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Sorption behaviour, diffusion mechanism of the iron metal ions in the environmental samples onto polyurethane foam

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ABSTRACT

The sorption properties of polyurethane foam (PUF) and chromatographic behaviour for separation and determination of iron metal ions were investigated. The diffusion mechanism of iron metal ions onto PUF was studied under particle diffusion conditions and limited batch technique. The maximum sorption of Fe (III) was in the pH values of 2.1. The variation of the sorption of the Fe(III) ions with temperature gives an average values of ΔH , ΔS and ΔG to be $-102.3 \text{ kJ mol}^{-1}$, $-314.0 \text{ J K}^{-1} \text{ mol}^{-1}$ and -9.7 kJ mol^{-1} , respectively. The average sorption capacity of PUF was 1.69 mmol g^{-1} for the preconcentration factors of values ~ 250 and the recovery 98% were achieved (RSD $\approx 0.48\%$). The modified of Morris-Weber equation, $y = a\sqrt{x} \pm b$ where $a = f(r^+, r', z, T, C)$ and $b = f(Qe)$ was examined for the interpretation of the diffusion mechanism of sorption of iron metal ions onto PUF. The determination of Fe(III) in the environmental samples using PUF was applied.

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KEYWORDS

Polyurethane foam;
Sorption behaviour;
Diffusion;
Determination;
Iron.

INTRODUCTION

Polyurethane foam (PUF) is an excellent sorbent for separation and preconcentration of the trace metal ions in environmental samples with an inexpensive method. This material has low density, good flexibility, high selectivity and good stability. For these reasons, a considerable interest in PUF had risen in the two last year^[1-9]. The kinetics study of sorption of metal ions onto PUF is important since it provides information on the mechanism of rate controlling process and on the reactions accompanying the extraction as well as on the internal physical structure of the PUF and the extracted ions.

Saeed et al.^[10,11] initiated the interpretation of kinetic data for the sorption of Co and Cd ions onto PUF either by diffusion or mass action transfer. The first interpretation of the kinetic data treated PUF as porous particles of spherical shapes and assumed that metal ions diffuse into these micropores. Assuming that the time dependency of bulk sorption was governed by intraparticle diffusion, the equation given by Morris-Weber (M-W), $Q_t = k_M \sqrt{t}$ was applied, the plot was linear but does not pass through the origin as predicted from equations, showing that the particle diffusion mechanism was not operative and did not control the kinetics of cobalt sorption on PUF. Hasany et al.^[12,13], El-Shahawi et al.^[14-16] and de Almeida et al.^[17] applied

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the M-W equation on the kinetics of Co, Ag, Hg, U, Se, Au and nitrophenol sorption onto PUF. The diffusion rate of these metal ions was rapid in the initial stages, and slowed down with the passage of time and the plot was deviated with increased time. Moawed et al.^[18-21] studied the kinetics of sorption of Li, Na, K, Ag, Ni, Cu, Pd, Cd, Hg, Au and U ions onto different type of PUF. The M-W equation was applied, the data obtained showed that the values of the interparticle rate constant was dependent on the ionic size of metal ions and the size of PUF. Finally, the M-W equation was applied on the sorption of Cr, Pb, Cd, Ni, Cu, and organic matter onto different sorbents e.g. sunflower stem^[22], XAD-16^[23,24], Styrofoam^[25], beach sand^[26], rice husk^[27], *Moringa oleifera* pods^[28] and poly(hydroxyethylmethacrylate)^[29]. The results obtained for these sorbents were in agreement with PUF.

The methodology of the present work is to study the chromatographic behaviour of extract of iron metal ions onto PUF in order to examine approaching of the exact condition of sorption of metal ions onto PUF. Also, we interpret the deviation for the application M-W equation on the sorption of metal ions onto PUF. Finally, we apply PUF for the preconcentration and determination of the Fe(III) metal ions in environmental samples.

EXPERIMENTAL

Reagents and materials

All reagents were prepared from analytical reagent grade chemicals and bidistilled water. A 1 mg mL⁻¹ stock solution of metal ions was prepared by dissolving Fe(NO₃)₃·9H₂O in water, the solution is then diluted to 100 mL in a measuring flask. A 4 mol L⁻¹ potassium thiocyanate solution was prepared by dissolving 97 g of KSCN in 250 mL of H₂O. Commercial white sheets (density ≈ 12-25 kg m⁻³) of open cell polyether type based polyurethane foam were used.

Apparatus

All spectrophotometric measurements were performed using spectro UV-Vis RS Digital spectrophotometer (Labomed, Inc). The pH measurements were carried out using a pH meter from Microprocessor pH Meter (HANNA Instruments).

RESULTS AND DISCUSSION

In order to estimate the best conditions for the determination of iron (III) metal ions and to interpret of the diffusion mechanism, we studied the sorption behaviour of Fe(III) ions onto PUF.

Optimum conditions for sorption of iron, cobalt and nickel onto PUF

The effect of pH on the separation of Fe(III) ions onto PUF was examined using a batch technique. A 0.1 g portion of the PUF mixed with 25 mL aliquot solution containing 4 µg mL⁻¹ of Fe(III) ions and 0.8 M of KSCN at different pH values. After shaking for 15 minutes, the solutions were separated and the concentration of metal ions was determined spectrophotometrically using thiocyanate method in acidic medium at λ_{max} 495 nm. The pH values were plotted against the uptake as shown in Figure 1. The optimum pH ranges to separate Fe(III) from aqueous solution was 1.4-2.4 and the uptake of [Fe (SCN)₆]³⁻ was decreased with increasing pH values 2.5-3.5. This result shows that controlling the pH can play a role to enhance the selectivity of Fe(III) ions separation with PUF.

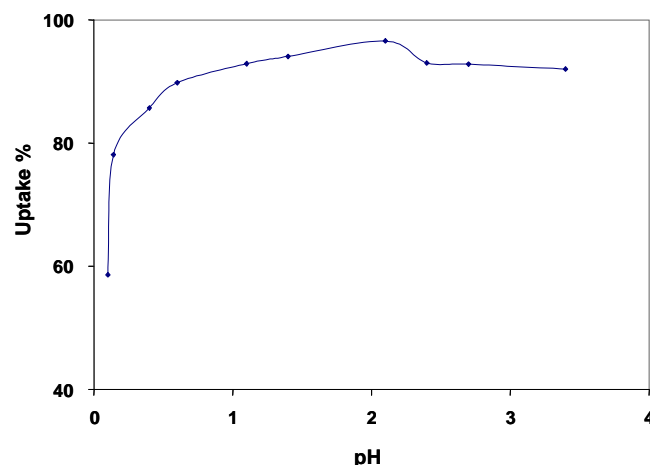


Figure 1 : Effect of pH on the sorption of iron (III) ions onto PUF

The uptake of Fe(III) ions (7.16×10^{-5} mol L⁻¹) with PUF was found to be strongly dependent on the thiocyanate concentration, thus the concentration of KSCN in the extraction medium was studied in the concentration range from 0.01 to 2 -mol L⁻¹ KSCN. From the results obtained, the sorption of iron (III) ions increases with the increasing of ligand concentra-

tion (from 0.01 to 0.80 mol L⁻¹), then it slightly changed with the increasing of KSCN concentration (0.4-8.0 mol L⁻¹). The optimum KSCN concentration ranges necessary for the maximum uptake of Fe (III) ions were 0.8-2.0 mol L⁻¹[30].

Uptake of the Fe(III) on PUF was determined as a function of metal ions concentrations in the aqueous solution. The linear plot of Q vs. [Mⁿ⁺] is shown in Figure 2. The resultant isotherms show a good linear relationship over a relatively wide range of [Mⁿ⁺] with zero intercept (0.0013) and a good correlation (r=0.9997). The low relative standard deviation values (RSD~ 1.79%) for the analysis of five samples replicates of the Fe (III) which indicates a good precision and accuracy of the proposed method.

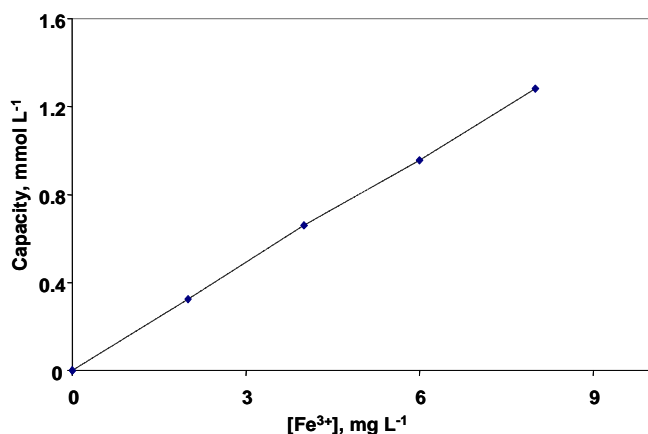


Figure 2 : Isotherm curve of the sorption of Fe(III) ions onto PUF

The results were analyzed using Dubinin Radushkevich ($\ln q_c = \ln k_{dr} - \beta \varepsilon^2$ & $\varepsilon = RT \ln[1 + \frac{1}{q_c}]$) equation, where “ q_c ” is the amount of Fe(III) ions sorbed per unit mass of PUF, “ q_c ” is the amount of metal ions sorbed at equilibrium and K_{DR} is a constant. The computed average value of β from the slopes is $-5.9 \times 10^{-3} \text{ kJ}^2 \text{ mol}^{-2}$. The activation energy of the cation diffusion process is very important since it reflect the ease with which cation can pass through PUF particles. The value of ΔE can be correlated to β ($E = 1/\sqrt{-2\beta}$). The evaluated average value of (E) is 9.2 kJ mol^{-1} for metal ions sorbed. The small value of ΔE suggests that the rate is particle diffusion controlled[31]. The average capacity of the PUF for iron metal ions was estimated to be 1.69 mmol g^{-1} .

The dependence of sorption of Fe(III) ions onto

PUF with temperature was evaluated using the equations: $\ln K_c = -\Delta H / RT + \Delta S / R$, and $\Delta G = \Delta H - T\Delta S$. The plot of $\ln K_c$ vs. $1/T$ gives the numerical values of ΔH and ΔS from the slope and the intercept, respectively (Figure 3). The uptake of metal ions decreases with the increasing of temperature. The average value of (ΔG) is -9.7 kJ mol^{-1} , the negative values of ΔG are attributed to the spontaneous nature of sorption process. Similarly, the negative values of ΔH (with average value $-102.3 \text{ kJ mol}^{-1}$) may be interpret as the exothermic chemisorptions process, while negative values of entropy (with average value $-314.0 \text{ J K}^{-1} \text{ mol}^{-1}$) may be indicative that the sorption is fast. The low activation energy of the sorption as compared to the enthalpy indicates the strong attraction operation during sorption and the uptake process can occur even under normal conditions.

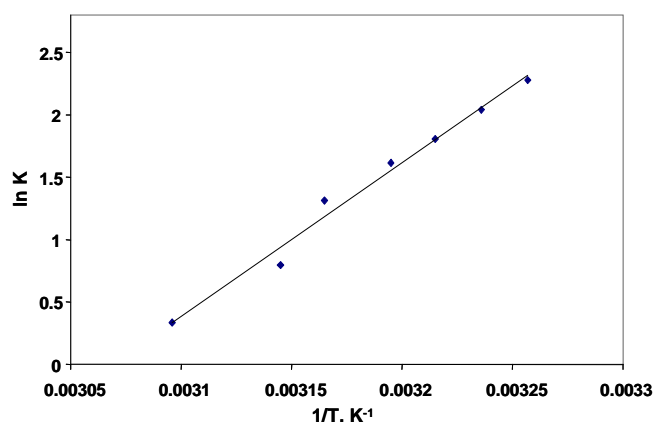


Figure 3 : Effect of temperature on the sorption of metal from aqueous solution

The performance of PUF in preconcentration of iron metal ions in different volumes of aqueous solution was studied. The effect of the sample volume (10-100 mL) to the weight of PUF (0.1 g) on the uptake was studied using batch technique. The data indicate that the maximum sorption of metal ions in batch factor (V/m) ranges from 200 to 300. The uptake of the iron (III) ions decreases with increasing of the sample volume (from 98% to 52.6%) in batch factor, $V/m \sim 750$.

The effect of different types of PUF which have different densities ($12-25 \text{ Kg m}^{-3}$) on the separation of Fe(III) was examined using batch technique. The density values of PUF were plotted against the uptake. The uptake of metal ions increases with decreasing the PUF density (93-98%). This result is due to the type of low

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density PUF that has a large pore size and more active centers than the high density PUF.

The influence of particle size of PUF (0.12–0.89 cm³) on the extraction of Fe(III) was studied. From the results obtained show that the uptake of the PUF for Fe(III) is slightly changed (94.2–98%) with the particle size of PUF due to using type of flexible polyurethane foam has low density.

The effect of various eluting agents like HCl, NaOH, NH₄OH, NaF, Na₂C₂O₄, (NH₄)₂C₂O₄, Na₃PO₄ and CH₃COCH₃ on the stripping of Fe(III) ions from PUF matrix was studied. It was observed that the Fe(III) was partially eluted by NaF, Na₃PO₄ and HCl, while NH₄OH, (NH₄)₂C₂O₄ and CH₃COCH₃ completely eluted the Fe (III) from the PUF matrix.

Sorption diffusion mechanism of iron onto PUF

The rate of sorption of Fe(III) ions onto PUF (0.28 cm³) was measured by batch extraction mode at different time intervals, i.e., 0.1–30 min. From the results obtained, the time required for sorption equilibrium for Fe(III) was found to be 5 minutes. This rapid extraction is due to the application of PUF by using batch technique.

Sorption of iron (III) ions on PUF may involve three steps: bulk transport of the solute in the solution, film transfer involving diffusion of the solute through a hypothetical film boundary layer and diffusion of the solute within the pore volumes of the adsorbent and along pore-wall surfaces to active adsorption sites^[10]. In previous published articles^[10–24], results of studies on the diffusion mechanism of metal ions onto PUF using the equation of M-W show that the plot of Q_t versus $t^{1/2}$ was linear but does not pass through the origin and deviated with the increasing of time. Therefore, we apply M-W equation to study the factor affect the diffusion mechanism of Fe(III) ions onto PUF and to interpret the deviation of these model on the sorption of metal ions onto PUF.

The obtained data show that the plot consists of three lines as predicted by the M-W equation (Figure 4). The lines do not pass through the origin. The diffusion rate is high in the initial stages and decreased with the passage of time. The time required for the initial stage is one minute and the average value of the uptake in this time nearly about 70% (n=5). Also, the time re-

quired for sorption in the second and third stages are 1 and 7 minutes (n=5), respectively and the uptakes for these times are 11.9 and 13.8%, respectively. The values of diffusion rate constant (k_M) are computed from the three distinct slopes (Figure 4). The average value (n=5) of k_M is estimated to be 0.73 mmol g⁻¹ min⁻¹ in the initial stage up to one minute and is reduced to 0.13 mmol g⁻¹ min⁻¹ up to one minute in the second stage, then to 0.03 mmol g⁻¹ min⁻¹ up to 7 minutes in the third stage. The decrease of k_M in the second and third steps is due to the retardation and blocking of the active centers which mean the saturation of the surface by adsorbed molecules. The values of intercept of the three lines of the plot are -0.23, +0.40 and +0.56, respectively. Finally, the equations of the three stages are $y = 0.73x - 0.23$ ($R^2 = 0.99$), $y = 0.13x + 0.40$ ($R^2 = 0.96$) and $y = 0.034x + 0.56$ ($R^2 = 0.97$), respectively (n=5).

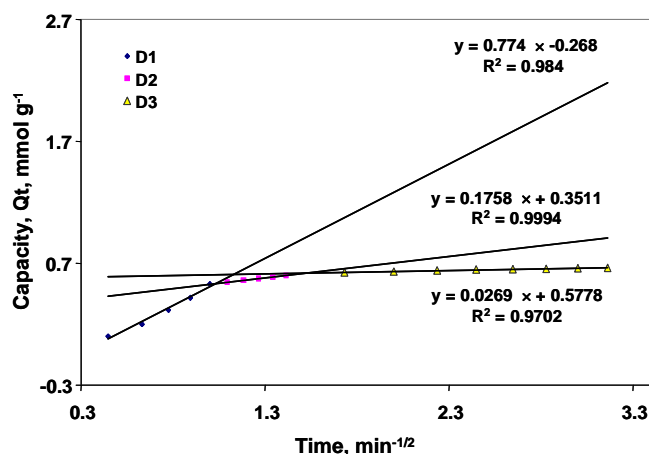


Figure 4 : Effect of batch factor (V/m) on the diffusion rate constant of Fe (III) onto PUF

The effect of particle size of PUF on the diffusion rate of iron (III) was studied. Three straight lines were obtained, which were taken as indication that the particle diffusion mechanism of Fe (III) onto PUF pass through three stages (steps). The results show that the three straight lines do not pass through the origin. The value of diffusion rate constant (slope) decrease in the first step and increases in the second step with increasing the particle size of PUF, but it does not change in the third step (TABLE 1). The values of the intercept of first and second lines have negative values when using large particle size of PUF. The values of slope and intercept of third step at different particle size of PUF are nearly equals, which show that the diffusion rate of third step is independent on the particle size of PUF.

TABLE 1 : Effect of particle size of PUF on the diffusion rate

Particle size, cm ³	Step-1	Step-2	Step-3
0.28	$y = 0.71x - 0.23$, $R^2 = 0.99$	$y = 0.17x + 0.36$, $R^2 = 1$	$y = 0.027x + 0.58$, $R^2 = 0.97$
0.37	$y = 0.41x - 0.13$, $R^2 = 0.98$	$y = 0.73x - 0.44$, $R^2 = 1$	$y = 0.028x + 0.57$, $R^2 = 0.94$
0.89	$y = 0.41x - 0.14$, $R^2 = 0.99$	$y = 0.72x - 0.45$, $R^2 = 1$	$y = 0.028x + 0.57$, $R^2 = 0.94$

The effect of pore size of PUF (using PUF with different densities, 12, 16, 21 and 25 Kg m⁻³) on the rate of diffusion of Fe (III) was studied. The results obtained show that the value of the diffusion rate constant decreases with increasing PUF density in the initial stage, but increases in the third step. The value of intercept increases with increasing the PUF density in the initial stage but decreased in the second and third steps (TABLE 2). These results show that the rate of diffusion is strongly dependent on the pore size or density of PUF.

TABLE 2 : Effect of polyurethane type (density) on the diffusion rate

Density, kg m ⁻³	Step-1	Step-2	Step-3
16	$y = 0.64x - 0.20$, $R^2 = 0.99$	$y = 0.24x + 0.22$, $R^2 = 0.99$	$y = 0.05x + 0.53$, $R^2 = 0.90$
21	$y = 0.53x - 0.16$, $R^2 = 0.99$	$y = 0.24x + 0.15$, $R^2 = 0.99$	$y = 0.08x + 0.42$, $R^2 = 0.95$
25	$y = 0.33x - 0.11$, $R^2 = 1$	$y = 0.14x + 0.11$, $R^2 = 1$	$y = 0.11x + 0.16$, $R^2 = 1$

The effect of temperature on the rate of diffusion of Fe(III) onto PUF was examined. It was found that the rate of diffusion decreases from 0.73 to 0.32 mmol g⁻¹ min⁻¹, and the intercept increases (from -0.23 to -0.11) by increasing the temperature from 25 to 53 °C in the first stage. But the values of slope increases and intercept decreases with the increasing of temperature in second and third stages (TABLE 3). These results may be attributed to the change of diffusion rate depending on temperature.

TABLE 3 : Effect of temperature on the diffusion rate

Temp, °C	Step-1	Step-2	Step-3
37	$y = 0.50x - 0.19$, $R^2 = 0.95$	$y = 0.40x - 0.05$, $R^2 = 0.98$	$y = 0.04x + 0.47$, $R^2 = 0.96$
48	$y = 0.37x - 0.13$, $R^2 = 0.99$	$y = 0.56x - 0.32$, $R^2 = 1$	$y = 0.04x + 0.41$, $R^2 = 0.98$
53	$y = 0.32x - 0.11$, $R^2 = 0.99$	$y = 0.50x - 0.28$, $R^2 = 1$	$y = 0.05x + 0.34$, $R^2 = 0.95$

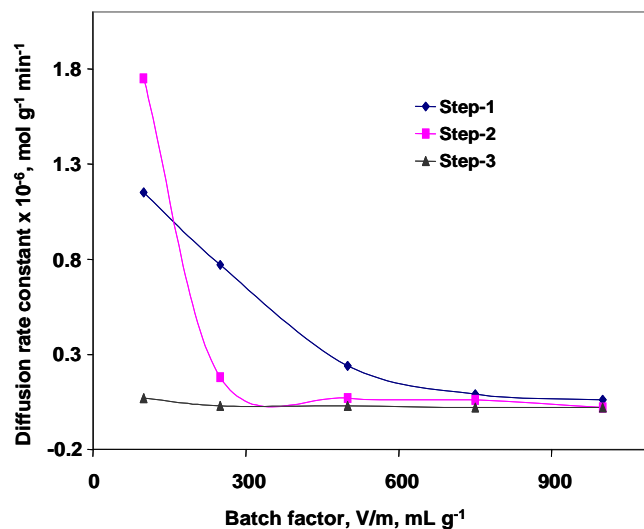
Effect of concentration of iron (0.2-1.8 × 10⁻⁴ M)

on the rate of diffusion was also studied. The diffusion rate constant increases with the increasing of concentration of metal ions (TABLE 4). It is clear that the intercept increases with increasing [Mⁿ⁺] in the case of second and third stages while it decreases in first stage. These results may be attributing to the strong dependency of the diffusion rate on the concentration of metal ions. The intercept values are also functions of the concentration of iron ($b = f[Fe(III)]$).

TABLE 4 : Effect of concentration of iron (III) on the diffusion rate

Conc., mg L ⁻¹	Step-1	Step-2	Step-3
2	$y = 0.31x - 0.08$, $R^2 = 0.97$	$y = 0.12x + 0.13$, $R^2 = 1$	$y = 0.02x + 0.27$, $R^2 = 1$
6	$y = 0.90x - 0.29$, $R^2 = 0.98$	$y = 0.40x + 0.24$, $R^2 = 1$	$y = 0.06x + 0.76$, $R^2 = 0.98$
8	$y = 1.07x - 0.35$, $R^2 = 0.99$	$y = 0.50x + 0.29$, $R^2 = 1$	$y = 0.11x + 0.94$, $R^2 = 0.97$

Studying the effect of batch factor, 100-1000 mL g⁻¹ (V/m, 0.1 g of PUF in 10-100 mL of solution) on the diffusion rate of Fe(III) onto PUF showed that the diffusion rate constant of Fe(III) ions decreases from 1.15 to 0.06 μmol g⁻¹ min⁻¹ with increasing of batch factor from 100 mL g⁻¹ (Figure 5). The intercept increases the first stage but it decreases with increasing batch factor in the second and third stages. These results may be shows to the diffusion rate strongly depend on the batch factor.

**Figure 5 : Morris-Weber (M-W) plot of diffusion rate Fe (III) ions onto PUF**

The diffusion rate of different metal ions (Fe, Co and Ni) onto PUF was studied. The obtained data

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reveals that the values of the diffusion rate constant sequence is in the order $\text{Co}^{2+} > \text{Fe}^{3+} > \text{Fe}^{2+} > \text{Ni}^{2+}$ (TABLE 5). These results reflect that the diffusion rate not only depends on the ionic size but it also depends on valence of metal ions and charge of complex. In our previous study, the values of k_M sequence is in the order $\text{Zn}^{2+} > \text{Cd}^{2+} > \text{Hg}^{2+}$ which shows that the diffusion rate depends on the size of metal ions^[32]. The plot of Co(II) and Ni(II) ions consists of a two-stage straight line while the plots of Fe(III) and Fe(II) consists of three stages. The diffusion rate of these metal ions is rapid in the initial stages, and then slows down with the passage of time.

TABLE 5 : Effect of different metal ions on the diffusion rate

Metal ions	Step-1	Step-2	Step-3
Fe (II)	$y = 0.66x - 0.20, R^2 = 1$	$y = 0.12x + 0.34, R^2 = 1$	$y = 0.02x + 0.49, R^2 = 0.97$
Co (II)	$y = 2.53x - 0.80, R^2 = 1$	$y = 0.27x + 1.47, R^2 = 1$	
Ni (II)	$y = 0.13x + 0.01, R^2 = 0.95$	$y = 0.018x + 0.21, R^2 = 0.97$	

Reichenberg equations $Q_t/Q_e = 1 - 6\pi^2 e^{-Bt}$ where $B = \pi^2 r^{-2} D_i$ was applied to study the particle diffusion mechanism. The results obtained for this model is in

agreement with M-W model. That is the diffusion rate of these matters is rapid in the initial stages, and slows down with the passage of time. The obtained plot consists of a three-stage line that does not pass through the origin (TABLE 6).

The kinetic data for the sorption of Fe(III) onto PUF was calculated according to the first order ($\log(Q_e - Q_t) = \log Q_e - k_1 t / 2.303$) and the second order ($t/Q_t = 1/k_2 Q_e^2 + t/Q_e$) reactions. A plot of $\log(Q_e - Q_t)$ vs. t shows a three-stage straight line (TABLE 6) which indicates that the process is a first order reaction for each of the three stages of the sorption of iron (III) onto PUF. The values of rate constants (k_{11}, k_{12}, k_{13}) of the three stages calculated from the slopes are 1.77, 0.83 and 0.48 min^{-1} , respectively. The values of half life of three stages of sorption of Fe(III) onto PUF are 0.39, 0.83 and 1.44 min, respectively. The plot of t/Q_t vs. t for the experimental data according to second order reaction model gives two linear relationships (second and third stages become one, TABLE 6). The model is not applied on the first stage due to the negative value of the slope of the straight line. The calculated values of rate constant (k_2) and half life ($t_{1/2}$) are 3.36 min^{-1} and 0.28 min, respectively.

TABLE 6 : Kinetic data of different model for the sorption of iron (III) onto PUF

Equation	Step-1	Step-2	Step-3
F (Qt/Qe) vs. t	$y = 0.60x + 0.18, R^2 = 0.91$	$y = 0.13x + 0.61, R^2 = 0.99$	$y = 0.01x + 0.87, R^2 = 0.98$
Bt vs. t	$y = 1.28x - 0.41, R^2 = 0.97$	$y = 0.68x + 0.12, R^2 = 1$	$y = 0.43x + 0.34, R^2 = 0.90$
Qe-Qt vs. t	$y = -0.54x + 0.67, R^2 = 1$	$y = -0.07x + 0.20, R^2 = 1$	$y = -0.006x + 0.05, R^2 = 0.95$
Log (Qe - Qt) vs. t	$y = -0.77x - 0.0476, R^2 = 0.95$	$y = -0.36x - 0.50, R^2 = 0.99$	$y = -0.21x - 0.68, R^2 = 0.90$
t/Qt vs. t	$y = -0.10x + 1.34, R^2 = 0.81$	$y = 0.97x + 0.28, R^2 = 1$	
1/Qt vs. 1/t	$y = 2.03x - 0.14, R^2 = 1$	$y = 0.43x + 1.47, R^2 = 0.99$	

Application

The analytical applicability of the polyurethane foam was tested for the separation of iron in different samples.

Fe (III) ions in the different samples of spring water from Al-Nefud Desert (water composition: Na: 17.9 mg L^{-1} ; K: 1.2 mg L^{-1} ; Ca: 10.0 mg L^{-1} ; Mg: 3.75 mg L^{-1} ; Fe: 0.01 mg L^{-1} ; TDS: 122.5 mg L^{-1} ; HCO_3^- : 28.5 mg L^{-1} ; Cl: 22.0 mg L^{-1} ; SO_4 : 20.5 mg L^{-1} ; NO_3^- : 4.5 mg L^{-1} ; F: 0.05 mg L^{-1} and pH: 7.2 had certified by Nova and Hayat Co) were removed using batch technique. A 25 mL aliquot of water sample was spiked with 100 μg of tested metal ions at the adjusted pH.

Then the solutions were shaken 10 min. The uptake percentage of Fe(III) ions from the water samples onto PUF was 99. The results show that the PUF is a suitable sorbent for removing metal ions from water. (RSD~0.69%, n=4).

PUF was used for determining iron content in multi-vitamin capsules using batch technique. A capsule (weighing 0.4196 g and containing Ca: 10.7 mg; Cu: 1 mg; Cr: 25 μg ; Fe: 4.9 mg; Mg: 19.2 mg; Mn: 1.9 mg; P: 8.0 mg; Se: 25 μg ; Zn: 7.6 mg) of AZINC (Arkopharma, Carros, France) was digested in a beaker with 2 mL of concentrated HNO_3 by slowly increasing the temperature to 150 °C until a solid residue

remained. After cooling, the residue was dissolved in 20 mL of concentrated HNO_3 . The solution was gently evaporated on a steam bath till a residue was again left. It was mixed with 50 mL of distilled water, and concentrated HNO_3 was added dropwise until a clear solution was obtained. The pH of solution was adjusted to 2.3 and the recommended procedure applied. The percentage of Fe(III) after recovery with 10 mL of acetone was determined spectrophotometrically. The average value of the recovered iron was 4.68 mg (95.5 %, RSD~1.03%, n=7). These results showed the suitability of the PUF for determination of iron in pharmaceutical samples.

The iron content of Granite reference sample, G2 (US Geological Survey Certificate of Analysis, USGS) was determined. A 0.1 g portion of Granite was digested with 5 mL conc. HNO_3 and 15 mL HCl until a solid residue remained. After cooling to room temperature the residue was dissolved in 10 mL of H_2O and 2 mL of conc. HNO_3 then diluted with distilled water to 100 mL. The pH of the solution was adjusted and the batch procedure was applied. Iron concentration was found to be 1.11 mg L^{-1} using PUF (RSD~0.25%, n=3). These results are in good agreement with the value of obtained by direct spectrophotometric measurements (1.16 mg L^{-1}) and the certified reference sample of Granite (1.06 mg L^{-1}).

CONCLUSION

The present work deals with the using of polyurethane foam as polymeric extractors to separate and determine of concentration iron metal ions in environmental samples. The sorption behaviour of Fe(III) onto PUF was studied. The maximum uptake was in the pH range of 0.4-2.4, and the average values of ΔG , ΔH and ΔS are -9.7 kJ mol^{-1} , $-102.3 \text{ kJ mol}^{-1}$ and $-314.0 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. The negative values of ΔG and ΔH indicate the spontaneous and exothermic nature of the sorption of these metal ions. Also, the average sorption capacity of PUF was 1.69 mmol g^{-1} , and preconcentration factor of value ~250 and the recovery of 96-99% were achieved.

The diffusion mechanism of iron (III) ions onto polyurethane foam was studied by using Morris-Weber equation results. From the results, we observed that: I)

the plot of Q_t versus $t^{1/2}$ is a three-stage line that does not pass through the origin with three-intercept value. II) The intercept value of the first stage is negative while those of the second and third stages are positive. III) The values of slopes in are order of second stage > first stage > third stage with increasing of temperature and particle size of PUF. IV) The values of intercepts of second stage are changed to negative values with increasing of temperature and the particle size of PUF. Therefore, we can write the modified model for M-W equation as $y = a\sqrt{x} \pm b$ where $a = f(r^+, r', z, T, C, V / m)$ and $b = f(Qe)$.

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