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ARTICLES

Use of Amberlite XAD-7HP for the Separation of Mn(II) and Mn(VII) in Waters[1]

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Abstract—A simple method is proposed for the determination and speciation of Mn(II) and Mn(VII) in waters utilizing a macroporous resin, Amberlite XAD-7HP. The batch method was employed and flame atomic absorption spectrometry was used in all determinations. Amberlite XAD-7HP resin was shown to retain Mn(VII) between pH 4 and 12. If the solution contains only one of the species, either Mn(II) or Mn(VII), the resin behaves selectively depending on the pH of the solution. The elution from the sorbent was realized using $K_2C_2O_4$ in HNO_3. The efficiency of the method was checked via spike recovery experiments. The proposed method was successfully applied to industrial wastewater samples and quantitative recoveries (≥96.0%) confirmed the accuracy of the method.

Keywords: manganese, speciation, flame atomic absorption spectrometry, amberlite XAD-7HP

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Manganese is a very abundant element in nature with an average concentration in natural waters in the range of 0.1–1.0 mg/L. It can be found in soils, surface and ground waters in the +1 through +7 oxidation states [1, 2]. It is an essential micro-nutrient that is present in all living cells. Its presence is important for the proper function of several enzymes and function of the brain, nervous system and normal bone growth [3]. It is used in various steel materials as a hardening agent and finds application in pharmaceutical preparations. However, it is toxic at high levels and can cause lesions, headache, psychotic behavior, drowsiness and other symptoms and conditions. The most prevalent oxidation states of manganese are Mn(II) and Mn(VII). It is known that excessive intake of Mn(II) affects human health. In public water supplies, Mn(VII) causes such difficulties as the staining of clothes and encrustation of pipelines. Mn(VII) is widely used as an oxidizing agent in analytical chemistry and also as a disinfectant. It has several important applications as oxidant in the organic chemical industry and in the cleaning preparation for the metallurgical industry. Therefore especially waste waters should be analyzed for their permanganate content to obtain correct information on toxicity and biotransformation of manganese species [4]. The behavior and the forms of manganese in waters can be predicted from its Eh–pH diagram [5]. Redox conditions and the acidity/alkalinity existing in the solution have a direct influence in manganese speciation [6–10].

The World Health Organization (**WHO**) guideline for manganese levels is 0.5 mg/L for health and 0.1 mg/L to avoid staining problems [11]. The limit value for manganese in drinking waters is 50 μg/L according to both EU and USA regulations [12]. The main source of manganese pollution in the water derives from industrial and metallurgical applications such as steel alloy, paint and varnishes, dry cell batteries, match and fireworks, electroplating, and mining industry. In a previous study, a manganese concentration of 2.0 mg/L was observed in some of the waters obtained from different areas in Bangladesh which is four-fold higher than the risk based drinking water criteria of WHO [13]. Therefore the accurate determination of Mn(II) and Mn(VII) ions in waters has become increasingly necessary to study problems associated with environmental water pollution.

There are not too many studies on manganese speciation and determimation in literature. A chelating poly(dithiocarbamate) resin (**PDTC**) has been proposed by Yebra-Biurrun et al. [14] for the preconcentration of manganese and determination by flame atomic absorption spectrometry (**FAAS**). Preconcentration of manganese can be achieved using small PDTC columns at high flow-rates (5–6 mL/min) and sample volumes (1500 mL). Qian et al. [10] described a novel method for the speciation and preconcentration of Mn(II)/Mn(VII) with crosslinked chitosan

[1] The article is published in the original.

Table 1. Properties of the sorbents used in Mn speciation at pH 3.0, 7.0 and 10.0

Sorbent	Property	Form
Diaion SK 116	Strong cation exchanger	Sodium
Diaion SK 1BS	Strong cation exchanger	Sodium
Diaion SA 20 A	Strong anion exchanger	Chloride
Amberlite IRN-78	Strong anion exchanger	Hydroxide
Amberlite IRA-743	Weak anion exchanger	Free Base
Amberlite IR 120 Plus	Strong cation exchanger	–
Dowex 1X4	Strong anion exchanger	Chloride
Dowex 50WX4	Strong cation exchanger	Hydrogen
Duolite C-467	Chelating resin	Sodium
Amberlite XAD-HP	Adsorbent	–

and determination by FAAS. Özdemir et al. [15] developed a speciation scheme for the identification of the chemical forms of manganese in tea leaves and tea infusions. In addition to studies with manganese determination/speciation, there is a still need to develop analytical methods not only to determine the total manganese content in different environmental samples but also to determine its species separately with sufficient precision and sensitivity.

In this study, a simple separation procedure has been proposed with Amberlite XAD-7HP resin for the speciation of Mn(II) and Mn(VII) in waters using FAAS.

EXPERIMENTAL

Reagents and materials. All reagents were of analytical reagent grade and highest purity. 18 MΩ·cm ultra pure water was used throughout the study. Glassware and plasticware were cleaned by soaking in 10% (v/v) nitric acid and rinsed with ultra pure water prior to use. Stock solutions of Mn(II) and Mn(VII) (1000 mg/L) were prepared by dissolving appropriate amounts of manganese sulfate ($MnSO_4$) and potassium permanganate ($KMnO_4$) in 100 mL of ultra pure water. Lower concentration standards were prepared daily from their stock standard solutions.

Instrumentation. An atomic absorption spectrometer, Thermo Elemental Solaar M6 Series with an air-acetylene burner assembly, was used in all measurements. In sorption studies with batch process, Yellowline RS 10 (Staufen, Germany) reciprocating shaker was used to provide efficient mixing. The pH measurements were performed by using Corning 450 pH/ion meter with a pH combination electrode.

Speciation of Mn(II) and Mn(VII) using solid sorbents. To find the appropriate sorbent for the speciation of Mn(II) and Mn(VII), experiments were performed with batch equilibration using various sorbents such as chelating and ion-exchange resins, natural and synthetic zeolites. As an initial study, 20.0 mL of 2.0 mg/L solutions of Mn(II) and Mn(VII) were prepared separately and their pH was adjusted to 7.0. About 0.100 g sorbent was added immediately after pH adjustment and the solutions were shaken for about 15 min. The contents were filtered through filter paper and the filtrate was used for the determination of percent sorption using FAAS. Of the sorbents investigated (Table 1), some were selected for the further studies. In the subsequent experiment, the pH of the solutions was adjusted to pH 3.0, 7.0 and 10.0 to determine the approximate sorption in acidic, neutral and basic media. The percent sorption was examined using the procedure mentioned above.

Effect of solution pH on the sorption of Mn(II) and Mn(VII). To see the change in uptake behavior of the sorbent Amberlite XAD-7 HP in a wide pH range (2.0–12.0), 2.0 mg/L solutions of Mn(II) and Mn(VII) were prepared separately and the pH of the solutions was adjusted to the desired value using NaOH (0.1–1.0 M) and HCl (0.1–1.0 M). The percent sorption of the solutions was determined by the procedure mentioned above.

Desorption from the sorbents. After collection of Mn(II) and Mn(VII) on Amberlite XAD-7HP, the release from the resin was investigated using various eluents namely 2 M HNO_3, 2 M HCl, 0.02 M KI/1 M HNO_3 and 0.01 M $K_2C_2O_4$/1 M HNO_3. For this purpose, Mn(VII) solutions (20.0 mL, 2.0 mg/L) were prepared and their pH was adjusted to 5.0. About 0.100 g of sorbent was added to each solution. After shaking for 15 min, the solutions were filtered and the sorbents left on the filter paper were placed into the eluent solutions one by one. The solutions were shaken again for 15 min for elution. After the end of this period, the solutions were filtered and the eluates were analyzed for their manganese content.

Recovery of the proposed method. In order check the total recovery of the method after sorption/elution stages, 15.0 mL of 2.0 mg/L solution of Mn(II), 15.0 mL of 2.0 mg/L soltion of Mn(VII) or 15.0 mL of 2.0 mg/L Mn(II) + 2.0 mg/L Mn(VII) together were

prepared separately and processed with the method. The final volume of the solution (0.01 M $K_2C_2O_4$/1 M HNO_3) was also 15.0 mL. Percent recovery values were calculated from the matrix-matched calibration plots.

RESULTS AND DISCUSSION

Analytical performance. In order to obtain the calibration plot for manganese, standards were prepared in concentrations from 0.01 to 2.5 mg/L. A good linearity is obtained even in 0.01 to 0.1 mg/L range: $y = 0.1133x - 0.0008$, $R^2 = 0.9987$ and $y = 0.1144x - 0.0013$, $R^2 = 0.9992$, for Mn(II) and Mn(VII), respectively. In addition, Mn(II) and Mn(VII) standards were prepared separately to check whether they give different responses. It was observed that the calibration plot is independent of the chemical form of the metal ($MnSO_4$ or $KMnO_4$). For the aqueous standards, the limit of detection (**LOD**) based on 3 times the standard deviation above the blank value is 0.54 μg/L.

Sorption studies. The form of manganese is very sensitive to redox conditions and pH of the natural matrices. Depending also on the presence of other ions in the solutions manganese can be found in different forms. In this study, our purpose was to find a proper method for the determination of Mn(II) and Mn(VII) in natural waters. For this purpose, several ion-exchange or chelating resins, natural and synthetic zeolites were tried as sorbents and their selectivity towards Mn(II) and Mn(VII) was examined following the sorption procedure explained in "Experimental."

Table 2 gives preliminary results about the uptake of selected sorbents towards Mn(II) and Mn(VII) species. In view of the fact that sufficient information could not be obtained from Table 2, it was decided to determine the percent sorption on various sorbents from acidic, neutral and basic media. For this purpose, the pH of the solutions was adjusted to 3.0, 7.0 and 10.0 and percent sorption was determined. The percentage sorption graphs for the selected sorbents at different pH values are shown in Fig. 1.

Among the sorbents tried, Amberlite XAD-7HP gave the most promising results for the speciation of manganese. Therefore, the further experiments were carried out with Amberlite XAD-7HP resin. It is a macro porous acrylic ester resin with no functional groups [16]. It resembles other XAD resins like XAD-1, -2, and -4 which comprise styrene polymers with divinylbenzene crosslinking. These XAD resins can be applied directly or after a chemical pretreatment step to introduce ionic groups. For example, Doğutan et al. [17] functionalized XAD-2 with palmitoyl quinolin-8-ol and used the modified resin to preconcentrate Mn(II) from natural waters. In our study, we did not apply a treatment step and used Amberlite XAD-7HP in its original form.

Table 2. Sorption (%) of Mn(II) and Mn(VII) towards selected sorbents (sample volume 20 mL, amount of resin 0.100 g, initial concentrations 2.0 mg/L for both Mn(II) and Mn(VII), $n = 3$)

Sorbent	Mn(II)	Mn(VII)
Alumina basic	~80	~40
Chelex 100	>95	~40
Duolite GT-73	>95	>95
Clinoptilolite	>95	>90
Zeolite beta	>95	>95
Zeolite Y	>95	>95
Zeolite ZSM-5	>95	>95
MCM-41	>95	>90
Chitin	~85	>95
Chitosan*	>95	>90
Chitosan**	~50	>95
Chitosan***	~65	>95
Amberlite IRN-78	>95	>95
Amberlite IRA-743	~80	~80
Amberlite IR 120	>95	~30
Dowex 1X4	>95	~30
Dowex 50 WX4	>95	>95
Duolite C-467	>95	~30
Diaion SK 116	>95	~40
Diaion SK 1BS	>95	~35
Diaion SA 20A	>95	~35
Rexyn 101	>95	~35
Amberlite XAD-7HP	~15	~80

* Low molecular weight, ** medium molecular weight, *** high molecular weight.

Extraction efficiency as a function of pH. The studies in which Amberlite XAD-7HP was used have shown that the preconcentration ability of the resin is pH-dependent. Many researchers mention the differences in the extraction efficiency of sorbents depending on the charge of the metal ion [16]. For this reason, the first experiment with the resin was about the determination of its extraction efficiency for Mn(II) and Mn(VII) at different pH values by batch equilibration.

As illustrated in Fig. 2, Mn(VII) is taken up by the resin almost quantitatively between pH 4 and 12 except pH 7 where the sorption is about 80%. It is also seen from the figure that Mn(II) adsorption is less than 20% from pH 2 to 8 and retention reaches a maximum value at a pH of 12. Without going further, based on this observation and the Eh–pH diagram of Mn it can be said that Mn(II) at this pH was not Mn^{2+} ion anymore but had been converted to MnO_2 (or an other

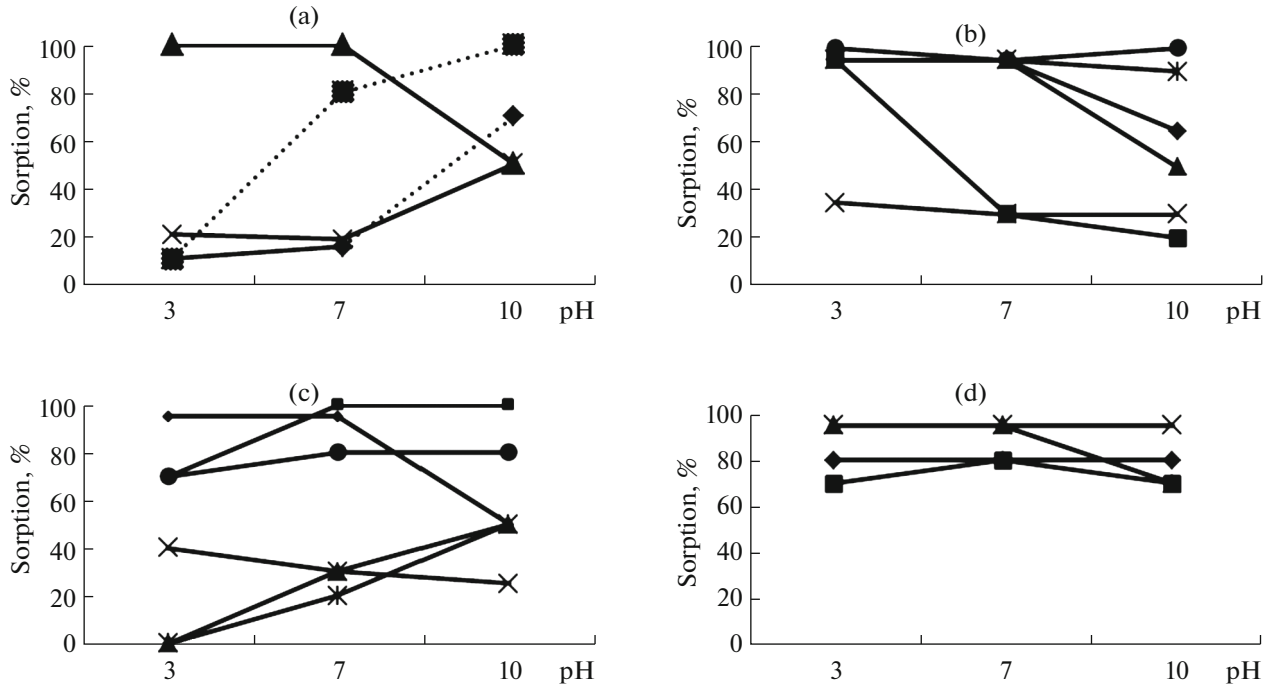

Fig. 1. Percentage uptake: (a) Amberlite XAD-7HP, Mn(II) (×), Mn(VII) (■); Duolite C-467 Mn(II) (▲), Mn(VII) (◆); (b) Diaion SK 1BS Mn(II) (◆), Mn(VII) (■); Diaion SK 116 Mn(II) (▲), Mn(VII) (×) and Dowex 50WX4 Mn(II) (×), Mn(VII) (●); (c) Amberlite 120 plus Mn(II) (◆), Mn(VII) (×); Diaion SA 20 A Mn(II) (×); Mn(VII) (■) and Dowex 1X4 Mn(II) (▲),Mn(VII) (●); (d) Amberlite IRA 743 Mn(II) (◆), Mn(VII) (■) and Amberlite IRN 78 Mn(II) (▲), Mn(VII) (×).

insoluble manganese species namely $Mn(OH)_2$, Mn_3O_4). So, it was the physical retention of solid MnO_2 on the resin particles, or more possibly on the filter paper during filtration rather than the ionic bonding of Mn^{2+} in the macro pores of Amberlite XAD-7HP resin. When the initial concentration of Mn^{2+} in the solution was 2.0 mg/L or lower, MnO_2 particles formed could not easily seen by the naked eye. When the concentration exceeded 2.0 mg/L, brownish-black MnO_2 was readily seen on the filter paper. (This experiment was repeated without adding Amberlite XAD-7HP and pH of solution was brought to 12 with the addition of 1 M NaOH. Meanwhile, a precipitate was obtained and filtered out.) Both the filtrate and the precipitate after dissolution in HCl were analyzed for their manganese content and it was found that more than 90% of the original manganese was in the solid phase, the rest in the filtrate. This finding confirmed the precipitation of MnO_2 (or other insoluble forms) under these conditions. In the next set of experiments, it was planned to repeat sorption studies at different pH values for Mn(II) alone, Mn(VII) alone and Mn(II) + Mn(VII) together. For this purpose three pH values were selected to work at; namely pH 1.0, 5.0, and 12.0. The results are given in Table 3.

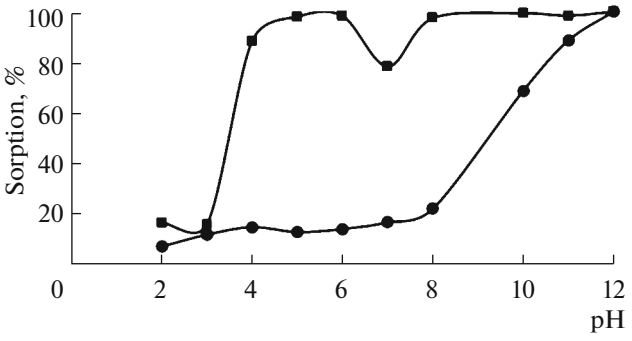

Fig. 2. Percentage uptake by Amberlite XAD-7HP resin for Mn(II) (●) and Mn(VII) (■) as a function of pH.

As can be understood from Table 3, the percent sorption results for Mn(II) and Mn(VII) when they are alone are in accordance with the previous findings. But when they were together in the same solution, they demonstrate very high take-up (>80%) even at pH 1. Although this result was thought to be wrong at first look, it is likely to be true due to the following reaction [18]:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightleftarrows 5MnO_{2(s)} + 4H^+. \quad (1)$$

It is mentioned that this reaction has an equilibrium constant of about 10^{47}; but the rate at which it occurs is said to be slow [18]. In our experiments during sorption, the solutions were shaken for at least 15 min, and this relatively long time must have been sufficient for the formation of MnO_2 precipitate. And again, since the mixture is filtered after shaking with

the resin (so that MnO_2 is removed), the filtrate is found to contain less manganese than expected. This finding can lead to further studies in which MnO_2 precipitation can be used to determine the concentration of Mn(II) in the original solution and/or it can be used for the coprecipitation of some trace elements in various samples [16].

Desorption studies. As explained under "Experimental," two strategies were followed for the desorption of manganese from Amberlite XAD-7HP resin. The first strategy was to wash the surface of the resin with strong acids and release the manganese species adsorbed by converting them into Mn^{2+} that is not adsorbed at low pH values. The second strategy was to apply several reactants such as KI and $K_2C_2O_4$ based on the reactions (2), (3):

$$MnO_{2(s)} + 4H^+ + 2I^- \rightarrow Mn^{2+} + I_2 + 2H_2O, \quad (2)$$

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightleftarrows 2Mn^{2+} + 10CO_{2(g)} + 8H_2O. \quad (3)$$

The results of the desorption (elution) studies are given in Table 4. As seen from the table, the most efficient eluent was 0.01 M $K_2C_2O_4$ (in 1 M HNO_3). It was so successful that it was able to desorb Mn(VII) species adsorbed on the resin and also readily dissolve MnO_2. To our knowledge, nobody has used this eluent before.

Total recovery of the proposed method for manganese determination. Based on the sorption–elution studies, the expected total recovery of the method must be greater than 90%. In order to check whether this is achieved, separate solution of Mn(II) alone, Mn(VII) alone, and Mn(II) + Mn(VII) together, were prepared and subjected to the sorption–elution steps as before. The results given in Table 5 indicate the efficiency of the method. When the solution contains only one of the species, namely either Mn(II) or Mn(VII), the resin behaves selectively depending on the pH of the solution. If pH is 2.0, neither Mn(II) nor Mn(VII) is adsorbed efficiently. The lower recoveries at acidic pH values must be due to the conversion of manganese species to Mn^{2+} which is not adsorbed by the resin. At pH 2.0, if the species had behaved as they were alone, we would have obtained recovery about 10–20%. Instead, 58% was obtained. This must be again due to the reaction (1) which MnO_2 could have been formed, collected on the filter paper and analyzed after dissolution in $K_2C_2O_4$ (1 M HNO_3). A similar effect is also observed at pH 5.0 together with the quantitative sorption of Mn(VII) on the resin. At pH 12.0 both species can be adsorbed (or collected) quantitatively. When analyzing real samples pH must be adjusted to 12.0 if both species are to be determined. The precipitate formed can be analyzed for manganese concentration.

Analysis of real samples. To explore the feasibility of the presented speciation procedure, the proposed procedure was applied for the determination of manganese species in industrial wastewaters. In order to verify the accuracy of the established procedure, recovery experiments were carried out by spiking the samples with different amounts of manganese species before any pretreatment. The results are presented in Table 6. A good agreement was obtained between added and found value of the analyte. As can be seen, recoveries between 96.0 and 103.3% were obtained, which confirm the accuracy of the presented method and could be applied successfully for the speciation of manganese species in water samples.

Table 3. Sorption (%) of manganese species by Amberlite XAD-7HP at different pH values (sample volume 20 mL, amount of resin 0.100 g, initial concentrations 2.0 mg/L for both Mn(II) and Mn(VII), $n = 3$)

Ion	pH 1.0	pH 5.0	pH 12.0
Mn(II) alone	31 (±5)	19 (±2)	95 (±3)
Mn(VII) alone	23 (±2)	98 (±1)	95 (±2)
Mn(II) + Mn(VII) together	83 (±3)	97 (±1)	93 (±3)

Table 4. Desorption of manganese species from Amberlite XAD-7HP

Eluent	Elution, %
2 M HNO_3	~45
2 M HCl	~45
0.02 M KI in 1 M HNO_3	<LOD
0.01 M $K_2C_2O_4$ in 1 M HNO_3	>95

Table 5. Recovery (%) of the proposed methodology (initial and final volumes 15 mL, initial concentrations 2.0 mg/L, eluent 0.01 M $K_2C_2O_4$ in 1 M HNO_3, $n = 3$)

Ion	pH 2.0	pH 5.0	pH 12.0
Mn(II) alone	6 (±1)	10 (±1)	96 (±2)
Mn(VII) alone	8 (±1)	97 (±1)	97 (±7)
Mn(II) + Mn(VII) together	58 (±4)	81 (±4)	96 (±6)

Comparison with other methods. A comparison of the represented method with other reported speciation methods for manganese is shown in Table 7. The comparison of the proposed method with the previously reported procedures for the speciation analysis of manganese indicates that the present procedure has the comparable or better LOD values than those reported previously. High sorption values, lower detection limits and good RSD values are some of the advantages of the proposed method. These characteristics are of key interest for routine laboratories in trace metal ion analysis.

An accurate, precise and simple method was developed for speciation and determination of Mn(II) and Mn(VII) ions in water samples. It was observed that

Table 6. Speciation analysis of manganese species in wastewater samples

Sampling region	Added, mg/L		Found, mg/L		Recovery, %	
	Mn(II)	Mn(VII)	Mn(II)	Mn(VII)	Mn(II)	Mn(VII)
Manisa*	–	–	<LOD	0.56 ± (0.04)	–	–
	0.5	0.5	0.48 ± (0.02)	1.02 ± (0.06)	96.0 ± (4.0)	96.0 ± (5.6)
Manisa*	–	–	<LOD	0.72 ± (0.02)	–	–
	0.5	0.5	0.51 ± (0.03)	1.26 ± (0.07)	102.0 ± (6.0)	103.3 ± (5.3)
Kemalpaşa**	–	–	<LOD	<LOD	–	–
	0.5	0.5	0.51 ± (0.02)	0.49 ± (0.01)	102.0 ± (4.0)	98.0 ± (2.0)

* Industrial wastewater sample Manisa region; ** industrial wastewater sample Kemalpaşa region.

Table 7. Comparison of the proposed method with some studies in literature for manganese

Solid phase	Elution solvent	Detection method	Detection limit, μg/L	Matrix	Reference
Amine-functionalized mesoporous silica UVM-7	Nitric acid	AT-FAAS	0.008	Natural water samples	[19]
Nickel–aluminum layered double hydroxide nano sorbent	Hydroxylamine hydrochloride	FAAS	0.47	Tap, sea lake and waste water	[4]
Crosslinked chitosan	Oxammonium hydrochloride	FAAS	1.98	Lake and tap water	[10]
Amberlite XAD-4 modified with 8-hydroxy-2-quinoline carboxaldehyde	Nitric acid	FAAS	0.26	River, sea and tap water	[20]
Naphthalene modified with 1-(2-pyridylazo)-2-naphthol	Dimethylformamide	FAAS	5	Lake water	[21]
Ambersorb 572	Nitric acid	FAAS	0.68	River and tap water	[22]
Kaolinite/5-Br-PADAP	Sulfiric acid	FAAS	4.3	Waters, air and human hair	[23]
Amberlite XAD-7HP	Potassium Oxalate	FAAS	0.54	Industrial wastewater	This work

the speciation of manganese ions is possible after adjusting the pH of sample solution. Amberlite XAD-7HP resin has been shown to retain Mn(VII) between pH 4 and 12. Mn(II) determination at mg/L level can be done by forming the MnO_2 precipitate at pH 12. The elution from the micro column and/or the dissolution of MnO_2 formed can be realized by $K_2C_2O_4$ in HNO_3 which have been shown to be very effective. The proposed procedure has comparable or better LOD values than those reported in literature. Quantitative recoveries (≥96%) with industrial wastewater samples were obtained which confirmed the accuracy of the presented method.

REFERENCES

1. Michalke, B. and Fernsebner, K.J., *Trace Elem. Med. Biol.*, 2014, vol. 28, no. 2, p. 106.
2. Oliveira, R.L.F., Pedrobom, J.H., Menegario, A.A., Domingos, R.N., Junior, D.A.P., and Kiang, C.H., *Anal. Chim. Acta*, 2013, vol. 799, p. 23.
3. Citak, D., Tuzen, M., and Soylak, M., *J. Hazard Mater.*, 2010, vol. 173, nos.1–3, p. 773.
4. Abdolmohammad-Zadeh, H. and Sadeghi, G.H., *Talanta*, 2012, vol. 94, p. 201.
5. Pacini, V.A., Ingallinella, A.M., and Sanguinetti, G., *Water Res.*, 2005, vol. 39, no. 18, p. 4463.
6. Yebra, M.C. and Moreno-Cid, A., *Anal. Chim. Acta*, 2003, vol. 477, p. 149.
7. Stumm, W. and Morgan, J.J., *Aqua Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, New York: Wiley, 1996, 3rd ed.
8. Florence, T.M., *Talanta*, 1982, vol. 29, p. 345.
9. Quddane, B., Martin, E., Boughriet, A., Fischer, J.C., and Wartel, M., *Mar. Chem.*, 1997, vol. 58, p. 189.
10. Qian, A.X.S., He, G.H.F., and Han, X., *Analyst*, 2001, vol. 126, p. 239.
11. *Guidelines for Drinking-Water Quality*, Geneva: World Health Org., 2008, 3rd ed.
12. Welz, B. and Sperling, M., *Atomic Absorption Spectrometry*, Weinheim: Wiley, 1999.

13. Frisbie, S.H., Ortega, R., Maynard, D.M., and Sarkar, B., *Environ. Health Perspect.*, 2002, vol. 110, no. 11, p. 1147.
14. Yebra-Biurrun, M.C., Garcia-Dopazo, M.C., Bermejo-Barrera, A., and Bermejo-Barrera, M.P., *Talanta*, 1992, vol. 39, p. 671.
15. Özdemir, Y. and Güçer, Ş., *Anal. Lett.*, 1998, vol. 31, no. 4, p. 679.
16. Alfassi, Z.B. and Wai, C.M., *Preconcentration Techniques for Trace Elements*, Eds., Boca Raton, FL:CRC, 1992.
17. Doğutan, M., Filik, H., and Apak, R., *Anal. Chim. Acta*, 2003, vol. 485, p. 205.
18. Skoog, D.A. and West, D.M., *Fundamentals of Analytical Chemistry*, New York: Holt–Saunders, 1997, 7th ed.
19. Shirkhanloo, H., Khaligh, A., Mousavi, H.Z., and Rashidi, A., *Microchem. J.*, 2016, vol. 124, p. 637.
20. Karadaş, C. and Kara, D., *J. Food Compos. Anal.*, 2013, vol. 32, p. 90.
21. Anjos, A.P., Cornejo-Ponce, L., Cadore, S., and Baccan, N., *Talanta*, 2007, vol. 71, p. 1252.
22. Kendüzler, E. and Türker, A.R., *Anal. Sci.*, vol. 18, no. 8, p. 917.
23. Afzali, D., Taher, M.A., Mostafavi, A., Ziae, S., and Mobarakeh, M., *Talanta*, 2005, vol. 65, p. 476.