ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Separation and Subsequent Determination of Iron in Aqueous and Non-Aqueous Solutions Using Modified Polymer

R.A.Mansour[1]*, Adel M. El-Menshawy[2] and A.M. Eldesoky[3]

1. *Engineering Chemistry Department, High Institute of Engineering & Technology (New Damietta), Egypt
2. Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt.
3. Engineering Chemistry Department, High Institute of Engineering &Technology (New Damietta), Egypt and Al-Qunfudah Center for Scientific Research (QCSR), Al-Qunfudah University College, Umm Al-Qura University ,KSA.

Manuscript Info

Manuscript History:

Received: 18 October 2014
Final Accepted: 29 November 2014
Published Online: December 2014

Key words: Polymer; Zincon; Sorption; Iron; Preconcentration

Corresponding Author

R.A.Mansour

Abstract

Iron has been eliminated from different media using Chloromethyl polystyrene polymer (CMPS-polymer) has been modified with 2-carboxy-2-hydroxy-5-sulfoformazyl benzene (Zincon) in batch and column modes. The obtained modified polymer was characterized by partial elemental analysis and infrared spectra. The extraction isotherm was applied at different pH's. Fe (III) was sorbed from aqueous solution at pH 2 - 7 and stripped using different concentrations of HCl. The maximum sorption capacity, the preconcentration factor and the detection limit of Fe (III) ion were 0.946 mmol g^{-1}, 300 and 6.7 ppb, respectively. The loaded zincon-polymer can regenerated for at least 50 cycles. The utility of the modified polymer was tested in water, ash coal, drugs, vitamin, kerosene and oil (food and petroleum) samples and showed RSD value of < 3% reflecting its accuracy and reproducibility. Iron (III) is highly extracted from mixtures containing different metal ions in the presence of thiocyanate and thiosulfate. The polymer is found highly sensitive to Fe (III) than thiocyanate. Iron (II) may be eliminated from iron (III) by controlling the pH. The method is successfully used for the removal of iron from crude phosphoric acid.

1. Introduction

The interest in the determination of trace heavy metals in natural waters has increased immensely in the last decades because of the environmental problems and public health studies. Iron in small amounts is essential for humans and animals. It is well known that iron deficiency causing anemia; much iron may cause several health problems (cancer, heart disease, arthritis, diabetes and liver diseases) [1]. Iron was restricted to 2 mg L^{-1} by World Health Organization [2] and 200 µgL^{-1} by European Legislation [3]. Due to the very low concentration of iron and the interfering effect of the matrix, its determination demand very sensitive analytical techniques [4-6]. Separation and preconcentration were applied to overcome these difficulties. Many procedures are well characterized for such a purpose [7 – 14]. Of all, solid phase extraction (SPE) has attracted a great attention owing to its simple operation, rapid phase separation, no emulsification, high enrichment factor and easily automation. Organic chelating resins [15], polymer inclusion sorbents [16], modified nanometer-sized alumina [17], C18-bonded silica gel [18], controlled-pore glass [19], activated carbon [20], ion exchange resins [21], thermal modified kaolinite [22], microcrystalline naphthalene [23 – 33], C60–C70 fullerene and its derivative [34] were used**.** In general, the lower sorption capacity, medium constituents and the use of expensive organic reagents are the common disadvantages. The use of modified polymer solved these difficulties [35].In continuation of our earlier work on separation of Cu (II) and Zn (II) ions by the same modified polymer, the present work introduced a new method for removal of iron from complex matrices including natural water, seawater, phosphoric acid, drugs, oils, and certified samples.

2. Experimental

2.1. Reagents and solutions

Fe (III) solution was prepared by dissolving 2.907 g of anhydrous $FeCl_3$ in absolute ethanol and diluted to one liter with ethanol while Fe (II) was obtained from $FeSO_4.7H_2O$. Commercial chloromethyl polystyrene copolymer with divinylbenzene (CMPS-polymer) (MP-500A; Bayer Co., Germany); 2% DVB; specific surface area (BET) is 66 m^2 g^{-1} and 46 meq g^{-1} resin was used. 2-Carboxy-2- hydroxy-5-sulfo-formazyl benzene, cetyltrimethyl ammonium bromide (CTAB) and the metal salts (Aldrich) were used. The reaction was followed up with the aid of FTIR spectroscopic analysis. The pH-metric measurements were performed using a Metrohm E53b Potentiograph equipped with a 665 DOSIMAT (Metrohm, Herisau, Switzerland). The combined glass electrode was standardized before and checked after each titration with buffer solutions produced by FISHER (New Jersy, USA). All titrations were carried out at temperatures 28–40 °C and ionic strength of 0.04-0.12 mol l^{-1} KCl. HCl, NaOH and the other reagents were analytical grade (BDH). The glassware used was cleaned by soaking overnight in aqueous HNO_3 (1:1), and then rinsing with distilled water several times. Fe(III) has been determined spectrophotometrically using KSCN and confirmed by FAAS.

2.2. Preparation of Z-polymer

In a 100 ml round bottom flask, 1 g of chloromethyl polystyrene polymer was soaked for three days in 25 ml chloroform as swelling medium. To the swollen polymer, 0.5 g Zincon; 0.1 g CTAB and 5 ml of 30% aqueous solution of Na_2CO_3 were added. The reaction mixture was heated under reflux on a water bath with magnetically stirring for 10 h. On cooling, the polymeric product was filtered off, washed thoroughly with acetic acid, distilled water, methanol, acetone and finally diethyl ether. The product was dried at 40°C overnight and characterized by elemental analysis and FTIR spectroscopy. The suggested structure of Z-polymer is shown in Scheme 1.

2.3. Equipment

A Perkin-Elmer Model 2380 atomic absorption spectrometer (USA) was used. The IR spectra were carried out using Mattson 5000 FTIR Spectrophotometer (4000 – 400 cm^{-1}) as KBr disk. The spectrophotometric measurements were performed on a Unicam 2001 UV-Vis Spectrophotometer using a 1 cm quartz cell. The pH values were measured using a pH-meter (Hanna Instruments, 8519, Italy) with accuracy of ±0.01 and standardized.

2.4. pH- metric titrations

All pH titrations were carried out at 25±2 ^{o}C. The following solutions were titrated against 0.0052 mol l^{-1} NaOH at ionic strength of 0.1 M KCl:

a) 1 ml of KCl + 2.5 ml HCl (0.0135 M)
b) 1 ml of KCl + 2.5 ml HCl (0.0135 M) + 50 mg DC20-DAPCH
c) 1 ml of KCl+2.5 ml HCl (0.0135 M)+50 mg DC20-DAPCH+1 ml Fe (III) [$1x10^{-3}$ M]

The volume completed to 25 ml with bidistilled H_2O, stirred and recorded the pH.

2.3. Investigation of the optimal conditions for Z-polymer

2.3.1. Batch method

A sample solution (100 ml) containing 50 µg ml^{-1} of Fe (III) was transferred to 250 ml glass stoppered bottle. After adjusting the pH to the optimum value, 100 mg of the modified zincon-polymer was added. The mixture was shaken for 60 min, filtered, washed with bidistilled water, and the sorbed Fe (III) was eluted with 5 ml of the suitable concentration of HCl, then determined spectrophotometrically or by taken 1 ml of the eluent, diluted with 100 ml distilled water and determined by AAS.

2.3.2. Column method

DC20-DAPCH (0.5 g) was firstly swollen for 24 h, packed in a glass column (4 cm length and 6 mm diameter), treated with 1 mol l^{-1} HCl (20 ml) at the optimum flow rate and washed with bidistilled water to become acid free. 100 ml of 100 µg ml^{-1} metal ion at the optimum pH, were passed through the column at the optimum flow rate, the column was washed with 100 ml of bidistilled water to remove any uncomplexed metal ions from resin bed.

The stripping of Fe(III) from resin was carried out by HCl. The eluted metal ion was collected in a 100 ml calibrated flask and determined.

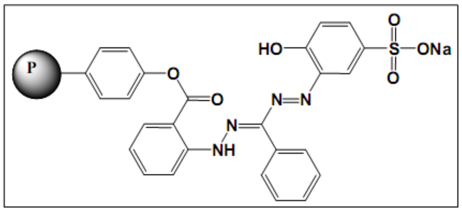
3. Results and discussion

3.1. Characterization of the Modified Z-Polymer

In order to verify the presence of the active functional groups of Zincon in the modified polymer, the IR spectra of CMPS-polymer and Z–polymer were recorded. The spectrum of CMPS-polymer exhibits a characteristic band at 701 cm^{-1} attributed to ν(C–Cl) and a broad band at 3400 cm^{-1} attributed to ν(OH) of water. Upon modification of CMPS-polymer with zincon (Scheme 1) , additional bands appeared at 3600-3500, 3160, 1708, 1655, 1630 and 1050 cm^{-1} attributed to $\nu(OH)_{phenolic}$, ν(NH), ν(N=N), ν(C=O), ν(C=N) and ν(N– N) bands, respectively[36]. Also, the high decrease in intensity of the 701 cm^{-1} band, the formation of a new one at 1050 cm^{-1} and the presence of the phenol OH were taken as evidence for the progress of the reaction through ester link.

Metal-Z-polymer interaction was confirmed by the change in color from red in Z-polymer to blue in the complexes. Also, by the shift of ν (C=O) and ν (N=N) bands to lower wave numbers by 30 and 20 cm^{-1}, respectively, and the absence of $\nu\ (OH)_{phenolic}$ band indicating the interaction of Z-polymer with Fe (III) ion.

The C, H and N content in the Z-polymer was estimated by elemental analysis [Found (Calcd. %): C = 58.9 (60.2%), H= 4.1 (4.0%), N = 9.0 (9.7%)] indicating the formation of Z-polymer. The modification was carried out by 92%. The nitrogen content was measured in Z-polymer which absent in CMPS-polymer. The shift observed in the pH titration curves (Fig.1) of Z-polymer with Fe (III) ion than the Z- polymer was taken as a support for the interaction of Z- polymer with the studied metal ions via liberation of hydrogen ions. The Fe (III)- Z-polymer is found below Z-polymer curve indicating that Fe (III) ion interact with the modified polymer. Water regain values were measured by recording the weight difference of the modified polymer after its storage at 120 °C for 48 h. The water regain value was found 0.30 g g^{-1} for Z-polymer. Comparison of this value with 0.12 g g^{-1} of CMPS-polymer indicates appreciable improvement of the sorption capacity of Z- polymer [37].



Scheme 1. Structure of the modified polymer (Z-polymer)

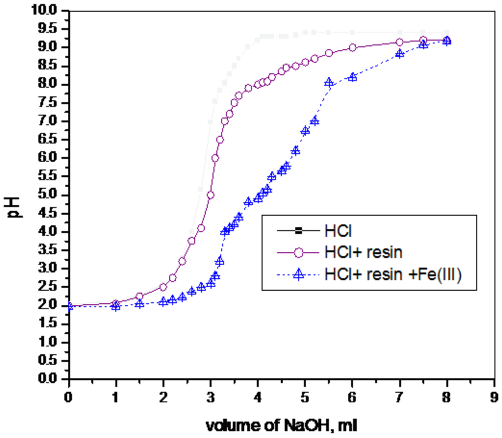


Fig.(1). The pH metric titrations of HCl, [HCl + Z-polymer] and [HCl + Z- polymer + Fe (III)] against 0.0052 mol l^{-1} NaOH.

3.2. Preliminary investigations

Batch and column preliminary experiments were carried out to investigate the quantitative sorption of Fe (III) by Z-polymer. It was found that, CMPS-polymer does not show any tendency for the sorption of Fe (III). On the other hand, the modified polymer is efficient due to the strong interaction between Fe (III) and the function groups in the loaded via complexation. The analytical variables have been studied through the batch and column techniques.

3.3. Batch technique

Effect of pH

To show the effect of pH (1.0–8.0) on the sorption of Fe (III) by batch equilibrium experiments, solution containing Fe (III) ion was shacked with the zincon-polymer for sufficient equilibrium time. Fig. (2) shows that, the maximum efficiency of Z-polymer for sorption of Fe(III) was achieved at pH 2.5–7.0. For subsequent experiments, the working media is adjusted at pH 3.0. The lower pH value is generally preferred for analyzing real samples (acidic biological and geological). In addition, these conditions prevent the precipitation of metal hydroxides.

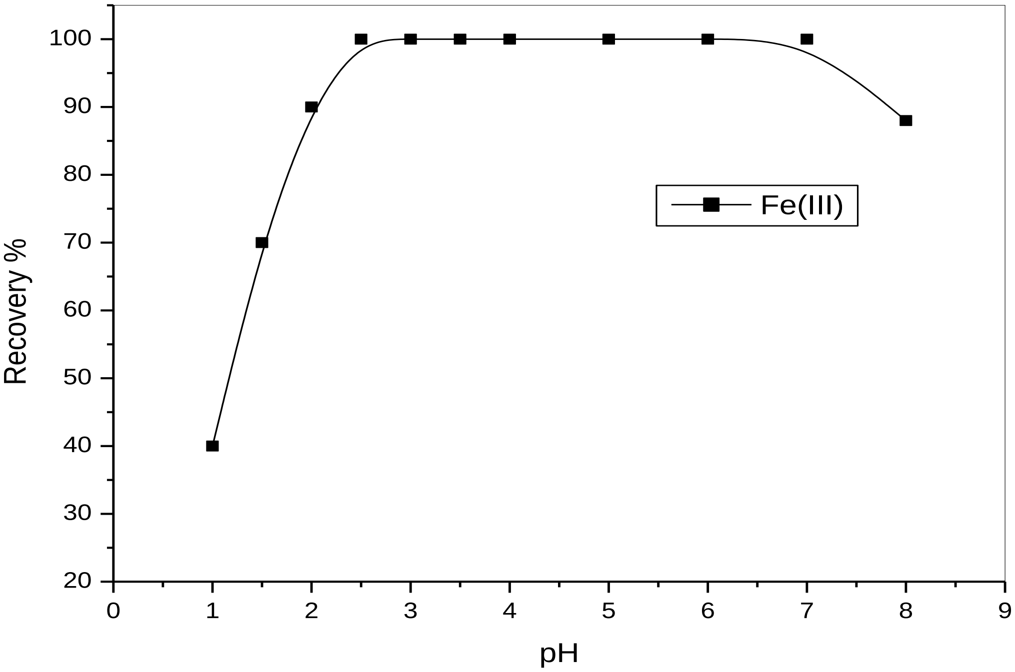


Fig .(2). Effect of pH on the recovery % of Fe(III) using 50 mg Z-Polymer and stirring time 30 min at 25°C

Sorption Capacity

The sorption capacity of Z- polymer towards Fe (III) was determined by shaking excess Fe (III) with 50 mg of Z-polymer under optimum conditions. The maximum sorption capacity is 0.946 mmol g^{-1}.

Effect of Amount of Z- Polymer

The amount of Z- polymer is an important parameter that affects the recovery of metal ion. Quantitative sorption is not obtained when the amount of resin is less than 50 mg. Large amount of Z-polymer restricts the elution of the sorbed Fe (III) by a small volume of eluent quantitatively. So, the used amount of resin must be optimized to 50 mg for subsequent experiments.

Effect of Stirring Time

To determine the rate of sorption of Fe (III) on Z-polymer, batch experiments were elaborated by shaking 50 mg of the Z-polymer with 100 ml of feed solution containing the metal ion at 25 and 50ºC. Aliquots of 0.5 ml solution were taken out for analysis at pre-determined intervals. The concentration of metal ion in the supernatant solution was determined and the amount of metal ion sorbed on Z-polymer was calculated.

The sorption half-time ($t_{1/2}$) was estimated Fig. (3) and the maximum sorption of Fe (III) with Z- polymer reached its equilibrium time after 15, 12 and 10 min at 25ºC in water, ethanol and acetone, respectively. The difference may be due to the hydration around Fe (III) is larger than salvation by ethanol or acetone. Therefore, the high polarity of water favors its interaction with the surface (less polar solvents such as acetone permit a great degree of interaction between metal ion and active centers on Z- polymer.

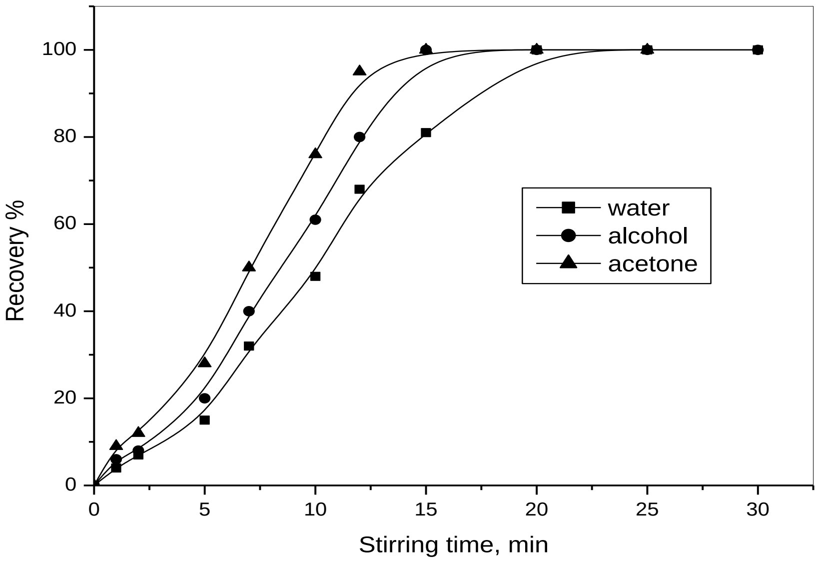


Fig.(3). Effect of Stirring Time on the Recovery % of Fe (III) Using 50 mg Z-Polymer at pH 3 in Water, Acetone and Ethanol at 25 °C.

Choice of Eluent

Choice of the most effective eluent for the quantitative stripping of the retained metal ion on Z- polymer is of special interest. The metal ion sorbed on the modified resin was eluted with acid solutions (HCl, HNO_3 and H_2SO_4) and EDTA into the aqueous phase. Literature showed that, AAS may be handicapped by the presence of a complex organic matrix that causes suppression of the analyte signal. So, acid solution is analytically preferred.

The data obtained in Fig.(4) indicate that, 0.5 mol l^{-1} of HCl could afford quantitative elution of Fe III) from the modified resin. Subsequent elution was carried out with HCl taken the advantage that, Cl^- is acceptable matrix for AAS and spectrophotometric determination.

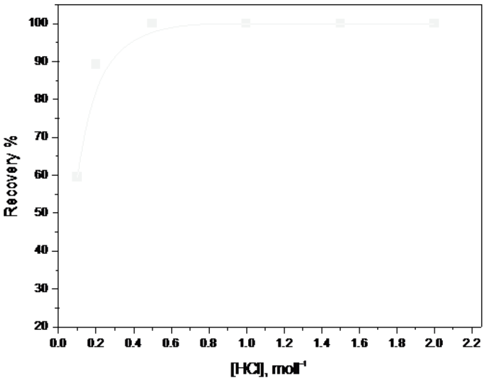


Fig. (4). Effect of [HCl] (5 ml) on the Recovery of Fe (III) Using 50 mg Z-Polymer and Stirring Time 5 min at 25 °C.

Interferences

The effect of interfering agents on the recovery of Fe (III) was studied. The influence of several cations and anions on its sorption and determination is summarized in Table. (1). Most of the examined ions did not interfere during the extraction and determination of Fe (III). However, the presence of oxalate, citrate and tartrate caused a remarkable suppression of sorption. PO_4^{3-} and SCN^- have no effect on the sorption of Fe (III). Moreover, Cu (II) interfered in the determination of Fe (III) in presence of SCN^-. The interference was eliminated by thiosulphate which turned Cu (II) to insoluble Cu (I), but doesn't interfere on the reaction of Fe (III) with Z- polymer. Fluoride could be used as a masking agent for Fe (III). NaH_2PO_4 has no effect; the method may be applicable for removal of iron from Egyptian crude phosphoric acid.

Table (1). Influence of interfering cations and anions on recovery percentage of 10 µg ml^{-1} Fe(III) ion using 50 mg of Z-polymer at 25°C.

Interfering Ion	Concentration (µg ml^{-1})	Fe(III) (R %)
K^+	200	99.5
Mg^+	200	98.5
Ca^{2+}	200	98.5
NH_4^+	200	99.0
Acetate	200	100.0
Oxalate	200	57.0
Citrate	200	50.0
Tartrate	200	66.0
PO_4^{3-}	200	96.0
SO_4^{2-}	200	99.0
NO_3^-	200	99.5
Cl^-	200	99.9
SCN^-	200	99.9
F^-	200	00.0
$S_2O_3^{2-}$	200	98.5
EDTA	200	80.0

Modified-polymer Stability and Reusability

The modified polymer (50 mg) was shaken with 100 ml of HCl (1– 6 mol l^{-1}) or 1 mol l^{-1} of NaOH and/or organic solvents (ethanol, acetone and chloroform) for 24 h, filtered and washed with bidistilled water. After air drying, various elemental constituents were investigated. It was found that, there was no change in the polymer composition suggesting a stable nature of the modified polymer.

The modified Z-polymer was subjected to several sorption and desorption cycles by stirring 50 mg with 100 ml of 25 mg l^{-1} solution containing Fe (III) for 1 h at room temperature. The concentration of Fe (III) was determined after elution with 5 ml of appropriate concentration of HCl. Less than 2 % sorption capacity for Fe(III) ion was found indicating that the modified polymer is highly stable and may be use for several times. Storing of the modified polymer for 6 months under the ambient conditions has no effect on the sorption capacity.

3.4. Column Technique

Effect of Flow Rate

The sorption of Fe (III) was investigated at different flow rates (0.5 - 10 ml min^{-1}) under the optimum conditions. The capacity of Fe (III) was found maximum at flow rate of 5 ml min^{-1} Fig. (5). The faster sorption of Fe (III) ion with the modified polymer is taken as an indication for its higher reactivity with the polymer.

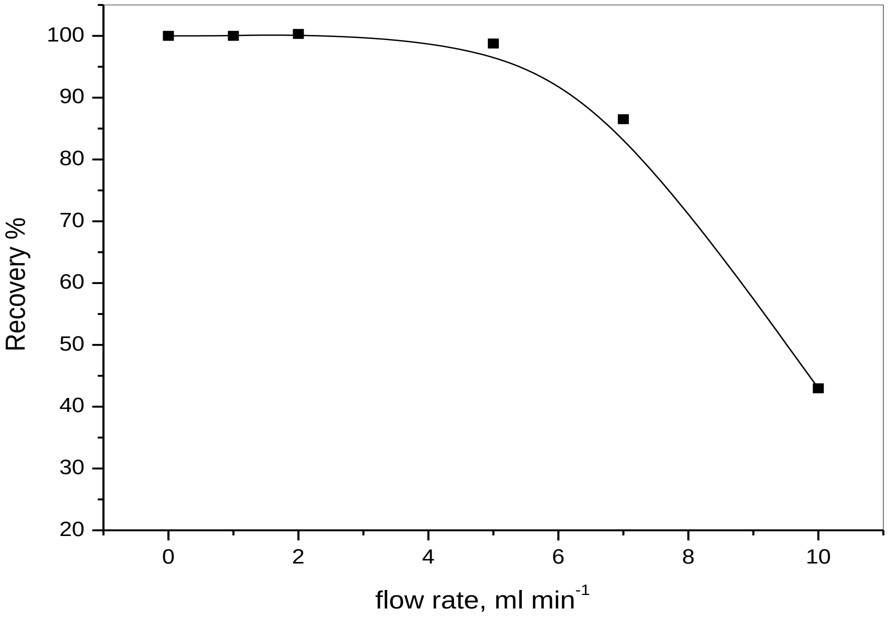


Fig. (5). Effect of Flow Rate on the Recovery of Fe (III) at 25 °C.

Breakthrough Capacity

To evaluate the amount of Fe (III) sorbed per gram on the modified polymer under the optimum conditions, a breakthrough capacity is operated. The column was packed with 0.5 g of the modified polymer and 50 µg ml^{-1} of Fe (III) at the optimal pH and flow rate. The receiving effluent after 5 min was fractionalized into 5 ml portions and in each the metal ion was determined. The breakthrough capacity Fig. (6) indicates that, the column is saturated with 48 mg g^{-1} of Fe (III) ion.

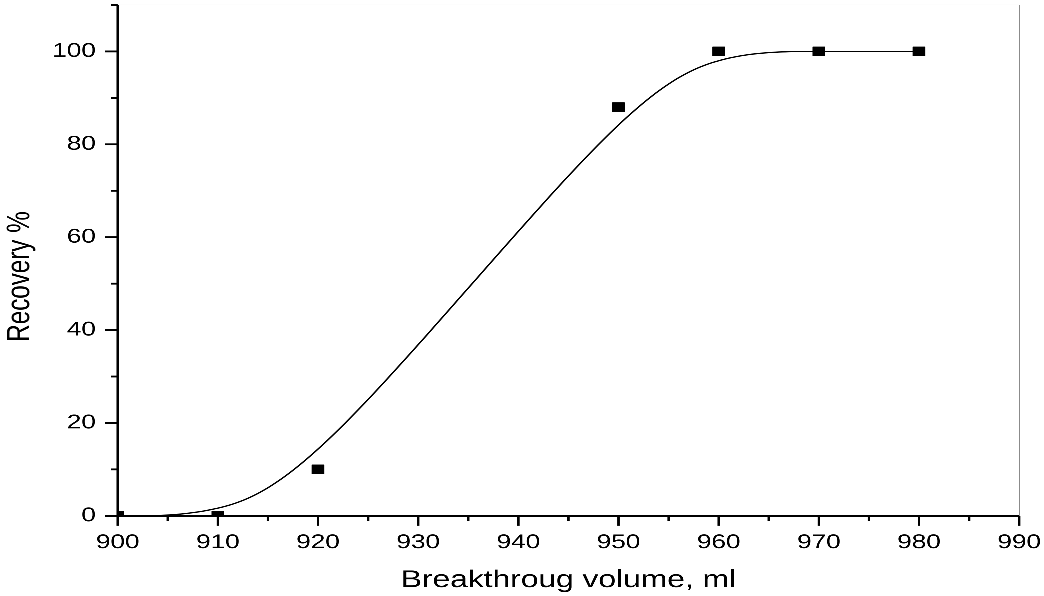


Fig.(6). Breakthrough Curve for Fe (III) Ion with Flow Rate 5 ml min^{-1} at 25 °C.

Column Reuse

To test the long-term stability of the column containing the modified polymer, successive sorption and elution cycles were carried out by passing the metal solution through the column at the optimum flow rate and then eluted. The procedure was carried out several times and the stability of the column was assessed by monitoring the change in the recoveries of the sorbed metal ion. The results of 100 sorption/desorption cycles indicated that, the recovery decreased by ≤ 3 %, reflecting good stability of the modified polymer.

Effect of Volume and Preconcentration Factor

Aqueous solutions (0.1–2.0L) containing 10 µg of Fe (III) were passed through the modified polymer bed, eluted with 5 ml of the appropriate concentration of HCl and determined. It was found that, Fe (III) ion may be removed quantitatively from volume up to 1500, then the recovery decreased remarkably. Therefore, on using 5 ml of appropriate concentration of HCl as eluent, the preconcentration factor is 300 folds which is found high comparing with previous work [38].

3.5. Detection Limits of the Metal Ions

The detection limit was investigated for 10^{-1} - 10^{-3} µg ml^{-1} Fe (III) solutions passing through the Z-polymer bed at a suitable flow rate. The limit of detection (LOD) is 6.7 ppb, showing high sensitivity of the modified polymer in preconcentrating trace iron.

3.6. Applications

Selective Separation of Fe (III) from Synthetic Mixtures

In order to separate selectively Fe (III) from mixtures with some metal ions, an aliquot of aqueous solution (0.5 L) containing 5 mg of Fe (III) and 50 mg of the added cation (s) was taken and the recommended procedure (column mode) was followed. The results summarized in Table (2) showed that Fe (III) sorbed by the polymer, even in the presence of 50 mg of the other interfering cations under the optimum conditions.

Table (2). Separation of Fe (III) (5 ppm) from synthetic mixture.
Conditions: flow rate = 5 ml min^{-1}, n = 5 at 25 °C.

Metal ion	Fe(III), ppm Found	Recovery %
Cu(II)^{a}	4.97	99.40+ 0.30
Co(II)^{b}	4.99	99.80+ 0.15
Ni(II)^{b}	4.98	99.60+0.33
Cu(II)+ Co(II)$^{a, b}$	4.96	99.20+0.25
Cd(II)+Pb(II)+Cu(II)^{a,b}	4.96	99.20+0.55
Zn(II)+Co(II)+Cd(II)^{a}	4.95	99.00+0.68
Cr(III)+Hg(II)+ Pb(II)^{a}	4.91	98.20+0.76

a: in presence of 10^{-3} mol $l^{-1}$$S_2O_3^{2-}$.
b: in presence of 10^{-3} mol l^{-1} SCN^-.

Selective Separation of Fe (III) from Natural Water

Surface water samples were collected from Nile River (Mansoura, Dameitta, Ras EL-Bar) and tap water from Mansoura city. All samples were filtered using a sintered glass G4 and the suspended matter is determined Table (3). The pH, total dissolved salts (TDS), dissolved oxygen (DO) and total alkalinity (mg $CaCO_3$ l^{-1}) were determined according to the previous methods.

Table (3). Water Quality Measurements for Samples Collected from Different Locations.

Type of water (Location)	Parameters				
	pH	TDS (gl^{-1})	TSM (gl^{-1})	TDO (mg O_2 l^{-1})	Alkalinity (mg $CaCO_3$ l^{-1})
Tap water (Mansoura city)	7.22	0.12	4.00	6.38	125.00
Nile river (Mansoura city)	7.83	0.50	4.00	5.54	144.00

Wastewater (Talkha from Meat Antar)	8.25	0.55	4.00	7.85	180.00
Nile water (Dameitta city)	8.20	29.20	321.00	5.56	185.00
Wastewater (Ras El-Bar from Elborg)	8.14	14.30	150.00	6.24	154.00
Sea water (Port Said from Suez canal)	8.19	46.10	346.00	5.74	132.00

The samples were acidified with concentrated HNO_3 to pH ~ 2 and preserved in polyethylene vessel. The organic matter was digested prior to the separation process. 0.5 g of $K_2S_2O_8$ and 5 ml of 98 % (w/v) H_2SO_4 were added to 500 ml of the water sample and heated for 30 min at 95 °C. After cooling to room temperature, 5 ml of 10^{-3} mol l^{-1} of SCN^- and $S_2O_3^{2-}$ solution were added and the pH was adjusted to 3 and passed through the column with flow rate 5 ml min^{-1} then eluted with 5 ml of 0.5 mol l^{-1} HCl and analyzed as previously described.

The quality of water is mentioned in Table (3). The tap, Nile and Sea water samples were analyzed for Fe (III) by the described procedure (Table 3). Preliminary investigation showed that the method is selective to sorb Fe (III) with high efficiency. Samples of wastewater from Talkha. Table.(4) showed high concentration of Fe (III); may be due to the agricultural effluents and domestic sewage. The RSD % is found < 1.0.

Table (4). Analysis of Water Samples Using AAS for Determination of Fe (III) Ion after Preconcentration with Z-polymer at pH 3, Flow Rate = 5 $ml.min^{-1}$, n = 5 at 25 °C.

Sample (Location)	Epermintal value of Fe(III) $\mu g ml^{-1}$
Tap water (Mansoura city)	0.50 ± 0.25
Nile river (Mansoura city)	1.45 ± 0.41
Wastewater (Talkha from Meat Antar)	2.26 ± 0.87
Nile water (Dameitta city)	2.11 ± 0.22
Wastewater (Ras El-Bar from Elborg)	3.32 ± 0.95
Sea water (Port Said from Suez canal)	2.50 ± 0.72

Determination of Fe (III) in Pharmaceutical Samples

A tablet of drug or vitamin was digested using 5 ml of concentrated HNO_3 and heated to near dryness. After cooling, the residue was dissolved with another 5 ml of acid. The solution was gently evaporated on a steam bath till a residue was again left. It was heated with 50 ml of doubly distilled water, filtered off and completed to 100 ml in a calibrated flask. After adjusting pH, the recommended procedure for the determination of Fe (III) was applied (column mode). The amount of recovered Fe (III) is determined as usual and the results of analysis are listed in Table (5).

Table (5). Preconcentration and Determination of Fe(III) in Pharmaceutical Tablets (mg $tablet^{-1}$). (Conditions: pH =3, flow rate = 5 ml min^{-1}, n = 5 at) 25°C.

Drug	Mineral composition (mg/tablet)	R% Fe (III)
Gerimax	Mg(150), Fe(14), Mn (2.5), Zn(15), Cr(0.05), Se(0.05), Mo(0.15), Cu(2.00)	14.00 ± 0.02
Recovery%		100%
Centrum	Ca(162), Fe(27), Mg(100), Mn(7.5), K(7.5), Zn(22.5), Cu(3.00)	26.77 ± 0.20
Recovery%		99.15%
Totavit.	Cr(25), Mn(2.5), Fe (18), Cu(2), Ni (0.005), Zn (15),	17.94 ± 0.05
Recovery%		99.66%

Determination of Fe (III) in Ash Coal

The ash coal was taken from the burner of Talkha electricity station; 0.5 g of the ash sample were digested with aqua regia and heated to near dryness. The residue is boiled with concentrated HNO_3 and heated gently on a steam bath to near dryness, then diluted with doubly distilled water and filtered. The filtrate was then buffered at the optimum pH, treated with suitable masking agent and the total volume was completed to 100 ml and the recommended procedure for the determination of Fe (III) was applied. The concentration of Fe (III) was found 0.15 mg l^{-1} with RSD of < 0.90 % (n = 3).

Determination of Fe (III) in Oil, Kerosene and Crude Petroleum

The introduced method was applied for separation of Fe (III) in food oil (collected from oils and soap factory), Kerosene (commercial from motor oil station), and crude petroleum oil (collected from Ballaiem wells). Fe (III) was determined in spiked and unspiked oil samples. For this purpose, different amounts of Fe (III) were added to the sample and the proposed method (column) was applied. The obtained results are given in Table (6). As can be seen, the method could be applied successfully for the separation of trace amount of Fe (III) in non-aqueous samples. The accuracy of the results is quite satisfactory. Relative error is less than 2 % for Fe (III).

Table (6). Determination of Fe(III) in Non-Aqueous Media (100 ml, n=5) Using Column Technique.

Samples	Added (ppm)	Found (ppm)	Recovery % ± R.S.D[a]
Food oil (90% in ethanol)	0.0	1.5	100.00+1.10
	5.0	6.49	99.85+1.30
	10.0	11.51	100.08+1.00
Kerosene (90% in ethanol)	0.0	0.51	100.0+1.00
	5.0	5.42	98.73+1.87
	10.0	10.50	99.90+1.20
Petroleum oil (10% in benzene)	0.0	5.6	100.0+1.20
	5.0	10.52	99.24+1.50
	10.0	15.62	100.13+1.30

[a] mean and R.S.D. of five determinations.

4. References

[1] C. Niederau,; R. Fischer,; A. Purschel,; W. Stremmel,; D. Haussinger,; Long-term survival in patients with hereditary hemochromatosis, Gastroenterology **1996**, 110, 1107–1119.

[2] WHO, Rolling revision of the WHO guidelines for drinking water quality, Nutrient minerals in drinking-water and the potential health consequences of long-term consumption of demineralized and remineralized and altered mineral content drinking-waters, **2003**.

[3] European Community, Directive 98/83/EC on the quality of water intended for human consumption, **1998.**

[4] A. Ceccarini,; I. Cecchini,; R. Fuoco,; Determination of trace elements in seawater samples by on-line column extraction/graphite furnace atomic absorption spectrometry, Microchem. J.**2005,** 79, 21–24.

[5] L. Elci,; A. A. Kartal,; M. Soylak,; Solid phase extraction method for the determination of iron, lead and chromium by atomic absorption spectrometry using Amberite XAD-2000 column in various water samples, J. Hazard. Mat. **2008**, 153, 454–461.

[6] L.H.J. Lajunen,; Spectrochemical Analysis by Atomic Absorption and Emission, The Royal Society of Chemistry, Cambridge, **1991**, p. 220.

[7] L.B. Xia,; Y.L. Wu,; Z.C. Jiang,; S.Q. Li,; B. Hu,; Speciation of Fe(III) and Fe(II) in water samples by liquid-liquid extraction combined with low-temperature electrothermal vaporization (ETV) ICP-AES, Int. J. Environ. Anal. Chem., **2003**, 83, 953-962.

[8] D. Kara,; M. Alkan,; Selective preconcentration, separation and speciation of ferric iron in different samples using N,N′-bis(2-hydroxy-5-bromo-benzyl)1,2-diaminopropane,Talanta **2001,** 55, 415-423

[9] M.H. Pournaghi-Azar,; B.M. Fatemi,; Simultaneous determination of ferric, ferrous and total iron by extraction differential pulse polarography: application to the speciation of iron in rocks, Microchem J. **2000**, 65 199-207.

[10] D.L. Giokas,; E.K. Paleologos,; M.I. Karayannis, Speciation of Fe(II) and Fe(III) by the modified ferrozine method, FIA-spectrophotometry, and flame AAS after cloud-point extraction, Anal. Bioanal. Chem. **2002**, 373, 237.

[11] H. Bagheri,; A. Gholami,; A. Najafi,; Simultaneous preconcentration and speciation of iron(II) and iron(III) in water samples by 2-mercaptobenzimidazole-silica gel sorbent and flow injection analysis system,Anal. Chim. Acta **2000**, 424, 233-242

[12] A. Kozak,; N. Jodlowska,; M. Kozak,; P. Koscielniak,; Simple flow injection method for simultaneous spectrometric determination of Fe(II) and Fe(III), Analytica Chimica Acta **2011**, 702, 213-217.

[13] Jong-Mi-Lee,; Edward A. Boyl,; Yolanda Echegoyen- Sanz,; Jessica N. Fitzsimmons,; Ruifeng Zhang,; Richard A. Kayser,; Analysis of trace (Cu, Cd, Pb and Fe) in sea water using batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry, Analytica Chimica Acta **2011**, 686, 93-101.

[14] Joffrey A. Hawkes,; Martha Gledhill,; Douglas P. Connelly,; Eric P. Acbterberg,; Characterization of iron binding ligand in seawater by reverse titration, Analytica Acta Acta **2013**, 761.

[15] B.C. Mondal,; D. Das,; A.K. Das,; Synthesis and characterization of a new resin functionalized with 2-naphthol-3,6-disulfonic acid and its application for the speciation of chromium in natural water, Talanta **2002**, 56, 145-152.

[16] Y.M. Scindia,; A.K. Pandey,; A.V.R. Reddy,; S.B. Manohar,; Selective Preconcentration and Determination of Chromium(VI) Using a Flat Sheet Polymer Inclusion Sorbent: Potential Application for Cr(VI) Determination in Real Samples, Anal. Chem. **2002**, 74, 4204-4212.

[17] X.L. Pu,; Z.C. Jang,; B. Hu,; H.B. Wang,; γ-MPTMS modified nanometer-sized alumina micro-column separation and preconcentration of trace amounts of Hg, Cu, Au and Pd in biological, environmental and geological samples and their determination by inductively coupled plasma mass spectrometry, J. Anal. At. Spectrom. **2004**, 19, 984.

[18] M.E. Mahmoud,; G.A. Gohar,; Silica gel-immobilized-dithioacetal derivatives as potential solid phase extractors for mercury(II), Talanta **2000**, 51, 77-87.

[19] C.G. Bruhn,; F.E. Pino,; V.H. Campos,; J.A. N´obrega,; On-Line preconcentration of Cr(III) and Mn(II) in FI-FAAS: A critical study involving interference effects and analytical use of an immobilized 8-hydroxyquinoline minicolumn, Anal. Bioanal. Chem. **2002**, 374, 131.

[20] S. Cerutti,; M.F. Silva,; J.A. G´asquez,; R.A. Olsina,; L.D. Martinez, On-line preconcentration/determination of cadmium in drinking water on activated carbon using 8-hydroxyquinoline in a flow injection system coupled to an inductively coupled plasma optical emission spectrometer, Spectrochim. Acta, Part B **2003**, 58, 43-50.

[21] H. Filik,; B.D. ¨ozt¨urk,; M. Do˘gutan,; G. G¨um¨us,; R. Apak,; Separation and preconcentration of iron(II) and iron(III) from natural water on a melamine-formaldehyde resin, Talanta **1997**, 44, 877-884.

[22] D. Afzali,; M.A. Taher,; A. Mostafavi,; S.Z.M. Mobarakeh,; Thermal modified Kaolinite as useful material for separation and preconcentration of trace amounts of manganese, Talanta **2005**, 65, 476-480.

[23] M.A. Taher,; Differential pulse polarography determination of indium after column preconcentration with [1-(2-pyridylazo)-2-naphthol]-naphthalene adsorbent or its complex on microcrystalline naphthalene, Talanta **2000**, 52, 301-309.

[24] M.A. Taher,; Atomic absorption spectrometric determination of trace zinc in alloys and biological samples after preconcentration with [1-(2-pyridylazo)-2-naphthol] on microcrystalline naphthalene, Analyst **2000**, 125, 1865-1868.

[25] M.A. Taher,; S. Puri,; R.K. Bansal,; B.K. Puri,; Derivative spectrophotometric determination of iridium after preconcentration of its 1-(2-pyridylazo)-2-naphthol complex on microcrystalline naphthalene, Talanta **1997**, 45, 411-416.

[26] W.H. Huang,; B. Hu,; H.C. Xiong,; Z.C. Jiang,; Separation and preconcentration combined with glow discharge atomic emission spectrometry for the determination of rare earth elements (La, Nd, Eu, Dy, Y) in geological samples, J. Anal. Chem. **2000**, 367, 254.

[27] H.C. Xiong,; B. Hu,; T.Y. Peng,; S.Z. Chen,; Z.C. Jiang,; Separation/Preconcentration of Lanthanum and Europium by Micro-Column Packed with Immobilized 1-Phenyl-3-methyl-4-bonzoyl-5-pyrazone on Microcrystalline Naphthalene and Determination by Electrothermal Vaporization Inductively Coupled Plasma-Atomic Emission Spectrometry, Anal. Sci. **1999**, 15, 737.

[28] M.S. Bispo,; M.G.A. Korn,; E.S.B. Morte,; L.S.G. Teixeira,; Separation/Preconcentration of Lanthanum and Europium by Micro-Column Packed with Immobilized 1-Phenyl-3-methyl-4-bonzoyl-5-pyrazone on Microcrystalline Naphthalene and Determination by Electrothermal Vaporization Inductively Coupled Plasma-Atomic Emission Spectrometry, Spectrochim. Acta, Part B **2002**, 57, 2175-2180.

[29] T. Nagahiro,; G.F. Wang,; M. Satake,; Column Preconcentration of Aluminum and Copper(II) in Alloys, Biological Samples, and Environmental Samples with Alizarin Red S and Cetyltrimethylammonium-Perchlorate Adsorbent Supported on Naphthalene Using Spectrometry, Microchem. J. **1995**, 52. 247-256.

[30] A.M.H. Shabani,; S. Dadfarnia,; N. Nasirizadeh,; Speciation analysis of mercury in water samples by cold vapor atomic absorption spectrometry after preconcentration with dithizone immobilized on microcrystalline naphthalene, Anal. Bioanal. Chem. **2004**, 378, 1388.

[31] P.G. Krishna,; J.M. Gladis,; U. Rambabu,; T.P. Rao,; G.R.K. Naidu,; Preconcentrative separation of chromium(VI) species from chromium(III) by coprecipitation of its ethyl xanthate complex onto naphthalene, Talanta **2004**, 63, 541-546.

[32] R.K. Dubey,; A. Bhalotra,; M.K. Gupta,; B.K. Puri,; Differential Pulse Polarographic Determination of Rhodium(III) and Ruthenium(III) in Synthetic Samples after Preconcentration of Their Quinolin-8-olate Complexes onto Microcrystalline Naphthalene, Microchem. J. **1998**, 58 117-126.

[33] Z.F. Fang,; B. Hu,; Z.C.; Jiang,; Speciation analysis of vanadium in natural water samples by electrothermal vaporization inductively coupled plasma optical emission spectrometry after separation/preconcentration with thenoyltrifluoroacetone immobilized on microcrystalline naphthalene, Spectrochim. Acta, Part B **2005**, 60, 65-71.

[34] J.R. Baena,; M. Gallego,; M. Valcarcel,; Speciation of Lead in Environmental Waters by Preconcentration on a New Fullerene Derivative, Anal. Chem. **2002**, 74, 1519-1524.

[35] Adel M. El-Menshawy,; Ahmed A. El-Asmy, ; Zincon polymer as a new modifier for selective separation and determination of copper and zinc from synthetic, water and drug samples,Indian J. science and technology **2009**, 2, 78-84.

[36] R. M. El-Shazly,; G. A. A. Al-Hazmi,; S. E. Ghazy,; M. S. El-Shahawi,; A. A. EI-Asmy,; Synthesis and spectroscopic characterization of cobalt(II) complexes with some thiosemicarbazone derivatives, J. Coord. Chem., **2006**, 59, 846-859.

[37] Das N.; Das J.; Preconcentration and separation of gold (III) and silver (I) from each other and from base metals using a chelating ion exchanger containing quinaldinic acid amide group, J. Ind. Chem. Soc. **1989**, 66, 724-27.

[38] M. M. Hassanein,; I. M. Kenawy,; A. M. EL-Menshawy,; A. A. EL-Asmy,; Separation and Preconcentration of Gallium(III), Indium(III), and Thallium(III) Using New Hydrazone-modified Resin, Analytical Sciences, Japn, **2007**, 23, 1403-1408.