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**Research Article** 

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# Chromatographic estimation of iron content in pharmaceutical samples using polyamine polyhalo polyurethane sorbent

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#### ABSTRACT

Polyurethane sorbent was developed by adding new chelating groups and changes the polarity of the matrix. The polyamine polyhalo polyurethane sorbent (PPPs) contains °1 amine, halogen, ether and urethane groups, which reveals its potential for extraction and recovery of iron(III) ions. The effects of different parameters including pH, shaking time, flow rate, temperature and initial concentration of iron were studied to optimize the presented procedure. Maximum sorption of Fe(III)ions on to PPPs was achieved in acidic medium (pH 1-2 and 5) at a period range 1-5 min. A perfect isotherm curve with zero intercepts (0.005), a good correlation ( $R^2$ =0.986) has been obtained. The values of LOD, LOQ and RSD (n=6) for determination of Fe(III) ions are 3.0 ng L<sup>-1</sup>, 10.1 ng L<sup>-1</sup>, and 0.75%, respectively. The batch capacities of the PPCIPs, PPBrPs and PPIPs were 0.133, 0.124 and 0.118mmolg<sup>-1</sup>, respectively. The accuracy of the procedure was verified by the analysis of iron drugs samples with recoveries were 100% which indicated that PPPs have a great potential to determine iron in real samples.

Keywords: Iron; Polyurethane sorbent; Pharmaceutical; Recovery; Extraction

### INTRODUCTION

Iron is essential micronutrients with a variety of bio chemical functions in all living organisms [1-4]. Iron plays a main functional role in hemoglobin, myoglobin, haemenzymes formation and oxidative processes of living tissues and iron deficiency is the most common cause of defective erythropoiesis and anemia [5, 6]. Also, the iron supplements are primarily used to treat anemia or other iron deficiencies. Direct determination of iron ionsin different medical and environmental purposesis to some extent a problem because of the high concentration of interfering matrix components [7, 8]. The coupling of a separation/preconcentration procedure and elimination of iron ions were considered: pH, initial concentrations, shaking time and solution temperature. The equilibrium, kinetic and thermodynamic models for the separation and recovery of iron ions was studied to optimize the condition for the estimation process.

The flexible polyurethane foam (PUF) is a copolymer consist from low molecular weight polyols [polyether,( $CH_2CH_2O$ )<sub>n</sub>]linkage through urethane groups (NHCOO)[9-11].Many reports used of PUF as a low cost sorbent [12-15].It is an excellent material due to cellular structure and high available of surface area, excellent thermal stability and solvent resistance [16-19].The PUF immobilized, incorporated or coupled with chelating ligands are used for preconcentration, separation and determination of trace metal ions [20-22]. The high density of PUF/ligand is an inconvenience, which they cause to decrease sorption capacity of PUF and decrease the extraction rate of metal ions. This problem demand preparation of low density PUF has high sorption capacity without an addition of these reagents. The modification of PUF surface by adding new chelating groups which to dissolve this problem [23, 24].In this study, Adding °1 amine and halogen (Cl, Br or I) groups is the basis to improve of the PUF surface and increasing of its sorption capacity. Modified PUF (PPPs) was prepared by refluxing of the low density PUF with HCl to produce a high number of amino groups, then diazotization of it by NaNO<sub>2</sub> followed by added of

CuCl, CuBr or KI solution. Although the simple and inexpensive of this procedure for modified of PUF, the PPPs has a high ability for complete extraction of heavy metal from aqueous solution.

#### **EXPERIMENTAL SECTION**

#### 2.1. Chemicals and reagents

PPPs were prepared according to Sand Meyer reaction [25, 26]. The substitution of an aromatic amino group is possible via preparation of its diazonium salt and subsequent displacement with a nucleophile e.g. Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>.

Stock solutions (1 mg mL<sup>-1</sup>) of Fe(III) was prepared by dissolving appropriate amounts of an analytical category of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (Merck, Germany)in distilled water containing 1mL conc. H<sub>2</sub>SO<sub>4</sub>. A series of 25 mL for metal standard solutions (0–20 mg L<sup>-1</sup>) were used for the preparation of calibrations curve.

#### 2.2. Apparatus

All absorbance measurements were monitored by Shimadzu Model UV-1800 (Shimadzu Corporation, Japan) and Jasco UV/VIS Spectrometer v-630 (Jasco, Japan). The pH measurements were carried out using a pH meter from Jenway 3510 PH-meter (Jenway, Beacon Road, Stone, Staffordshire, ST15 OSA, UK).

#### 2.3. Recommended procedures

Extraction of Fe(III) ions was carried out by a batch technique at 25 °C. Adsorption experiments were carried out by agitating 0.1 g of PPPs with 25 mL of Fe(III) solution (8mg L<sup>-1</sup>) in a shaker adjusted to the desired speed. After shaking 60 min, the iron concentrations remaining in the supernatant solution and recovering from PPPs by 0.1 M HCl were determined by using UV-Vis spectrophotometer as thiocyanate complex. The following equations were used to calculate the uptake percentage of iron ( $\% E = ((C_o - C)/C_o) \times 100$ ) and capacity of PPPs ( $Q = EC_oV/m$ )where C<sub>o</sub> and C are the initial and final concentrations of iron in solution, respectively. V is the volume of iron solution and m is the mass of PPPs.

In the dynamic experiments, 1.0 g portion of PPPs was packed into a column (15-cm long and 1.5 cm in diameter). 25 mL of Fe(III) solution (0.2mg L<sup>-1</sup>) was passed through the PPPs column (L= 6 cm) at flow rate 2 mL min<sup>-1</sup>. Effluents werecollected and analyzed spectrophotometrically. The elution of the iron from the PPPs columns was carried out using (0.3mol L<sup>-1</sup>)KCl then the amount of iron was determined spectrophotometrically.

#### **RESULTS AND DISCUSSION**

#### **3.1. Optimum condition for extraction of iron(III) ions onto PPPs**

The effect of pH on the extraction of Fe(III) ions from thiocyanate solution using PPPs has been examined by batch technique. The pH the ironsolution was adjusted before equilibration usingHCl and NaOH solutions. The uptake percentage of iron was plotted against the pH value. Iron(III) was completely extracted onto PPPs as anion thiocyanate complex from aqueous solution at pH 1-2 then decreased to 80% at pH 7 (Fig. 1). At pH < 3.3, the surface of the PPPs is positively charged; the result shows that the extraction process mainly depends on the ion association complex formed between the PPPs cation in acidic medium (pH < 3.3) and the anion metal thiocyanate complexes (PPPs<sup>+</sup>: [M(SCN)<sub>n</sub>]<sup>m</sup>). While the sorption Fe(III) ions onto PPPs at pH between 3.3 and 7 as chelation process. At pH 1-2, the sorption percentage of Fe(III) onto PPCIPs > PPBrPs > PPIPs. While the iron(III) ions onto PPIPs is more sorbed than PPCIPs and PPBrPs at pH 5. This result shows that the sorption process is depended on the type of sorbent due to the polarity of functional groups.

The sorption rate of iron onto PPCIPs, PPBrPs and PPIPs has been measured using batch extraction mode at different time intervals (1-30 min). The result obtained shows that the time required for complete extraction of Fe(III) onto PPCIPs, PPBrPs and PPIPs are2, 15 and 15min, respectively (Fig. 1). This indicated that the rate of sorption of the iron ions onto PPCIPs was rapid than PPBrPs and PPIPs due to the nature of reaction between the PPPs and iron(III) thiocyanate complex.

The pseudo-first order [  $\log(Q_e - Q_t) = (\log Q_e) - (k_1 t / 2.303)$  ] and pseudo-second order [

 $t/Q_t = (1/k_2Q_e^2) + (t/Q_e)$ ] kinetic models are tested for the sorption of Fe(III) ions onto PPCIPs, PPBrPs and PPIPs (Fig. 2). The R<sup>2</sup> value for pseudo-first order sorption model (0.802) is lower than the value of R<sup>2</sup> (0.999) for pseudo-second order kinetic. This suggests that the pseudo-second order sorption mechanism is predominant. Comparing the correlation coefficient (R<sup>2</sup>) values, we found that the sorption kinetics was best described by the pseudo-second order model. The R<sup>2</sup> values for pseudo-second order sorption model (0.999) are higher than those for

pseudo-first order kinetic (0.803). This suggests that the pseudo-second order adsorption mechanism is predominant and that the overall rate of the iron sorption process appears to be controlled by chemisorption process. The values of the initial rate constant  $(h=k_2Q^2)$  were 0.108, 0.043 and 0.041 mol g<sup>-1</sup> min<sup>-1</sup> for sorption of Fe(III) ions onto PPCIPs, PPBrPs and PPIPs, respectively. The values of *h* sequence were in order PPCIPs>PPBrPs and PPIPs. This result indicates that the rate of sorption is depending on the polarity of sorbent. The values of the rate constant of the sorption ( $k_2$ ) calculated from the line slope were88.2, 40.0 and 40.0 g mmol<sup>-1</sup> min<sup>-1</sup>, respectively. The values of the half-life ( $t_{1/2} = 1/Ck_2$ ) were0.6, 1.3 and 1.3 min for the sorption of iron(III) onto PPCIPs, PPBrPs and PPIPs, respectively.



Fig. 1: Effect of initial pH, contact time, sample volume and dose of PPPs on the extraction of iron



Fig. 2: The pseudo first order and pseudo second order for the sorption of iron on to PPCIPs, PPBrPs and PPIPs

The effect of iron concentration on the capacities of PPCIPs, PPBrPs and PPIPs was studied. The relation between the amount of sorbed iron per unit mass of PPPs and the initial Fe(III) concentration (Fig. 3). A perfect linear curve with zero intercept (0.0052) and good correlation ( $R^2$ =09861) has been obtained (Table 1). It is clear that the capacity was increased with increasing the initial concentration and reached a plateau (maximum uptake capacity values) were obtained. The sorption capacities of PPCIPs, PPBrPs and PPIPs for iron from thiocyanate solution were estimated to be 0.133, 0.124 and 0.118mmol g<sup>-1</sup>, respectively. The capacity sequence was in order PPCIPs >PPBrPs > PPIPs due to the polarity of sorbents which agreement with theresult obtained from the breakthrough curve (Fig 3). The achieved results illustrated thatthe PPPs is more efficient than another type of PUF [27-30].

Table 1:	Characteristics o	f the isotherm	curve for sorption	of iron(III)	onto PPPs
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Sorbent	Least squa	are equation	correlation coefficient ( $\mathbf{P}^2$ )	Capacity
Sorbein	Slope	Intercept	correlation coefficient (K)	mmol g <sup>-1</sup>
PPClPs	0.190	0.0056	0.984	0.133
PPBrPs	0.184	0.0038	0.988	0.124
PPIPs	0.161	0.0064	0.987	0.118



Fig. 3: Isotherm and breakthrough curves for extraction of iron(III) using PPPs sorbents

The detection limit (LOD) was established by analyzing four blank solutions (LOD =  $3 \sigma$ , where  $\sigma$  is the standard deviation of blank determination). The value of LOD of Fe (III) was 0.042 ng mL<sup>-1</sup> (Table 2) Also, the limit of quantitation (LOQ =  $10 \sigma$ ) was 0.140 ng L<sup>-1</sup>. The LOD and LOQ value for the studied ions with the PPPswould enable the use of this material in collection of iron ions at a trace concentration prior to their determination with high accuracy.

	Table 2: The detection limit of iron(III) ions,	recovery percentage and relative standard deviation
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Sorbont	LOD	LOQ	Recovery	RSD
Sorbein	ng L <sup>-1</sup>	ng L <sup>-1</sup>	%	%
<b>PPC1Ps</b>	3.9	13.4	95.56	1.07
PPBrPs	2.1	6.8	89.94	0.40
PPIPs	3.1	10.2	90.06	0.79

The accuracy and precision for the different fortification levels of the sample were estimated. The recoveries percentage values using batch technique ranged from 90.3 % to 95.6 % with the low relative standard deviation values (RSD=0.75%) for the analysis of six samples replicates of Fe(III) indicate a good precision and accuracy of the proposed method. This result shows that the PPPsare suitable for the determination of tested metal ions in water samples. The values of LOD and RSD% due to the application of PPPs method for the determination of Fe(III) indicate that the PPPs sorption method is more efficient than other methods [17, 31-34].

The effect of solution temperature on the extraction of Fe(III) using PPCIPs, PPBrPs and PPIPs has been studied (Fig. 4). The result shows that the maximum sorption of Fe(III) occurs at high temperature and the extraction

percentage of iron(III) ions increases with the increasing of the temperature. Thermodynamic parameters for the sorption of Fe(III) were calculated using the equations:  $\ln K = -\Delta H/RT + \Delta S/R$ ,  $K = ((C_o - C)/C)$  and  $\Delta G = \Delta H - T\Delta S$  where K is the distribution coefficient for sorption. The plot of ln K vs. 1/T gives the numerical values of  $\Delta H$  and  $\Delta S$  from slope and intercept of the plot (R<sup>2</sup>=0.551). The positive value of  $\Delta H$  (15.6 kJ mol<sup>-1</sup>) indicate that the sorption process of iron is endothermic chemisorption (Table 3). While the average value of the entropy (67.6 J K<sup>-1</sup>mol) is an indication of the faster sorption of Fe(III) onto PPPs. The  $\Delta G$  have been evaluated using the equation:  $\Delta G = \Delta H - T\Delta S$ . The negative values of  $\Delta G$  (-4.5 kJ mol<sup>-1</sup>) indicate that the feasibility of the process and its spontaneous nature without induction period.

Sorbent	$\frac{\Delta G}{kJ \text{ mol}^{-1}}$	$\frac{\Delta H}{kJ \text{ mol}^{-1}}$	$\frac{\Delta S}{J \text{ mol}^{-1}}$
DDCID	7.1	10 (	

Table 3: The thermodynamic parameters for extraction of iron(III) onto PPPs



Fig. 4:Thermodynamic parameters for the sorption of Fe(III) onto PPPs sorbents

The effect of batch factor (sample volume 10-125 mL to the 0.1 g of PPPs, V/m) on the recovery of Fe(III) ions was studied (Fig. 1). The result indicated that the maximum recovery of iron in batch factor (V/m) 100–250 then the recovery decreases with the increasing of the batch factor. Also, the effect of volume (25 mL) to the 0.01-0.2 g of PPPs on the recovery of iron was studied. The maximum recovery of the iron in a batch factor (V/m) ranged from 125 to 250then decreased to 50% in V/m 1250.

The sample flow rate through the PPPs columns is a very important parameter since it controls the time of analysis. The dependence of the uptake of the Fe(III) on the flow rate (0.5-20 mL min<sup>-1</sup>) was studied and the uptake percentage of the iron (III) ions was estimated. The maximum uptake percentage(100%) observed in the range 1–5 mL min<sup>-1</sup>. Faster flow rates than 5 mL min<sup>-1</sup> led to decrease the uptake percentage (95%).

The effect of various eluting agents like HCl, H<sub>2</sub>SO<sub>4</sub>, NaOH, NH<sub>4</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, Na<sub>2</sub>SO<sub>4</sub>, KCl, (1:1) HCl and KCl on the stripping of iron from PPPs column was tested. It is observed that Fe(III) was completely eluted from PPPs with 25 mL of 2 mol L<sup>-1</sup>KCl. Also, the elution of 2 mg of Fe(III) from the PPPs columns by using 0.3 mol L<sup>-1</sup>KCl was tested at various flow rates (0.5-5 mL min<sup>-1</sup>). The chromatograms indicate that iron was completely eluted within the first 5-30 mL (Fig 5).



Fig. 5: Effect of eluent flow rates on the recovery of iron(III) from PPPs columns

#### **3.2Applications**

The validity and accuracy of the PPPs column and batch procedure were successfully assessed by estimate of iron content in cement, fertilizer and pharmaceutical samples.

The iron content in the Haemojetampoule (European Egyptian Pharm. Ind., Alexandria, Egypt), Ferro-6Capsule (Pharco Pharmaceuticals, Alexandria, Egypt) and Ferro- ZSyrup (Napco PharmaIndustrial, 10th Of Ramadan City, Egypt) wereestimated. Samples were digested in 2 mL of concentrated HNO<sub>3</sub> by slowly increasing the temperature up to 150 °C till dryness. After cooling, the residue was dissolved in 20 mL of concentrated HNO<sub>3</sub>. Then the solution was gently evaporated on a steam bath till dryness then left to cool down. The residue was mixed with distilled water and few drops of concentrated HNO<sub>3</sub> until a clear solution was obtained and the pH was adjusted to the recommended value and finally transferred into a 25 mL graduated measuring flask and filled up with distilled water to the mark. Then dynamic procedures were applied. The chromatograms of eluted ironwere shown in Figure 6. The iron estimated is in agreement with the values in certified samples.



Fig. 6: Chromatograms of iron recoveries from the drug samples from PPPs columns

#### CONCLUSION

The present work is concerned with the preparation of new sorbent (PPPs) containing primary amine and halogen groups. The PPCIPs, PPBrPs and PPIPs were used for recovery and determination of iron(III) traces. The maximum extraction of anionic iron thiocyanate complex occurs in acidic medium (pH 1-2). The kinetic and thermodynamic parameters for the extraction of the Fe(III) ions onto PPPswereestimated. The negative values of  $\Delta G$  indicated that the spontaneous nature of the sorption of Fe(III). The sorption mechanism of iron ions onto PPPs may proceed via the ion association and chelation processes. This study could conclude that PPPs has the ability to recovery and determine iron in pharmaceutical samples.

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