Studii şi Cercetări Ştiinţifice
Chimie şi Inginerie Chimică, Biotehnologii, Industrie Alimentară

Scientific Study & Research
Chemistry & Chemical Engineering, Biotechnology, Food Industry

2017, **18** (1), pp. 045 – 052

ISSN 1582-540X

ORIGINAL RESEARCH PAPER

RAPID METHOD FOR EVALUATION OF METALLIC MOBILE FRACTION FROM SEWAGE SLUDGE SAMPLES

Nicoleta M. Marin[1,2*], Gabriela G. Vasile[1], Marius Simion[1], Luoana F. Pascu[1], Carol B. Lehr[1]

[1]National Research and Development Institute for Industrial Ecology, Drumul Podu Dambovitei no 71-73, district 6, Bucharest, Romania
[2]University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, Blvd. Regina Elisabeta, no 2-14, 030018, Bucharest, Romania

*Corresponding author: nicoleta_mirela02@yahoo.com

Received: June, 24, 2016
Accepted: February, 23, 2017

Abstract: This study presents a modified extraction method for evaluation of mobile fraction from sewage sludge samples. The mobile content of As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn was detected using three different single chemical extraction procedures and also the leaching test according to SR EN ISO 12457-2/2003 standard. The experimental data show that the optimal extraction method was the one with diethylenetriamine pentaacetic acid (DTPA), $CaCl_2$ and triethanolamine (TEA) and a modified ratio solid: solution = 1 : 10 (mass per volume). The selected method provides a better assessment of the ability of metals to leach from sewage sludge during storage than leaching test method.

Keywords: *agriculture improver, bioavailability index, extraction method, leached, metals*

INTRODUCTION

Toxic metals that are present in wastewater have a high tendency to accumulate in sewage sludge collected from treatment plants, caused of their reduced biodegradability. The content of metallic mobile fraction provides important information about metals bioavailability from the sewage sludge structure.

External factors such as: *p*H, oxidants or reductants products can move bounded metals that exist in different fractions from one form to another, over time. Evaluation of the total content and soluble fractions provide comprehensive information about the influence of environmental hazardous metals [1 – 6]. Accumulation of toxic metals in sewage sludge restricts its use as soil fertilizer. For this reason is necessary to determine the metal content in sewage sludge in order to establish the final destination: either as waste (inert, non-hazardous, or dangerous) or as fertilizer in agriculture [7, 8].

In order to achieve this goal, standardized methods are used only for the total content of the metals and for the leached metals [9, 10]. Extraction of mobile metallic fraction from environmental samples, such as soil, sludge and sediment, is usually performed using different single chemical extraction procedures [10 – 15].

The purpose of this study was to establish a single chemical extraction method in order to rapid evaluation of the content of metallic mobile fraction in sewage sludge samples from wastewater treatment plants.

MATERIALS AND METHODS

Three different sewage sludge samples were collected from Wastewater Treatment Plants Vaslui, Buzau and Satu Mare (Romania).

Preparation of the materials

The chemical extraction solutions were prepared with triethanolamine, calcium chloride anhydrous, diethylenetriamine pentaacetic acid, ammonium acetate and ammonium nitrate in distilled water and were purchased from Sigma Aldrich.

Hydrochloric acid 37 % and nitric acid 67 % used to prepared aqua regia mixture were obtained from Merck. For the calibration curve a Multielement Certified Reference Material 100 $mg \cdot L^{-1}$ XVI Certipur for ICP, Merck quality, was used.

Extraction of mobile metallic fraction

The sewage sludge samples were dried at 25 ± 2 ºC air temperature, milled in a RM 100 Retsch Mill and sieved with a Fritsch Analysette 3 Spartan System. In order to determinate the total and mobile fraction content, the fraction with the particle size less than 150 μm was separated.

For the metallic mobile fraction determination, three standardized single chemical extraction procedures were applied (Table 1). Method 1 was performed with a modified ratio solid: liquid from 1 : 2 to 1 : 10, in order to improve the capacity of the extraction solution to remove metallic elements from the sewage structure [12].

As is presented in Table 1, the extraction time for the methods 1 to 3 is 2 hours, in comparison with leaching method, where are necessary 24 hours of extraction. The reagents used in methods 1 to 3 are a combination of organic and inorganic salts, instead in the leaching test was used only distilled water.

The extraction with aqua regia (mixture of hydrochloric acid 37 % and nitric acid 67 %) was performed in order to determinate the total metallic content [9].

Table 1. *Single chemical extraction procedures applied to sewage sludge samples*

No	Method	Extraction conditions	References
1	Aqua regia extraction	HCl-HNO_3 3 : 1 = 21 mL HCl + 7 mL HNO_3	[9]
2	SR ISO 14870/2002	0.005 M DTPA + 0.01 M $CaCl_2$ + 0.1 M TEA, solid/solution = 1 : 10*, shaken 2 h at 40 rpm·min^{-1}	[13]
3	Standard ONORM L 1094-2/1994	1M CH_3COONH_4, pH = 7 ± 0.02, solid/solution = 1 : 10, shaken 2 h at 40 rpm·min^{-1}	[11]
4	Standard DIN 19730/1997/ONORM L 1094-1/1994	1M NH_4NO_3, pH = 7 ± 0.02, solid/solution = 1 : 2.5 shaken 2 h at 40 rpm·min^{-1}	[11]
5	SR EN 12457-2/2003	Distilled water, solid/aqueous solution = 1 : 10, shaken 24 h at 40 rpm·min^{-1}	[10]

**Modified ratio solid: solution*

Calibration curves were prepared in the range 0.5 to 2.5 mg·L^{-1}, using the specified extraction solutions for each method (Table 1).

The content of As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Se and Zn (total and mobile) was determinate with an ICP-EOS Optima 5300 DV Perkin Elmer Spectrometer. In Table 2 are presented the Spectrometer operating parameters.

Table 2. *The emission wavelengths and the spectrometer operating parameters used in ICP-OES determinations*

Metallic elements	ICP-OES Wavelength [nm]	ICP-OES Spectrometer parameters	
As	188.979	Delay time	40 [s]
Cd	228.802	Replicates	2 times
Cr	267.716	**Plasma parameters**	
Cu	327.393	Plasma flow rate	15 [L·min^{-1}]
Mo	202.031	Auxiliar flow rate	0.2 [L·min^{-1}]
Ni	231.604	Nebulizer flow rate	0.7 [L·min^{-1}]
Pb	220.353	Power RF	1400 [W]
Sb	206.836	Plasma view	15.0 [mm]
Zn	206.200	View distance	15.0 [mm]
Co	228.616	-	-

RESULTS AND DISCUSSION

The total metallic concentrations were compared with sewage sludge reference values imposed by the Romanian Order 344/2004 [7]. As is presented in Table 3, total concentrations of As, Cr and Ni were situated above the maximum admissible values (MAV) in sample 1 and only As overflow the MAV in sample 3.

Table 3. *The total metallic content in different sewage sludge samples*

Metallic elements	Unit	Sample 1	Sample 2	Sample 3	MAV*
As	[mg·kg^{-1}] d.m.	**11.4**	2.90	**16.9**	10
Cd	[mg·kg^{-1}] d.m.	2.20	5.60	0.41	10
Cr	[mg·kg^{-1}] d.m.	**1249**	61.9	19.7	500
Cu	[mg·kg^{-1}] d.m.	287	189	22.6	500
Mo	[mg·kg^{-1}] d.m.	31.8	22.8	<0.03	-
Ni	[mg·kg^{-1}] d.m.	**119**	92.5	33.3	100
Pb	[mg·kg^{-1}] d.m.	73.1	146	3.30	300
Sb	[mg·kg^{-1}] d.m.	<0.15	25.6	1.22	-
Zn	[mg·kg^{-1}] d.m.	1730	590	88.0	2000
Co	[mg·kg^{-1}] d.m.	13.4	6.20	5.41	50

Results notated with < represent values situated below the quantification limit
**Maximum admissible value accepted according to Romanian Order no. 344/2004 [7]*

In Tables 4 to 6 are presented mobile metal concentrations obtained with the extraction methods 1 to 4 indicated in Table 1. The experimental results were compared with the reference values imposed by the Romanian Order 95/2005 for inert, non-hazardous and hazardous wastes.

The sewage sludge sample 1 will be classified as non-hazardous waste, if methods 2, 3, 4 are applied only, but the Zn content extracted with method 1 was situated above the maximum limit for hazardous waste (Table 4).

Table 4. *Mobile metallic concentrations in sample 1*

Metallic elements	Unit	SR ISO 14870/ 2002 (1)	DIN 19730/ 1997 (2)	ONORM L1094-2/1994 (3)	SR EN 12457-2/2003 (4)	MAV*		
						inert waste	non-hazardous	hazardous
As	[mg·kg^{-1}] d.m.	0.21	0.20	1.61	<0.07	0.5	2	25
Cd	[mg·kg^{-1}] d.m.	0.92	<0.01	0.13	<0.01	0.04	1	70
Cr	[mg·kg^{-1}] d.m.	0.13	0.23	0.32	2.42	0.5	10	100
Co	[mg·kg^{-1}] d.m.	0.51	0.22	0.20	0.23	-	-	-
Cu	[mg·kg^{-1}] d.m.	**70.3**	2.81	3.13	0.72	2	50	100
Mo	[mg·kg^{-1}] d.m.	0.70	<0.01	1.34	<0.01	0.5	10	30
Ni	[mg·kg^{-1}] d.m.	6.62	3.44	0.82	0.11	0.4	10	40
Pb	[mg·kg^{-1}] d.m.	7.03	<0.07	0.20	0.14	0.5	10	50
Sb	[mg·kg^{-1}] d.m.	0.12	0.11	< 0.06	0.12	-	-	-
Zn	[mg·kg^{-1}] d.m.	**629**	13.6	33.6	49.3	4	50	200

*Results notated with < represent values situated below the quantification limit *Maximum admissible value accepted according to Romanian Order no. 95/2005 [8]*

Table 5. *Mobile metallic concentrations in sample 2*

Metallic elements	**Unit**	**SR ISO 14870/ 2002 (1)**	**DIN 19730/ 1997 (2)**	**ONORM L1094-2/1994 (3)**	**SR EN 12457-2/2003 (4)**	**MAV***		
						inert waste	**non-hazardous waste**	**hazardous waste**
As	[mg·kg^{-1}] d.m.	*<0.07	<0.07	<0.07	<0.07	0.5	2	25
Cd	[mg·kg^{-1}] d.m.	1.51	<0.01	<0.01	<0.01	0.04	1	70
Cr	[mg·kg^{-1}] d.m.	<0.01	<0.01	<0.01	<0.01	0.5	10	100
Co	[mg·kg^{-1}] d.m.	0.42	0.07	0.13	<0.01	-	-	-
Cu	[mg·kg^{-1}] d.m.	**37.1**	<0.01	**18.1**	1.04	2	50	100
Mo	[mg·kg^{-1}] d.m.	0.13	**21.6**	0.61	<0.01	0.5	10	30
Ni	[mg·kg^{-1}] d.m.	1.14	0.41	0.63	0.11	0.4	10	40
Pb	[mg·kg^{-1}] d.m.	**37.8**	0.04	**3.32**	0.13	0.5	10	50
Sb	[mg·kg^{-1}] d.m.	0.21	0.34	<0.06	<0.06	-	-	-
Zn	[mg·kg^{-1}] d.m.	**90.0**	1.01	**36.5**	0.42	4	50	200

*Results notated with < represent values situated below the quantification limit *Maximum admissible value accepted according to Romanian Order no. 95/2005 [8]*

The sample 2 is classified as inert waste if method 4 is applied or non-hazardous waste if method 3 is used, but the results obtained with single chemical extraction method 1 and method 2 indicated that sewage sludge is a hazardous waste because Pb and Zn have high values according to method 1 and Mo present a content above the limit according to method 2 (Table 5).

Using methods 2, 3, 4, the sewage sludge sample 3 is classified as inert waste or non-hazardous waste if method 1 is applied (Table 6).

Table 6. *Mobile metallic concentrations in sample 3*

Metallic elements	**Unit**	**SR ISO 14870/ 2002 (1)**	**DIN 19730/ 1997 (2)**	**ONORM L1094-2/1994 (3)**	**SR EN 12457-2/2003 (4)**	**MAV***		
						inert waste	**non-hazardous waste**	**hazardous waste**
As	[mg·kg^{-1}] d.m.	<0.01	<0.01	<0.01	0.03	0.5	2	25
Cd	[mg·kg^{-1}] d.m.	<0.01	<0.01	<0.01	<0.01	0.04	1	70
Cr	[mg·kg^{-1}] d.m.	<0.01	<0.01	<0.01	0.03	0.5	10	100
Co	[mg·kg^{-1}] d.m.	0.10	<0.01	<0.01	<0.01	-	-	-
Cu	[mg·kg^{-1}] d.m.	1.70	0.17	0.60	0.04	2	50	100
Mo	[mg·kg^{-1}] d.m.	<0.01	<0.01	0.10	<0.01	0.5	10	30
Ni	[mg·kg^{-1}] d.m.	0.10	<0.03	<0.03	<0.03	0.4	10	40
Pb	[mg·kg^{-1}] d.m.	0.30	<0.07	<0.07	<0.07	0.5	10	50
Sb	[mg·kg^{-1}] d.m.	<0.06	0.06	<0.06	<0.06	-	-	-
Zn	[mg·kg^{-1}] d.m.	**6.60**	0.90	1.00	0.24	4	50	200

*Results notated with < represent values situated below the quantification limit *Maximum admissible value accepted according to Romanian Order no. 95/2005 [8]*

The experimental data presented in Table 4 to 6 indicate that the improved standardized extraction method SR EN ISO 14870/2002 can be successfully used for obtaining rapid information about pollutants behavior in environmental real conditions, about the ability of metals to be released from sludge structure and migrate into groundwater and plants.

Metallic mobile fraction in sewage sludge – Index of Bioavailability (iBA), [%]

The transfer of the metal to the environment was evaluated using bioavailability index [16 – 17] according to equation (1):

$$iBA\% = \frac{Cm \cdot 100}{Cm(total)} \tag{1}$$

where: *Cm* is the mobile metal content, solubile in aqueous or extraction solutions;
Cm(total) represents the total content of metal in sewage sludge samples.

The bioavailability indices indicate a low transfer of As, Cd, Cr, Mo, Ni, Co, Sb to the environment for all samples. Even if the total content of As, Cr and Ni are higher that the maximum admissible values for sample 1 and As for sample 3, the metals are bounded in the sewage structure.

The comparison between values of bioavailability indices for Cu and Zn in sample 1 and, respectively for Cu, Pb and Zn in sample 2 were presented in Figure 1 and Figure 2.

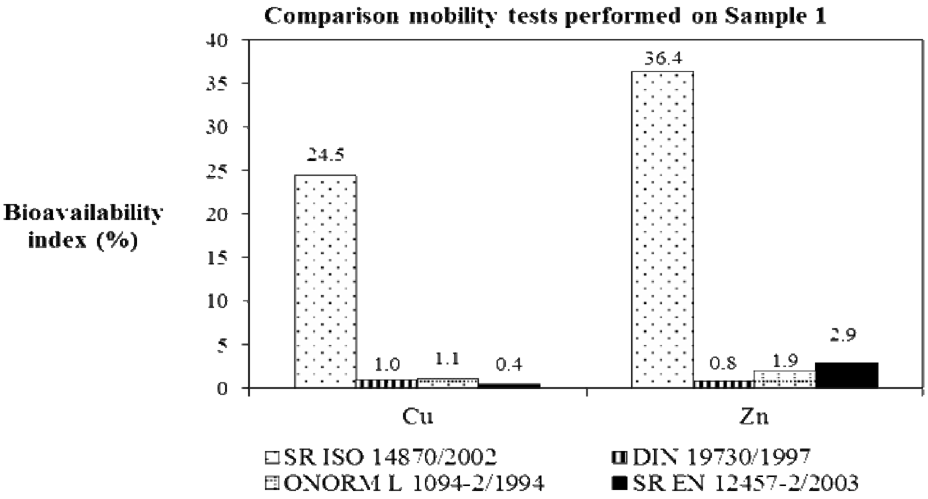

Figure 1. *Comparison of bioavailability indices for Cu and Zn with standardized methods 1 to 4*

The data presented in Figure 1, respectively Figure 2 indicate that the highest bioavailability index was obtained with DTPA, $CaCl_2$ and TEA single chemical extraction procedure (method 1).

When modified method 1 is applied on sample 3, low percentages of bioavailability index were obtained. So, for Cu and Zn mobile the index was 7.5 %, the highest value was recorded for Pb (9.1 %). The index was zero for As, Cd, Cr, Mo and only 1.85 % for Co.

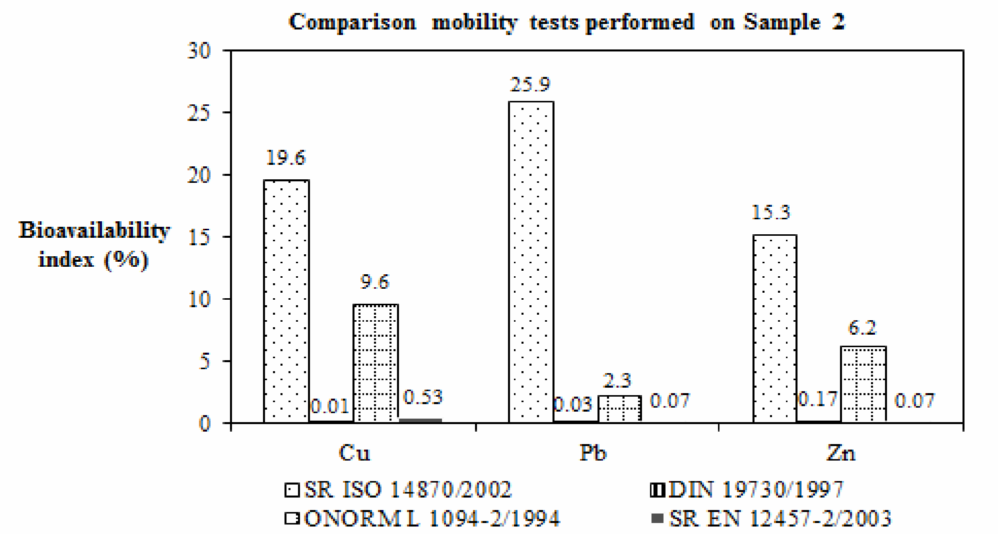

Figure 2. *Comparison of bioavailability indices for Cu, Pb and Zn with standardized methods 1 to 4*

CONCLUSIONS

This study proposed a rapid extraction method for quantitative determinations of metallic mobile fraction from sewage sludge samples, in order to establish the final destination, as improver in agriculture or as a waste storage (inert, non-hazardous or hazardous). The results show that the single chemical extraction procedure according to the modified SR EN ISO 14870 standard (ratio solid: liquid = 1 : 10) can be successfully used for estimation the content of metallic mobile fraction, which can be available from sewage sludge samples.

Acknowledgement

The authors are grateful for the financial support of project PN 16 25 01 09- 2016 (Contract no. 38N/2016).

REFERENCES

1. Jarosław, G., Barbara, G.: Mobility of Heavy Metals in Municipal Sewage Sludge from Different Throughput Sewage Treatment Plants, *Polish Journal of Environmental Studies*, **2012**, **21** (6), 1603-1611;
2. Bacon, R. J., Davidson, M.C.: Is there a future for sequential chemical extraction, *Analyst*, **2008**, 25-46;
3. Hsiau, P., Lo, S.: Extractabilities of heavy metals in chemically-fixed sewage sludges, *Journal of Hazardous Materials*, **1998**, **58**, 73-82;
4. Alvarez, A.E., Mochon, C.M., Sanchez, J.C.J., Rodriguez, T.M.: Heavy metal extractable forms in sludge from wastewater treatment plants, *Chemosphere*, **2002**, **7**, 765-775;

5. Albores, F.A., Cid, P.B., Gomez, F.E., Lopez, F.E.: Comparison between sequential extraction procedures and single extractions for metal partitioning in sewage sludge samples, *Analyst*, **2000**, **125**, 1353-1357;
6. Fuentes, A., Lloréns, M., Sáez, J., Soler, A., Aguilar, I.M., Ortuño, F.J., Meseguer. F.V.: Simple and sequential extractions of heavy metals from different sewage sludges, *Chemosphere*, **2004**, **54** (8), 1039-1047;
7. Romanian Order no. 344/**2004** regarding Technical rules on environmental and in particular, soils when are used amended sewage sludge in agriculture;
8. Romanian Order no. 95/**2005** establishing acceptance criteria and preliminary procedures for acceptances of waste storage and national list of waste accepted in each class of landfill;
9. SR EN 16174/**2013:** Sludge, treated biowaste and soil - Digestion of aqua regia soluble fractions of elements;
10. SR EN 12457-1/**2003**: Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 4: One stage batch test at a liquid to solid ratio of 10 $L \cdot kg^{-1}$ for materials with particle size below 10mm (without or with size reduction);
11. Vasile, G., Cruceru, L., Petre, J., Iancu, V., Mitran, R.: Analytical investigation concerning the methodology for extraction of exchangeable forms of heavy metals from different types of soils, *Journal of Environmental Protection and Ecology*, **2006**, **7** (3), 562-569;
12. Vasile, G., Cruceru, L.: Optimised method for extraction of mobile species of heavy metals from polluted soils, *Journal of Environmental Protection and Ecology*, **2007**, **8** (4), 801-805;
13. SR ISO 14870:**2002**: Soil quality. Extraction of microelements with buffer solutions of DTPA;
14. Malinowska, E.: The effects of soil liming and sewage sludge application on dynamics of copper fractions and total copper concentration, *Environmental Monitoring and Assessment*, **2016, 188**;
15. Elouear, Z., Bouhamed, F., Boujelben, N., Bouzid, J.: Assessment of toxic metals dispersed from improperly disposed tailing, Jebel Ressas mine, NE Tunisia, *Environmental Earth Sciences* **2016**, **75**;
16. Kim, L., Vasile, G.G., Stanescu, B., Calinescu, S., Batrinescu, G.: Distribution and bioavailability of mobile arsenic in sediments from a mining catchment, *Journal of Environmental Protection and Ecology*, **2015**, **16** (4), 1307-1315;
17. Kim, L., Vasile, G.G., Stanescu, B., Dinu, C., Ene C.: Distribution of Trace Metals in Surface Water and Streambed Sediments in the Vicinity of an Abandoned Gold Mine from Hunedoara County, Romania, *Rev.Chim. (Bucharest),* **2016**, **67** (8) 1441-1446.