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Synthesis of ion-selective imprinted polymer for manganese removal from environmental water

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Abstract In this study, ion-imprinted polymer was prepared for manganese(II) by formation of binary (1-(2-pyridylazo)-2-naphthol) complex in methanol (porogen) following copolymerization with 4-vinylpyridine (VP), ethyleneglycoldimethacrylate (EDMA), and 2,2′-azobisisobutyronitrile (AIBN) as a functional monomer, cross-linking agent, and initiator, respectively. The standardized effects of the independent variables and their interactions were also investigated using Pareto chart. Results of the two-level fractional factorial design (2^{4-1}) based on an analysis of variance demonstrated that only pH of solution, amount of polymer, and adsorption time were seen to be statistically significant. For optimization of manganese removal from aqueous solution by manganese-imprinted polymer (Mn-IP) a three-factor, three level Box-Behnken design techniques combining with response surface methodology (RSM) was used on 15 different experimental data obtained in a batch study. The significance of independent variables and their interactions were tested by the analysis of variance (ANOVA) with 95% confidence limits. The optimal conditions were 9.7, 44.4 mg, and 19.1 min for pH of solution, amount of polymer, and adsorption time, respectively. Under the optimized experimental conditions, the detection limit of the proposed procedure followed by ICP-OES was found to be 0.6 μg L^{-1}. Furthermore, the distribution ratio and selectivity coefficients of manganese and other selected ions were investigated. The method was applied to the determination of manganese in water samples.

Keywords Manganese · Response surface methodology · Box-Behnken design · Imprinted polymer · Water samples

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Introduction

Manganese(II) is a biometal with low contents in natural waters. Therefore, manganese ions in natural waters always involve biocycles. Lack of this metal in the human organism leads to the bones and cartilages deformation and destroys platelet aggregation [1]. The good diversity of procedures concerning the determination of trace levels of Mn, in different matrices, demonstrates the importance of this element [2].

The solid phase extraction (SPE) procedures using molecular-imprinted polymers (MIPs) are the established procedures for preconcentration and separation of the trace elements [3, 4]. The SPE is replacing liquid–liquid extraction due to the following merits [5, 6]: (i) absence of emulsion, (ii) high preconcentration factor, (iii) low costs, (iv) low organic solvent consumption, (v) less processing time, (vi) simpler processing methods, (vii) ease of automation, and (viii) eco-friendly. The MIP technique has shown considerable promise as a procedure for preparing materials which are capable of ion recognition [7]. In this method, appropriate polymerizable binding group is linked to a template molecule that is co-polymerized in the presence of a cross-linking agent to form a cross-linked polymer. The removal of the template leaves binding sites processing the shape corresponding to that of the template. The resulting polymer contains specific binding sites that recognizes the imprint molecule and can exhibit a high selectivity for rebinding the template utilized in its preparation [4]. Sacco et al. [8] have studied synthesis of manganese porphyrinosilica imprinted with templates using the sol–gel process.

The Box-Behnken is a second-order multivariate design based on three-level incomplete factorial designs that received widespread application for assessment of critical experimental conditions, that is, maximum or minimum of response functions. The number of experiments (N) required for the development of this design is defined as $N = 2k\ (k - 1) + C_0$, where k is the factor number and C_0 is the replicate number of the central point [9–12].

This study proposes a preconcentration method using manganese-imprinted polymer (Mn-IP) for determination of manganese in water samples by inductively coupled plasma optical emission spectrometry (ICP-OES). The optimization of the preconcentration procedure is performed exploiting the Box-Behnken design.

Materials and methods

Apparatus

The measurements were performed with a simultaneous ICP-OES (Varian Vista-Pro, Springvale, Australia) coupled to a V-groove nebulizer and equipped with a charge coupled device (CCD). The ICP conditions are shown in Table 1. The pH was determined with a model 630 Metrohm pH meter with combined glass-calomel electrode.

Table 1 ICP-OES instrumental conditions

Plasma	Argon
RF generator power (kW)	1.5
Plasma gas flow rate (L min^{-1})	15.0
Auxiliary gas flow rate (L min^{-1})	1.5
Frequency of RF generator (MHz)	40.0
Observation high (mm)	8.0
Nebulizer pressure (kPa)	240

Materials

1-(2-Pyridylazo)-2-naphthol (PAN), ethanol, methanol, and acetic acid were obtained from Merck (Darmstadt, Germany). VP, EDMA, and AIBN were obtained from Aldrich (Milwaukee, WI, USA). Reagent grade $MnSO_4{\cdot}H_2O$ and nitrate or chloride salts of other cations were obtained from Merck. Stock solution of Mn (1000 mg L^{-1}) was prepared by dissolving the proper amount of $MnSO_4{\cdot}H_2O$ in doubly distilled water in a 10-mL flask and diluting to the mark with water. Dilute solutions were prepared by appropriate dilution of the stock solution in doubly distilled water.

Preparation of polymer

The following method was used for synthesizing the polymer: 0.17 g of $MnSO_4{\cdot}H_2O$ and 0.25 g of PAN were weighed in a glass tube and dissolved in 15 mL of methanol. 4 mmol of VP, 20 mmol of EDMA, and 50 mg of AIBN were added into the solution sample. The oxygen of the solution was removed by bubbling of nitrogen through it for 10 min, then freezed with liquid nitrogen, and sealed under vacuum. The polymerization reaction was carried out in a water bath at 60 °C for 5 h. The synthesized polymer was ground in a mortar, dried, and sieved to get particles with diameters in the range of 55–75 μm. Fine particles were removed by suspending polymer beads in methanol and decantation of methanol for three times. To remove templates, the remaining particles were treated with 2 mol L^{-1} of HCl for 72 h and the excess amount of HCl was washed by methanol. For confident of complete removal of template from polymer, the concentration of manganese ions in aqueous phases after desired treatment periods were measured by ICP-OES. Finally, the particles were dried at 80 °C. Figure 1 schematically shows the synthesis of MIP.

Procedure

Adsorption of manganese from aqueous solutions was investigated in batch experiments. Adsorptions were performed in test tubes containing 12.5-μg manganese in 25-mL deionized water. According to a preliminary experimental design, the pH was adjusted by drop-wise addition of 1-mol L^{-1} sodium hydroxide and 1-mol L^{-1} hydrochloric acid; and appropriate imprinted polymer was added

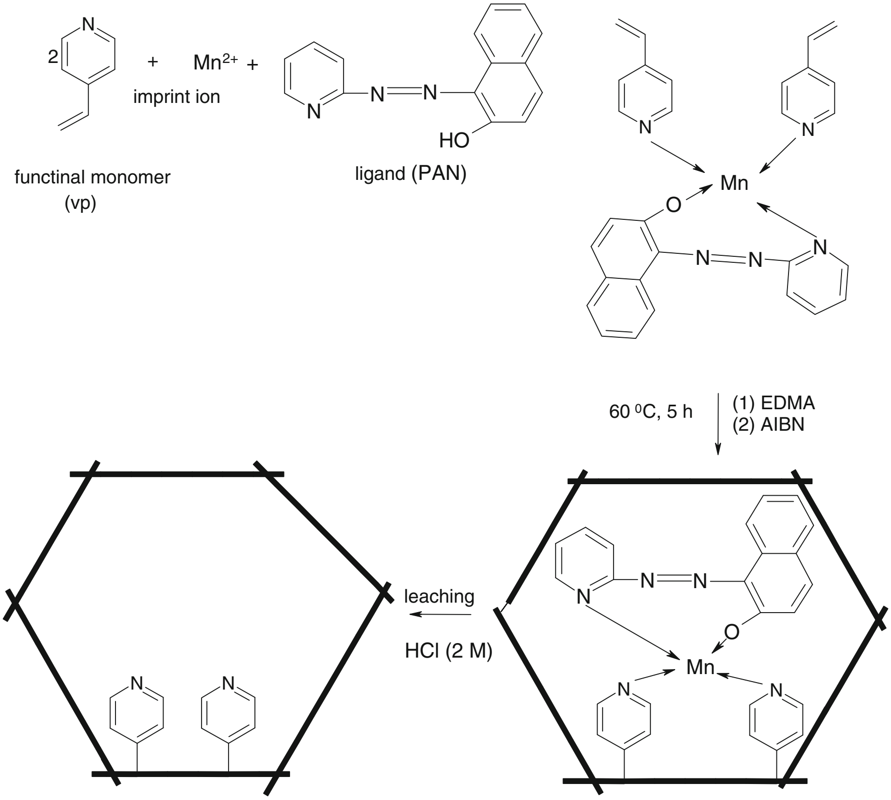

Fig. 1 Preparation of ion imprinted polymer material

into solutions. After that, the mixture was shaken for a suitable time. Finally, the amount of manganese ions in the solution was determined by ICP-OES. The instrument response was periodically checked with known manganese standard solutions. Three replicate extractions and measurements were performed for each solution. Percent extraction (*E%*) of Mn of was calculated using the formula:

$$E\% = 100(C_0 - C_\mathrm{f})/C_0, \tag{1}$$

where C_0 and C_f are the concentrations of manganese ion before and after adsorption in the solution, respectively.

The distribution ratio (*D*) was calculated using the formula:

$$D = \left(\frac{C_0 - C_\mathrm{f}}{C_\mathrm{f}}\right)\left(\frac{V}{m}\right), \tag{2}$$

where *m* is the mass of the polymer in g and *V* is the volume of the solution in mL, respectively.

Adsorbed manganese(II) ions were desorbed from the imprinted polymer by putting washed polymer particles into 10 mL of CH_3COOH:HNO_3 (1:1, v/v). The imprinted polymer containing Mn was placed in the desorption medium and stirred continuously at 600 rpm at room temperature for 50 min. The final manganese concentration in the solution was determined by ICP-OES. The unbound manganese amount to the polymer was obtained by subtracting the manganese bound amount to the polymer from that of the initial manganese loaded to the polymer.

Surface area measurement

The surface area of the MIP was measured by methylene blue adsorption as this material is known to be adsorbed as a monolayer only on solid adsorbents [13]. A standard solution of methylene blue was prepared (17.8 mg L^{-1}). A calibration curve for this material was drawn ($\lambda = 600$ nm) by measuring diluents from standard stock solution. In order to calculate the surface area, 0.1 g of Mn-IP was treated with 25 mL of methylene blue. The treatment lasted until there was no further decrease in absorbance. The amount of methylene blue adsorbed was calculated based on concentration difference between the initial and equilibrium valves, which were measured by spectrophotometry [3].

Factorial design

A two-level factorial ($2^{4\text{-}1}$) design with two replicates of center point was carried out to determine the effect of these factors (pH of solution, amount of polymer, and ligand and adsorption time) by their interactions. The fractional factorial design was evaluated using analytical response (A) of manganese. An analysis of the variance (ANOVA) demonstrated that, within the experimental range, only pH, amount of polymer (w), and adsorption time (t) were statistically significant.

Box-Behnken design

The significant variables like pH of solution, w and t were chosen as the critical variables and designated as X_1, X_2, and X_3, respectively. The low, middle, and high levels of each variable were designated as $-$, 0, and $+$, respectively. The actual design of experiments is given in Table 2.

In a system involving three significant independent variables X_1, X_2, and X_3, the mathematical relationship of the response on these variables can be approximated by the quadratic (second degree) polynomial equation:

$$\begin{aligned} Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \\ + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2, \end{aligned} \tag{3}$$

where Y is estimate response, β_0 constant, β_1, β_2, β_3 are linear coefficients, β_{12}, β_{13}, β_{23} interaction coefficients between the three factors, and β_{11}, β_{22}, β_{33} quadratic coefficients.

A multiple regression analysis is done to obtain the coefficients and the equation can be used to predict the response. The degree of experiments chosen for this study was Box-Behnken, a fractional factorial design for three independent variables. It is applicable once the critical variables have been identified. In the model given in

Table 2 Variable levels used for the trials and the Box-Behnken design for the optimization of the Mn-IP

Trial no.	pH	*w*	*t*	*A*
1	8.0	20	30	0.07490
2	11.0	20	30	0.08604
3	8.0	80	30	0.07080
4	11.0	80	30	0.08509
5	8.0	50	10	0.07669
6	11.0	50	10	0.08533
7	8.0	50	50	0.07636
8	11.0	50	50	0.09046
9	9.5	20	10	0.09755
10	9.5	80	10	0.09463
11	9.5	20	50	0.09752
12	9.5	80	50	0.09652
13	9.5	50	30	0.09765
14	9.5	50	30	0.09702
15	9.5	50	30	0.09736

Eq. 4, interactions higher than second order have been neglected. A total of 15 experiments were necessary to estimate of the full model.

Results and discussion

Characterization of polymer

The FT-IR spectra of leached and unleached Mn-IP materials were recorded using KBr pellet method. As is seen on Fig. 2, no band in the region of 1648–1638 cm^{-1} is present indicating the absence of vinyl groups in polymer materials, confirming the polymerization is complete. There is a difference between the FT-IR spectra of the leached and unleached polymer. The band located at 1561 cm^{-1} which is assigned to v (C=N) stretching vibration of pyridyl nitrogen in leached polymer was shifted to lower wavenumber (1541 cm^{-1}) on complexation with manganese ion in unleached polymer. A weak band of the aromatic ring near 1251 cm^{-1} v (C–N) present in the unleached polymer was also shifted to about 1255 cm^{-1} in the leached polymer indicating the involvement of C=N group of VP in interaction with manganese ions.

Surface area measurement

The surface area of Mn-IP was calculated using the formula [3, 13]:

$$A_s = \frac{GN_{Av}\phi 10^{-20}}{MM_w}, \quad (4)$$

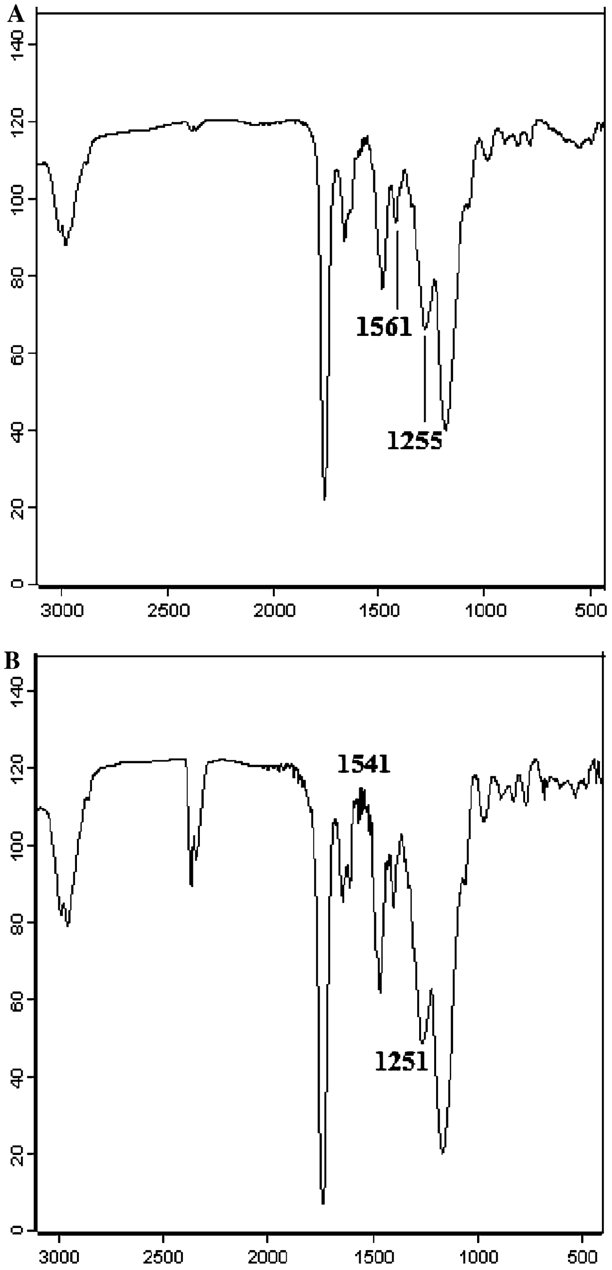

Fig. 2 FT-IR spectra of leached (**a**) and unleached (**b**) Mn-imprinted polymer

where A_s is the imprinted polymer surface area in $m^2\ g^{-1}$, G is the amount of methylene blue adsorbed (g), N_{AV} is the Avogadro's number ($6.02 \times 10^{23}\ mol^{-1}$), ϕ is the methylene blue molecular cross section ($197.2\ A^{o2}$), M_w is the molecular weight of methylene blue (373.9 g mol^{-1}), and M is the mass of adsorbent (g). The surface area ($\text{m}^2\ \text{g}^{-1}$) of Mn-IP was 295.

Optimization of the preconcentration procedure

The optimization step of the Mn-IP procedure was carried out using a Box-Behnken design.

The number of experiments needed to investigate the previously noted three parameters at three levels would be 27 (3^3). Therefore, this was reduced to 15 using a Box-Behnken experimental design. The results from this limited number of experiments provided a statistical model, which was used to identify high yield trends for the extraction process. Table 2 shows the matrix and the responses as analytical signals for manganese. The following equations illustrate the relationship of the three variables, that is, pH of solution, w, t, and analytical response (A).

$$\begin{aligned}A = {} & -0.571887 + 0.138915(\text{pH}) - 0.000017(w) - 0.000597(t) - 0.007218(\text{pH})^2 \\ & - 0.000002(w)^2 + 0.000003(t)^2 + 0.000018(\text{pH})(w) + 0.000045(\text{pH})(t) \\ & + 0.000001(w)(t). \end{aligned} \tag{5}$$

The response surface consideration of the equation is shown in Fig. 3. The derivation of this general equation as pH, w, and t results in three new equations:

$$\frac{\delta(A)}{\delta(\text{pH})} = 0.138915 - 0.014436(\text{pH}) + 0.000018(w) + 0.000045(t),$$

$$\frac{\delta(A)}{\delta(W)} = -0.000017 + 0.000018(\text{pH}) - 0.000004(w) + 0.000001(t),$$

$$\frac{\delta(A)}{\delta(t)} = -0.000597 + 0.000045(\text{pH}) + 0.000001(w) + 0.000006(t).$$

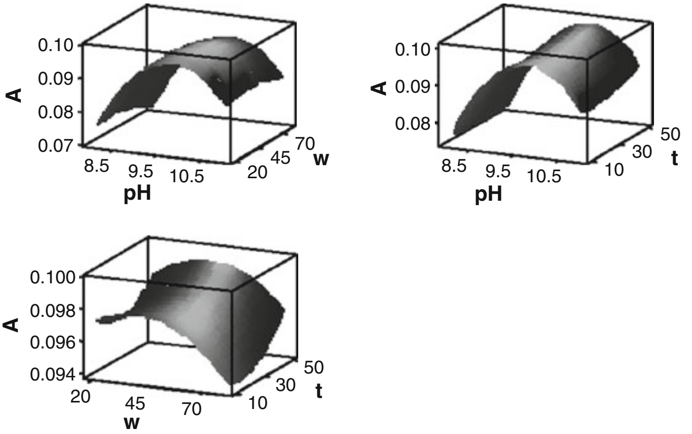

Fig. 3 Three-dimensional response surface plot for the effect of pH, w, and t versus analytical response

The critical point in the response surface are found by solving these equation systems for the condition of $\frac{\delta(A)}{\delta(\mathrm{pH})} = 0$, $\frac{\delta(A)}{\delta(W)} = 0$ and $\frac{\delta(A)}{\delta(t)} = 0$. The way of calculating these critical points has been published in previous [14]. The summery of the analysis of variance (ANOVA) is shown in Table 3. The calculated values for the critical point are as follows: pH = 9.7, $w = 44.4$ mg, and $t = 19.1$ min. According to the ANOVA (Table 3), the F values indicate that most of the variation in response might be explained by the regression equation. The p value is used to estimate whether F is large to indicate statistical significance. If $p > F$ value is less than 0.05, then it indicates that the model is statistically significant [15, 16]. The probability p (0.001) is lower than 0.05. This indicates that the model term is significant at 95% of probability level. Any factor or their interaction with $p < 0.05$ is significant. The model gives adjusted R^2 value of 0.995. Figure 3 shows the response surface plots obtained for removal of manganese from aqueous solution. For the validation, triplicate confirmatory experiments were conducted using the optimized parameters. In the optimal condition, the percent extraction was more than 99%.

Effect of pH

The effect of pH on the extraction of manganese ions was studied. Results showed that the percent extraction was nearly constant and quantitative in the pH of 9.7. At the pH values below 9.7, the percent extraction was decreased. Perhaps, the complex of Mn-PAN was destruction. This result is similar to the results reported by other authors [1, 2].

Effect of adsorption time

The adsorption time was also optimized in order to minimize the time needed for sample processing. The experimental results showed that the quantitative adsorption was obtained when the adsorption time was greater than 19 min. It is evident from the results that the adsorption time needed to attain equilibrium is dependent on the

Table 3 ANOVA analysis for response manganese

Source	Sum of squares	Degree of freedom	Mean square	F value	p
Regression	1.313 E−03	9	1.46 E−04	311.38	<0.0001
Linear	1.041 E−03	3	3.47 E−04	740.43	<0.0001
Square	9.97 E−04	3	3.32 E−04	709.04	<0.0001
Interaction	1.1 E−05	3	4.0 E−06	7.72	0.025
Residual	2.0 E−06	5	4.0 E−07		
Lack-of-fit	2.0 E−06	3	6.7 E−07	7.19	0.125
Pure error	9.38 E−07	2	4.688 E−07		
R^2	0.995				

initial concentration of manganese ions. For the same concentration, the percent adsorption of manganese ions increases with increase of adsorption time.

Effect of polymer mass

The influence of the mass of polymer used for quantitative extraction of manganese was investigated. Optimum amount of polymer was 45 mg. As the mass of polymer increased, the percent recovery of manganese was increased. It is apparent that the percent extraction of manganese ions increases rapidly with increase in the mass of the polymer particles due to the greater availability of the exchange sites or surface area.

Analytical performance

In this study, the standard aqueous calibration was used. Under the optimum conditions described, the calibration curve was linear over the concentration range from 30 to 150 μg L^{-1}. The least square equation at above dynamic linear range was as follows:

$$A = 0.0038\,C\,\left(\mu\text{g L}^{-1}\right) - 0.0035 \qquad \left(r^2 = 0.991\right). \tag{6}$$

The limit of detection (LOD) of the proposed method for the determination of manganese was studied under the optimal experimental conditions. The LOD obtained from $\text{LOD} = 3(\sigma)_{\text{blank}}/m$, where σ is the standard deviation of 10 consecutive measurements of the blank and m is the slope of the calibration curve. The LOD was 0.6 μg L^{-1}. The experimental preconcentration factor defined as the ratio of the slopes of calibration graphs with and without preconcentration was 18.9. The accuracy of the procedure was confirmed by determination of Mn in standard reference material, NIST SRM 1643e Trace element in water, with certified Mn content of 38.97 ± 0.45 μg L^{-1}. The obtained value for Mn using proposed method was 39.45 ± 3.1 μg L^{-1}.

Selecting coefficients of manganese ions over the other selected inorganic cations that co-existed with manganese ions in natural sources were studied by batch method. The Mn-IP particles were tested for separation of 12.5 μg manganese ions in 25-mL sample solution and 25 μg from Cu^{2+}, Zn^{2+}, Co^{2+}, Pb^{2+}, and Ni^{2+} ions either individually or in their mixtures. The concentrations of these metals were determined by ICP-OES. The selectivity of the manganese ions versus another cation was determined by the ratio of the two partition coefficients, D_{Mn}^{2+} and D_m^{n+}, which is referred to the selectivity factor, α:

$$\alpha = \frac{D_{\text{Mn}}^{2+}}{D_m^{n+}}. \tag{7}$$

The obtained results are summarized in Table 4. As it is clear from the results, quantitative separation of manganese from other cations is possible. Compared to other metal ions, the selectivity factor values demonstrate that the Mn-IP synthesized for the Mn^{2+} has a higher selectivity for this ion due to match the charge, coordination geometry, coordination number, and size of cavity of Mn-IP

Table 4 Selectivity factors and distribution ratios of manganese

Foreign ion	Distribution ratio (*D*)	Selectivity factor (α)
Mn^{2+}	1296	–
Cu^{2+}	228	5.7
Zn^{2+}	195	6.6
Co^{2+}	210	6.2
Pb^{2+}	102	12.7
Ni^{2+}	270	4.8

Table 5 Determination of manganese in water samples ($N = 3$)

Samples	Manganese content (μg L^{-1})		*R* (%)
	Added	Found	
Tap water	0.0	94.2 ± 2.9	–
	5.0	99.13 ± 3.1	98.6
River water	0.0	68.5 ± 3.5	–
	5.0	73.47 ± 2.8	99.4
Underground water	0.0	27.9 ± 2.1	–
	5.0	32.82 ± 2.2	98.4
Mineral water	0.0	6.1 ± 3.4	–
	5.0	11.0 ± 3.2	98.0

polymer. Other cations with a higher ionic radius than manganese could not enter easily in the cavity, therefore, the recovery of these cations were decreased [17].

Analytical application

In order to assess the applicability of the procedure to real samples with different matrices, it was applied to the extraction and separation of manganese ions from 100 mL of four different samples. Table 5 shows the extraction of 0.5 μg of added manganese ions from 100 mL of different samples. As seen, the results of three analysis of each sample show that the manganese recovery was almost quantitative.

Conclusion

Ion-imprinted polymers bead find broad application as excellent adsorbents for metal ions. In the present study, a Mn-IP particle was prepared using the combination of VP, EDMA, AIBN, and Mn-PAN complex as functional monomers, cross-linking agent, initiator, and template, respectively. The LOD of this method was compared with other manganese sorbent. The LOD of the proposed method was 0.6, whereas, in previously published paper, the LOD was 5.0 μg L^{-1} [1], 5.0 μg L^{-1} [2], and 0.5 μg L^{-1} [18]. The Mn-IP adsorbent, which was highly selective toward manganese ions, is expected to be a useful material for the interference-free extraction and preconcentration of manganese ions.

The application of a three-factor, three-level Box-Behnken matrix became possible, rapid, economical, and efficient way of an optimization strategy of the proposed procedure. The proposed mathematical procedure also provided a critical analysis of the simultaneous interactive influences of independent variables such as pH of solution, amount of polymer, and adsorption time for better understanding of the Mn(II) removal process. The optimal variables were found to be 9.7 for pH, 44.4 mg for amount of polymer particles, and 19.1 min for adsorption time.

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