

Separation and Adsorption Properties of Poly Styrene-Graft-Ethyl Methacrylate Copolymer for Zinc, Copper, and Cobalt Ions in Water Samples

Harun Ciftci

Department of Chemistry, Faculty of Science and Arts, Ahi Evran University, Kirsehir, Turkey

In this article, separation and adsorption properties of poly styrene-graft-ethyl methacrylate copolymer for zinc, copper, and cobalt ions in water samples were investigated. For this aim, some experimental and analytical parameters such as solution pH, sample flow rate, type of eluting agent, and sample solution volume were optimized. The adsorbed metal ions on polymeric resin were eluted with 5 ml of 2 mol l⁻¹ HNO₃ and they were determined by flame atomic absorption spectrometry. In optimized conditions, the adsorption capacities for Zn, Cu, and Co were obtained as 6.8, 5.2, and 7.5 mg g⁻¹, respectively. The detection limits were calculated as 0.82 μg l⁻¹ for Zn, 1.24 μg l⁻¹ for Cu, and 0.68 μg l⁻¹ for Co from standard deviation of the blank (50 ml, pH 5.8) measurements 10 replicates. The relative standard deviation of recoveries for seven replicate analyses of Zn, Cu, and Co ions (50 ml of 0.10 mg l⁻¹) were found as 2.4, 2.8, and 1.5%, respectively. The accuracy of method was checked with certified reference material (NIST SRM 1643e, trace elements in water) and the developed method was successfully applied to tap water, commercial drinking water, and mineral water samples. POLYM. ENG. SCI., 54:1555–1559, 2014. © 2013 Society of Plastics Engineers

INTRODUCTION

Copper, cobalt, and zinc are essential micronutrients that need to be consumed in adequate amounts for normal physiological functions of organisms [1]. Those trace elements transfer to living organisms through drinking water, food, drug, and inhalation [2] and can have toxic effects when taken in excessive amounts [3]. Therefore, it is vital to determine the level of trace elements in environmental and food samples.

Neutron activation analysis [4], inductively coupled plasma (ICP) mass spectrometry [5, 6], ICP atomic emission spectrometry [7], electrothermal atomic absorption spectrometry [8], and flame atomic absorption spectrometry (FAAS) [9, 10] are the main instrumental techniques

determining trace elements in various samples. FAAS has been widely used for the determination of trace amounts of metal ions. However, due to insufficient sensitivity and matrix effects, direct determination of metal ions at low levels in environmental samples by FAAS is limited [11–13]. Therefore, separation and preconcentration techniques such as precipitation and coprecipitation, cloud point extraction, ion-exchange, dispersive liquid–liquid micro-extraction, and solid-phase extraction (SPE) are needed to determine metal ions [14].

SPE has been widely used for separation and sensitive determination of metal ions, mainly in water samples. SPE has some advantages of being rapid, simple, sensitive, and economic, requiring low solvent usage and having lower extraction time [15–17].

In SPE process of trace elements needs sorbent materials some of which are Amberlite and Duolite XAD resins, activated carbon, cellulose, modified silica gel, polymeric resin, and biomass [18–21]. The mechanism of retention of those materials is performed by means of simple adsorption, chelating, and ion-exchange [22].

In this study, separation and adsorption properties of poly styrene-graft-ethyl methacrylate copolymer for zinc, copper, and cobalt ions in water samples were investigated by using column chromatography. The optimum experimental parameters such as sample solution pH, eluent type and volume, flow rate of sample solution for the quantitative recovery of the analytes were examined and optimized.

EXPERIMENTAL SECTION

Apparatus

Metal determinations were carried out using a Perkin Elmer AAnalyst model 400 (Shelton, CT, USA) Flame Atomic Absorption Spectrometer with a hollow cathode lamp for working elements and a deuterium background corrector in air–acetylene flame. Working parameters of the equipment were established according to the manufacturer's guideline for each element.

Correspondence to: Harun Ciftci; e-mail: harunciftci@yahoo.com

DOI 10.1002/pen.23698

Published online in Wiley Online Library (wileyonlinelibrary.com).

© 2013 Society of Plastics Engineers

Reagents and Solutions

All reagents and solvents were analytical grade and used without further purification. Deionized water was used for all reagents preparation. Standard solutions of copper, zinc, and cobalt were prepared by appropriate dilution of the stock standard solution (Merck, 1000 mg l⁻¹). Other chemical reagents were obtained from Merck (Darmstadt, Germany).

Poly styrene-*graft*-ethyl methacrylate copolymer was prepared from poly (styrene-*co-p*-chloromethyl styrene)s, 1,2-dipiperidinoethane, and ethyl methacrylate (EMA) at 130°C in *N,N*-dimethyl formamide according to literature [23].

Preparation of Separation Column

1.0–2.0 g of resin was treated with nitric acid (50 ml of 2 mol l⁻¹) for the removal of impurities in a beaker. It was filtrated and washed with deionized water until pH of the supernatant was neutral. Then, it was dried in an oven at 80°C for 8 h and 0.5 g of dried resin was packed into a glass column (100 × 8 mm² i.d.) plugged with small portion of glass wool at both ends. Before each use, the column was preconditioned by passing the blank solutions in working pH. The sample solution was permitted to flow through the column under gravity [24].

Separation/Preconcentration Procedure

The column method was used to obtain optimum conditions for separation/preconcentration of the metal ions. Preconcentration of copper, zinc, and cobalt ions was performed by using 50-ml test solution containing 0.1 mg l⁻¹ of each metal ion. Test solutions were passed through the column after adjusting to the optimum experimental conditions. The adsorbed ions on the resin in the column were eluted with 5 ml of 2 mol l⁻¹ HNO₃ solution that had a flow rate of 4 ml min⁻¹ and were determined by FAAS.

Analysis of Water Samples

Tap water was collected from our research laboratory at Ahi Evran University. Commercial drinking water and mineral water were collected from local market in Turkey. For analysis, a 250 ml sample was placed in beaker and it was filtered through 0.45 μm cellulose nitrate membrane filters (Millipore) to remove suspended organic and other particles. Afterward, known amounts of copper, zinc, and cobalt solutions were spiked into samples and then pH was adjusted to pH 5.8 with sodium acetate-acetic acid buffer solutions. Finally, the preconcentration procedure was applied.

RESULTS AND DISCUSSION

Effect of Test Solution pH on Recovery of Metal Ions

pH of medium is of prime importance for efficient retention and recovery of the metal ions on the resin. Its

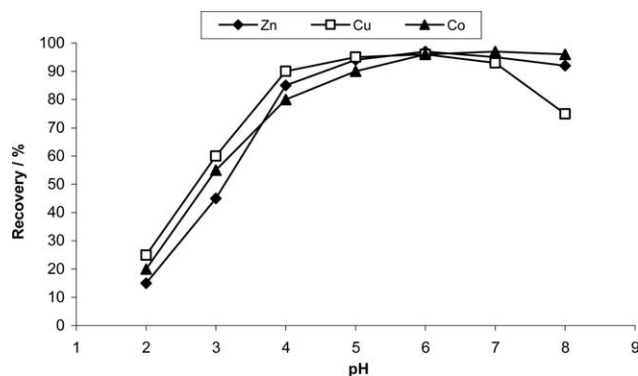


FIG. 1. The effect of pH on the recoveries of Zn, Cu, and Co from aqueous solutions.

influence strongly depends on the nature of the sorbent used. Hence, the effect of pH on the recovery of analyte ions was studied in the range of 3.0–8.0. Prepared solutions which have working pH were passed through the column at an optimized flow rate. Effect of the pH on the recovery values was summarized in Fig. 1. As shown in this figure, optimum recoveries were found between the pH value of 5.0–7.5 for zinc, 5.0–6.5 for copper, and 5.5–8.0 for cobalt. If pH values are lower than 5.0, retention of metal ions on copolymer due to the competition between protons and the metal ions for the adsorption sites of the sorbent are decreased. The decrease in recovery of metal ions when pH >7.5 is probably due to the precipitation of metal ions and hydroxide ions. The pH values for simultaneous preconcentration of Zn, Cu, and Co ions must be between the pH values of 5.5–6.5. Therefore, a pH of 5.8 in sodium acetate-acetic acid buffer was selected in further experiments.

Choice of Eluents Agents

The type and concentration of eluent is also important for the analytical parameters of a column solid-phase preconcentration system. Inorganic acids such as HCl and HNO₃ are recommended in desorption of metal ions from polymeric materials because they rapidly decrease the pH of the medium and assist the protons exchange to replace the bounded metal ions in the solid phase. For this purpose, HCl and HNO₃ solutions in different concentration and volume were used. The effects of various eluent on the recoveries of metal ions are given in Table 1. The obtained results show that the maximum recoveries of studied metal ions were found by using 5 ml of 2 mol l⁻¹ HNO₃ or 5 ml of 3 mol l⁻¹ HNO₃ solutions. If concentrated acid (3 mol l⁻¹ HNO₃) is used as eluent agent, polymer surfaces would be infected. Therefore, 5 ml of 2 mol l⁻¹ HNO₃ solutions was used for maximum elution of Zn, Cu, and Co.

Effect of Sample Flow Rate

The sample flow-rate should be optimized to ensure quantitative recovery along with decreasing the time

TABLE 1. Effect of type and concentration of eluting agent on zinc, copper, and cobalt ion recoveries from aqueous solutions.

Eluent	Recovery/% (wt) ^a		
	Zn	Cu	Co
1 mol l ⁻¹ HCl, 5 ml	88 ± 2	78 ± 2	85 ± 2
2 mol l ⁻¹ HCl, 5 ml	95 ± 2	84 ± 1	92 ± 2
3 mol l ⁻¹ HCl, 5 ml	96 ± 2	88 ± 1	94 ± 1
2 mol l ⁻¹ HNO ₃ , 5 ml	98 ± 2	96 ± 2	100 ± 2
3 mol l ⁻¹ HNO ₃ , 5 ml	98 ± 1	97 ± 1	98 ± 1

^aMean value and standard deviation of three replicate analyses.

required for sample processing. The flow rate of sample solution on the retention of metal ions was examined in the range of 1.0–6.0 ml min⁻¹ at optimum conditions. Results are shown in Fig. 2. The recoveries of metal ions are in the range between 95 and 100% at flow rates varying from 1.0 to 4.0 ml min⁻¹ for Zn and Co, and 1.0 to 3.0 ml min⁻¹ for Cu. If sample flow rates are higher than these values, it is obtained that recoveries are decreased because of the insufficient interaction time between the metal ions and resin. Accordingly, the optimum flow rate was recommended as 3 ml min⁻¹ for simultaneous separations of all worked metal ions.

Effect of Sample Volume

To calculate preconcentration factor for each metal ion, optimization of sample volume is required as a main factor. To determine the maximum applicable sample volume, solutions containing 2.5 µg of each metal ion were varied in the range of 50–1000 ml under the optimum conditions and were passed through a column. The results are shown in Fig. 3.

It was obtained that if the sample volume ranged between 50 and 800 ml for copper, 50 to 1000 ml for Zn and Co, recoveries were higher than 95%. By analyzing 5 ml of the final solution after the preconcentration of sample solution, preconcentration factors were found as 200, 160, and 200 for zinc, copper, and cobalt, respectively.

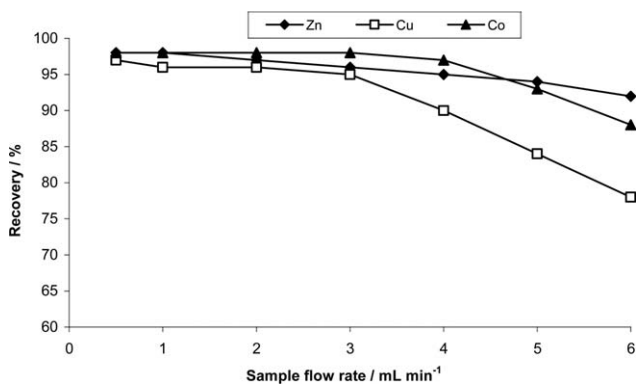


FIG. 2. The effect of sample flow rate on the recoveries of Zn, Cu, and Co from aqueous solutions.

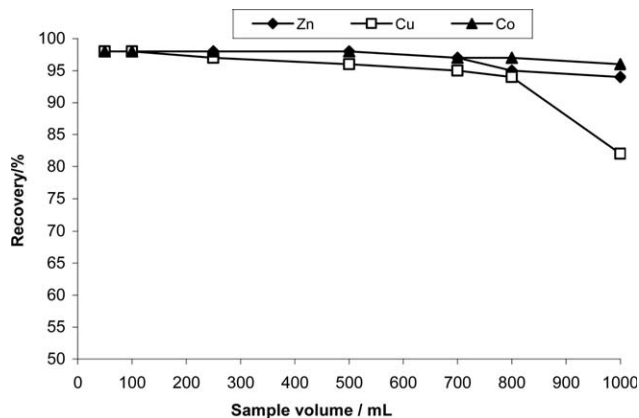


FIG. 3. The effect of sample volume on the recoveries of Zn, Cu, and Co from aqueous solutions.

Adsorption Capacity of Resin

The adsorption capacity is an important factor in the evaluation of the property of a sorbent, because it determines how much sorbent is required to quantitatively concentrate the analyte ions from a given solution [25–27]. To determine adsorption capacity, 0.2 g of resin was added into a beaker which has 50 ml of aqueous solution including 25 mg of each metal ion in optimum pH and stirred for 60 min with a magnetic stirrer. Then, metal ions in solution were determined by using FAAS after needed dilution process. The calculated adsorption capacities for Zn, Cu, and Co were 6.8, 5.2, and 7.5 mg g⁻¹, respectively. Adsorption capacity for metal ions depends on several parameter such as pH of solution, temperature, ionic strength, the sorbent surface areas, the effects of other species in the matrix, the particle size, the forces of interaction between the adsorbed species with the sorbent, particle diameter, particle charge, complexation capacities, conditional binding constant, particle ratios, and sorption coefficient of each species. Therefore, adsorption capacities of the sorbent material for different metal ions in the same matrixes may be different. The capacities of the adsorbent did not significantly change up to 50 cycles.

Influence of Interfering Species

Effect of various ions present in water on the recoveries of analyte ions was investigated under optimized experimental conditions. Synthetic 50 ml of solutions containing 5 µg of zinc, copper, and cobalt ions and various amounts of possible interfering ions were used for this aim. The recovery values for different amounts of foreign ions were given in Table 2. As can be seen, added ions have no significant effect on the recovery of analyte ions.

Analytical Features and Applications of Method

The limit of detections (LOD)s are calculated according to 3Sd/(m.PF) criteria, where Sd is the standard deviation of the blank (50 ml, pH 5.8) measurements 10

TABLE 2. Effects of the matrix ions on the recoveries of zinc, copper, and cobalt ions from aqueous solutions.

Interfering ions	Mass concentration/mg l ⁻¹	Recovery/(wt) ^a		
		Zn	Cu	Co
K ⁺	1000	100 ± 1	98 ± 2	97 ± 2
Na ⁺	1000	101 ± 2	96 ± 2	98 ± 1
Ca ²⁺	500	98 ± 2	95 ± 3	96 ± 2
Mg ²⁺	200	96 ± 2	97 ± 2	99 ± 3
Zn ²⁺	5	–	101 ± 2	97 ± 3
Cu ²⁺	5	99 ± 2	–	96 ± 1
Co ²⁺	5	98 ± 2	102 ± 2	–
Ni ²⁺	5	100 ± 3	98 ± 2	98 ± 2
Cd ²⁺	5	98 ± 2	95 ± 2	96 ± 1
Pb ²⁺	5	99 ± 1	96 ± 2	95 ± 2
Cr ³⁺	5	96 ± 1	95 ± 2	101 ± 2
Al ³⁺	5	95 ± 2	100 ± 2	98 ± 2
Fe ³⁺	5	97 ± 2	96 ± 2	98 ± 1
NO ₃ ⁻	1000	97 ± 2	96 ± 2	95 ± 3
Cl ⁻	1000	95 ± 1	95 ± 2	96 ± 2

^aMean value and standard deviation of three replicate analyses.

replicates, *m* is the slope of calibration curve, and PF is preconcentration factor for proposed procedure. The LODs for Zn, Cu, and Co were calculated as 0.82, 1.24, and 0.68 μg l⁻¹, respectively. To determine the precision

TABLE 3. Analysis of cobalt, copper, and zinc in the certified reference material NIST SRM 1643e (trace elements in water).

Element	Mass concentration/μg l ⁻¹		Recovery/(wt)
	Found ^a	Certified	
Co	28.12 ± 0.86	27.06 ± 0.32	103.9
Cu	23.26 ± 1.12	22.76 ± 0.31	102.1
Zn	77.6 ± 4.4	78.5 ± 2.2	98.8

^aMean and standard deviation from three determinations.

of the proposed method, the test solutions (50 ml) containing 0.1 mg l⁻¹ of each metal ions were used. The relative standard deviation (RSD) for seven replicate analyses of Zn, Cu, and Co ions was found as 2.4, 2.8, and 1.5%, respectively.

The developed method was applied to standard reference material (50 ml NIST SRM 1643e, trace elements in water) for the determination of cobalt, zinc, and copper. The results, based on the average of three replicates, are given in Table 3, which shows that the results are in good agreement with the certified values. The improved method was applied to water samples. The validity of the proposed method was further proven by analyzing spiked analyte ions samples. Experimental results are given Table 4.

TABLE 4. Mass concentrations of cobalt, copper, and zinc in drinking, tap and mineral waters and their recoveries from spiked water samples.

Sample	Zn			Cu			Co		
	Added/μg l ⁻¹	Found ^a /μg l ⁻¹	Recovery/(wt)	Added/μg l ⁻¹	Found ^a /μg l ⁻¹	Recovery/(wt)	Added/μg l ⁻¹	Found ^a /μg l ⁻¹	Recovery/(wt)
Drinking water A	0	14.4 ± 0.8		0	4.5 ± 0.4		0	ND ^b	
	5.0	18.8 ± 1.2	96.9	5.0	9.4 ± 0.5	98.9	5.0	5.2 ± 0.4	104
Drinking water B	0	ND ^b		0	ND ^b		0	ND ^b	
	5.0	5.0 ± 0.6	100	5.0	4.9 ± 0.5	98	5.0	5.1 ± 0.4	102
Tap water	0	24.6 ± 1.4		0	6.4 ± 0.7		0	2.4 ± 0.2	
	10.0	35.3 ± 2.6	102.8	5.0	11.2 ± 0.8	98.2	5.0	7.3 ± 0.5	98.6
Mineral water	0	84.4 ± 5.8		0	25.5 ± 1.8		0	8.5 ± 0.6	
	50.0	138 ± 6.4	102.6	10.0	37.2 ± 2.2	104.7	5.0	13.2 ± 1.1	97.7

^aMean ± *t*.*s*/*N* at 95% confidence level: *t* = 1.96; *s* is the standard deviation of three determinations and *N* the number of samples (3).

^bNot detected.

TABLE 5. Comparison of the proposed method for preconcentration of Zn, Cu, and Co ions in water samples with other methods described in the literature.

Adsorbent	Enrichment factor			LOD/μg l ⁻¹			RSD/%			Ref.
	Zn	Cu	Co	Zn	Cu	Zn	Zn	Cu	Co	
Nano hybrid material (ZrO ₂ /B ₂ O ₃)	–	10	10	–	3.3	3.8	–	3	3	[28]
Chloromethyl polystyrene polymer modified with 2-carboxy-2-hydroxy-5-sulfo-formazyl benzene	300	250	–	5.0	4.0	–	2.25	1.25	–	[29]
Silica gel modified with <i>p</i> -dimethylamino-benzaldehyde	125	125	–	6.50	0.69	–	<5.0	<5.0	–	[30]
4,6-Dihydroxy-2-mercaptopyrimidine loaded on activated carbon	–	260	260	–	2.9	3.4	–	1.2	1.3	[31]
<i>Penicillium digitatum</i> immobilized on pumice stone	50	50	–	1.3	1.8	–	2.0	3.0	–	[32]
Tween 80 coated alumina	–	8.8	8.3	–	0.4	1.2	–	1.9	2.6	[33]
Poly S-g-EMA	200	160	200	0.82	1.24	0.68	2.4	2.8	1.5	This work

Comparison to Other Procedure

A comparison of the proposed procedure with other reported preconcentration procedures is summarized in Table 5. Analytical characteristics obtained for this study are comparable to many procedures in the table. The LODs of present procedure are better than some of the other reported preconcentration methods [28, 29, 31, 32]. Preconcentration factor is relatively higher than similar procedure reported in literature [28, 30, 32, 33] and the RSD (%) of this work is comparable to given procedure in Table 5.

CONCLUSIONS

It has been demonstrated that the poly styrene-graft-ethyl methacrylate copolymer provides high enrichment factors (200, 160, and 200 for Zn, Co, and Co, respectively), high tolerance limit of interfering ions, and low detection limits ($0.82 \mu\text{g l}^{-1}$ for Zn, $1.24 \mu\text{g l}^{-1}$ for Cu, and $0.68 \mu\text{g l}^{-1}$ for Co) for separation/preconcentration and determination of copper, cobalt, and zinc ions at trace levels using FAAS technique in water samples. Adsorption capacities for Zn, Cu, and Co ions were obtained as 6.8, 5.2, and 7.5 mg g^{-1} , respectively. This material was stable with a period greater than 50 cycles and can be safely used an alternative sorbet to separate trace metals in different samples

ACKNOWLEDGMENT

The author is thankful to Dr. M. Mursit Temuz for synthesis of graft polymer.

REFERENCES

1. S.B. Goldhaber, *Regul. Toxicol. Pharmacol.*, **38**, 232 (2003).
2. L. Noel, R. Chekri, S. Millour, C. Vastel, A. Kadar, V. Sirot, J.C. Leblanc, and T. Guerin, *Food Chem.*, **132**, 1502 (2012).
3. S.L. Davydova, *Crit. Rev. Anal. Chem.*, **28**, 377 (1998).
4. N.A.A. Salim, A.K. Wood, A.M. Yusof, M.S. Hamzah, M.S. Elias, and S.A. Rahman, *Fresenius Environ. Bull.*, **18**, 1618 (2009).
5. M.M. Hassanien, *Environ. Monit. Assess.*, **167**, 587 (2010).
6. Z. Fiket, V. Roje, N. Mikac, and G. Kniewald, *Croat. Chem. Acta*, **80**, 91 (2007).
7. M. Faraji, Y. Yamini, and M. Rezaee, *Talanta*, **81**, 831 (2010).
8. G. Pavlovska, K. Cundeve, and T. Stafilov, *Croat. Chem. Acta*, **74**, 121 (2001).
9. H. Ciftci, *Clean*, **38**, 657 (2010).
10. H. Ciftci, *Desalination*, **256**, 18 (2010).
11. A. Afkhami, T. Madrakian, R. Ahmadi, H. Bagheri, and M. Tabatabaee, *Microchim. Acta*, **175**, 69 (2011).
12. T. Shamspur and A. Mostafavi, *J. AOAC Int.*, **92**, 1203 (2009).
13. C.F. Harrington, R. Clough, H.R. Hansen, S.J. Hill, and J.F. Tyson, *J. Anal. At. Spectrom.*, **25**, 1185 (2010).
14. K. Pyrzynska, *Trends Anal. Chem.*, **29**, 718 (2010).
15. S. Matsuoka and K. Yoshimura, *Anal. Chim. Acta*, **664**, 1 (2010).
16. M.L. Kim and M.B. Tudino, *Talanta*, **82**, 923 (2010).
17. A.R. Turker, *Sep. Purif. Rev.*, **41**, 169 (2012).
18. R. Arimian, F. Piri, B. Karimi, and A. Moghimi, *Croat. Chem. Acta*, **84**, 111 (2011).
19. R. Say, A. Tuncel, and A. Denizli, *J. Appl. Polym. Sci.*, **83**, 2467 (2002).
20. X. Wang, X. Zhang, H. Guo, L. Yuan, and P. Liu, *Polym. Eng. Sci.*, **52**, 972 (2012).
21. S. Baytak, F. Zereen, and Z. Arslan, *Talanta*, **84**, 319 (2011).
22. V. Camel, *Spectrochim. Acta B*, **58**, 1177 (2003).
23. M. Coskun and M.M. Temuz, *J. Polym. Sci. Polym. Chem.*, **41**, 668 (2003).
24. H. Ciftci, T. Tunc, I.H. Tasdemir, and E. Ciftci, *Environ. Toxicol. Chem.*, **30**, 616 (2011).
25. E. Eren, O. Cubuk, H. Ciftci, B. Eren, and B. Caglar, *Desalination*, **252**, 88 (2010).
26. O.M. Kalfa, O. Yalcinkaya, and A.R. Türker, *Inorg. Mater.*, **45**, 988 (2009).
27. A. Karatepe, M. Soylak, and L. Elçi, *Clean*, **39**, 502 (2011).
28. O.M. Kalfa, O. Yalcinkaya, and A.R. Türker, *J. Hazard. Mater.*, **195**, 332 (2011).
29. A.M. El-Menshawey and A.A. El-Asmy, *Indian J. Sci. Technol.*, **2**, 78 (2009).
30. Y. Cui, X. Chang, X. Zhu, H. Luo, Z. Hu, X. Zou, and Q. He, *Microchem. J.*, **87**, 20 (2007).
31. M. Ghaedi, F. Ahmadi, and A. Shokrollahi, *J. Hazard. Mater.*, **142**, 272 (2007).
32. S. Baytak, E. Kenduzler, A.R. Turker, and N. Gok, *J. Hazard. Mater.*, **153**, 975 (2008).
33. S.Z. Mohammadi, H. Hamidian, L. Karimzadeh, and Z. Moeinadini, *Arab. J. Chem.*, Available at: <http://dx.doi.org/10.1016/j.arabjc.2012.02.002>.