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Thermal modified Kaolinite as useful material for separation and preconcentration of trace amounts of manganese ions

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Abstract

This work assesses for the first time the potential of natural Kaolinite as adsorptive material for preconcentration of metal traces. Manganese is quantitatively retained by 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) on thermal modified Kaolinite by column method in pH range of 8.5–10.0 at flow rate of 2 ml min^{-1}. Manganese was removed from column with 5.0 ml of H_2SO_4 4 mol l^{-1} and determined by flame atomic absorption spectrometric at 279.5 nm. In this case, 0.l μg of manganese can be concentrated from 800 ml of aqueous sample (where concentration is as low as 0.125 μg l^{-1}). Detection limit is 4.3 μg l^{-1} ($3\,\delta_{bl}$ m^{-1}) and analytical curve is linear in the 0.02–10 mg l^{-1} in final solution with correlation coefficient 0.9997 and relative standard deviation for eight replicate determination of 5 μg of manganese in final solution is 0.71%. The interference of a large number of anions and cations has been studied in detail to optimize the conditions and method was successfully applied for determination of manganese in complex materials.

Keywords: Manganese determination; Kaolinite; Solid-phase extraction; 5-Br-PADAP

1. Introduction

A large number of industries discharge metal-containing effluents into water resources without adequate treatment. Contamination of the environment by manganese is currently an area of concern. Although, manganese is an essential micronutrient, over-exposure causes poisonous effects such as memory impairment, disorientation, hallucinations speech disturbance, compulsive behavior and acute anxiety [1,2]. Manganese is present in many alloys and is found in a number of pharmaceutical, biological and environmental samples. The world health organization study group suggested occupational limits of manganese are 0.2 mg m^{-3} and 0.03 mg l^{-1} in air and water, respectively [1]. Very low concentrations of manganese are present in various complex samples. Therefore, it is important from analytical point of view to develop sensitive, selective and economical method for determination of the trace amounts of manganese [3–5].

The most technique available for preconcentration of metals from aqueous sample are solvent extraction and solid-phase extraction using various adsorbents such as activated carbon [6], adsorption resins [7], cellulose [8], microcrystalline naphthalene [9–11], Amberlite XAD-2 resins [12], octadecylsilica membrane disk [13] and synthetic Zeolites [14]. Some of these adsorbents may be fairly effective for preconcentration of metal ions, but their methods of preconcentration are lengthy and involve rigid control of conditions and they are commonly expensive. Kaolinite is a 1:1 aluminosilicate consisting of stacked pairs of tetrahedral silica sheets and octahedral alumina sheets. Each pair of sheet is bound together through common oxygen atoms and successive pairs are held together by hydrogen bonding between Si–OH and Al–OH groups. The resulting crystal has a silica face of SiO_2 tetrahedral, and alumina face carrying Al–OH groups and edges, which carry both Si–OH and Al–OH sites

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[15]. Isomorphism substitution of Al^{3+} for Si^{4+} in the silica layer leaves that face with a small permanent negative charge, while the charge alumina face and on the edges is pH-dependent. Pure Kaolinite ($Al_2Si_2O_5$ $(OH)_4$) is one of the more highly weathered clay minerals. The adsorptive properties of Kaolinite make its valuable both scientifically and commercially. Kaolinite has been utilized in removal of organic and metal ions from wastewater [16–20]. In present work, we have investigated for the first time potential of thermal modified Kaolinite as adsorptive materials for preconcentration of traces manganese. We have found, modified Kaolinite has advantages than other sorbents including, large surface area (because kaolinite is porous) and good chemical stability in different media. We have developed a flame atomic absorption spectrometry method for determination of trace amounts of manganese after adsorption onto thermal modified Kaolinite loaded with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and subsequent desorption with 5.0 ml of 4 mol l^{-1} H_2SO_4. The developed method is found to be sensitive and selective and has been employed for estimation of manganese in various complex samples.

2. Experimental

2.1. Apparatus

A Varian model SpectrAA 220 flame atomic absorption spectrometer was used in following conditions: wavelength, 279.5 nm; lamp current, 5.0 mA; slit width, 0.2 nm; acetylene flow, 1.5 l min^{-1}; air flow as oxidant, 3.5 l min^{-1}.

A Beckman pH meter was employed for pH measurement. A funnel-tipped glass tube (80 × 10 mm) was used as column for preconcentration. All glassware and columns were washed with mixture of concentrated hydrochloric acid and concentrated nitric acid (1:1) before use.

2.2. Reagents

All chemical materials were analytical reagent grade. Manganese (II) sulfate monohydrate from Aldrich was dissolved in double distilled water, diluted to 1000 ml in a standard volumetric flask, and standardized by known method [21]. Buffer solution with pH 8.5–10.0 was prepared by mixing an appropriate ratio 0.5 mol l^{-1} ammonia and ammonium acetate. A 0.02% solution of 5-Br-PADAP in ethanol was prepared. Solution of various metals was used to study the interference of ions. Natural Kaolinite was collected from Rayen area, Kerman region in Iran.

2.3. Preparation of thermal modified Kaolinite

After purification of Kaolinite, it was heated to 850 °C and then was sieved to obtain a particle size <45 μm (350 mesh). Then, sulfuric acid 5 mol l^{-1} was added to it for removal of the cation exit in Kaolinite, especially manganese ion for 24 h, finally Kaolinite was washed with distilled water until pH was neutralized. Adsorbent was dried at 110 °C in an oven and stored in calcium chloride desiccators until used.

2.4. Preparation of column loaded with 5-Br-PADAP

One gram of thermal modified Kaolinite was treated with an ethanol:sulfuric acid:water (2:1:1) solution overnight, then Kaolinite was washed with distilled water. The Kaolinite was saturated with 5-Br-PADAP reagent by passing 2 ml of 0.02% 5-Br-PADAP solution in ethanol at flow rate of 0.5 ml min^{-1}. Afterward it was washed with water until excess reagent was eliminated from Kaolinite. Passing a buffer solution must precondition before sample load the column. Then column could be used repeatedly for eight times at least.

2.5. Procedure for the sorption of manganese by column

An aliquot of the solution containing 0.1–50 μg of manganese was taken in a 100 ml beaker and it was added to it 5.0 ml of buffer solution with pH 9.0, then diluted to 50 ml with distilled water. This solution was passed through the column at a flow rate of 2 ml min^{-1}. After passing this solution, the column was washed with 5 ml of distilled water. The adsorbed manganese on the column was eluted with 5 ml of 4 mol l^{-1} sulfuric acid, at a flow rate 1.0 ml min^{-1}. The eluent was collected in a 5.0 ml volumetric flask and manganese was determined by flame atomic absorption spectrometry.

3. Results and discussion

3.1. Reaction conditions

The reaction conditions were investigated with 5.0 μg of manganese. The sorption of manganese on the column was found to be a maximum in the pH range of 8.5–10.0 (Fig. 1). In

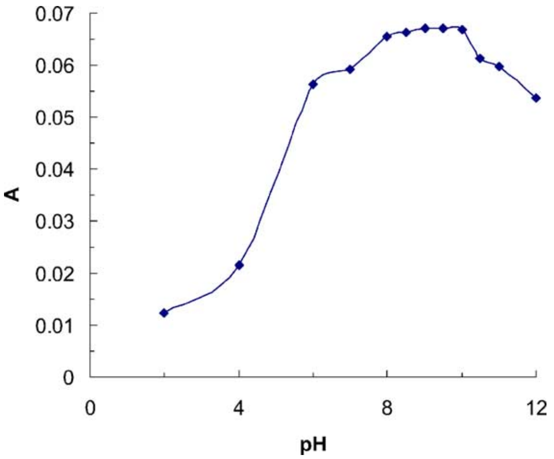

Fig. 1. Effect of pH on adsorption of manganese. Conditions: Mn, 5.0 μg; flow rate of sample, 2 ml min^{-1} and eluent solution, 5.0 ml H_2SO_4 of 4 mol l^{-1} with flow rate 1 ml min^{-1}. Instrumental setting: wavelength, 279.5 nm; lamp current, 5.0 mA; slit width, 0.2 nm; acetylene flow, 1.5 l min^{-1} and air flow as oxidant, 3.5 l min^{-1}.

subsequent studies, the pH was maintained at approximately nine.

The flow rate was varied from 0.2–3 ml min^{-1} did not affect adsorption. A flow rate of 2 ml min^{-1} was recommended in all experiments.

The volume of the aqueous phase was varied in the range of 50–1000 ml under optimum conditions, keeping the other variable constant. It was observed that the absorption was almost constant up to 800 ml. However, for convenience, all the experiments were carried out with 50 ml of aqueous phase.

Preliminary observation indicated that manganese was desorbed completely with 5 ml of 4 mol l^{-1} sulfuric acid. Therefore, 5.0 ml of sulfuric acid 4 mol l^{-1} was used in the present work.

3.2. *Sorption capacity of modified Kaolinite for manganese*

The sorption capacity of modified Kaolinite for manganese was evaluated. In this case, the column containing 1.0 g of modified Kaolinite was used and different volume of 100 mg l^{-1} manganese solution was passed through the column. Each time, the solution of after passing the column, was determined manganese until the solution showed the manganese. The modified Kaolinite has a sorption capacity of 1.83 mg manganese per gram modified Kaolinite.

3.3. *Analytical curve and sensitivity*

It is possible to retain 0.1 μg of manganese from 800 ml of solution passing through the column where concentration is as 0.125 μg l^{-1} in aqueous solution. Detection limit is 4.3 μg l^{-1} and analytical curve is linear in the 0.02–10 mg l^{-1} in final solution with correlation factor of 0.9997 (Fig. 2). Eight replicate determination of 5.0 μg of manganese in final solution gave a mean absorbance of 0.067 with a relative standard deviation of 0.71%. Sensitivity for 1% absorbance was 51 μg l^{-1}.

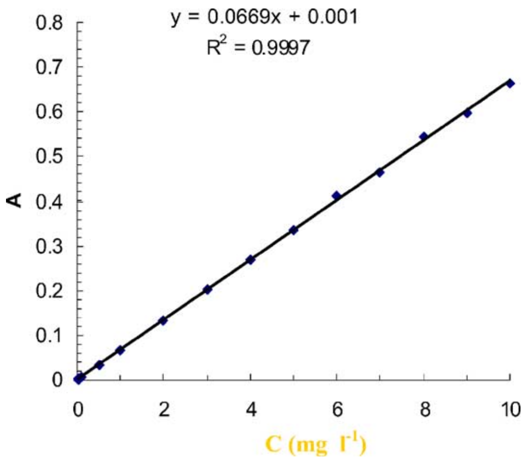

Fig. 2. Analytical curve for manganese. Conditions and instrumental setting were same as Fig. 1.

Table 1
Effect of diverse salts and metal ions

Salt or ion	Tolerance limit (mg)
$CH_3COON_a \cdot 3H_2O$	700
KNO_3	730
$Na_2S_2O_3$	180
$Na_2C_2O_4$	100
NaCN	50
Na_2 EDTA	0.08
Cu(II)	0.07, 3[a]
Mg(II), Ca(II)	100
Sb(III)	50
Tl(I)	30
Pb(II)	10
Cd(II)	0.02, 2[b]
Ni(II)	0.06, 3[a]
Fe(III)	2.3
Zn(II)	0.05, 3[a]
Cr(III)	7.5
Hg(II)	3

Conditions: Mn, 5.0 μg; flow rate of sample, 2 ml min^{-1} and eluent solution, 5.0 ml H_2SO_4 of 4 mol l^{-1} with flow rate 1 ml min^{-1}. Instrumental setting: wavelength, 279.5 nm; lamp current, 5.0 mA; slit width, 0.2 nm; acetylene flow, 1.5 l min^{-1} and air flow as oxidant, 3.5 l min^{-1}.

[a] After masked with 5 ml of 0.1 mol l^{-1} sodium oxalate.

[b] After masked with 3 ml of 0.01 mol l^{-1} sodium cyanide.

3.4. *Effect of diverse ions*

Various salts and metal ions were added individually to a solution containing of 5.0 μg manganese and the general procedure was applied. The tolerance limit was set, as the diverse ion amount require causing ±3% error in the determination of manganese. The results obtained are given in Table 1. Among the anion examined, most could be tolerated up to gram or milligram levels except EDTA, obviously the stability constant of Mn-EDTA complex must be near that of the Mn-5-Br-PADAP complex. Most of the metal ions examined did not interference up to milligram level except of cadmium, nickel, copper and zinc ions. Copper, nickel and zinc ions were masked with 5 ml of 0.1 mol l^{-1} sodium oxalate and cadmium ion with 3 ml of 0.01 mol l^{-1} sodium cyanide. Thus, the proposed method is selective and can be used for determination of manganese in complex samples without any prior separation.

3.5. *Analysis of manganese in standard alloys*

The method was applied to the determination of manganese in Nippon Keikinzoku Kogyo (NKK) CRM No. 916 and No. 920 Aluminum alloy, NKK No. 1021 Al, Si, Ca, Zn alloy, NIST SRM 629 Zinc alloy, NIST SRM 627 Zn-base alloy CE and Japanese Standards of Iron and Steel (JSS) 157–3 stainless steel. A 0.l g sample of the standard alloy or steel was completely dissolved in 10 ml of hydrochloric acid (1:1) by heating on a water-bath and then 3 ml of 0.1 mol l^{-1} sodium oxalate was added to it to reduce the manganese ions to manganese(II). The solution was filtered and diluted to 100 ml with distilled water in a standard flask. An aliquot of

Table 2
Analysis of manganese in standard alloys

Sample	Composition (%)	Found[a]
NKK CRM No. 916 Aluminum Alloy	Si, 0.41; Fe, 0.54; Mg, 0.10; 0. Cr, 0.05; Zn, 0.030; Ti, 0.10; Sn, 0.05; P, 0.04; Sb, 0.01; B, 0.006; Zr, 0.05; Bi, 0.03; Co, 0.03; Ni, 0.06; V, 0.02; Cu, 0.27; Mn, 0.11	0.114 ± 0.006
NKK CRM No. 920 Aluminum Alloy	Si, 0.78; Fe, 0.72; Mg, 0.46; Cr, 0.27; Zn, 0.80; Ti, 0.15; Bi, 0.06; Ga, 0.05; Ca, 0.03; Co, 0.10; Ni, 0.29; V, 0.15; Cu, 0.71; Mn, 0.20	0.197 ± 0.006
NKK CRM No. 1021 Al, Si, Cu, Zn Alloy	Cr, 0.03; Zn, 1.76; Ti, 0.04; Sn, 0.10; Pb, 0.18; Sb, 0.01; Zr, 0.01; Bi, 0.01; V, 0.007; Ca, 0.004; Ni, 0.14; Cu, 2.72; Mn, 0.21	0.209 ± 0.004
NIST SRM 629 Zinc Alloy	Fe, 0.017; Cu, 1.5; Al, 5.15; Mg, 0.094; Sn, 0.012; Cr, 0.0008; Cd, 0.0155; Ni, 0.0075; Pb, 0.0135; Si, 0.078; Mn, 0.0017	0.0018 ± 0.0001
JSS 157-3 Stainless Steel	C, 0.21; S, 0.025; Al, 0.017; Si, 0.21; Ni, 0.11; Cr, 0.10; P, 0.020; Cu, 0.10; Mn, 0.61	0.616 ± 0.008

Conditions and instrumental setting were same as Table 1.

[a] Mean of five determination, ± standard deviation.

this sample was taken and procedure was applied. The results obtained are given in Table 2. These results are in agreement with certified values.

3.6. Analysis of manganese in human hair, water and air samples

The method has been employed for determination of manganese in well water, river water and drinking water of several cities. A 50 ml of water sample was adjusted to pH 1 with nitric acid and 10 ml of 0.1 mol l^{-1} of sodium oxalate added to it, filtered and analyzed by general procedure. The results are given in Table 3.

Table 3
Analysis of manganese in waters, air and human hair

Sample	Manganese found[a]
River water (Rayen, Kerman)	3.8 ± 0.1[b]
Well water (Kerman)	24.3 ± 0.4[b]
Rayne drinking water	13.4 ± 0.3[b]
Kerman drinking water	18.3 ± 0.3[b]
Sirjan drinking water	16.8 ± 0.3[b]
Air (Shahid Bahonar University)	0.243 ± 0.003[c]
Air (Analytical Laboratory, Shahid Bahonar University)	0.378 ± 0.005[c]
Human hair (male)	17.3 ± 0.3[d]
Human hair (female)	21.6 ± 0.4[d]

Conditions and instrumental setting were same as Table 1.

[a] Mean of five determination, ± standard deviation.

[b] $\mu g\,l^{-1}$.

[c] $mg\,m^{-3}$.

[d] $\mu g\,g^{-1}$.

The method was applied to the determination of manganese in the air. The manganese in the air was trapped in 20 ml concentrated HNO_3 by a Rotary Vane Vacuum Pump MLW type DS_1 with Saugvermogen 1 $m^3\,h^{-1}$. Then general procedure was applied after neutralizing the acid and adding sodium oxalate. The results are given in Table 3.

To determine manganese in human hair, 10.0 g of sample, after washed with acetone, was decomposed with 30 ml concentrated nitric acid and 6 ml of 50% perchloric acid, and then the solution was heated until dried. The distilled water was added to it, filtered and diluted to 250 ml in calibration flask. An aliquot of this solution was taken through the general procedure after adding sodium oxalate. The results obtained are given in Table 3.

4. Conclusion

Many methods have reported for preconcentration and determination of manganese. The main advantage of this procedure are: (I) natural Kaolinite is very cheap; (II) during manganese desorption the 5-Br-PADAP reagent remain in the Kaolinite, what allows using column for several times; (III) a good preconcentration factor (160) can be achieved; (IV) the preparation of the extractor system is simple and fast. The procedure used for measurement of manganese in standard alloy show a good accuracy. The proposed procedure has been applied for the determination of manganese in complex samples. The 5-Br-PADAP is fairly sensitive and selective for manganese but with the preconcentration step and the use of atomic absorption spectrometry, its sensitivity and selectivity have been further improved.

References

[1] P.L. Malvankar, V.M. Shinde, Analyst 116 (1991) 1081.
[2] H.G. Seiler, A. Sigle, Hand book on toxicity of inorganic compounds, Marcel-Dekker, New York, 1998.
[3] J. Wang, J. Lu, Talanta 42 (1995) 331.
[4] M.A. Taher, A. Mostafavi, J. AOAC Int. (USA) 84 (3) (2001) 706.
[5] A. Miyazaki, H. Tao, J. Anal. Atom. Spectrom. 6 (1991) 173.
[6] B.M. Randerborght, R.E. Vangrieken, Anal. Chem. 40 (1991) 311.
[7] M. Soylak, L. Elci, Int. J. Environ. Anal. Chem. 66 (1997) 81.
[8] P. Burba, P.G. Willmer, Talanta 30 (1983) 381.
[9] M.A. Taher, Anal. Sciences 17 (2001) 969.
[10] M.A. Taher, B.K. Puri, R.K. Bansal, J. Microchem. 58 (1998) 21.
[11] M.A. Taher, Talanta 52 (2000) 181.
[12] S.L.C. Ferreria, C.F.D. Brito, A.F. Danats, Talanta 48 (1999) 1137.
[13] M. Bagheri, M.H. Mashhadizadeh, S. Razee, Talanta 60 (2003) 839.
[14] Y.P. Pena, W. Lopez, J.L. Burguera, M. Burguera, M. Gallignani, R. Brunetto, P. Carrero, C. Rondon, F. Imbert, Anal. Chim. Acta 403 (2000) 249.
[15] R.G. Harris, J.D. Wells, B.B. Johnson, J. Colloids Surf. Physicochem. Engi. Aspects 180 (2001) 131.
[16] S. Yariv, D.K. Ghosh, L.G. Hepler, J. Chem. Soc. Faraday Trans. 87 (1991) 1201.
[17] P.A. Odey, G.A. Parks, Clays Clay Minear. 42 (1994) 337.
[18] M.H. Koppelman, J.G. Biard, Clays Clay Minear. 25 (1977) 457.
[19] H. Bilinski, S. Kozar, M. Plavisc, Z. Kwokal, M. Branica, Marine. Chem. 32 (1991) 225.
[20] G. Suraj, C.S.P. Iyer, M. Lalithambika, Appl. Clay Science. 13 (1998) 293.
[21] A.I. Vogel, Text Book of Quantitative Chemical Analysis, 6th edn., Longman, London, 2000.