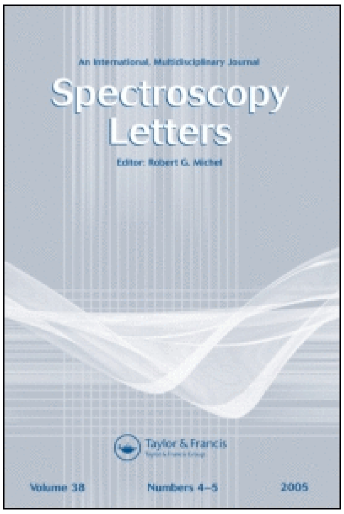

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Spectrophotometric Determination of Malachite Green Residue in Water Samples After Preconcentration on Surfactant-Coated Alumina

Khalil Farhadi[a]; Ramin Maleki[b]; Nasim Mohammad Nezhad[a]; Naser Samadi[a]
[a] Department of Chemistry, Faculty of Science, Urmia University, Urmia, Iran [b] Food & Chemical Analysis Research Lab., Iranian Academic Center for Education, Culture & Research (ACECR), Urmia Branch, Urmia, Iran

To cite this Article Farhadi, Khalil , Maleki, Ramin , Nezhad, Nasim Mohammad and Samadi, Naser(2010) 'Spectrophotometric Determination of Malachite Green Residue in Water Samples After Preconcentration on Surfactant-Coated Alumina', Spectroscopy Letters, 43: 2, 101 — 107

To link to this Article: DOI: 10.1080/00387010903278309

URL: http://dx.doi.org/10.1080/00387010903278309

Spectroscopy Letters, 43:101–107, 2010

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903278309

Taylor & Francis
Taylor & Francis Group

Spectrophotometric Determination of Malachite Green Residue in Water Samples After Preconcentration on Surfactant-Coated Alumina

Khalil Farhadi[1],
Ramin Maleki[2],
Nasim Mohammad Nezhad[1],
and Naser Samadi[1]

[1]Department of Chemistry, Faculty of Science, Urmia University, Urmia, Iran
[2]Food & Chemical Analysis Research Lab., Iranian Academic Center for Education, Culture & Research (ACECR), Urmia Branch, Urmia, Iran

ABSTRACT A new, simple, and reliable method for rapid preconcentration of trace levels of malachite green from water samples is developed using a sodium dodecyl sulfate coated alumina solid phase. The effects of pH, flow rate of sample solution, and foreign ions on the sorption of malachite green have been investigated. Two micrograms of malachite green from 250 mL of aqueous phase could be quantitatively extracted into a 500 mg of SDS coated alumina. The collected malachite green molecules were eluted with 2 mL of acetonitrile and determined spectrophotometrically at 617 nm. The detection limit corresponding to three times of the standard deviation of the blank was found to be $3.2\,\mu g\,L^{-1}$. The proposed method was used for the separation and preconcentration of malachite green with high enrichment factor (about 250) from water samples.

KEYWORDS determination, malachite green, preconcentration, spectrophotometry, surfactant coated alumina

INTRODUCTION

Malachite green (MG) is a triphenylmethane dye (Fig. 1), originally used as a dyeing agent in the textile industry, has also been widely used in the fish farming industry for many decades. The reason for its popularity is derived from its broad antimicrobial spectrum and effectiveness in the prevention and treatment of certain fish diseases compared to other fishery chemicals.[1] On the other hand, it is also used as a dye in silk, wool, and jute and in leather cotton, paper, and acrylic industries.[2] However, MG has now become a highly controversial compound due to the risks it poses to the consumers of treated fish, including its effects on the immune system and reproductive system and its genotoxic and carcinogenic properties.[3–6]

Due to the vital importance of MG analysis, several analytical methods for its quantitative determination have been reported. These include spectrophotometric after solid-phase extraction using magnetic affinity adsorbent[7] liquid chromatography (LC) with visible detection,[8,9] LC–mass spectrometry

Received 14 August 2008;
accepted 18 June 2009.

Address correspondence to Khalil Farhadi, Department of Chemistry, Faculty of Science, Urmia University, Urmia, Iran. E-mail: khalil.farhadi@yahoo.com, kh.farhadi@mail.urmia.ac.ir

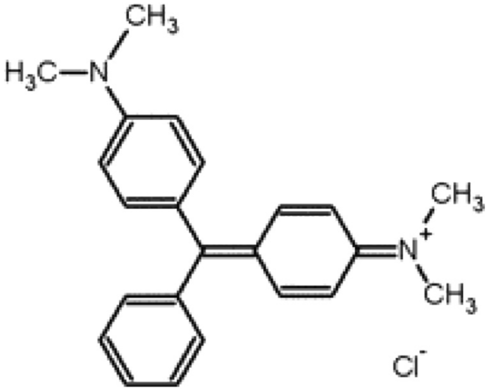

FIGURE 1 The structure of MG.

(LC–MS),[10,11] gas chromatography–MS (GC–MS),[12] and capillary electrophoresis.[13] Some of these methods are laborious and require sophisticated instruments; thus, the need still exists for the development of simple, sensitive, fast, and inexpensive methods.

In recent years, solid-phase extraction using surfactant-coated alumina columns have been used as new sorbent materials for the extraction or preconcentration of inorganic and organic compounds.[14–20] Adsorption of ionic surfactants on mineral oxides is a cooperative process. First, a monolayer of surfactant (i.e., hemimicelles) is formed with the surfactant head-group facing toward the oxide surface, and its hydrocarbon tail-groups protrude into the solution, interacting laterally between them. After that, surfactant adsorption occurs through hydrophobic interactions between hydrocarbon tail-groups, which results in the formation of discrete surface aggregates, termed admicelles. Because of the amphiphilic character of surfactants, admicelles are aggregates in which there are regions of different polarity, acidity, etc. This feature makes these aggregates extremely versatile extractants.

Recently, the modified Al_2O_3-SDS system has been used as a suitable solid phase for the preconentration and determination of Pd(II) and U(IV).[21,22] In the present work, the unmodified SDS-coated alumina was used for the preconcentration of MG from a large volume of aqueous samples. The adsorbed MG was eluted from the column and determined spectrophotmetrically. To the best knowledge of the authors, there is no report about the preconcentration and determination of MG using the proposed method in literature.

MATERIALS AND METHODS

Reagents

Pure MG, sodium dodecyl sulfate (SDS), and γ-type alumina were analytical grade and purchased from E. Merck (Darmstadt, Germany). All of the other solvents and chemicals were purchased from Scharlau (Barcelona, Spain) and used without further purification. Millipore filters were purchased from FILALBERT S. L. (Barcelona, Spain). Working solutions were prepared from the stock solution by serial dilutions with doubly distilled water.

Apparatus

All pH measurements were made with a Metrohm 744 pH meter (Switzerland) using a combined pH electrode. A Perkin Elmer model Lambda 25 (Waltham, MA, USA) UV-visible spectrophotometer equipped with 10-mm quartz cells was used for absorbance measurements. The flow of the sample through the column was adjusted with a vacuum pump model C55JXHRL-4205 (J/B Industries Inc., Aurora, IL, USA). Determination of MG was carried out on an HP 1100 series high performance liquid chromatograph (Agilent Technologies, Wilmington, Delaware, USA) controlled by Chemstation software, equipped with a diode array detector and a 20-μL injection loop.

Preparation of Solid-Phase Extraction Particles

For the preparation of SDS-coated alumina, purified alumina particles (γ-type; 5 g) were suspended in 500 mL of water containing 500 mg SDS and 1.25 g sodium chloride, and then the pH was adjusted to 4.5 ± 0.1 with a hydrochloric acid solution (1 M), and the suspension was stirred for 24 h. After shaking, the supernatant was discarded and the modified alumina was washed with doubly distilled water and dried at 60°C for 24 h. For preparation of the solid-phase extraction column, 500 mg of SDS-coated alumina was transferred to a Millipore filter holder for the preparation of a column (5 mm in height × 9 mm in diameter). A 0.45-μm Millipore filter was inserted between the packed column and a sintered glass disk to prevent the disk from clogging. The column was packed with SDS-coated alumina particles. Then the column was washed with 5 mL of acetate buffer (0.01 M, pH = 4.7) before use.

Solid-Phase Extraction and Quantification of MG

After preparation of extraction column, 250 mL of a solution containing MG (pH = 4.7) were passed through the column at a flow rate of 2 ± 0.1 mL min^{-1}. Then the retained MG was eluted from the column with 2 mL of acetonitrile and collected in a test tube, and its absorbance was measured at 617 nm against a reagent blank solution.

RESULTS AND DISCUSSION

Metal oxide, such as alumina, possesses a high surface area, but its surface is hydrophilic and has low adsorption affinity for organic compounds. Alumina can be modified by surfactant coating to enhance their sorptive capacity toward organic compounds.[23,24] Adsorption of surfactant on metal oxides occurs through coulombic attraction between charged alumina surface and the oppositely charged surfactant head-group. Vander Waals forces between the long chains of surfactants lead to the formation of admicelles and hemimicelles on the surface.[25] It is important to note that the adsorption on metal oxide is pH sensitive,[26] and also the concentration of SDS must be lower than the critical micelle concentration (CMC) of SDS (8×10^{-3} M), because when SDS concentration is higher than the CMC, the excess amount of SDS would form micelles in an aqueous solution so their sorption on the alumina surface is reduced.

Effect of SDS Amount

The concentration and type (hemimicelles, mixed hemimicelles/admicelles, or admicelles) of surfactant aggregates on mineral oxides depend mainly on the surfactant/oxide weight ratio. The influence of SDS amounts on the extraction performance of SDS-coated alumina was investigated by varying the concentration of anionic surfactant added between 0 and 500 mg/g alumina. The obtained results are summarized in Fig. 2. As can be seen, hemimicelles were formed at SDS concentrations lower than 50 mg/g alumina, mixed hemimicelles/admicelles between 50 and 250 mg/g alumina and admicelles in high amount of SDS (>250 mg/g alumina).[18] Thus, SDS amount about 100 mg/g alumina was selected in further studies.

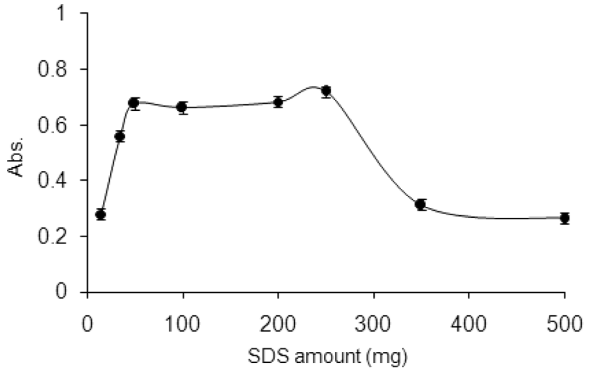

FIGURE 2 Influence of the amount of SDS on the adsorption of MG. Conditions: Operation in the batch mode; MG concentration, 20 μg L^{-1}; amount of alumina, 1.0 g; pH, 4.7.

Effect of Sorbent Amount on Recovery of MG

The influence of sorbent amount on the adsorption of MG was investigated by using of different sorbent amounts and evaluating their ability in the extraction of 20 μgL^{-1} of MG from 250-mL water samples. The obtained results are shown in Fig. 3. As can be seen, by using 500 mg of sorbent, MG is quantitatively extracted, and a decrease in recovery values was observed by decreasing the amount of sorbent. Therefore, 500 mg of sorbent was chosen for further studies.

Effect of pH

In solid-phase extraction studies, pH is an important parameter for quantitative recovery of

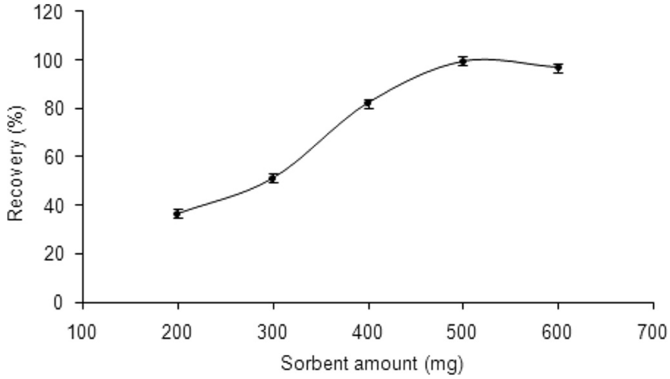

FIGURE 3 Effect of sorbent amount on extraction recovery. Conditions: MG concentration, 20 μg L^{-1}; sample solution volume, 250 mL; sample solution flow rate, 2 mL min^{-1}; pH, 4.7.

analytes.[20] The effect of pH on the extraction of MG was investigated in the pH range of 3–7. The adjustment of the pH of the solutions was performed by the addition of diluted NaOH or HCl. The obtained results are shown in Fig. 4. The progressive decrease in the adsorption of MG at $\mathrm{pH} < 4.5$ is probably related to the increase of a protenated form of MG that has no significant interaction with formed hemimicelles/admicelles on alumina. In $\mathrm{pH} > 5$, the decrease in absorbance is most probably related to poor fixation of SDS on alumina, so that in $\mathrm{pH} > 8$, all of the immobilized SDS is completely removed from the surface of solid support. Similar phenomena have been shown in the separation of traces of some cations and ketoconazole using SDS-coated Al_2O_3 solid-phase.[27,28] As a further confirmation, the amount of MG was determined in obtained acetonitrile solutions using high performance liquid chromatography (HPLC) (see Fig. 4). As seen, chromatographic results have been completely matched with spectrophotometric data in various tested pHs. Therefore, pH 4.7 was chosen as optimum for the quantitative separation, and the solution pH was fixed using 1 mL of acetate buffer (1.0 M).

Effect of Flow Rate

The influence of flow rates of the sample solution on extraction of MG was investigated by passing 250 mL of a sample containing $20\,\mu g\,L^{-1}$ of MG followed by elution of the column with 2 mL of acetonitrile at a flow rate of $1\,mL\,min^{-1}$. The obtained recovery values at three different sample flow rates were studied, and the obtained results show that in high flow rates, the recovery of MG diminishes (probably due to very low extraction times) and reaches maximum values in low flow rate values (Fig. 5). Thus, due to the importance of extraction time, $2\,mL\,min^{-1}$ was chosen as the optimum flow rate for the stripping step in further experiments.

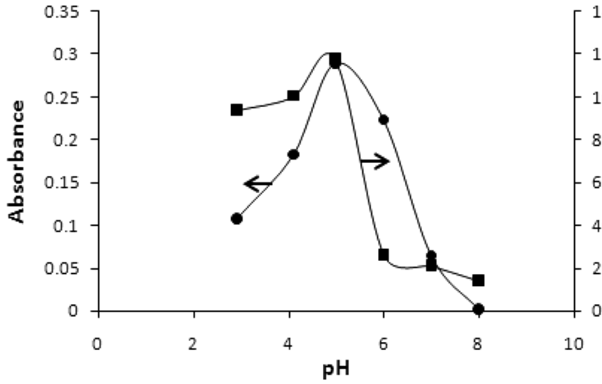

FIGURE 4 Influence of sample solution pH on extraction of $200\,\mu g\,L^{-1}$ of MG from 100 mL water on SDS coated alumina solid phase. Chromatographic conditions: column, C18, 15 cm × 4.6 mm i.d., $5\,\mu m$; mobile phase, acetonitrile, 50 mM ammonium acetate (85:15 v/v); flow rate, $1.5\,mL\,min^{-1}$; wavelength, 617 nm.

Elution of MG from the Column

The nature and concentration of eluents have an important effect on the desorption of analyte from the extraction column. Therefore, the elution of MG by various eluents was examined, and the results are shown in Fig. 6. As can be seen among the tested reagents, acetonitrile was suitable for the elution of MG from the extraction column. Also the influence of elution solvent volume was studied, and it was observed that 2 mL of acetonitrile completely desorbed MG from the column, and increasing the eluent volume only decreased the preconcentration factor.

Effect of Foreign Metal Ions

The recovery of MG in the presence of foreign ions was investigated (Table 1). The obtained results indicated that there is no considerable decrease in recoveries of MG. The tolerance limit was set as the amount of ion required to cause a ±3% error in the recovery values of $25\,\mu g$ MG. As seen, the proposed method is free from interference from a large number of transitions and nontransition cations at high concentration ranges (milligrams). Also, it is noteworthy that no decrease in recovery values was observed for MG in the presence of various anions at the milligram ranges.

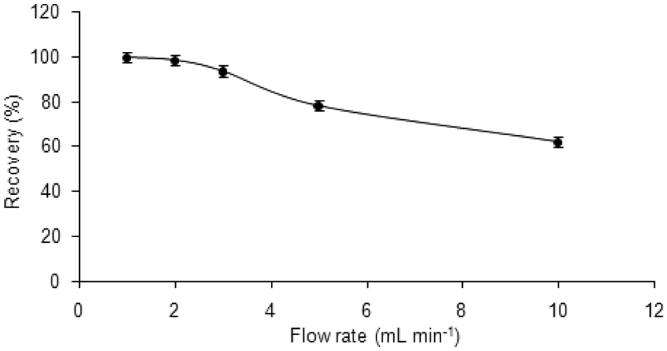

FIGURE 5 Effect of sample solution flow rates on recovery of MG from 100 mL water. Conditions: MG concentration, $50\,\mu g\,L^{-1}$; amount of sorbent, 500 mg; pH, 4.7.

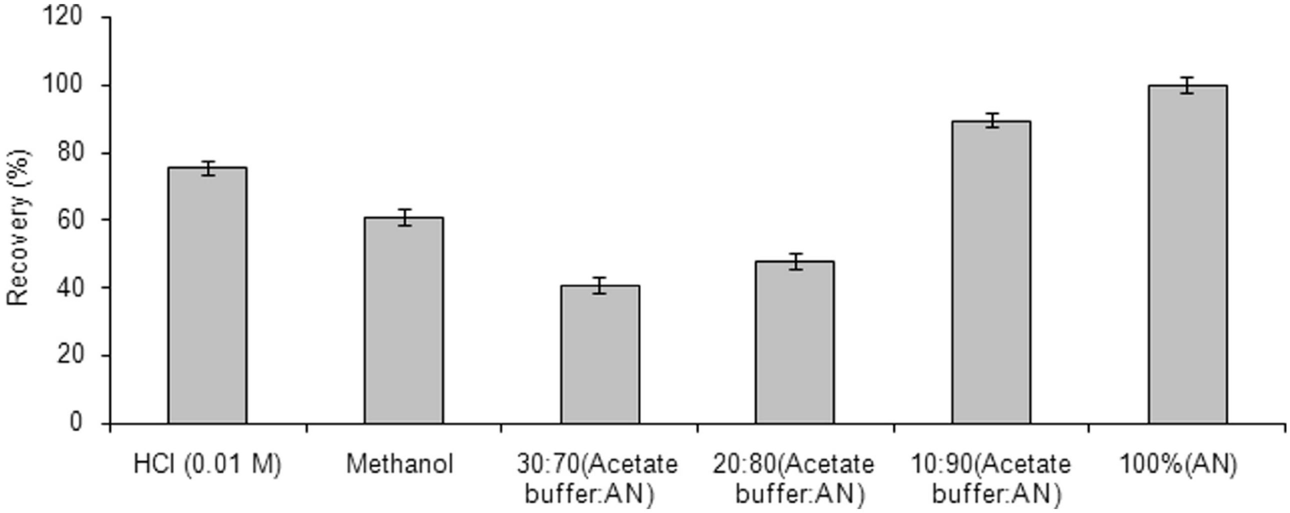

FIGURE 6 Influence of nature and concentration of eluents on extraction recovery. Conditions: MG concentration, 20 μg L^{-1}; amount of sorbent, 500 mg; sample solution flow rate, 2 mL min^{-1}; pH, 4.7.

TABLE 1 Recovery of 25 μg MG from Water Solutions Containing Other Cations

Interfering ion	Added as	Tolerance limit (mg cation)[a]
Na^+	NaCl	120
K^+	KCl	117
Ca^{+2}	$CaCl_2$	85
Mg^{+2}	$MgCl_2$	85
Ba^{+2}	$BaCl_2$	75
Fe^{+3}	$FeCl_3$	23
Co^{+2}	$Co(CH_3COO)_2 \cdot 4H_2O$	25
Pb^{+2}	$Pb(NO_3)_2$	17
Cu^{+2}	$CuSO_4 \cdot 5H_2O$	25
Zn^{+2}	$Zn(CH_3COO)_2 \cdot 2H_2O$	40

[a] Average of three replicate determinations.

Conditions: MG concentration, 50 μg L^{-1}; sample volume, 500 mL; amount of sorbent, 500 mg; sample solution flow rate: 2 mL min^{-1}; pH, 4.7.

Study of Preconcentration Factor

To determine the preconcentration factor, different volumes of sample solutions containing 10 μg of MG were passed through the column and washed with 2 mL of acetonitrile. It was found that there is no considerable effect with changing the volume of the sample solution up to 500 mL. Therefore, a preconcentration factor of 250 can be achieved. The obtained relative standard deviations (RSD%) of MG recoveries under optimal conditions for three replicate measurements at a concentration range level of 5–50 μg L^{-1} were between 2.5–3.4%. It must be noted that a prepared column can be used three times for quantitative recovery of MG without any regeneration. The capacity of SDS-Al_2O_3 on the sorption of MG was examined and found to be 2.78 mg/g of the solid phase.

TABLE 2 Results of MG Determination and Recovery from Water Samples

Sample (250 mL)	Added (μg · L^{-1})	Proposed method[a]	RSD (%)	Recovery (%)	HPLC method[a]	RSD (%)	Recovery (%)
Fish farming water sample 1	—	ND[b]	—	—	—		—
	20	20.6 ± 0.7	3.4	103	19.9 ± 0.5	2.5	99.5
	50	48.4 ± 1.3	2.7	96.8	49.7 ± 0.8	1.6	99.4
Fish farming water sample 2	0	7.6 ± 0.2	2.6	—	7.7 ± 0.1	1.9	—
	20.0	27.4 ± 0.7	2.5	99.3	27.5 ± 0.5	1.8	99.0
River water	—	ND[b]	—	—	—	—	—
	5.0	4.92 ± 0.16	3.25	98.4	4.96 ± 0.1	2.2	99.2

[a] Average of three replicate determinations.

[b] ND, not detected.

TABLE 3 Comparison of the Proposed Method with Other Methods

Recovery data	LOD	Detection	Clean-up	Matrix	Ref.
22.0%	0.5–1 μg/L	LC-UV/VIS (620 nm)	Magnetic SPE	Water	7
95.4%	10 μg/L	LC-UV/VIS (618 nm)	SPE:Diol column + filtrated	Water	29
99.4%	1.2 μg/L	LC-UV/VIS (618 nm)	—	Fish farming and river water	30
—	1–2 μg/Kg	LC-SERS[b]	Silver colloids in a PDMS[a] microlfuid channel + filtrated	Water	31
41.8%	0.28 μg/L	LC-amperometric detection at a carbon fiber electrode	Cyano SPE	Water	32
76.0%	—	LC-UV/VIS (615 nm)	—	Water	33
95.9%	3.2 μg/L	UV/VIS (618 nm)	SPE (surfactant coated alumina)	Water	This work

[a] Polydimethylsiloxane.
[b] Surface-enhanced Raman spectroscopy.

Analytical Applications

The calibration curve, which is plotted as absorbance against concentration of MG in water sample, indicated a wide linear range (5–100 $\mu g\,L^{-1}$) with good linearity ($r = 0.9947$). The limit of detection (LOD) of the proposed method for determination of MG based on 3σ of the blank is 3.2 $\mu g\,L^{-1}$. To assess the applicability of the method to real samples, it was applied to the extraction, preconcentration, and determination of MG from fish farming water samples. A 250-mL aliquot of a water sample containing MG was adjusted at pH 4.7, and then the MG was extracted using the proposed column and determined spectrophotometrically. The obtained results of spectrophotometric determinations compared with the HPLC method[29] (stationary phase: C18 column with 25-cm length, 4.6-mm i.d., and 5-μm particle size; mobile phase: a mixture of acetonitrile–acetate buffer [50 mM, pH 3.9], 85:15 v/v). MG was determined by isocratic elution (flow rate, 1.5 $mL\,min^{-1}$) with visible detection at $\lambda = 618$ nm. The results clearly indicated a satisfactory agreement between the determination of MG in water samples by the proposed method and HPLC method (see Table 2).

A comparison of the proposed method with other methods[7,29–33] (see Table 3) indicated that the analytical performance of the proposed method is comparable with other works; in the case of simplicity and low cost, it is superior.

CONCLUSION

The proposed method for solid-phase extraction of MG based on SDS-coated alumina phase is very simple, sensitive, economic, and reproducible. Due to a relatively high preconcentration factor, trace amounts of MG at ppb level can be determined accurately. The proposed method is free from interference for a large number of diverse ions that are associated with MG in various water samples.

ACKNOWLEDGMENTS

The authors wish to thank Mr. Y. Nikkhahi for his technical assistance.

REFERENCES

1. Alderman, D. J. Toxicological effects of malachite green. *J. Fish Dis.* **1985**, *8*, 289–298.
2. Culp, S. J.; Beland, F. A. Malachite green: A toxicological review. *J. Am. Coll. Toxicol.* **1996**, *15*, 219–238.
3. Alderman, D. J.; Clifton-Hadley, R. S. Malachite green: A pharmacokinetic study in rainbow trout, *Oncorhynchus mykiss* (Walbaum). *J. Fish Dis.* **1993**, *16*, 297–311.
4. Fernandes, C.; Lalitha, V. S.; Rao, V. K. Enhancing effects of malachite green on the development of hepatic preneoplastic lesions induced by *N*-nitrosodiethylamine in rats. *Carcinogenesis* **1991**, *12*, 839–845.
5. Rao, V. K. Inhibition of DNA synthesis in primary rat hepatocyte cultures by malachite green: a new liver tumor promoter. *Toxicol. Lett.* **1995**, *81*, 107–113.
6. Gouranchat, C. *Malachite Green in Fish Culture* (*State of the Art and Perspectives*). *Bibliographic Studies*; Ecole Natl. Veterinaire ENVT: Nantes, France 2000; 142.
7. Safarik, I.; Safarikova, M. Detection of low concentrations of malachite green and crystal violet in water. *Water Res.* **2002**, *36*, 196–200.
8. Mitrowska, K.; Posyniak, A.; Zmudzki, J. Determinatiovn of malachite green and leuomalachite green in water using liquid chromatography with visible and fluorescence detection and confirmation by tandem mass spectrometry. *J. Chromatogr. A* **2008**, *1207*(1–2), 94–100.
9. Andersen, W. C.; Turnipseed, S. B.; Roybal, J. E. Quantitative and confirmatory analyses of malachite green and leucomalachite green residues in fish and shrimp. *J. Agric. Food Chem.* **2006**, *54*, 4517–4523.

10. Valle, L.; Diaz, C.; Zanocco, A. L.; Richter, P. Determination of the sum of malachite green and leucomalachite green in salmon muscle by liquid chromatography–atmospheric pressure chemical ionisation-mass spectrometryionization. *J. Chromatogr. A* **2005**, *1067*(1–2), 101–105.
11. Lee, K. C.; Wu, J. L.; Cai, Z. Determination of malachite green and leucomalachite green in edible goldfish muscle by liquid chromatography–ion trap mass spectrometry. *J. Chromatogr. B* **2005**, *843*(2), 247–251.
12. Turnipseed, S. B.; Anderson, W. C.; Robal, J. E. Determination and confirmation of malachite green and leucomalachite green residues in salmon using liquid chromatography/mass spectrometry with no-discharge atmospheric pressure chemical ionization. *J. AOAC Int.* **2005**, *88*, 1312–1317.
13. Tsai, C. H.; Chan, P. H.; Lin, C. H.; Chang, T. C.; Chia, C. T. A new approach for the detection of a nonfluorescent compound by CE-resonance Raman spectroscopy based on the sweeping-MEKC mode. *Electrophoresis* **2006**, *27*, 4688–4693.
14. Cantero, M.; Rubio, S.; Ṕerez-Bendito, D. Determination of non-ionic polyethoxylated surfactant in wastewater and river water by mixed hemimicelle extractrion and liquid chromatography – ion trap mass spectrometry. *J. Chromatogr. A* **2005**, *1067*, 161–170.
15. Merino, F.; Rubio, S.; Perez-Bendito, D. Evaluation and optimization of an on-line admicell-based extraction–liquid chromatography approach of ionic organic compounds. *Anal. Chem.* **2004**, *76*, 3878–3886.
16. Moral, A.; Sicilia, M. D.; Rubio, S.; Perez-Bendito, D. Determination of bisphenols in sewage based on supramolecular solid phase extraction liquid chromatography/fluorimetry. *J. Chromatogr. A* **2005**, *1100*, 8–14.
17. Lopez-Jim, F. J.; Rubio, S.; Perez-Bendito, D. Determination of phthalate esters in sewage by hemimicelles-based solid-phase extraction and liquid chromatography–mass spectrometry. *Anal. Chim. Acta* **2005**, *551*, 142–149.
18. Moral, A.; Sicilia, M. D., Rubio, S.; Pérez-Bendito, D. Sodium dodecyl sulphate-coated alumina for the extraction/preconcentration of benzimidazolic fungicides from natural waters prior to their quantification by liquid chromatography/fluorimetry. *Anal. Chim. Acta* **2006**, *569*, 132–138.
19. Li, J.; Shi, Y.; Cai, Y.; Mou, S.; Jiang, G. Adsorption of diethyl-phthalate from aqueous solutions with surfactant-coated nano/microsized alumina. *Chem. Eng. J.* **2008**, *140*, 214–220.
20. Ghaedi, M.; Niknam, K.; Shokrollahi, A.; Niknam, E.; Rajabi, H. R.; Soylak, M. Flame atomic absorption spectrometric determination of trace amounts of heavy metal ions after solid phase extraction using modified sodium dodecyl sulfate coated on alumina. *J. Hazard. Mat.* **2008**, *155*, 121–127.
21. Farhadi, K.; Teimouri, G. Preconcentration of palladium in aqueous samples using a surfactant-coated alumina modified with thioridazine. HCl and its determination by atomic absorption spectrometry. *Anal. Lett.* **2004**, *37*, 1457–1468.
22. Farhadi, K.; Abdollahnezhad, N.; Maleki, R. Separation and preconcentration of uranium (VI) from aqueous samples using a surfactant-coated alumina modified with meloxicam. *Intern. J. Environ. Anal. Chem.* **2008**, *88*, 725–735.
23. Valsaraj, K. T. Partitioning of hydrophobic nonpolar volatile organics between the aqueous and surfactant aggregate phases on alumina. *Sep. Sci. Technol.* **1989**, *24*, 1191–1205.
24. Valsaraj, K. T. Adsorption of trace hydrophobic compounds from water on surfactant-coated alumina. *Sep. Sci. Technol.* **1992**, *27*, 1633–1642.
25. Attwood, D.; Florence, A. T. *Surfactant Systems: their Chemistry, Pharmacy and Biology*; Chapman and Hall: London, 1983.
26. Somasundaran, P.; Feurstenau, D. W. Mechanism of alkyl sulfonate adsorption at the alumina–water interface. *J. Phys. Chem.* **1964**, *70*, 90–95.
27. Farhadi, K.; Sheikhloei Bonab, S. Separation and kinetic-spectrophotometric determination of ketoconazole from formulations using SDS-coated Al_2O_3 and $KMnO_4$ in alkaline-SDS micellar medium. *J. Chin. Chem. Soc.* **2004**, *51*, 743–750.
28. Hiraide, M.; Iwasawa, J.; Kawaguchi, H. Collection of trace heavy metals complexed with ammonium pyrrolidinedithiocarbamate on surfactant-coated alumina sorbents. *Talanta* **1997**, *44*, 231–237.
29. Allen, J. L.; Meinertz, J. R; Gofus, J. E. Determination of malachite green and its leuco form in water. *J. AOAC Int.* **1992**, *75*, 646–649.
30. Pourreza, N.; Elhami, S. Spectrometric determination of malachite green in fish farming water samples after cloud point extraction using noionic surfactant Triton-X 100. *Anal. Chim. Acta* **2007**, *596*, 62–65.
31. Lee, S.; Choi, J.; Chen, L.; Park, B.; Kyong, J. B.; Seong, G. H.; Choo, J.; Lee, Y.; Shin, K. H.; Lee, E. K.; Joo, S. W.; Lee, K. H. Fast and sensitive trace analysis of malachite green using a surface-enhanced Raman microfluidic sensor. *Anal. Chim. Acta* **2007**, *590*, 139–144.
32. Sagar, K.; Smyth, M. R.; Wilson, J. G.; Mclaughlin, K. High performance liquid-chromatographic determination of the triphenylmethane dye, malachite green, using amperometric detection at a carbon fiber microelectrode. *J. Chromatogr. A* **1994**, *659*, 329–336.
33. Meinertz, J. R.; Stehly, G. R.; Gingerich, W. H.; Allen, J. L. Residues of [14C]-malachite green in eggs and fry of rainbow trout, *Oncorhynchus mykiss* (Walbaum), after treatment of eggs. *J. Fish Des.* **1995**, *18*, 239–247.