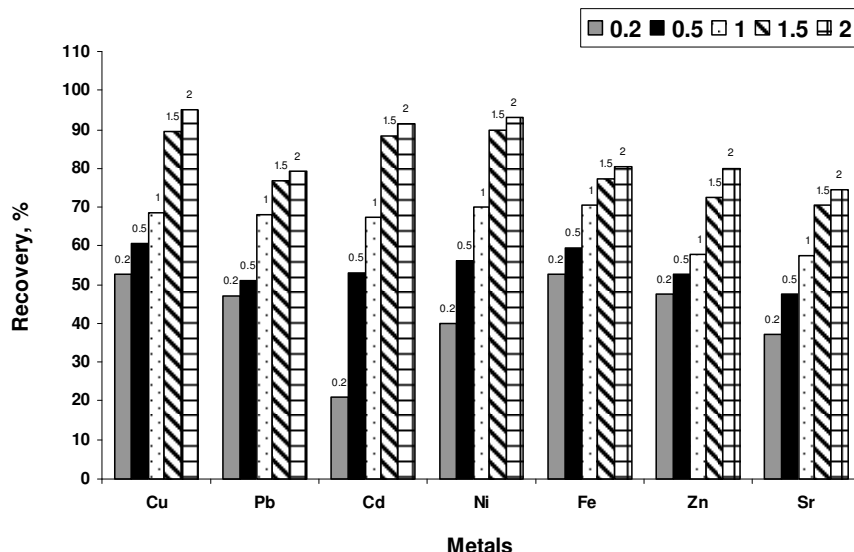
Figure 3. Effect of time of stirring on the separation of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+}.
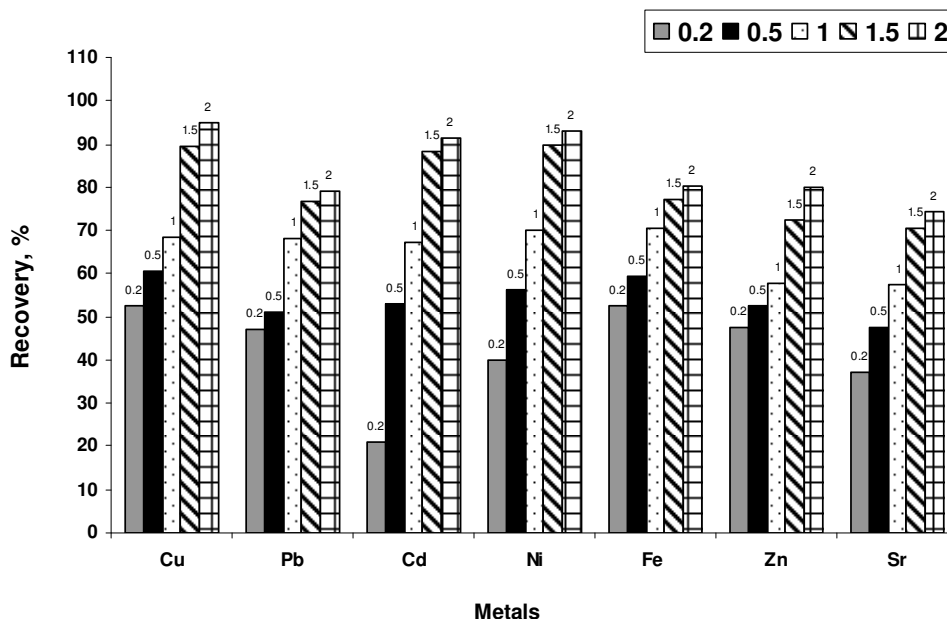
Figure 4. Effect of concentration of HCl used for elution on the recovery of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+}.

(%) increases with time of stirring up to 30 min, then becomes independent on the time of stirring at pH = 5.0-5.5 using SZP (Figures. 3).

Effect of eluting acid concentration on metal recovery

The optimum conditions of separation of studied heavy metal ions are pH= 5.0 -5.5, time of stirring= 30 min, and mass of modified silica gel ion sorbent≥20 mg. These conditions were applied to collect studied metal ions as well as to study the effect of eluting acid (10 ml of HCl and HNO_3). Figures 4 and 5) show the effect of concentration of eluting acids on the recovery of the investigated metal ions. The results showed that HNO_3 (Figure 5) releases the investigated metal ions from the ion sorbent more efficiently than HCl (Figure 4).
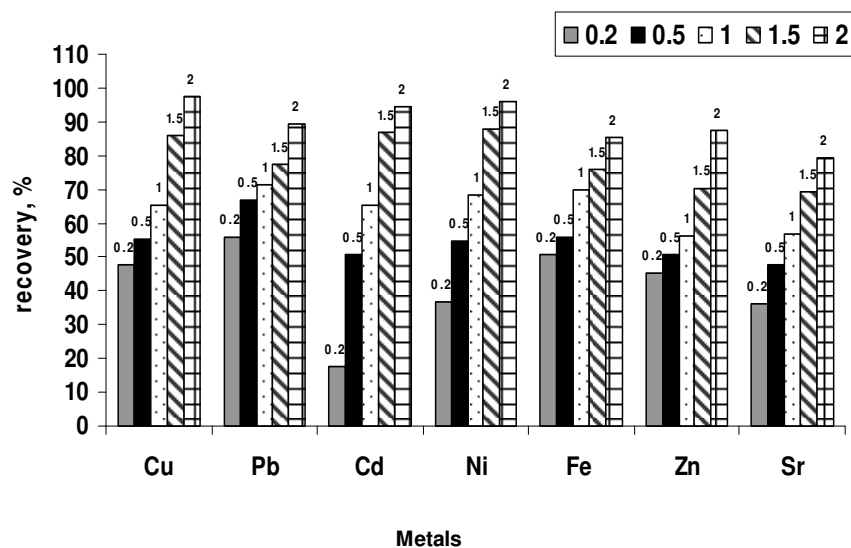
Figure 5. Effect of concentration of HNO_3 used for elution on the recovery of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+} and Fe^{3+}.

Table 1. Effect of some common

Ionic Species	Recovery %					
	Cu	Pb	Zn	Cd	Ni	Fe
None	92.2	90.7	86.6	92.8	89.7	88.7
EDTA	60.6	77.8	43.1	61.5	58.7	57.3
Acetate	92.3	90.7	86.5	92.3	89.2	88.5
Sulphate	80	91.7	85.4	93.4	89.8	90.1
Citrate	90.7	61.7	81.9	83.2	80.1	82.4
Oxalate	93.2	92.7	90.7	93.5	90.7	87.9
Nitrate	91.8	90.2	85.1	90.3	87.4	87.3
Phosphate	97.4	93.5	94.9	95.6	92.9	89.2

Ionic species on the separation of investigated metal ions on SZP.

Effect of interfering ions

The analytical preconcentration procedure for trace metal ions can strongly interfere with matrix constituents, and then the tested preconcentration procedure must be examined in the presence of the possible matrix elements. The effect of EDTA, acetate, sulphate, citrate, oxalate, nitrate and phosphate which represent the common ionic species in natural water samples were studied applying the optimum conditions detected above. As shown in Table 1, EDTA caused serious interference with the detected metal ions; this interference was attributed to competition between the complexation of the metal ions with the phosphate substrate on silica and with the interfering species in solution. Therefore, EDTA could be used successfully with HNO_3 acid as a good eluent for metal ions from the loaded SZP. On the other hand, oxalate, sulphate and citrate showed slight interference for all metal ions, while the investigated metal ions using silica gel-based zirconyl phosphate ion sorbent, showed a good resistance to most interfering ions such as acetate and nitrate.

Application

The SPE method was applied for the preconcentration and separation of Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} in water samples where the procedure was applied to one litre of sample. The analytical results of different samples of water collected from the northern part of Suez Gulf starting from summer 2004 until spring 2005 using SZP are shown in Tables 2 to 7. A comparison was performed with the standard solvent extraction method (APDC/MIBK).

In the case of using APDC/MIBK for the

Table 2. Copper concentration (µg/L) in seawater of Suez Gulf during period of study (2004 - 2005).

Season Station	Summer SZP	Summer APDC/MIBK	Winter SZP	Winter APDC/MIBK	Autumn SZP	Autumn APDC/MIBK	Spring SZP	Spring APDC/MIBK	Annual Mean SZP	Annual Mean APDC/MIBK
1	3.99±0.04	3.73±0.03	4.59±0.02	4.42±0.02	4.48±0.03	4.37±0.03	4.27±0.04	3.98±0.04	4.33±0.03	4.13±0.03
2	2.34±0.01	2.04±0.01	3.60±0.01	3.26±0.01	3.72±0.03	3.35±0.03	3.75±0.04	2.59±0.02	3.35±0.02	2.81±0.02
3	2.44±0.03	2.10±0.02	2.95±0.02	1.94±0.01	3.97±0.01	3.69±0.01	2.76±0.02	2.18±0.01	3.03±0.02	2.48±0.01
4	3.78±0.02	2.37±0.01	3.92±0.02	2.84±0.01	4.14±0.03	3.91±0.04	3.61±0.01	2.93±0.01	3.86±0.02	3.01±0.02
5	3.76±0.04	3.37±0.03	4.03±0.02	3.80±0.02	4.27±0.03	3.73±0.02	3.77±0.04	3.54±0.03	3.95±0.03	3.61±0.03
6	1.97±0.01	1.26±0.01	3.11±0.01	2.31±0.02	3.54±0.01	2.48±0.02	2.07±0.02	1.82±0.01	2.67±0.01	1.97±0.01
7	2.36±0.02	1.57±0.01	3.16±0.02	2.88±0.01	3.59±0.01	3.45±0.01	2.19±0.01	1.91±0.01	2.82±0.01	2.45±0.01
8	3.26±0.02	3.18±0.02	3.75±0.02	3.60±0.01	4.12±0.02	3.85±0.01	4.12±0.05	3.77±0.04	3.81±0.03	3.60±0.02
9	3.50±0.03	2.39±0.01	3.74±0.01	2.94±0.01	4.28±0.02	3.78±0.01	3.29±0.03	2.85±0.02	3.70±0.02	2.99±0.01
10	2.78±0.01	2.44±0.01	3.35±0.01	3.05±0.01	4.16±0.02	3.88±0.01	3.06±0.03	2.98±0.02	3.33±0.02	3.09±0.01
Mean	3.02±0.02	2.45±0.01	3.62±0.01	3.10±0.01	4.03±0.02	3.65±0.02	3.29±0.03	2.86±0.02	3.49±0.02	3.02±0.02

Table 3. Zinc concentration (µg/L) in seawater of Suez Gulf during period of study (2004 - 2005).

Season Station	Summer SZP	Summer APDC/MIBK	Winter SZP	Winter APDC/MIBK	Autumn SZP	Autumn APDC/MIBK	Spring SZP	Spring APDC/MIBK	Annual Mean SZP	Annual Mean APDC/MIBK
1	6.63±0.05	6.16±0.04	11.92±0.07	11.72±0.07	10.71±0.06	10.61±0.06	9.11±0.06	8.97±0.04	9.59±0.02	9.37±0.05
2	5.30±0.03	3.92±0.02	10.17±0.05	9.11±0.06	8.68±0.03	8.29±0.03	7.70±0.02	7.48±0.03	7.96±0.01	7.20±0.04
3	3.89±0.02	3.26±0.02	10.35±0.04	9.98 ±0.01	8.10±0.02	7.93±0.02	6.09±0.01	5.96±0.01	7.11±0.01	6.78±0.02
4	5.10±0.03	4.13±0.02	10.53±0.05	10.39±0.04	8.32±0.03	8.17±0.06	7.12±0.03	6.92±0.03	7.76±0.01	7.40±0.03
5	8.16±0.04	7.19±0.04	15.33±0.09	13.69±0.08	11.21±0.09	11.13±0.07	10.71±0.04	10.46±0.05	11.35±0.03	10.62±0.06
6	2.09±0.01	1.76±0.01	5.12±0.03	4.83±0.03	5.09±0.06	4.65±0.05	4.09±0.01	4.15±0.01	4.09±0.03	3.85±0.03
7	3.49±0.02	2.71±0.01	7.23±0.04	6.54±0.01	5.10±0.05	4.75±0.01	4.29±0.01	4.41±0.02	5.03±0.03	4.60±0.01
8	4.74±0.02	3.77±0.01	8.38±0.04	8.16±0.04	6.92±0.03	6.81±0.03	6.01±0.02	5.73±0.02	6.51±0.03	6.12±0.02
9	4.41±0.02	4.33±0.02	6.90±0.03	5.61 ±0.02	6.29±0.02	4.81±0.04	4.92±0.03	4.48±0.04	5.63±0.02	4.81±0.03
10	4.34±0.02	4.27±0.02	5.32±0.08	4.93±0.07	6.50±0.03	5.96±0.01	5.01±0.05	4.84±0.04	5.29±0.05	5.00±0.04
Mean	4.82±0.02	4.15±0.02	9.13±0.05	8.49±0.04	7.69±0.04	7.31±0.04	6.51±0.03	6.34±0.03	7.04±0.04	6.57±0.03

preconcentration and separation of Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} and Ni^{2+} and Fe^{3+} in water, the metal ion concentrations were in the range of [(3.02-4.03), (4.82–9.13), (0.59-1.41), (0.39-0.69), (0.89-1.57) and (7.82-12.08) µg/L], respectively. On a seasonal scale, trace metal concentrations increased gradually from their minimum values during spring and summer to their maximum values during winter and autumn except for Pb, which recorded its highest concentration during spring. This decrease in concentration during spring may be due to their consumption by

Table 4. Lead concentration (µg/L) in seawater of Suez Gulf during period of study (2004-2005).

Season Station	Summer		Winter		Autumn		Spring		Annual Mean	
	SZP	APDC/MIBK	SZP	APDC/MIBK	SZP	APDC/MIBK	SZP	APDC/MIBK	SZP	APDC/MIBK
1	0.61±0.02	0.51±0.01	0.97±0.06	0.85±0.06	0.88±0.03	0.57±0.03	1.77±0.04	1.59±0.03	1.06±0.04	0.88±0.03
2	0.37±0.01	0.33±0.01	0.92±0.01	0.75±0.01	0.27±0.01	0.23±0.01	1.58±0.03	1.48±0.03	0.79±0.02	0.69±0.02
3	0.49±0.01	0.42±0.01	1.03±0.02	0.93±0.02	0.63±0.01	0.49±0.01	0.91±0.02	0.77±0.01	0.77±0.02	0.65±0.01
4	0.66±0.03	0.45±0.02	1.09±0.02	0.97±0.02	0.72±0.02	0.69±0.01	1.07±0.02	0.91±0.02	0.89±0.02	0.75±0.02
5	1.26±0.02	1.13±0.01	1.52±0.02	1.37±0.02	0.95±0.03	0.77±0.02	1.55±0.03	0.98±0.02	1.32±0.03	1.06±0.02
6	0.26±0.02	0.23±0.01	0.45±0.03	0.39±0.03	0.47±0.03	0.39±0.02	0.48±0.02	0.40±0.02	0.42±0.03	0.35±0.02
7	0.29±0.02	0.26±0.03	0.65±0.03	0.57±0.02	0.58±0.02	0.42±0.02	0.60±0.03	0.49±0.02	0.53±0.03	0.43±0.02
8	1.27±0.03	1.22±0.02	2.03±0.03	1.90±0.01	1.30±0.04	1.22±0.03	2.12±0.06	1.95±0.04	1.68±0.04	1.57±0.03
9	0.31±0.05	0.15±0.03	0.61±0.03	0.54±0.01	0.90±0.04	0.75±0.04	1.95±0.04	1.62±0.03	0.94±0.04	0.76±0.03
10	0.34±0.02	0.19±0.03	0.51±0.04	0.49±0.02	0.94±0.03	0.87±0.03	2.04±0.05	1.73±0.04	0.96±0.03	0.82±0.03
Mean	0.59±0.02	0.49±0.01	0.98±0.03	0.88±0.02	0.76±0.02	0.64±0.02	1.41±0.03	1.19±0.02	0.94±0.02	0.80±0.02

Table 5. Cadmium concentration (µg/L) in seawater of Suez Gulf during period of study (2004-2005).

Season Station	Summer		Winter		Autumn		Spring		Annual Mean	
	SZP	APDC/MIBK	SZP	APDC/MIBK	SZP	APDC/MIBK	SZP	APDC/MIBK	SZP	APDC/MIBK
1	0.29±0.01	0.24±0.01	0.72±0.02	0.45±0.01	0.38±0.01	0.29±0.01	0.36±0.03	0.29±0.01	0.44±0.02	0.31±0.01
2	0.61±0.02	0.40±0.01	1.08 ±0.02	0.94 ±0.01	0.72±0.02	0.50±0.01	0.64±0.01	0.48±0.03	0.76±0.02	0.58±0.01
3	0.29±0.03	0.13±0.01	0.73±0.02	0.65±0.01	0.49±0.02	0.25±0.01	0.36±0.01	0.29±0.01	0.47±0.02	0.33±0.01
4	0.36±0.03	0.15±0.02	0.74±0.02	0.66±0.01	0.47±0.03	0.30±0.01	0.33±0.02	0.24±0.01	0.47±0.03	0.33±0.01
5	0.41±0.05	0.28±0.02	0.80±0.03	0.83±0.02	0.56±0.03	0.49±0.02	0.59±0.02	0.45±0.03	0.59±0.03	0.51±0.02
6	0.19±0.01	0.10±0.01	0.42 ±0.01	0.29±0.02	0.30±0.01	0.13±0.01	0.25±0.02	0.12±0.01	0.29±0.01	0.16±0.01
7	0.22±0.01	0.11±0.01	0.45±0.01	0.36±0.01	0.30±0.01	0.15±0.01	0.39±0.01	0.25±0.02	0.34±0.01	0.21±0.01
8	0.58 ±0.03	0.37±0.03	0.84 ±0.01	0.72±0.01	0.53±0.02	0.39±0.01	0.50±0.01	0.38±0.03	0.61±0.02	0.46±0.02
9	0.47±0.06	0.22±0.04	0.55±0.02	0.37±0.01	0.35±0.03	0.28±0.02	0.43±0.02	0.32±0.04	0.45±0.03	0.29±0.03
10	0.44±0.04	0.23±0.03	0.61±0.02	0.44±0.01	0.40±0.02	0.31±0.02	0.49±0.04	0.33±0.03	0.48±0.03	0.32±0.02
Mean	0.39±0.03	0.22±0.01	0.69±0.02	0.57±0.01	0.45±0.02	0.31±0.01	0.43±0.02	0.32±0.02	0.49±0.02	0.35±0.01

phytoplankton. During the period of study, it can be seen that, spring showed the highest concentration of Pb (2.12 µg/dm³) at El-Adabyiastation and this may be due to that, this station considered the most active and largest fishing harbour in the Gulf of Suez and the loaded gasoline spelt in the water surface during the fishing ships loaded. The high concentration of trace metals in winter as compared with other seasons may be attributed to terrestrial inputs of dust particles containing metal ions and strong winds throughout the water column including

Table 6. Nickel concentration (µg/L) in seawater of Suez Gulf during period of study (2004-2005).

Season / Station	Summer SZP	Summer APDC/MIBK	Winter SZP	Winter APDC/MIBK	Autumn SZP	Autumn APDC/MIBK	Spring SZP	Spring APDC/MIBK	Annual Mean SZP	Annual Mean APDC/MIBK
1	0.88±0.01	0.78±0.01	2.07±0.05	0.95 ±0.04	1.90±0.05	1.10±0.02	1.89±0.03	1.10±0.02	1.68±0.03	0.98±0.02
2	1.32±0.02	1.21±0.02	2.21±0.04	1.99 ±0.03	2.20±0.04	1.80±0.03	2.34±0.02	1.82±0.03	2.01±0.03	1.70±0.03
3	1.14±0.01	1.03±0.01	1.55±0.03	1.39±0.01	1.10±0.02	0.87±0.01	1.24±0.02	0.79±0.01	1.25±0.02	1.02±0.01
4	0.92±0.01	0.89±0.01	1.78±0.04	1.26±0.03	1.50±0.02	0.98±0.01	1.35±0.03	0.83±0.01	1.38±0.03	0.99±0.01
5	0.97±0.03	0.91±0.02	1.50±0.06	1.18±0.04	2.10±0.06	1.80±0.04	2.11 ±0.03	1.62±0.03	1.67±0.05	1.37±0.03
6	0.67±0.01	0.54±0.01	1.03±0.02	0.83 ±0.01	0.90±0.02	0.74±0.01	0.72±0.02	0.65±0.01	0.83±0.02	0.69±0.01
7	0.69±0.01	0.56±0.01	1.14 0.02	0.98 ±0.01	0.95±0.01	0.82±0.01	0.84±0.01	0.68±0.01	0.90±0.01	0.76±0.01
8	0.81±0.02	0.78±0.02	1.68±0.02	1.13 ±0.02	1.07±0.02	0.92±0.01	1.36±0.03	0.86±0.01	1.23±0.02	0.92±0.01
9	0.75±0.02	0.60±0.02	1.40±0.02	1.05±0.02	1.10±0.03	0.97±0.02	1.48±0.03	1.01±0.03	1.18±0.03	0.90±0.02
10	0.77±0.02	0.67±0.02	1.30±0.03	1.02±0.02	1.08±0.03	0.91±0.02	1.32±0.02	0.96±0.01	1.11±0.03	0.89±0.02
Mean	0.89±0.01	0.79±0.01	1.57±0.03	1.18±0.02	1.38±0.03	1.09±0.02	1.47±0.02	1.03±0.01	1.32±0.03	1.02±0.01

Table 7. Iron concentration (µg/L) in seawater of Suez Gulf during period of study (2004-2005).

Season / Station	Summer SZP	Summer APDC/MIBK	Winter SZP	Winter APDC/MIBK	Autumn SZP	Autumn APDC/MIBK	Spring SZP	Spring APDC/MIBK	Annual Mean SZP	Annual Mean APDC/MIBK
1	7.29 ±0.01	6.71±0.03	17.12±0.09	9.58±0.04	12.10 ±0.05	7.80±0.03	9.50±0.04	7.95±0.04	11.50±0.05	8.01±0.03
2	7.39±0.01	6.89±0.05	13.48±0.06	11.49 ±0.05	12.40±0.06	8.90±0.04	9.57±0.01	7.76±0.04	10.71±0.03	8.76±0.04
3	8.67±0.01	5.97±0.02	11.84±0.05	10.95±0.05	10.40±0.04	8.50±0.04	9.05±0.01	7.33±0.04	9.99±0.03	8.18±0.03
4	9.84 ±0.03	7.02±0.03	11.68±0.03	10.87±0.04	10.50±0.05	9.70±0.04	10.14±0.05	8.63±0.01	10.54±0.04	9.05±0.03
5	13.34±0.04	10.44±0.04	18.42±0.07	15.93±0.07	15.10±0.02	13.4 0±0.06	14.42±0.06	12.31±0.02	15.32±0.05	13.02±0.05
6	5.33 ±0.02	5.05 ±0.02	7.95±0.04	6.76 ±0.01	7.09±0.04	6.45±0.01	7.01±0.01	5.45±0.02	6.84±0.03	5.92±0.01
7	4.59 ±0.02	4.19 ±0.01	8.03±0.09	6.95 ±0.03	7.24±0.04	6.63±0.01	7.14±0.03	6.27±0.02	6.75±0.04	6.01±0.02
8	7.45 ±0.01	5.92 ±0.02	11.51±0.05	8.66±0.01	10.70±0.05	7.50±0.02	8.34±0.01	6.82±0.03	9.50±0.03	7.22±0.02
9	7.29±0.03	6.39±0.04	10.08±0.02	7.88±0.02	9.40±0.05	8.85±0.04	8.05 ±0.06	7.49±0.05	8.70±0.04	7.65±0.04
10	7.05±0.04	6.03±0.03	10.70±0.02	7.26±0.06	9.70±0.07	8.92±0.05	8.32±0.05	8.17±0.04	8.94±0.04	7.59±0.03
Mean	7.82±0.02	6.46±0.03	12.08±0.05	9.63±0.04	10.46±0.05	8.67±0.03	9.15±0.03	7.82±0.03	9.87±0.04	8.14±0.03

favourable conditions for metal ions to be transferred from solid suspended. The results indicated that, the northern part of Suez Gulf was more polluted than the southern part may be due to presence of different sources of pollutants such as the corrosion of ships hull coating with antifouling paints and the presence of many oil piers in this area. On the other hand, the western part of the gulf was highly polluted than the

Table 8. Efficiency for removal of metal ions (%) at ambient conditions.

Metal \ Station	Efficiency of separation, %				
	Zaitiya	NIOF	Adabyia	El-Kahraba	Uyun Mousa
Cu	34.39	9.16	26.43	6.20	17.99
Cd	34.43	32.14	70.27	42.5	18.42
Ni	43.55	8.38	45.38	59.09	20.69
Pb	21.65	23.85	47.57	5.08	26.15
Zn	3.39	4.79	32.52	5.02	9.98
Fe	3.08	3.33	29.06	3.06	7.01
Sr	59.02	26.08	11.32	26.00	27.14
Mg	38.52	42.26	12.13	15.61	62.00
Ca	9.56	7.68	14.23	10.62	7.41

eastern part due to the presence of much sources of pollution in this area except for Ni and Cd; their high concentration in the eastern side may be due to the presence of power thermal station at Aeon Mousa. Tables 2 to 7 showed that, Ain Sukhna station (St. VI) has the lowest concentrations of heavy metal ions, these values for Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} were (1.97, 2.09, 0.26, 0.19, 0.67 and 5.33 µg/L, respectively). According to the data about metal level in water, it can be observed that, Cd and Ni give their maximum values at El-Zeitiya station 1.08 and 2.34 µg/L, respectively. These results may be due to this station characterized by the presence of refinery factories and power plant discharge. While the lowest value of Cd and Ni (0.19 and 0.67) µg/L, respectively were recorded at Ain Sukhna station. Regionally the lowest value of copper (1.97 µg/L) occurred at Ain Sukhna station and this may be due to remoteness of this station from any sources of pollution. On the other hand the highest concentration of copper was found at 4.59 µg/L at Summer Balas. This is probably due to the emotion of this station by small fishing boats, touristic impact and corrosion of ships hull coating with antifouling paints. The presence of the highest concentration of Zn and Fe at NIOF may be due to the leaching of metals from the ships passing through the Suez Canal. While the lowest concentrations of these metals were recorded at Sand Beach station and this may be due to remoteness of this station from any sources of pollution. Ion exchange method (SZP) showed the same results but with values lower than that of SZP method. However it was found that there is no significant difference was found between the values obtained by the ion exchange and that of solvent extraction methods; the reliability of the two methods will be examined statistically. Also the results of APDC/MIBK system showed that, Ain Sukhna station has the lowest concentrations of heavy metal ions (Tables 2 to 7). Comparing the results obtained from the present study with those reported in the early studies (Hamed, 1996) (Abdel-Azim, 2002), there is an increasing in the heavy metal concentrations can be observed. This was explained by the increasing of factories along the coast of northern part of the Gulf of Suez and presence of more sources of pollution along this area.

Utilization of silica for the removal of metal ions at ambient conditions

Marine pollution may be due different sources; almost 80% of this pollution and coastal deterioration in Egypt coasts are attributed to different land activities whether industrial, agricultural, urban or physical, in particular those produced wastes and emissions that are not treated in a sound environmental manner (GESAMP, 1993). The remaining 20% is due to other sources ahead of which are marine sources i.e. different offshore activities such as oil, mineral and natural gas exploration and drilling operations, besides fishes, shipping and unloading and marine transportation (EL-Shenawy et al., 2006). Most toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution. (Lin and Juang 2002) Pb^{2+}, Cu^{2+}, Fe^{3+}, and Cr^{3+} are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders (Erdem et al., 2004). Various treatment processes are available; among which ion exchange is considered cost- effective if low-cost ion sorbents such as zeolites are used (Bailey et al., 1999).

Table 8 shows the results of treatment of trace metals for the highest polluted locations at ambient conditions (natural pH of the environment of studied area).It was found that, the highest percentage of the efficiency for copper (II) (34.39%) was recorded at Zaitiya location at which strontium also was co-sorbed with 59.02%. Adabyia location represented the maximum percent for the removal of cadmium (II) (70.27%). Power Station (St. IV) represented the highest percent for Ni^{2+} efficiency (59.09%) while; Adabyia station has the maximum percentage for Pb^{2+}, Zn^{2+}, Fe^{3+} and Ca^{2+} ions (47.57, 32.52, 29.06 and 14.23%, respectively).

Table 9. Statistical evaluation for Cu (II) analysis in natural water samples after preconcentration by solvent extraction (method 1) and Ion sorbent (method 2), n =5.

| Location | Method 1 | | Method 2 | | S_P | t- Test | Two- tailed F- test |
	$\overline{X_1}$ ng/ml	S_1	$\overline{X_2}$ ng/ml	S_2			
1	4.59	0.069	4.55	0.067	0.068	1.31	1.06
2	3.60	0.062	3.59	0.058	0.060	0.37	1.14
3	2.95	0.042	2.92	0.039	0.040	1.65	1.15
4	3.92	0.052	3.89	0.049	0.050	1.32	1.12
5	4.03	0.079	3.99	0.065	0.072	1.23	1.47
6	3.11	0.039	3.09	0.034	0.036	1.22	1.31
7	3.16	0.051	3.13	0.042	0.046	1.43	1.47
8	3.75	0.070	3.72	0.062	0.066	1.01	1.27
9	3.74	0.081	3.70	0.063	0.072	1.23	1.65
10	3.35	0.053	3.31	0.045	0.049	1.81	1.38

Table 10. Statistical evaluation for Zn (II) analysis in natural water samples after preconcentration by solvent extraction (method 1) and Ion sorbent (method 2), n =5.

| Location | Method 1 | | Method 2 | | S_P | t- Test | Two- tailed F- test |
	$\overline{X_1}$ ng/ml	S_1	$\overline{X_2}$ ng/ml	S_2			
1	11.92	0.179	11.89	0.129	0.156	0.43	1.92
2	10.16	0.168	10.11	0.162	0.165	0.68	1.07
3	10.35	0.169	10.30	0.135	0.152	0.73	1.56
4	10.53	0.149	10.50	0.139	0.144	0.47	1.15
5	15.33	0.301	15.31	0.229	0.267	0.17	1.72
6	5.12	0.070	5.09	0.067	0.068	0.98	1.09
7	7.23	0.121	7.19	0.113	0.117	0.76	1.14
8	8.37	0.150	8.34	0.124	0.137	0.48	1.46
9	6.91	0.129	6.87	0.121	0.125	0.71	1.14
10	5.32	0.088	5.28	0.08	0.084	1.06	1.21

Statistical evaluation of the ion exchange method compared with the standard solvent extraction method

The statistical analysis of the results was performed on commercial software. The agreement between a series of results measured by computing their mean deviation. This was evaluated by determining the arithmetical mean of the results (X), then calculating the deviation of each individual measurement from the mean and finally dividing the sum of the deviations, regardless of sign, by the number of measurements (n).

$$\text{Mean} = \overline{X} = X_1 + X_2 + \ldots\ldots X_n \qquad \frac{X_1 + X_1 + \ldots\ldots X_n{}^2}{n} \qquad (3)$$

In analytical chemistry, one of the most employed common statistical terms is the standard deviation (s) of a population of observations. This is also called the root mean square deviation, as it is the square root of the mean of the sum of the squares of the differences between the values and the mean of those values (El-Moursi, 2001).

$$S = \sqrt{\frac{\sum(X_i - \overline{X})^2}{n-1}} \qquad (4)$$

The comparison between the means of the two analytical methods can be performed by $|t_2|$ – test (Miller and Miller, 1986) at P= 0.05. F-test was also used for comparison of standard deviation, that is, the random error for two sets of data given by two analytical methods (EL-Shenawy et al., 2006). Tables 9-14 show the statistical analysis (mean values, standard deviation and "$|t_2|$" values) for heavy metal samples collected during

Table 11. Statistical evaluation for Pb (II) analysis in natural water samples after preconcentration by solvent extraction (method 1) and Ion sorbent (method 2), n =5.

Location	Method 1		Method 2		S_P	t- Test	Two- tailed F- test
	$\overline{X_1}$ ng/ml	S_1	$\overline{X_2}$ ng/ml	S_2			
1	0.97	0.080	0.92	0.075	0.077	1.44	1.13
2	0.92	0.071	0.89	0.069	0.070	0.95	1.05
3	1.03	0.070	0.99	0.059	0.064	1.38	1.40
4	1.09	0.050	1.06	0.044	0.047	1.42	1.29
5	1.52	0.029	1.50	0.023	0.026	1.70	1.58
6	0.45	0.072	0.41	0.066	0.069	1.29	1.19
7	0.66	0.022	0.65	0.017	0.019	1.13	1.67
8	2.03	0.061	1.99	0.052	0.056	1.57	1.37
9	0.61	0.030	0.59	0.021	0.025	1.72	2.04
10	0.49	0.019	0.48	0.016	0.017	1.27	1.41

Table 12. Statistical evaluation for Cd (II) analysis in natural water samples after preconcentration by solvent extraction (method 1) and Ion sorbent (method 2), n =5.

Location	Method 1		Method 2		S_P	t- Test	Two- tailed F- test
	$\overline{X_1}$ ng/ml	S_1	$\overline{X_2}$ ng/ml	S_2			
1	0.72	0.061	0.68	0.059	0.060	1.49	1.06
2	1.08	0.069	1.03	0.057	0.063	1.76	1.46
3	0.75	0.052	0.72	0.048	0.050	1.34	1.17
4	0.74	0.071	0.71	0.061	0.066	1.01	1.35
5	0.84	0.061	0.83	0.052	0.056	0.39	1.37
6	0.42	0.050	0.40	0.047	0.048	0.92	1.13
7	0.45	0.070	0.44	0.060	0.065	0.34	1.36
8	0.84	0.051	0.81	0.041	0.046	1.44	1.54
9	0.55	0.059	0.51	0.054	0.056	1.58	1.19
10	0.61	0.059	0.59	0.050	0.054	0.81	1.39

Table 13. Statistical evaluation for Ni (II) analysis in natural water samples after   preconcentration by solvent extraction (method 1) and Ion sorbent (method 2), n =5.

Location	Method 1		Method 2		S_P	t- Test	Two- tailed F- test
	$\overline{X_1}$ ng/ml	S_1	$\overline{X_2}$ ng/ml	S_2			
1	2.07	0.032	2.05	0.022	0.027	1.60	1.95
2	2.21	0.039	2.19	0.036	0.037	1.17	1.13
3	1.55	0.026	1.54	0.019	0.022	0.97	1.85
4	1.78	0.092	1.75	0.089	0.090	0.73	1.06
5	1.50	0.099	1.46	0.086	0.093	0.96	1.32
6	1.03	0.072	0.99	0.064	0.068	1.31	1.26
7	1.14	0.090	1.11	0.050	0.072	0.92	3.23
8	1.68	0.073	1.65	0.069	0.071	0.94	1.11
9	1.40	0.028	1.39	0.025	0.026	0.83	1.19
10	1.32	0.072	1.30	0.062	0.067	0.66	1.35

Table 14. Statistical evaluation for Fe (III) analysis in natural water samples after preconcentration by solvent extraction (method 1) and Ion sorbent (method 2), n =5.

Location	Method 1		Method 2		S_P	t- Test	Two- tailed F- test
	$\overline{X_1}$ ng/ml	S_1	$\overline{X_2}$ ng/ml	S_2			
1	17.12	0.265	17.09	0.191	0.231	0.29	1.91
2	13.48	0.238	13.44	0.225	0.232	0.38	1.11
3	11.85	0.199	11.81	0.146	0.174	0.51	1.84
4	11.68	0.175	11.66	0.166	0.170	0.26	1.10
5	18.42	0.368	18.40	0.261	0.319	0.14	1.98
6	7.95	0.112	7.93	0.102	0.107	0.41	1.19
7	8.03	0.134	7.99	0.110	0.122	0.72	1.47
8	11.51	0.217	11.49	0.209	0.213	0.20	1.07
9	10.07	0.201	10.02	0.184	0.192	0.57	1.18
10	10.70	0.184	10.65	0.172	0.178	0.62	1.13

Table 15. Correlation between parameters using Solvent extraction (SE) method during period of study (2004-2005) at P <0.05.

Metals	Cu (SE)	Zn (SE)	Pb (SE)	Cd (SE)	Ni (SE)	Fe (SE)	Temp.	pH	S‰	D O	NO_2	NO_3	NH_3	PO_4
Cu (SE)	1.00													
Zn (SE)	0.73	1.00												
Pb (SE)	0.73	0.49	1.00											
Cd (SE)	0.40	0.52	0.59	1.00										
Ni (SE)	0.61	0.81	0.37	0.79	1.00									
Fe (SE)	0.70	0.97	0.57	0.58	0.77	1.00								
Temp.	0.25	-0.04	-0.06	-0.02	0.03	-0.03	1.00							
pH	0.16	0.47	0.29	0.28	0.24	0.57	-0.05	1.00						
S‰	0.44	0.17	0.20	0.27	0.32	0.21	0.66	0.25	1.00					
D O	0.11	-0.17	0.28	-0.22	-0.26	-0.26	-0.35	-0.61	-0.45	1.00				
NO_2	0.51	0.65	0.81	0.65	0.50	0.68	-0.19	0.29	0.00	0.25	1.00			
NO_3	0.59	0.76	0.79	0.74	0.67	0.79	-0.18	0.45	0.12	0.12	0.94	1.00		
NH_3	0.61	0.81	0.73	0.69	0.69	0.80	-0.16	0.28	0.00	0.19	0.95	0.95	1.00	
PO_4	0.44	0.86	0.52	0.52	0.63	0.85	-0.23	0.54	-0.09	-0.03	0.83	0.87	0.90	1.00

the period of study (2004-2005). $|t_2|$ and F values were less than the tabulated ones indicating that the SPE method is precise and accurate.

Correlation coefficients were carried out using statistical computer program. They were calculated between all pairs of measured variables

for the two methods; solvent extraction with APDC/MIBK (Table 15) and SPE using SZP (Table 16). The results showed that:

Table 16. Correlation between parameters using ion exchange (SZP) method during period of study (2004-2005) at P <0.05.

Metals	Cu (SZP)	Zn (SZP)	Pb (SZP)	Cd (SZP)	Ni (SZP)	Fe (SZP)	Temp.	pH	S‰	D O	NO$_2$	NO$_3$	NH$_3$	PO$_4$
Cu (SZP)	1.00													
Zn (SZP)	0.71	1.00												
Pb (SZP)	0.75	0.42	1.00											
Cd (SZP)	0.47	0.61	0.60	1.00										
Ni (SZP)	0.26	0.61	0.20	0.89	1.00									
Fe (SZP)	0.48	0.84	0.36	0.67	0.67	1.00								
Temp.	-0.07	-0.09	-0.09	-0.07	-0.01	0.09	1.00							
pH	0.17	0.42	0.22	0.42	0.39	0.69	-0.05	1.00						
S‰	0.23	0.09	0.18	0.23	0.23	0.23	0.66	0.25	1.00					
D O	0.24	-0.12	0.35	-0.24	-0.47	-0.47	-0.34	-0.62	-0.45	1.00				
NO$_2$	0.55	0.64	0.82	0.73	0.46	0.57	-0.19	0.29	0.00	0.25	1.00			
NO$_3$	0.62	0.74	0.77	0.83	0.63	0.69	-0.18	0.45	0.11	0.11	0.94	1.00		
NH$_3$	0.61	0.80	0.71	0.78	0.60	0.67	-0.16	0.28	0.00	0.18	0.95	0.95	1.00	
PO$_4$	0.46	0.85	0.47	0.67	0.61	0.78	-0.23	0.54	-0.09	-0.03	0.83	0.87	0.90	1.00

1. Temperature is correlated with salinity, where positive correlation (r= 0.66). This due to salinity increases during hot seasons and vice versa.

2. The high significant positive correlation coefficient was found between nutrient salts and trace metals (Tables 15 and 16) indicate that the factors responsible for their distribution are similar.

3. There is high significant positive correlation between Cu and Fe (r =0.70) in the case of using APDC/MIBK method for preconcentration and separation of metal ions and the moderate correlation for SZP (r =0.48). This positive correlation indicates that Cu is mostly adsorbed by amorphous iron (Johnson, 1986).

4. Zn is highly correlated with Fe and Cu, where high significant positive correlations for APDC/MIBK method (r= 0.97 and 0.73, respectively) while, for SZP (r = 0.84 and 0.71, respectively). These correlations are due to adsorbing Zn by hydrous iron oxide (Kester, 1974). However, the obtained correlation between Zn and Cu is due to that both metals are insoluble in the oxidized states and form sulphides in reducing conditions.

Conclusion

The optimum conditions for the concentration of Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} using chemically-modified silica with zirconium phosphate are pH= 5.0-5.5, time of stirring=30 min and eluent acid 2M HNO_3. Citrate and EDTA cause strong interference therefore digestion of organic matter should be performed prior to the separation process with the ion sorbent.

The SPE method was applied for preconcentration and separation of Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} in the water samples in comparison with the standard solvent extraction method. On a seasonal scale, trace metal concentrations increased gradually from their minimum during spring and summer to their maximum during winter and autumn except for Pb, which recorded its high concentration during spring. This decrease in concentration during spring may be due to their consumption by phytoplankton. During the period of study, it can be seen that, spring showed the highest concentration of Pb (2.12 µg/L) at El-Adabyia station and this may be due to that, this station considered the most active and largest fishing harbour in the Gulf of Suez and the loaded gasoline spelt in the water surface during the fishing ships loaded. The ion sorbent (SZP) can be used in the separation and preconcentration of Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Ni^{2+} and Fe^{3+} with high distribution coefficient at optimum conditions with no interference from common ionic species.

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