فصل وتقدير نسبة الحديد و المنجنيز في الماء باستخدام مستخلص بولي هيدروكسيل بولي يورثان الرغوي

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الملخص:

مستخلص البولي هيدروكسيل بولي يورثان الرغوي استخدم كمستخلص جديد لفصل وتركيز وتقدير أيونات المنجنيز والحديد الموجودة في عينات المياه الطبيعية. تمت دراسة أفضل الظروف التجريبية لفصل فعال لمستوى أثر الأيونات عند إختلاف المعاملات التجريبية في المجموعات والطرق والديناميكية. لقد وجد بأن أعلى نسبة فصل للحديد والمنجنيز عندما تكون درجة الحموضة بين 6−8. إن حركية الفصل للحديد والمنجنيز باستخدام البولي هيدروكسيل بولي يورثان الرغوي سريعة جداً وأن قيمة متوسط عمر–الزمن اللازم لعملية الفصل هو 11.7 دقيقة. لقد وجد أيضاً بأن السعة الكلية للفصل باستخدام البولي هيدروكسيل بولي يورثان الرغوي تساوي 8.7 ميكرومول للجرام الواحد وأن أقل حد لتقدير العناصر في الماء هو 0.08 ميكروجرام لكل لتر وقد تم حسابه باستخدام طريقة الطيف. وأخيرا فقد وجد بأن ربط أيونات المعادن قيد الدراسة مع البولي هيدروكسيل بولي يورثان الرغوي كانت مفيده لإزالة المعادن الملوثة من عينات حقيقية.

University of Bahrain

Journal of the Association of Arab Universities for Basic and Applied Sciences

ORIGINAL ARTICLE

Separation and determination of iron and manganese in water using polyhydroxyl polyurethane foam

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Abstract The polyhydroxyl-polyurethane foam (PPF) was used as a new sorbent for separation, preconcentration and determination of manganese and iron ions in natural samples. Experimental conditions for effective separation of trace levels of the metal ions were optimized with respect to different experimental parameters in batch and dynamic processes. The maximum sorption of Mn(II) and Fe(III) was in the pH range of 6–8. The kinetics of sorption of the Mn(II) and Fe(III) by the PPF was found to be fast with an average value of half-life of sorption ($t_{1/2}$) of 11.7 min. The sorption capacity of PPF was 8.7 μmol g^{-1} and the recovery of tested ions 99–100% was achieved. The lower detection limit, 0.08 μg L^{-1} was evaluated using spectrophotometric method. The relative standard deviation (*RSD*) under optimum conditions is 1.3% (n = 5). The bonding of the studied metal ions by the PPF is useful for the removal of metal contamination from real samples.

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1. Introduction

Some of the trace elements including iron, manganese, zinc and copper are essential micronutrients with a variety of biochemical functions in all living organisms. However, the benefits of these micronutrients may be completely reversed if present at high concentrations. Some heavy metals particularly cadmium and lead, not essential elements for human nutrition,

on the other hand, have been considered serious soil and environment pollutant due to their potential toxicity at low concentrations (Hicsonmez et al., 2012; Seiler et al., 1998). Trace metals are ubiquitous environmental contaminants. Environmental samples take up trace metals from soils, fertilizers, air, industrial process and transportation. Heavy metals are mobile and easily taken up by plants in the environment (Tuzen et al., 2009; Zhu et al., 2007). Due to these important points, the accurate determinations of trace heavy metals are important part of the studies in analytical chemistry (Kong et al., 2007; Soylak and Cay, 2007).

The determination of heavy metals has been receiving much attention. Considering the low manganese and iron concentration levels in natural samples, sensitive analytical techniques are required to obtain adequate detection limits. To solve this problem, preconcentration/separation procedures have been proposed. Preconcentration is a very important issue for

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achievement of low detection limits (Ahmadi et al., 2007; Ensafi and Shiraz, 2008). Solid-phase extraction (SPE) is a very important place in preconcentration studies due to its simplicity, high preconcentration factors, environmental friendly, etc. (Ensafi and Ghaderi, 2008; Yamini et al., 2008). The SPE technique is also used to improve the sensitivity and selectivity of spectrophotometric methods for determination of heavy metal ions. It has been successfully used in connecting with the enrichment procedures for determination of ultra trace metals in various food and water samples (Malc et al., 2005; Venkatesh et al., 2005). In addition, it has some extra advantages: large availability, easy recovery of the solid phase, attainability of large preconcentration factors and facility for separation using various systems. The most convenient sorbent materials are C18 (Ali et al., 1999), amberlite or Chelex (Ferreira et al., 2000), activated carbon (de Pena et al., 1995) and polyurethane foam (PUF) (Anthemidis et al., 2002).

The PUF is an excellent sorbent material due to its high available surface area and extremely low cost. In addition, it is stable in acids and bases, it will not change its structure when heated up to 180 °C (El-Shahat et al., 2008; Moawed, 2006). Thus, it is a very suitable material for batch and column techniques. The aim of this study is first to highlight the method of modification of polyurethane foam with polyhydroxyl groups, because these groups act as selective ligands with high bond stability for transition metal ions (Abdel Azeem et al., 2010; Moawed, 2011). The second aim is to develop a new, simple, cheap and rapid separation and determination procedure for Mn and Fe in trace level from natural samples using the modified PUF. The great advantage of this modified PUF is that it can extract metal ions without prior complexation.

2. Experimental

2.1. Apparatus

All spectrophotometric measurements of Mn and Fe were recorded using a Shimadzu Model UV-1800 spectrophotometer (Shimadzu Corporation, Japan). The pH measurements were carried out using the microprocessor pH meter BT 500 BOECO, Germany. Doubly distilled water (DDW) was obtained from two successive distillations using Hamilton laboratory glass instrument (Europe House, Sandwich Industrial Estate, Sandwich Kent, England). Glass columns of about 25-cm long and 1.5 cm in diameter were employed in the chromatographic separation experiments.

2.2. Reagents and materials

Stock solutions of the studied metal ions were prepared by dissolving appropriate amounts of analytical reagent grade of $Mn(NO_3)_2$ and $Fe(NO_3)_3$ in double distilled water (DDW). Commercial PUF, open-cell polyether-type, (30 kg m^{-3}) was supplied from the Egyptian company for foam production, Cairo, Egypt.

Polyhydroxyl polyurethane foam was prepared by cut of PUF into similar cubes (~ 0.125 cm^3), washed by a 2 mol L^{-1} solution of HCl, followed by doubly distilled water and acetone then left to dry at room temperature. 5 g PUF cubes were soaked in an HCl (1:1) for 1 h to liberate the maximum number of free amino groups. It was washed with water, placed

into a 0.1 mol L^{-1} HCl solution and then cooled in an ice bath. The PUF was diazotized by the drop wise addition of 25 mL of $NaNO_2$ (2 mol L^{-1}) to the cold solution containing the PUF, and stirred vigorously until the yellow color appeared due to the formation of diazonium chloride. Then, it was boiling for 2 h to replace the diazonium chloride group with hydroxyl group. The orange PPF material was washed with distilled water followed by acetone and then air-dried.

2.3. General procedures

2.3.1. Batch technique

Removal of Mn(II) and Fe(III) was carried out by a batch technique at 25 °C except otherwise specified. A 0.1 g portion of the PPF was mixed with 25 ml aliquot of metal ion solution (5 μg mL^{-1}) in a shaker. After shaking for 30 min, aliquots of solution were withdrawn and the concentration of metal ions was determined spectrophotometrically.

2.3.1.1. Effect of pH. A 25 mL portion of metal ion solutions (5 μg mL^{-1}) of Mn(II) and Fe(III) from single element aqueous solutions, was shaken with 0.1 g of PPF for 30 min. The pH of the metal ion solution was adjusted before equilibration with HCl or NaOH over a range of 1–8. After the equilibration, the remained metal ions were determined by the recommended method.

pH_{ZPC} is the pH when the charge on the PPF surface is zero (zero point charge). To determine the pH_{ZPC} of the PPF surface, we take 25 mL of solution in a series of 100 mL flasks of pH in the range 1–13. The initial pH (pH_i) of the solutions was determined and 0.1 g of the PPF was added to each flasks. After completion of 24 h, the final pH (pH_f) of the solutions was measured. The difference between the initial and final pH values ($\Delta pH = pH_f - pH_i$) was plotted against the pH_i. The pH_{ZPC} was noted at the pH in which the initial pH equals the final pH.

2.3.1.2. Effect of shaking time. The effect of shaking time on the extraction efficiency of Mn(II) and Fe(III) was studied. For that purpose, 0.1 g of PPF was added to 25 mL of sample at the optimum pH and automatic shaking for different time intervals (1–60 min).

2.3.1.3. Effect of sorbent amount. The effect of different PPF amounts on the sorption of Mn(II) and Fe(III) was examined. Different amounts of PPF (0.1–0.5 g) were equilibrated with sample solutions adjusted at the optimum pH, which was automatically shaken for 30 min at room temperature. After equilibration, the remaining metal ion in the solution was determined.

2.3.2. Dynamic experiments

To study the preconcentration, the breakthrough capacities, the chromatographic behavior, and the separation of Mn(II) and Fe(III) ions, a compact column of 15×1.5 cm id was packed with 1 g of the PPF, by the procedure described previously (Burham et al., 2009). Solutions were passed through the column at a flow rate of 2 mL min^{-1}.

2.3.2.1. Effect of flow rate. The dependence of the uptake of the metal on the flow rate was studied for Mn(II) and Fe(III), the

sample (50 mL, 1 µg mL^{-1}) flow rate being varied from 0.5 to 10 mL min^{-1} and the retention percentage of the metal ion into the column was determined.

2.3.2.2. Breakthrough capacity. Two hundred and fifty milliliter samples containing Mn(II) and Fe(III) ions separately at concentrations (5 µg mL^{-1}), were passed through foam columns, at flow rates 4 mL min^{-1}. Each solution was adjusted to the optimum pH and the effluent was collected in 5 mL fractions where the amount of metal ions in each fraction was determined by the recommended method.

2.3.2.3. Preconcentration. Preconcentration of the studied metal ions was investigated from model solutions prior to the determination in the real samples. Fifty to two thousand five hundred milliliter solutions containing 20 µg of Mn(II) and Fe(III) were passed through the column after adjusting to the optimum pH value and the flow rate. The stripping of the metal ions from the PPF column was carried out by 0.1 mol L^{-1} HCl solutions and the amount of Mn(II) and Fe(III) in the eluate was determined by the recommended method.
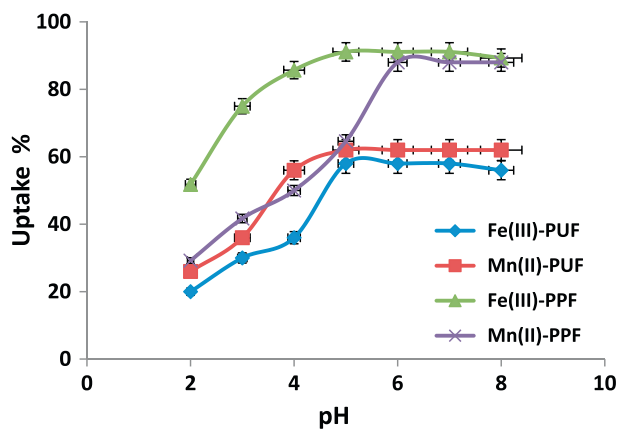
2.3.3. Analysis of real samples

For real water analysis one-liter volume of water sample was collected from Qaroun Lake and Bahr Youssef, Fayoum City spiked with 20 µg of the metal ions, adjusted to pH 6 and passed through the modified foam columns at a flow rate of 2 mL min^{-1}. The columns were rinsed with 20 mL DDW and the metals were eluted by 0.1 mol L^{-1} HCl solution. The concentration of each metal ion was determined by the recommended method. The experiment was repeated three times and the recovery percentage and relative standard deviation (*RSD*) were calculated.

3. Results and discussion

3.1. Batch technique

The effect of pH on the recovery of Mn(II) and Fe(III) ions by PUF and PPF is presented in Fig. 1. The pH of the aqueous solution was clearly an important parameter that controlled the uptake process. The results show that the maximum re-

moval efficiency reached 88–91% for Mn(II) and Fe(III) ions by using PPF in the pH ranges 6–8 and 5–8, respectively. While the maximum sorption of these metal ions by PUF was 58–62%. The uptake sequence was in order PPF > PUF, which depends on the functional group of the PPF molecule. At pH, less than 2 the uptake of the studied metal ions is too small and then increases rapidly with increasing the pH value. The optimum pH value to remove the studied ions from aqueous solution is 6–8. Based on the behavior of Mn(II) and Fe(III) ions extraction on the PPF, we have speculated that ion exchange and hydrogen bonding may be the principal mechanism for the removal of these heavy metal ions (Ajmal et al., 1998). The similarity of the curves of PPF and the PUF could reasonably suggest that the sorption of metal ion onto PUF may proceed via both mechanism, weak anion exchange and ion association mechanism. The possible mechanisms that have been previously proposed for the sorption of metal ions onto PUF are surface sorption (El-Shahawi and Nassif, 2003), etherlike solvent extraction (Huang et al., 1992), anion exchanger (Hasany et al., 2000), cation chelation (Hasany et al., 2001), and ion association (Fong and Chow, 1992).

The pH$_{ZPC}$ value was determined to be approximately 4.7 for the PPF. At pH lower than the pH$_{ZPC}$ (pH < 4.7), the surface of the PPF is positively charged while at pH greater than pH$_{ZPC}$, the surface of the PPF becomes negatively charged. Therefore, the metal ions (Mn^{2+} and Fe^{3+}) are adsorbed due to electrostatic interaction of metal ions with the negatively charged surface of the PPF. Hence, there is an increase in adsorption after pH greater than pH$_{ZPC}$.

The kinetics of sorption is important from the point of view that it controls the process efficiency. The curves are continuous and smooth suggesting a stable and uniform sorption process. The faster uptake of these metal ions on the new modified PUF probably reflects a better accessibility of the studied analyte ions to the new chelating sites in the PPF. This rapid extraction is due to the application of PPF by using batch technique, which is relatively fast and efficient of PPF sorbent as compared to other sorbents (Ho and Ofomaja, 2006; Zhou et al., 2009; Zou et al., 2011).

The sorption of Mn and Fe ions on PPF may involve three steps: bulk transport of solute in solution, film transfer involving diffusion of solute through a hypothetical film boundary layer, and diffusion of the solute within the pore volumes of
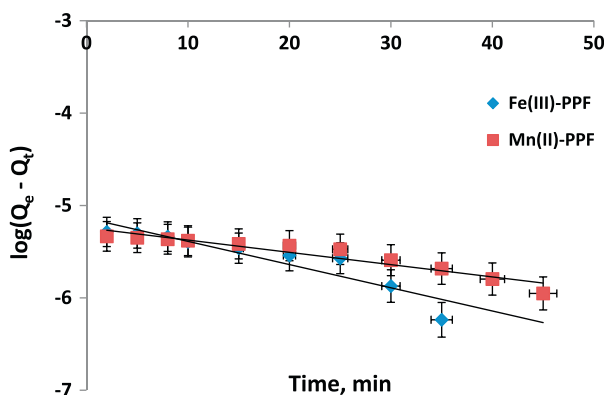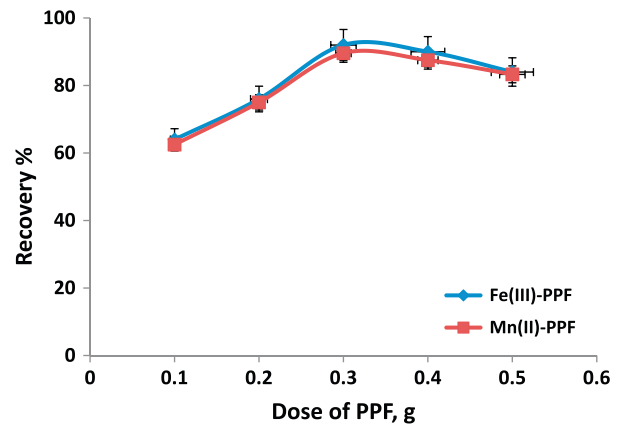

Figure 1 Effect of pH on the extraction of iron(III) and manganese(II) onto PPF.
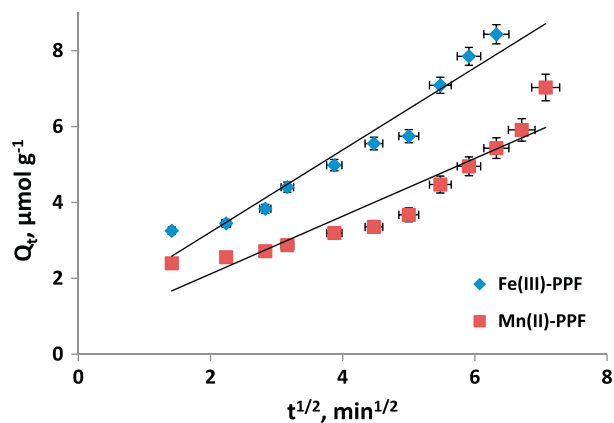
Figure 2 Morris–Weber model for sorption of iron(III) and manganese(II) onto PPF.

Table 1 Diffusion rate for the sorption of Fe(III) and Mn(II) ions.

Ions	Weber–Morris model		Bangham model	
	k_i	r	α	r
Fe(III)	1.08	0.97	0.37	0.94
Mn(II)	0.76	0.94	0.36	0.9

the adsorbent and along pore-wall surfaces to active adsorption sites (Moawed, 2011). In order to study the particle diffusion mechanism of the sorption of Mn and Fe onto PPF, the Morris–Weber ($q_t = k_M\sqrt{t}$) equation was applied (Fig. 2). Where q_t is the amount of metal ions sorbed at time t and k_M is the rate constant of interparticle transport. The obtained data show that the plots of q_t vs. $\sqrt{t}$ are linear and the values of k_M are 1.08 and 0.76 μmol g^{-1} min$^{-1/2}$ for the sorption of Mn and Fe, respectively (Table 1). The k_i values sequence was in order Fe(III) > Mn(II) which indicates that diffusion rate depends on the ionic size. For the pore diffusion mechanism, the kinetic data for the sorption of Mn and Fe onto PPF were analyzed by using Bangham model ($\log\log(C_o/C_o - Q_t m) = \log(k_o m/2.303V) + \alpha\log(t)$). The linearity (Table 1, $r = 0.923$) of the Bangham plot shows that the diffusion of Mn and Fe into pores of the PUF is also the rate controlling step.

The pseudo first order [$\log(Q_e - Q_t) = (\log Q_e) - (k_1 t/2.303)$] and pseudo second order [$t/Q_t = (1/k_2 Q_e^2) + (t/Q_e)$] kinetic models are tested to fit the experimental data for sorption of Mn and Fe. The average value of correlation coefficient (r) value for pseudo first order sorption model ((Fig. 3, $r = 0.94$) is nearly equals to r-value for pseudo second order kinetic (0.93). Therefore, the chi-square model ($X^2 = \sum(Q_c - Q_e)^2/Q_e$) was used for comparing between the

Figure 4 The effect of PPF dose on the sorption of iron(III) and manganese(II) onto PPF.
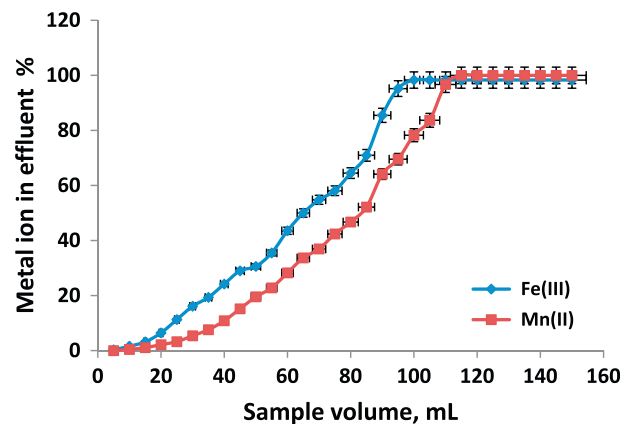
Figure 5 Breakthrough capacity of PPF column for the sorption of metal ions.

experimental sorption capacity against those obtained from predicted pseudo first order and pseudo second order equations. From Table 2 it was seen that the value of X^2 (0.20) obtained from pseudo first order model is also nearly equals to X^2 value for pseudo second order kinetic (0.12). This suggests that the pseudo first order and pseudo second order adsorption mechanisms are predominant. The average value of initial sorption rate ($h = k_2 Q_e^2$) and k_1 (first order rate constant) were in order Fe(III) > Mn(II) which indicate that the rate of sorption depends on the ionic size.

The effect of different PPF amounts (0.1–0.5 g) was examined. These results show that the maximum uptake percentage is in 0.3 g of PPF and decreases with decreasing of amount of PPF (from 92 to 63.5% in $V/m > 250$, Fig. 4). The batch

Figure 3 Pseudo first order plot for sorption of iron(III) and manganese(II) onto PPF.

Table 2 Kinetic parameter of pseudo first order and pseudo second order models.

| Ions	Pseudo-first-order			Pseudo-second-order		
	k_1	r	X^2	h	r	X^2
Fe(III)	0.06	0.93	0.15	0.9	0.95	0.19
Mn(II)	0.03	0.95	0.24	0.48	0.91	0.05
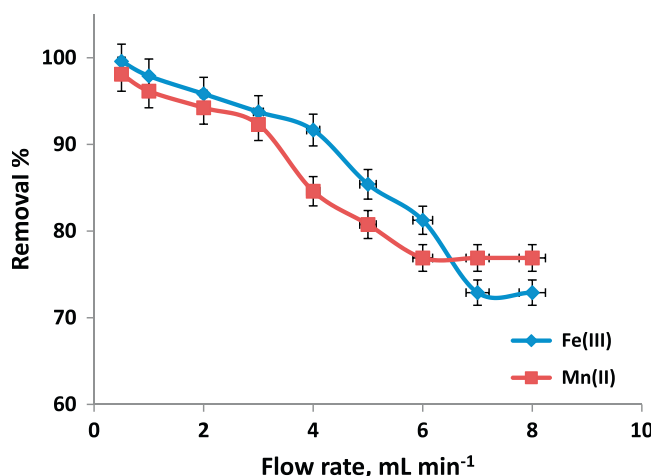
Figure 6 Effect of sample flow rate on the sorption of metal ions using PPF column.

factor (V/m) was estimated to be 250 with an average value of $RSD \approx 0.8\%$ ($n = 3$).

The relationship between the amount of a substance extracted at a constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The capacity of PPF was found to be 8.13 and 9.25 μmol g^{-1} ($RSD = 1.3\%$, $n = 5$) for Mn and Fe, respectively. This confirms that the new modified foam has greater affinity against these metal ions.

3.2. Column procedure

The capacity of PPF column containing one gram of the PPF could be determined from the curves obtained by plotting the
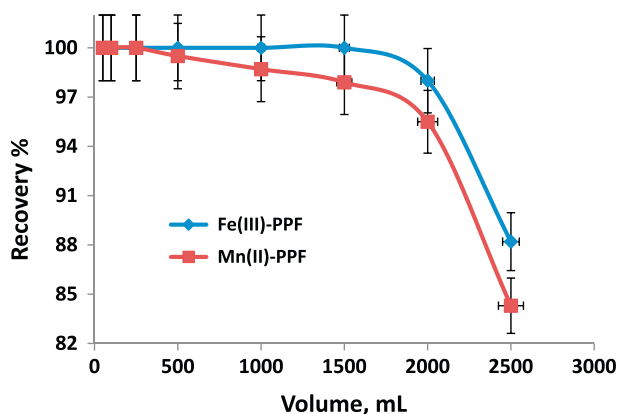
Figure 7 Effect of the sample volume on the sorption of metal ions onto PPF.

amount of metal ion emerged from the column versus the volume of effluent collected. PPF column is saturated with Mn and Fe under the optimum conditions. From the breakthrough curve presented in Fig. 5, the saturation of each column is reached after passing 115 mL and 100 mL of Mn and Fe, respectively. The average value of the capacity of PPF column for Mn(II) and Fe(III) is estimated to be 9.8 μmol g^{-1}. These results are in a good agreement with the values of capacities obtained using batch technique (8.7 μmol g^{-1}).

The sample flow rate through the PPF column is a very important parameter since it controls the time of analysis. The loading of the tested analytes through PPF columns was examined at different flow rates between 0.5 and 10 mL min^{-1}. The maximum and quantitative recovery was observed in the short-range 0.5–3 mL min^{-1} (Fig. 6). Faster flow rates than 3 mL min^{-1} led to decrease in the recovery percentage ($<91.7\%$). This confirms the relation of retention sensitivity and contact time between Mn(II) and Fe(III) and PPF.

In order to explore the possibility of enriching low concentrations of analyte from large volume by the batch procedure, the effect of sample volume on the recovery of Mn and Fe ions was also investigated. For this purpose, 50–2500 mL of sample solutions containing 20 μg of Mn and Fe was allowed to pass through the PPF columns at a flow rate of 1 mL min^{-1}. It was found that quantitative uptake 98.6–99.7% ($RSD = 1.3$, $n = 6$) was obtained for tested metal ions up to a sample volume of 1500 mL (Fig. 7). The elution of Mn and Fe from PPF column was occurred with recovery percentages of 95.8–97.9% with 0.75 mol L^{-1} HCl ($RSD = 2.1$, $n = $ n). These results show that the Mn and Fe can be concentrated effectively from the dilute aqueous solutions using PPF columns.

The limit of detection (LOD) is defined as 3σ where σ is the standard deviation of blank determination. The proposed method for the determination of the investigated ions was studied under the optimal experimental conditions by applying the procedure for blank solutions. The detection limits were established by analyzing five blank solutions. The σ value was estimated by Microsoft office excel 2007 program. The LOD of Mn and Fe was found to be 0.05 and 0.11 μg L^{-1}, respectively ($RSD = 1.3\%$, $n = 5$). Also, limits of quantitation ($LOQ = 10\sigma$) for Mn(II) and Fe(III) is 0.15 and 0.36 μg L^{-1}, respectively (Table 3). The sensitivity sequence was in order, $Fe^{3+} > Mn^{2+}$, which may be attributed to their different ionic sizes. The LOD and LOQ values for the studied ions with the new extractor enable the use of this material in collection of Mn and Fe ions at a trace concentration prior to their determination with high accuracy. The values of LOD and RSD due to the application of PPF for determination of Mn(II) and Fe(III) indicate that the PPF sorption method is more efficient than other sorbents (Abdel Azeem et al., 2010; Burham et al., 2009; Nitiyanontakit et al., 2011; Rahman et al., 2011; Tuzen et al., 2009).

Table 3 Characteristics of the isotherm curves of the sorption of metal ions.

Metal ions	Detection limit (μg L^{-1})		RSD (%)	Capacity Q (μmol g^{-1})
	LOD	LOQ		
Fe(III)	0.11	0.36	1.8	9.25
Mn(II)	0.05	0.15	0.9	8.13

Table 4 Determination of metal ions water sample using PPF column.

Metal ions	Added μg	Qaroun Lake			Bahr Youssef		
		μg	%	RSD (%)	μg	%	RSD (%)
Fe(III)	20	36	102	1.8	20.7	104	2.6
Mn(II)		21.2	106	1.5	20.6	103	1.2

The accuracy and precision for the different fortification levels of the sample were estimated. The recoveries percentage are 98–100% with the value of *RSD* 0.9 and 1.8% for Mn and Fe, respectively (n = 5). These results show that the PPF is suitable for the determination of tested metal ions in water samples.

4. Analytical application

The proposed column method was applied for the determination of analyte ions in Nile river water (Bahr Youssef) and lake water (Qaroun Lake) samples. Lake or tap water sample was adjusted to the optimum conditions. A 100 mL aliquot of water sample was spiked with twenty micrograms of the analyte ions. Then the solutions were allowed to pass through the PPF columns at a flow rate of 2 mL min^{-1} and then desorbed by 0.75 mol L^{-1} HCl solution. The results are listed in Table 4, the average recovery percentage was 102–106% (RSD = 1.8%, n = 4). The results indicate the suitability of the PPF column for the determination and quantitative recovery of the studied ions from natural water samples.

The separation and determination of mixture of Mn(II) and Fe(III) in water samples using PPF column were examined. The mixture solution was passed through the PPF column. Mn(II) and Fe(III) were eluted using 1 mol L^{-1} HCl at a flow rate of 2 mL min^{-1}. The results show that Mn(II) can be separated from white iron material. This technique allows the determination of each metal ion from the other ions in mixture.

5. Conclusion

The polyhydroxyl polyurethane foam showed several good characteristics, such as fast extraction kinetics, low price and low *LOD* for Mn and Fe. This modified foam can be potentially used as a solid-phase extraction material for the preconcentration, separation and determination, when coupled with spectrophotometer, of trace Mn and Fe in environmental samples. The new extractor has good chemical and physical stability feature, rapid equilibration in the recovery of the studied analyte ions and can be used many times without losing its uptake capacity. This extractor expected to be a useful material for the extraction and preconcentration of Mn and Fe ions.

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