

## Research Article

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# Separation and Preconcentration of Fe(III) from Aqueous and Nonaqueous Media using 1-(3,4-Dihydroxybenzylidene)-2-acetylpyridinium chloride Hydrazone Modified Resin

Ibrahim M. Kenawy<sup>1</sup>, Bakir Geragh<sup>2</sup>, Adel M. El-Menshawy<sup>1</sup> and Ahmad A. El-Asmy<sup>1,2,\*</sup><sup>1</sup>Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt<sup>2</sup>Chemistry Department, Faculty of Science, Kuwait University, Kuwait\*Corresponding Author, E-mail: [aelasmy@yahoo.com](mailto:aelasmy@yahoo.com) Tel: 0020502261734

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**Abstract:** 1-(3,4-Dihydroxybenzylidene)-2-acetylpyridinium chloride hydrazone (DAPCH) loaded on Duolite C20 has been investigated to be used in the elimination of Fe(III) from different media by batch and column techniques. The obtained modified resin (DC20-DAPCH) and the Fe(III) chelate were characterized by partial elemental analysis and IR spectra. The extraction isotherm was applied at different pH. Fe(III) was sorbed from aqueous solution at pH 3 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<sup>-1</sup>, 300 and 1.0 ppb, respectively. The loaded resin was regenerated for at least 50 cycles. The utility of the modified resin 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 modified resin was found highly sensitive to Fe(III) than thiocyanate. Fe(II) may be eliminated from Fe(III) by controlling the pH. The method is successfully used for removing Fe(III) from crude phosphoric acid.

**Keywords:** Resins; Hydrazones; Sorption; Iron; Preconcentration

## 1. INTRODUCTION

The interest in the separation and determination of trace metals in natural waters has increased in the last decades because of the environmental problems and public health studies. Iron in small amounts is essential for humans and animals. Iron deficiency caused anemia and much may cause several health problems (cancer, heart disease, arthritis, diabetes and liver diseases) [1]. Iron was restricted to 2 mg L<sup>-1</sup> by World Health Organization [2] and 200 µg L<sup>-1</sup> 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 [7-11]. 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 for easily automation. Organic chelating resins [12], polymer inclusion sorbents [13], modified nanometer-sized alumina [14], C18-bonded silica gel [15], controlled-pore glass [16], activated carbon [17], ion exchange resins [18], thermal modified kaolinite [19], microcrystalline naphthalene [20–29], C60–C70 fullerene and its derivative [30] were used. In general, the time length of preparation, the lower sorption capacity and the use of expensive organic reagents are the common disadvantages. Introducing modified ion-exchange resins solved these difficulties, but suffers from the presence of electrolytes [31]. The separation of Fe(III) was achieved using aluminon by flotation method in the pH range 2-3 [32]. A wide variety of collectors has been used for the flotation of iron ores containing different iron and gangue minerals. Heavy metal pollution is spreading throughout the world with the expansion of industrial activities [33]. These heavy metals, which find many useful applications in our lives, are very harmful if they are discharged into natural water resources and may pose finally serious health hazards [34, 35]. Industrial wastewater contains high levels of heavy metals and to avoid water pollution, treatment is needed before disposal.

The use of low-cost sorbents has been thoroughly investigated instead of other more inexpensive materials, for example, natural and waste materials coming from industrial, agriculture and forestry activities have high capacity for removing metal ions [36]. In continuation of earlier work on the separation of Ga(III), In(III) and Tl(III) [37] and speciation of Cr(III) and Cr(VI) [38] by the same resin, the present work introduced a new method for the removal of iron from 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<sub>3</sub> in absolute ethanol and diluted to one liter with ethanol while Fe(II) was obtained from FeSO<sub>4</sub>·7H<sub>2</sub>O. Girard's reagent P (GP), sodium chloride and 3, 4-dihydroxybenzaldehyde was purchased from Aldrich. Duolite C20 from Rohm and Hass Co. 1-(3,4-dihydroxybenzylidene)-2-acetylpyridinium chloride hydrazone (DAPCH) and its modified resin (DC20-DAPCH) were prepared as described earlier [37,38]. HCl, NaOH and the other reagents were analytical grade (BDH). The glassware used was cleaned by soaking overnight in aqueous HNO<sub>3</sub> (1:1), and then rinsing with distilled water several times. Fe(III) has been determined spectrophotometrically using KSCN and confirmed by FAAS.

### 2.2. Equipment

A Perkin-Elmer Model 2380 atomic absorption spectrometer (USA) was used in the determination of Fe with the following instrumental parameters: wavelength (nm) 248.3; lamp current (μA) 13; air flow rate (l min<sup>-1</sup>) 21; fuel flow rate (cm min<sup>-1</sup>) 6; burner height (cm) 2.1 and working range 0-6 (μg ml<sup>-1</sup>). The IR spectra were carried out using Mattson 5000 FTIR Spectrophotometer (4000–400 cm<sup>-1</sup>) 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.

### 2.3. pH- metric titrations

All pH titrations were carried out at 25±2 °C. The following solutions were titrated against 0.0052 mol l<sup>-1</sup> NaOH at ionic strength of 0.1 mol l<sup>-1</sup> KCl: a) 1 ml of KCl + 2.5 ml HCl (0.0135 mol l<sup>-1</sup>); b) 1 ml of

KCl + 2.5 ml HCl ( $0.0135 \text{ mol l}^{-1}$ ) + 50 mg DC20-DAPCH and c) 1 ml of KCl + 2.5 ml HCl ( $0.0135 \text{ mol l}^{-1}$ ) + 50 mg DC20-DAPCH+1 ml Fe(III) [ $1 \times 10^{-3} \text{ mol l}^{-1}$ ]. The volume completed to 25 mL with bidistilled  $\text{H}_2\text{O}$ , stirred and recorded the pH.

## 2.4. Separation procedures

### 2.4.1. Batch method

A sample solution (100 ml) containing  $50 \mu\text{g mL}^{-1}$  of Fe(III) was transferred to 250 mL glass stoppered bottle. After adjusting the pH to the optimum value, 100 mg of the modified resin 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 FAAS.

### 2.4.2. 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  $1 \text{ mol l}^{-1}$  HCl (20 mL) at the optimum flow rate and washed with bidistilled water to become acid free. 100 mL of  $100 \mu\text{g mL}^{-1}$  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 ions were collected in a 100 mL calibrated flask to be ready for the determination.

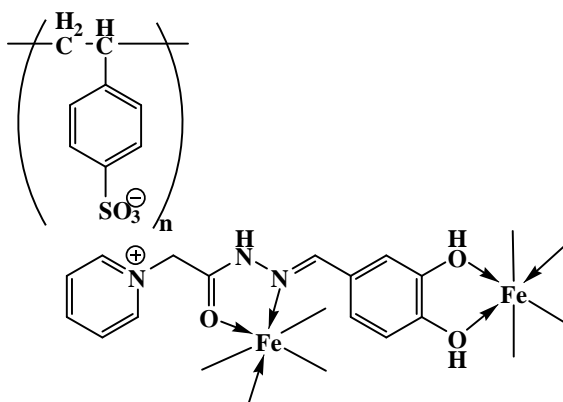
## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of the modified resin

The resin containing hydrazone was confirmed by the nitrogen content [Found 7.6 (Calcd. 9.2%)]. The absence of  $\text{Cl}^-$  ions indicates that the resin is modified by  $0.32 \text{ g g}^{-1}$ . The water content increases from  $0.18 \text{ g g}^{-1}$  in Duolite C20 to  $0.37 \text{ g g}^{-1}$  in DC20-DAPCH indicating an appreciable improvement of the sorption capacity of the modified resin [24]. This is also supported by the hydrogen content [Found 9.5 (Calcd. 4.6)].

In order to verify the presence of the active functional groups of DAPCH in the modified resin, the IR spectra of Duolite C20, DAPCH and DC20-DAPCH resin were compared. The IR spectrum of DC20 exhibits bands at 1212, 1173 and  $1127 \text{ cm}^{-1}$  attributed to  $\nu(\text{SO}_3^-)$  [26] while the less intense band at  $600 \text{ cm}^{-1}$  is assigned to  $\nu(\text{C-S})$  [38]. The abroad band at  $3450 \text{ cm}^{-1}$  is due to hydrated water. The spectrum of the DAPCH is characterized by strong bands at 3440, 3160,  $1700 \text{ cm}^{-1}$  assigned to  $\nu(\text{OH})$ ,  $\nu(\text{NH})$  and  $\nu(\text{C=O})$  groups; the less intense bands at 3003, 2953, 2901 are attributed to the pyridinium group. Upon modification, the pyridinium bands are weakened and slightly shifted to lower wavenumbers, where the  $-\text{SO}_3^-$  bands are shifted to lower wavenumbers indicating the formation of ionic bond. The metal-ligand coordination on the resin was confirmed by the shift of  $\nu(\text{C=O})$  in the spectrum of Fe(III) complex isolated at pH 3. The azomethine group is found broad and shifted by  $25 \text{ cm}^{-1}$ . The band located at 3540, assigned to phenolic OH, is shifted to lower wavenumber by  $15 \text{ cm}^{-1}$  indicating that Fe(III) is bonded with the two adjacent phenolic OH and this is taken as an indication for the increase of the sorption capacity of Fe(III) compared with previous work [39]. The proposed structure of the chelate is shown in Scheme 1.

The pH-metric titration curves (Fig. 1) of HCl, DC20-DAPCH and DC20-DAPCH-Fe(III) were taken as a strong support for the complex formation. The curve of DC20-DAPCH-Fe(III) is found different from that of DC20-DAPCH indicating the reaction of Fe(III) ions with the liberation of  $\text{H}^+$ .



Scheme 1. Proposed structure for the Fe(III) chelate formed at pH 3.

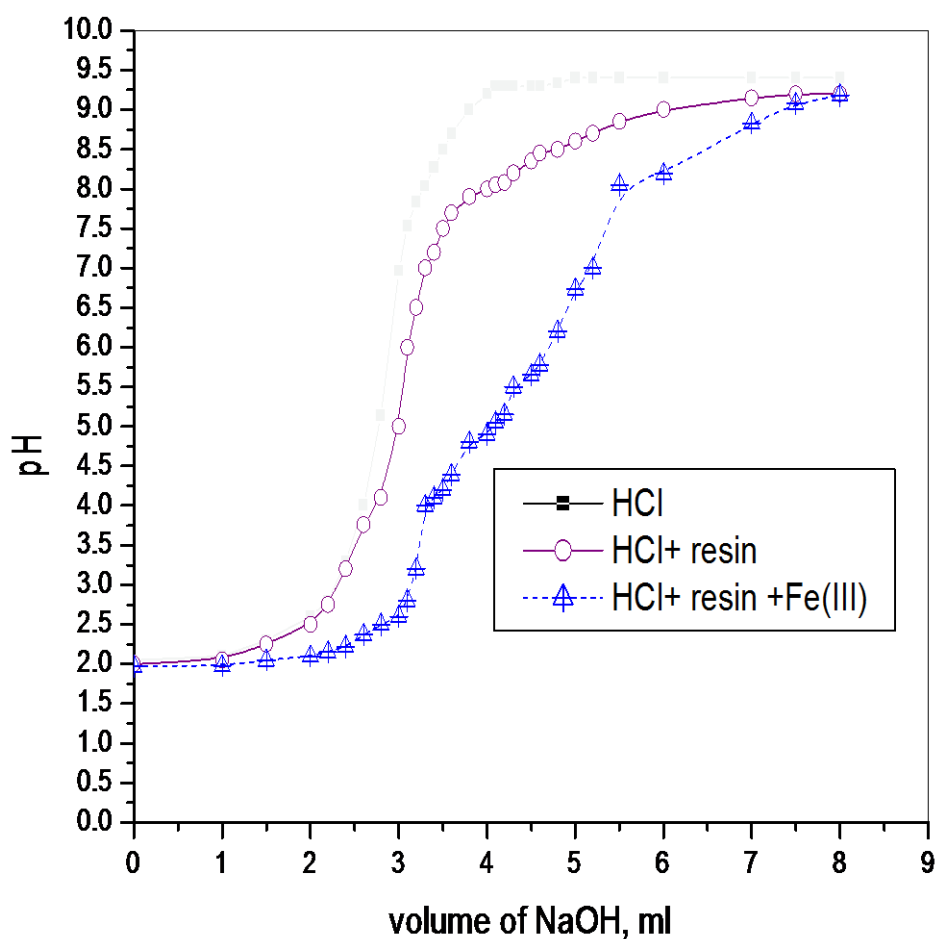


Figure 1. The pH metric titrations of HCl, [HCl + resin] and [HCl + resin + Fe(III)] against  $0.0052 \text{ mol l}^{-1}$  NaOH.

### 3.2. Preliminary investigations

Batch and column preliminary experiments were carried out to investigate the quantitative sorption of Fe(III) by Duolite C20 and DC20- DAPCH. It was found that, Duolite C20 have no sorption of Fe(III). On the other hand, the modified resin was found the superior due to its strong interaction with the Fe(III) ions through the active chelating groups in the loaded hydrazone *via* complexation. The analytical variables have been studied through the batch and column techniques.

#### 3.2.1. Batch technique

##### 3.2.1.1. 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 shaken with the modified resin for sufficient equilibrium time. Figure 2 shows that, the maximum efficiency of DC20-DAPCH 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 where this pH is preferred in the analysis of real samples (acidic biological and geological) and prevent the precipitation of metal hydroxides. Also, the lower stability of the resin at higher pH makes its use for sorption of metal ions in alkaline solutions unsuitable.

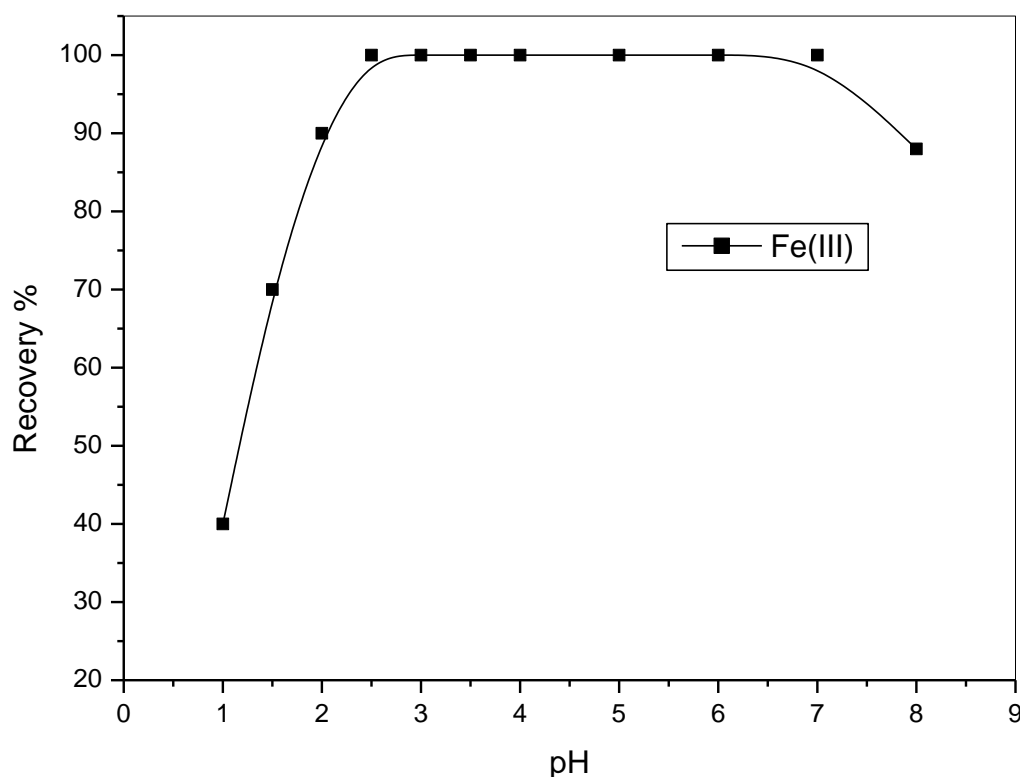


Figure 2. Effect of pH on the recovery % of Fe(III) using 50 mg DC20- DAPCH and stirring time 30 min at 25°C

### 3.2.1.2. Sorption capacity

The sorption capacity of DC20-DAPCH towards Fe(III) was determined by shaking excess Fe(III) with 50 mg of the resin and optimizing the conditions. The maximum sorption capacity is  $0.946 \text{ mmol g}^{-1}$ . The loading capacity of the modified resin is more than reported for *Rhizopus arrhizus* and *Chlorella vulgaris* [40]. The static adsorption capacity for Fe(III) selective iron(III) ion uptake using CuO-TiO<sub>2</sub> nanostructure by ICP-OES was calculated to be  $110.06 \text{ mg g}^{-1}$  [41].

### 3.2.1.3. Effect of amount of DC20-DAPCH

The amount of DC20-DAPCH 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 resin restricts the elution of the sorbed Fe(III) by a small volume of eluent quantitatively. So, the amount of resin must be optimized to 50 mg for subsequent experiments.

### 3.2.1.4. Effect of stirring time

To determine the rate of sorption of Fe(III) on DC20-DAPCH, batch experiments were elaborated by shaking 50 mg of the resin with 100 ml of feed solution containing Fe(III) ion at 25 and 50 °C. Aliquots of 0.5 mL solution were taken out for analysis at pre-determined intervals. The concentration of Fe(III) in the supernatant solution was determined and the sorbed amount was calculated.

The sorption half-time ( $t_{1/2}$ ) was estimated and the maximum sorption of Fe(III) reached its equilibrium time after 15, 12 and 10 min at 25 °C in water, ethanol and acetone, respectively (Fig. 3). The difference may be due to the hydration around Fe(III) is larger than solvation by ethanol or acetone. Therefore, the high polarity of water favors its interaction with the surface (less polar solvent such as acetone permits a great degree of interaction between metal ion and active centers on DC20-DAPCH) [42].

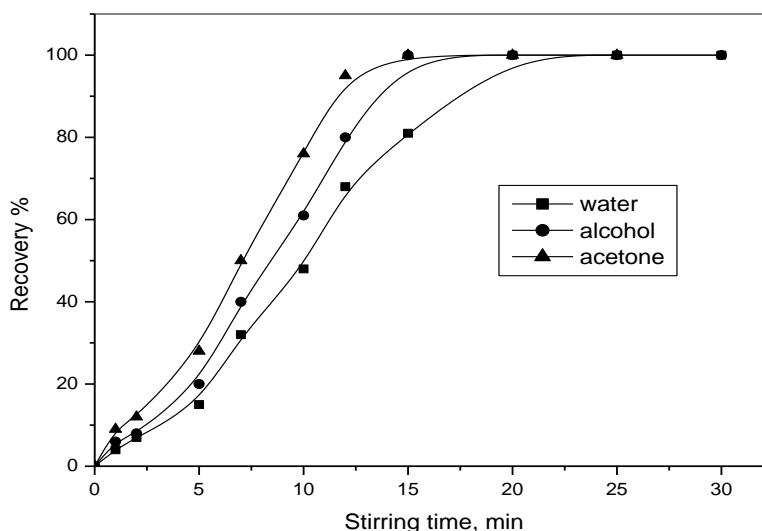


Figure 3. Effect of stirring time on the recovery % of Fe(III) using 50 mg DC20-DAPCH at pH 3 in water, acetone and ethanol at 25 °C

### 3.2.1.5. Choice of eluent

Choice of the most effective eluent for the quantitative stripping of the retained Fe(III) on Duolite C20-DAPCH is of special interest. The sorbed Fe(III) on the modified resin was eluted with acid solutions (HCl, HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>) 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 in Fig. 4 indicate that, 0.5 mol l<sup>-1</sup> of HCl affording quantitative elution of Fe(III) from the modified resin. Subsequent elution was carried out with HCl taken the advantage that, Cl<sup>-</sup> is acceptable matrix for AAS and spectrophotometric determination.

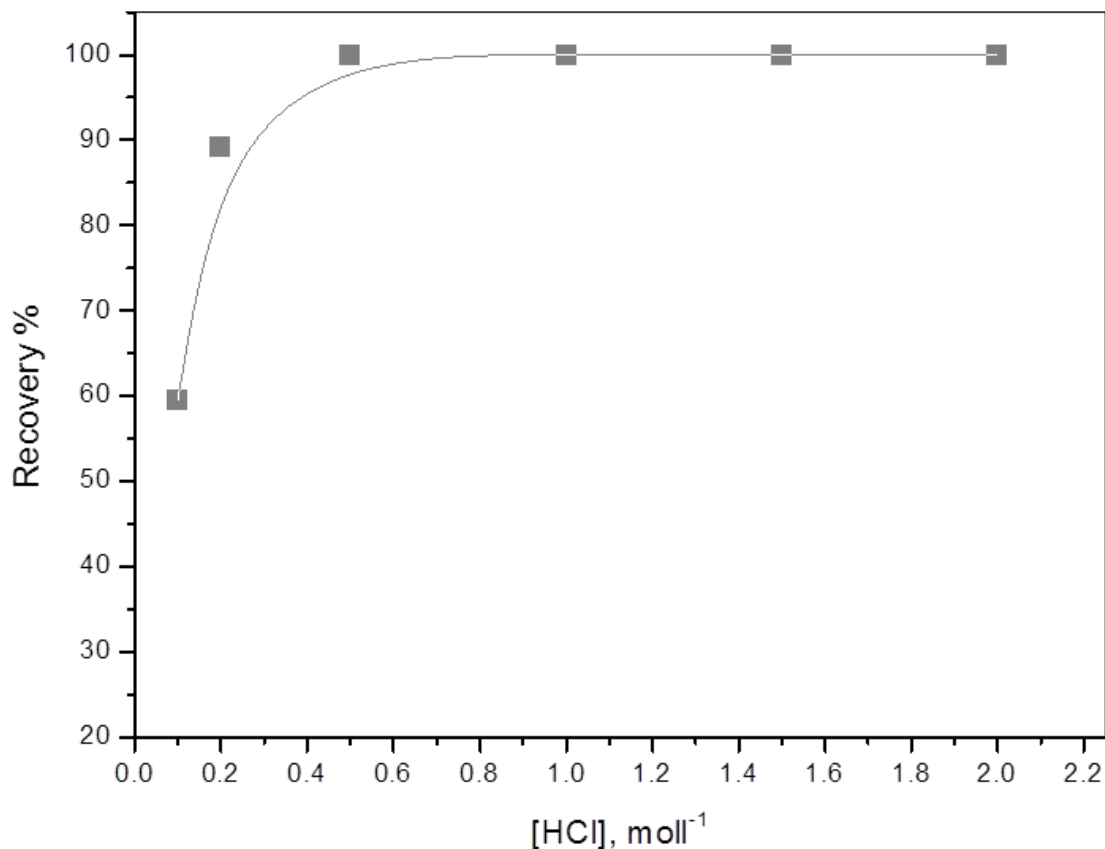


Figure 4. Effect of [HCl] (5 ml) on the recovery of Fe(III) using 50 mg DC20-DAPCH and stirring time 5 min at 25 °C.

### 3.2.1.6. Interferences

The effect of interfering cations and anions on the recovery of Fe(III) was studied and the results are summarized in Table 1. Most of the ions did not interfere during the extraction and determination of Fe(III). However, oxalate, citrate and tartrate caused a remarkable suppression of sorption. PO<sub>4</sub><sup>3-</sup> and SCN<sup>-</sup> have no effect on the sorption of Fe(III). Moreover, Cu(II) interfered in the determination of Fe(III) in presence of SCN<sup>-</sup>. The interference was eliminated by adding thiosulphate which turned Cu(II) to insoluble Cu(I), but doesn't interfere on the reaction of Fe(III) with DC20-DAPCH. Fluoride could be used as a masking agent for Fe(III). NaH<sub>2</sub>PO<sub>4</sub> has no effect; the method may be applicable for the removal of iron from Egyptian crude phosphoric acid.

Table1. Influence of interfering cations and anions on recovery percentage of  $10 \mu\text{g ml}^{-1}$  Fe(III) ion using 50 mg of Duolite C20-DAPCH at  $25^\circ\text{C}$ .

Interfering ion	Concentration ( $\mu\text{g ml}^{-1}$ )	Fe(III) (R %)
$\text{K}^+$	200	99.5
$\text{Mg}^+$	200	98.5
$\text{Ca}^{2+}$	200	98.5
$\text{NH}_4^+$	200	99.0
Acetate	200	100.0
Oxalate	200	57.0
Citrate	200	50.0
Tartrate	200	66.0
$\text{PO}_4^{3-}$	200	96.0
$\text{SO}_4^{2-}$	200	99.0
$\text{NO}_3^-$	200	99.5
$\text{Cl}^-$	200	99.9
$\text{SCN}^-$	200	99.9
$\text{F}^-$	200	00.0
$\text{S}_2\text{O}_3^{2-}$	200	98.5
EDTA	200	80.0

### 3.2.1.7. Resin stability and reusability

The modified resin (50 mg) was shaken with 100 mL of HCl ( $1-6 \text{ mol l}^{-1}$ ),  $1 \text{ mol l}^{-1}$  of NaCl, KCl or  $\text{NaNO}_3$  and organic solvents (ethanol, acetone or chloroform) for 24 h, filtered and washed with bidistilled water. After air drying, various elemental constituents were investigated. It was found that, no change in the resin composition suggesting a stable nature of the modified resin. It was noticed that, the hydrazone attached resin in the acid media began to dissociate in alkaline solution ( $\text{pH} > 9$ ) and the dissociation increases with increasing pH.

The modified resin was subjected to several sorption and desorption cycles by stirring 50 mg with 100 mL of  $25 \text{ mg l}^{-1}$  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) was found indicating that the modified resin is highly stable and may be used for several times. Storing the modified resin for ~ 6 months under the ambient conditions has no effect on its sorption capacity.

### 3.2.2. Column technique

#### 3.2.2.1. Effect of flow rate

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



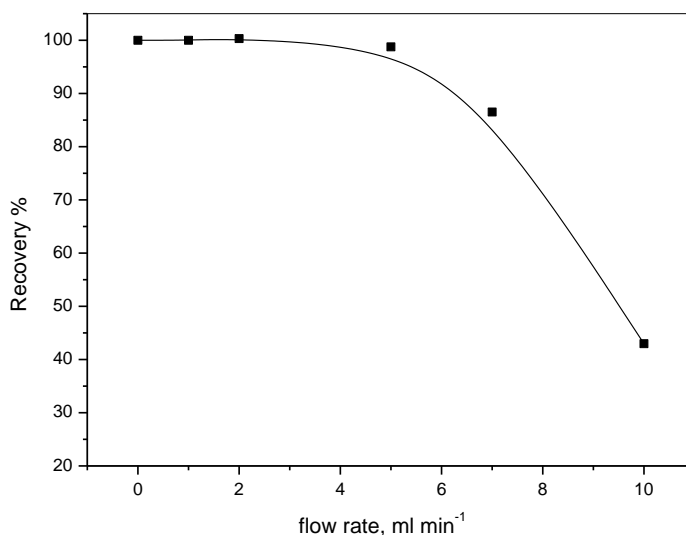


Figure 5. Effect of flow rate on the recovery of Fe(III) at 25 °C.

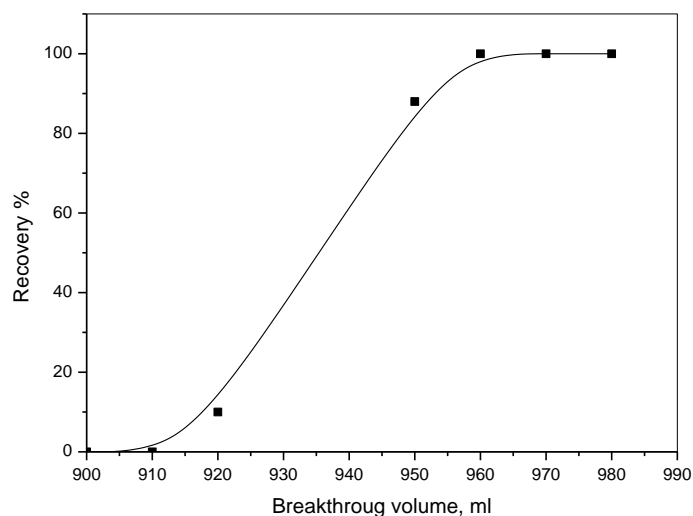


Figure 6. Breakthrough curve for Fe(III) ion with flow rate 5 ml min<sup>-1</sup> at 25 °C.

### 3.2.2.2. Breakthrough capacity

To evaluate the amount of Fe(III) sorbed on the modified resin under the optimum conditions, a breakthrough capacity is operated. The column was packed with 0.5 g of the modified resin and 50  $\mu\text{g ml}^{-1}$  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, Fe(III) was determined. The capacity (Fig. 6) indicates that, the column is saturated with 48  $\text{mg g}^{-1}$  of Fe(III).

### 3.2.2.3. Column reuse

To test the long-term stability of the column containing the modified resin, successive sorption

and elution cycles were carried out by passing Fe(III) solution through the column at the optimum flow rate, 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 Fe(III). The results of 100 sorption/desorption cycles indicate that, the recovery decreases by  $\leq 3\%$  reflecting good stability of the modified resin.

#### 3.2.2.4. Effect of volume and preconcentration factor

Aqueous solutions (0.1–2.0 L) containing 10  $\mu\text{g}$  of Fe(III) were passed through the modified resin bed, eluted with 5 ml of the appropriate concentration of HCl and determined. It was found that, Fe(III) may be removed quantitatively from volume up to 1.5 L, then the recovery decreases remarkably. Therefore, on using 5 mL of appropriate concentration of HCl as eluent, the preconcentration factor is 300 folds which are found high comparing with previous work [34].

#### 3.2.2.5. Detection limits

The detection limit was investigated for  $10^{-1}$ - $10^{-3}$   $\mu\text{g ml}^{-1}$  Fe(III) solutions passing through the resin bed at a suitable flow rate. The limit of detection (LOD) is 1.0 ppb, showing high sensitivity of the modified resin in preconcentrating trace Fe(III).

### 3.3. Applications

#### 3.3.1. Selective separation of Fe(III) from synthetic mixtures

In order to separate selectively Fe(III) from mixtures containing 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 suggested procedure (column mode) was followed. The results summarized in Table 2 showed that Fe(III) was sorbed by the resin, 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<sup>-1</sup>,  $n = 5$  at 25 °C.

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

*a: in presence of  $10^{-3}$  mol l<sup>-1</sup> S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. b: in presence of  $10^{-3}$  mol l<sup>-1</sup> SCN.*

#### 3.3.2. 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. The pH, total dissolved salts (TDS), dissolved oxygen (DO) and total alkalinity (mg CaCO<sub>3</sub> l<sup>-1</sup>) were determined according to the previous methods [20]. The quality of water was mentioned in Table 3.

Table 3. Water quality measurements for samples collected from different locations.

Type of water (Location)	Parameters				
	pH	TDS ( $\text{g l}^{-1}$ )	TSM ( $\text{g l}^{-1}$ )	TDO ( $\text{mg O}_2 \text{ l}^{-1}$ )	Alkalinity ( $\text{mg CaCO}_3 \text{ l}^{-1}$ )
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

Table 4. Analysis of water samples using AAS for determination of Fe(III) ion after preconcentration with DAPCH- resin at pH 3, flow rate =  $5 \text{ ml min}^{-1}$ ,  $n=5$  at  $25^\circ \text{C}$ .

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

The samples were acidified with concentrated  $\text{HNO}_3$  to  $\text{pH} \sim 2$  and preserved in a polyethylene vessel. The organic matter was digested prior to the separation process. 0.5 g of  $\text{K}_2\text{S}_2\text{O}_8$  and 5 mL of 98 % (w/v)  $\text{H}_2\text{SO}_4$  were added to 500 mL of the water sample and heated for 30 min at  $95^\circ \text{C}$ . After cooling to room temperature, 5 mL of  $10^{-3} \text{ mol l}^{-1}$  of  $\text{SCN}^-$  and  $\text{S}_2\text{O}_3^{2-}$  solution were added and the pH was adjusted to 3 and passed through the column with flow rate of  $5 \text{ ml min}^{-1}$ , then eluted with 5 mL of  $0.5 \text{ mol l}^{-1}$  HCl and analyzed as previously described.

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

### 3.3.3. Determination of Fe(III) in pharmaceutical samples

A tablet of drug or vitamin was digested using 5 mL of concentrated  $\text{HNO}_3$  and heated to near

dryness. After cooling, the residue was dissolved with another 5 ml of the acid. The solution was gently evaporated on a water 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 the pH, the procedure for the determination of Fe(III) was applied (column mode). The recovered amount of Fe(III) was determined and the results are listed in Table 5.

Table 5. Preconcentration and determination of Fe(III) in pharmaceutical tablets ( $\text{mg tablet}^{-1}$ ) at pH =3, flow rate =  $5 \text{ ml min}^{-1}$ , n = 5 and  $25 \text{ }^\circ\text{C}$ .

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)	$14.00 \pm 0.02$
Recovery%		100%
Centrum	Ca(162), Fe(27), Mg(100), Mn(7.5), K(7.5), Zn(22.5), Cu(3.00)	$26.77 \pm 0.20$
Recovery%		99.16%
Totavit.	Cr(25), Mn(2.5), Fe (18), Cu(2), Ni (0.005), Zn (15),	$17.94 \pm 0.05$
Recovery%		99.66%

Table 6. Determination of Fe(III) in non-aqueous media (100 ml, n=5 ) using column technique.

Samples	Added (Ppm)	Found (Ppm)	Recovery % $\pm \text{R.S.D}^a$
Food oil	0.0	1.50	$100.00+1.10$
(90% in ethanol)	5.0	6.49	$99.85+1.30$
	10.0	11.51	$100.08+1.00$
Kerosene	0.0	0.51	$100.00+1.00$
(90% in ethanol)	5.0	5.42	$98.73+1.87$
	10.0	10.50	$99.90+1.20$
Petroleum oil	0.0	5.60	$100.00+1.20$
(10% in benzene)	5.0	10.52	$99.24+1.50$
	10.0	15.62	$100.13+1.30$

<sup>a</sup> mean and R.S.D. of five determinations.

### 3.3.4. Determination of Fe(III) in ash coal

The ash coal was taken from the burner of Talkha electricity station; 0.5 g of the sample was digested with aqua regia and heated to near dryness. The residue is boiled with concentrated  $\text{HNO}_3$  and heated gently on a water bath to dryness, then diluted with doubly distilled water and filtered. The filtrate was then adjusted at the optimum pH, treated with suitable masking agent and the total volume was

completed to 100 mL and the procedure for the determination of Fe(III) was applied. The concentration of Fe(III) was found  $0.15 \text{ mg l}^{-1}$  with RSD of  $<0.90 \%$  ( $n = 3$ ).

### 3.3.5. Determination of Fe(III) in oil, kerosene and crude petroleum

The introduced method was applied for the 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 column procedure was applied. The results are given in Table 6. As 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 with Relative error less than 2 % for Fe(III).

## 4. CONCLUSION

A highly sensitive method was investigated to use 1-(3,4-Dihydroxybenzylidene)-2-acetylpyridinium chloride hydrazone (DAPCH) loaded on Duolite C20 in the removal of Fe(III) from different matrices. It was sorbed from aqueous solution at pH 3 and stripped using HCl. The maximum sorption capacity, the preconcentration factor and the detection limit of Fe(III) ion were  $0.946 \text{ mmol g}^{-1}$ , 300 and 1.0 ppb, respectively. The use of the resin was tested in water, ash coal, drugs, vitamin, kerosene and oil samples and showed RSD value of  $< 3\%$  reflecting its accuracy and reproducibility. Fe(III) is extracted from mixtures containing different metal ions in the presence of thiocyanate and thiosulfate. The resin was found sensitive to Fe(III) than thiocyanate.

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