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Chemical Speciation of Particular Heavy Metals in Sewage Sludge Using Sequential Extraction Procedure

M. S. Rizk[*], M. M. Yehia[**] and S. E. Gaber[**]

* Department of Chemistry, Faculty of Science, Cairo University, Egypt
** Central Laboratory for Environmental Quality Monitoring, National Water Research Center, Egypt

Summary: Sequential extraction was employed to investigate metal speciation using two different methods; Tessier's five steps extraction procedure and Commission of the European Communities Bureau of Reference (BCR) three steps sequential extraction procedure both include the utilization of a series of chemical extractants in a sequence of increasing strength. For each extraction step, a particular chemical form of the metal is expected to be dissolved. Principal physical, chemical properties and the total metal contents including Zn, Cu, Cr, Ni, and Pb were also carried out. It was observed by using a sequential extraction procedure in sewage sludge that fractions of heavy metals extractable e.g. water-soluble, exchangeable and carbonate-bound fractions are very low for Cu, Cr and Pb (0.27- 3.15%)., and higher for Zn and Ni (22.3% and 28.5%, respectively) The portions of other heavy metals bound to iron and manganese oxides and hydroxides fraction were below 15% and ranged from 13.8% for Cu, 10.23% for Cr and 13.2% for Pb. more than 55% Cu was mostly released in the moderately soluble fraction (heavy metals bound to organic matter and sulphides) which indicated that Cu was associated with strong organic ligands due to its affinity to form stable complexes.

Introduction

The consequence of the purification of municipal and industrial wastewater is a usual production of sewage sludge in great quantities, which elimination shows underestimated problems due to the large amount of organic matter, heavy metals, and pathogens accumulated in it. Heavy metals not only are not biodegradable and become toxic at some concentrations, but also they tend to accumulate along the food chain where man is the last link.[(1)]

The determination of total heavy metal content of sewage sludge does not provide useful information about the risks of bioavailability, the capacity for remobilisation and the behaviour of the metals in the environment.[(2)] While, the chemical forms of a metal or speciation allows the estimation of heavy metal bioavailability and is related to the different natures of the metals, their bonding strength, either in free ionic form or complexed by organic matter, or incorporated in the mineral fraction of the sample. The speciation of each metal in the sewage sludge depends on its initial chemical state in the sewage, the adsorption and precipitation mechanisms in sludge, and the effect of stabilization of the material and the

humification process that occurs during composting on the chemical form of the metal. [3]

The aim of this work is to assess the potential impact of studied heavy metals availability in sewage sludge and to evaluate its toxicity by chemical sequential extraction procedures and deciding the suitability of studied sludge for land application. The main physico-chemical analyses were carried out and a sequential extraction method was applied on sewage sludge for Zn, Cu, Cr, Ni and Pb using two different methods Tessier's five-steps extraction procedure[4] and BCR three-steps sequential extraction procedure.[5-6] The results obtained from both schems were compared with each other. The accuracy of extraction methods could be evaluated from the elemental recovery after whole extraction procedure.

Experimental

Sampling:

All the studied sewage sludge were taken from oxidation ponds in El-Sadat City, an industrial city in Egypt, in which About 15000 m^3 of wastewater (domestic 5000 m^3 and industrial 10000 m^3) are received per day. Freshly deposited sludge was collected in polyethylene bags and brought to the laboratory, air dried and stored in refrigerator for further analysis.

Characterization of the sludge

On aliquots of these samples the following physico-chemical analyses were made:

pH and EC : 5 g of the air dried sample was taken in 50 ml distilled water and agitated for 5 min. The solution was left for 1 h with occasional shaking. pH and EC were measured in sludge extracts, using a pH and conductivity meters, respectively.

Organic matter: Organic matter in the sediment was determined as Total Organic Carbon (TOC) using Dohrmann carbon analyzer; the reported data are the sum of soluble and insoluble organic carbon.

Total nitrogen: Total Kjeldahl Nitrogen TKN was measured by Kjeldahl method

Total P and total K: dry ash was prepared by leaving the residue at 500 ^oC overnight after cooling, these ashes were dissolved with 5% HCl in preparation for Optical Emission Spectrometry (ICP) analysis.

Total metal Extraction:

The total metals were extracted from the sediment samples using microwave-assisted total digestions using an acid digestion mixture (HNO_3-HCl-HF). A 0.5 g of sludge was treated with the acid mixture.

Heavy metal Speciation:

I- Tessier's five-steps sequential extraction procedure:

Using 1.0 gm of dried sewage sludge samples, a series of reagents was applied sequentially according to Table 1.

II- Communities Bureau of Reference (BCR) three-steps sequential extraction procedure:

The BCR three steps sequential extraction procedure was applied to 1.0 gm of dried sample according to the scheme in Table 2. For internal check on the procedure an additional step was applied after the sequential extraction steps (the insoluble residue metals) [7].

Table 1: Extractants and experimental conditions used to determine various extractable heavy metal forms

Step	Extractant	shaking duration and condition	Heavy metal form
1	8 ml 1 M $MgCl_2$ pH 7	1 h at room temp.	Exchangable
2	8 ml 1 M NaOAc, HOAc pH 5.0	5 h at room temp.	bound to carbonates
3	20 ml 0.04 M $NH_2OH.HCl$ in 25% HOAc	6 h at 96^{O}C Occasional agitation	bound to Fe-Mn oxides
4	5 ml 30% H_2O_2 and 3 ml 0.02 M HNO_3 adj. pH 2 after cooling 3 ml H_2O_2 pH 2 by HNO_3 after cooling add 5ml 3.2M NH_4OAc in 20% HNO_3 adjusting to 20 ml	2 h at 85^{O}C Occasional agitation 3 h at 85^{O}C intermediate agitation (30 min.)	bound to organic matter
5	HNO_3-HCl-HF	Microwave digestion	residual

Each experiment was carried out in triplicate. Samples were extracted in 100 ml polypropelene centrifuge tubes. After each extraction step samples were centrifuged at 4,000 rpm for 30 min. the subnatant was analyzed for heavy metals by Optical Emission Spectrometry using Perkin-Elmer Inductively Coupled Plasma (ICP-OES) Optima 3000 and The supernatant was washed with 8 (v/m) (Tessier), 20 (v/m) BCR,

shaking for 15 minutes and centrifuging. Decant the supernatant and discard before the next step.

Table 2: BCR sequential extraction procedure

Step	Extractant	shaking duration and condition	Heavy metal form
1	40 ml 0.11 M acetic acid pH 2.8	shaking for 16 h at ambient temp.	bound to carbonates and Exchangeable
2	40 ml 0.1 M $NH_2OH.HCl$ acidified pH 2 with HNO_3	shaking for 16 h at ambient temp.	bound to amorphous Fe -Mn oxides and hydroxide
	10 ml H_2O_2 stabilized by HNO_3 to pH 2-3	digest 1h room temp. with Occass. Manual shaking, digest 1 h 85^oC	
3	reduce vol. to few ml & add further 10 ml of H_2O_2	digest 1 h 85^oC	bound to organic matter and sulfides
	add 50 ml 1M amm. Acetate	Shake 16 h at room temp.	
4	aqua regia	Microwave digestion	residual

Results and discussion

Sewage sludge properties

The main physico-chemical properties of the raw sludge are presented in Table 3. The pH values ranged from 7.1 to 8.21 which indicate that the sludge is slightly alkaline. Electrical conductivity in a water extract of sewage sludge ranged from 1.802 mS/cm in sample No. 4 to 3.00 mS/cm in sample No.11 which did not exceed the salinity limit value of 3 mS/ cm to be used in good fertilizers.[8]

Table 3: Physico-chemical properties of sewage sludge

Sample	1	2	3	4	5	6	7	8	9	10	11	12
pH	7.19	7.82	7.86	7.71	7.1	7.63	8.21	8.17	7.59	7.57	7.46	7.45
EC mS/cm	2.84	2.42	2.14	1.802	2.27	2.74	2.26	2.56	2.58	2.05	3.00	2.09
TOC g/kg	249	175	342	428	265	388	200	177	382	275	283	351
TKN g/kg	14	10.07	27.53	28.94	17.38	25.33	13.58	10.47	20.27	14.3	17.79	18.65
Total P g/kg	6.59	12.1	10.7	11.4	14.6	10.5	12.5	9.7	12.1	10.52	6.59	10.9
Ca g/kg	52.71	40.6	32.5	26.59	33.7	39.4	29	43.5	45.32	30.54	48.65	28.45
K g/kg	5.25	3.6	2.5	2.32	3.42	3.29	2.81	4.3	5.12	3.15	6.54	4.2
Mg g/kg	7.55	6.4	7.4	5.6	6.8	5.82	5.4	5.66	7.8	5.7	8.45	6.23
Na g/kg	4.24	2.2	1.45	1.8	2.4	1.74	1.8	3.6	3.2	2.11	4.6	3.71

The tested samples of sewage sludge have a high percentage of organic matter and nitrogen which may be present in the ammonium, nitrate and organic forms. As regarded cationic macroelments, calcium is the most abundant, followed by magnesium, potassium and sodium in all the sludge tested samples. All the parameters closely reflect those found by the bibliography of sludges of similar characteristics, some of which have been used for soil amendment.[9-10]

Total metal content

Total metal concentrations of Zn, Cu, Cr, Ni and Pb in sewage sludge determined after nitric, hydrochloric and hydrofluoric acid Microwave digestion of samples are presented in Table 4. Concentrations are expressed on a dry mass basis. Table 4 also includes comparisons with sludge legal standard established by U.S.EPA-40 [11] and standard by EU Commission [12]

According to Table 4, the total metal concentrations ranged from 555 to 1026 mg/kg for Zn, 256-802 mg/kg for Cu, 125-510 mg/kg for Cr, 170-385 mg/kg for Ni and 100-215 mg/kg for Pb. These data show a wide variation of the concentration ranges of heavy metals that may be due to irregular input from the industrial waste water. Also sludges are exceeding the allowed limits of the EU Commission standard, (with exception of Zn). In contrast, according to U.S.EPA-40, the sludge could be disposed to agricultural land. Comparisons among total amount of heavy metals, however, are very general and imply that all forms of a given metal are equally soluble[13] and exert the same impact on the environment.[14]

Table 4: Total metal content (dry Mass basis) in sewage sludge samples and comparisons with sludge legal standard

Metal	Min-Max conc. In Sludge samples (mg/kg)	U.S.EPA CRF 503.13 (mg/kg)	EU commission (mg/kg)
Zn	555 -1026	2800	1500
Cu	256 - 802	1500	600
Cr	125 - 510	3000	Not available
Ni	170 - 385	420	100
Pb	100 - 215	300	200

The total heavy metals concentration values are excellent criteria to define the extent of metals contamination in the sludge when this is the final destination of the

sludge. But to forecast the ecological impact, the total content is of little value, since it has been observed that plant metal concentrations are not only correlated with soil total metal content.[15] Besides the determination of the total metals concentration, a deep investigation of the metals speciation in the sludge, emphasizing the mobility capacity of these metals should be done.[16]

Sequential extraction using Tessier's procedure

Figure 1 shows the extraction percentage of metals obtained with sequential extraction using Tessier's scheme. Zn is shown to be mainly bound to Fe/Mn oxides about 42%, Cu and Cr is mainly bound to organic matter (71% and 53% respectively), while Ni is present in all the fractions especially bound to Fe/Mn (about 33%), Pb is almost 66% in the residual portion.

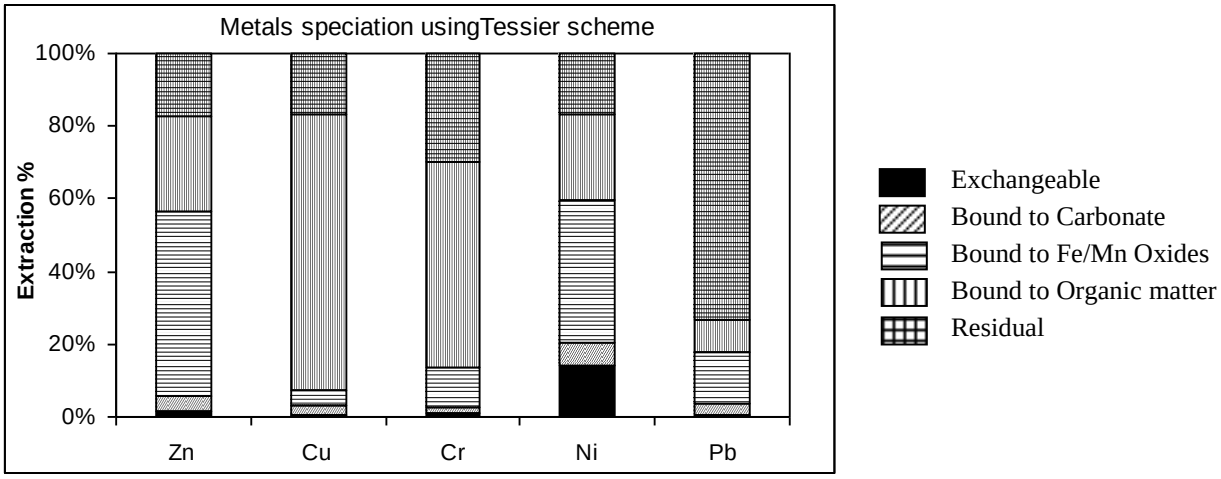

Fig. 1: extraction percentage of metals obtained with sequential Extraction using Tessier's scheme

Sequential extraction using BCR procedure

Figure 2 shows the extraction percentage of metals obtained with sequential extraction using BCR scheme. Zn showed the greatest degree of mobility as seen from the high proportion of metal extracted in the "exchangeable" and "reducible" fractions, Cu mainly associated to organic matter (about 61%). The sum of the last two fractions accounted more than 95% of the total Cu, while Cr was principally distributed between the third and the fourth fractions as mentioned in the literature.[17-18] Ni was extracted in large quantities during the first extraction step. This metal was distributed in the four fractions, the sum of the first two fractions being about 46% of

the total metal concentration. Pb was distributed between the third and fourth fractions about (22% and 52% respectively).

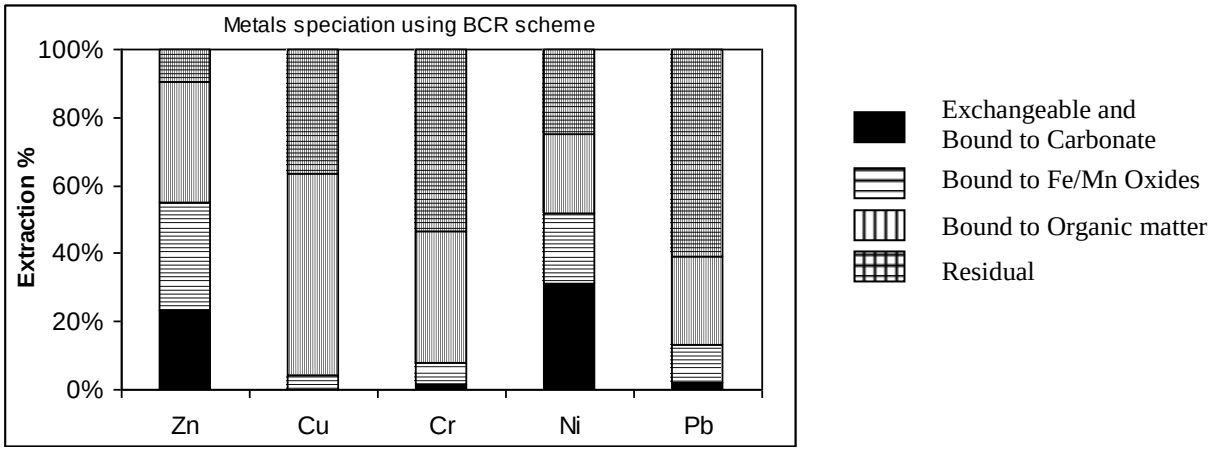

Fig. 2: extraction percentage of metals obtained with sequential extraction using BCR scheme

A comparison between Tessier's and BCR procedures showed a good correlation between the metal extracted in the corresponding steps of both procedures. However, there are some differences between Zn extracted by Tessier in exchangeable and bound to carbonate fraction was lower than that extracted by BCR procedure. For Cu and Cr The Tessier's method extracts higher concentrations in the organic fraction in contrast to the BCR which extracts greater concentrations from the Fe-Mn oxide fraction.

The accuracy of determination of heavy metals after microwave digestion was checked by analyses of standard materials. The mean values of three parallel heavy metal determinations are plotted with time as X-bar quality control charts Fig 3. From analysis of these charts it can be seen that in a time span of one year the measurement process was stable and the heavy metal concentrations were accurately determined. Comparing the total metal content measured by ICP-OES after microwave digestion to that extracted by both Tessier's and BCR Methods the recoveries obtained ranged from 84 to 94.13% for Tessier's and from 86 to 95.5% for BCR method. The relative standard deviation "R.S.D." was found to be better than 3% for all heavy metals determined in the present work. For the partitioning of heavy metals the R.S.D. of parallel three determinations in each particular step was found to be better than 5% for all studied heavy metals.

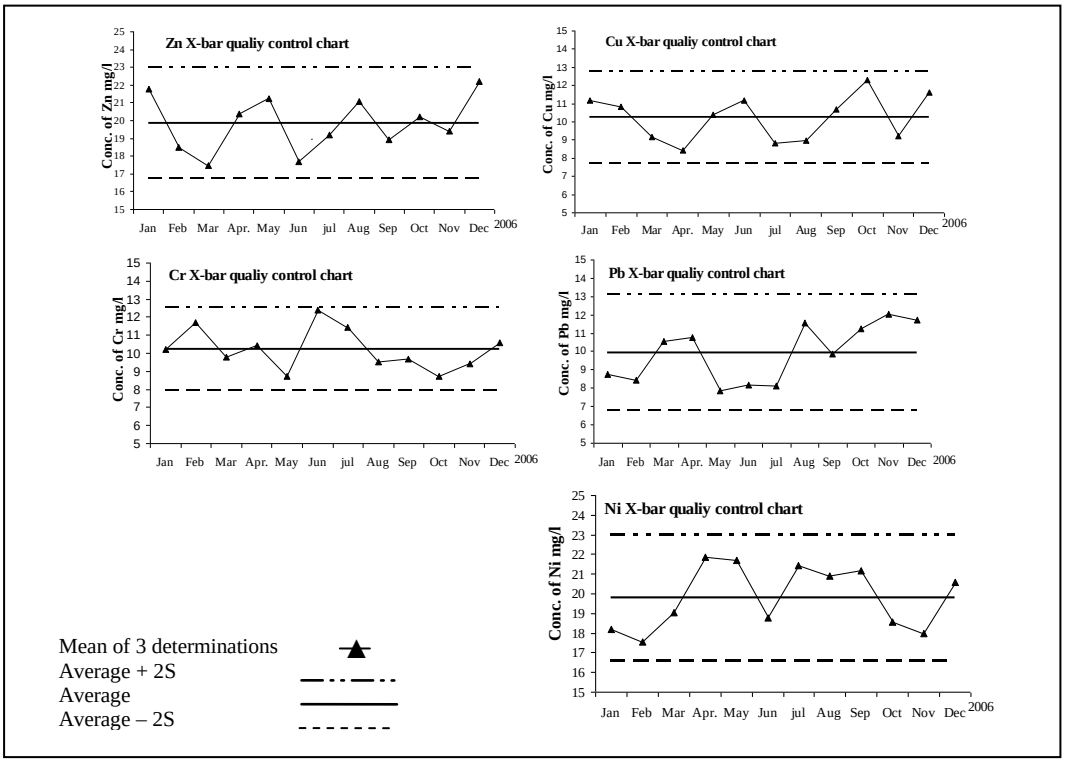

Fig. 3, X-Bar Quality control chart for heavy metals analysis by ICP-OES

It is evident from the data of Fig. 1 and Fig.2 that the fractions of heavy metals extractable in water-soluble, exchangeable and carbonate-bound fractions are very low for Cu, Cr and Pb (0.27-3.15%)., and higher for Zn and Ni (22.3% and 28.5%, respectively) Taking into consideration the high mobility and potential bioavailability of heavy metals in this fraction and their total concentrations, it can be concluded that sewage sludge cannot be used in agriculture due to the potentially hazardous effects of Ni on the terrestrial environment. Namely, the concentration of 385 mg/kg Ni in this fraction alone is much than that allowed for total metal concentrations by the legislation of EU Commission for sludge to be used in agriculture (Table 4). The portions of other heavy metals bound to iron and manganese oxides and hydroxides fraction were below 15% and ranged from 13.8% for Cu, 10.23% for Cr and 13.2% for Pb. Cu was mostly released in the moderately soluble fraction (heavy metals bound to organic matter and sulphides) where their proportions are more than 55% which indicated that Cu was associated with strong organic ligands due to its affinity to form stable complexes. Pb and Cr were found in high proportions in the most sparingly soluble fraction (residue fraction) more than 50 and 30% respectively.

Conclusions

Sequential extraction schemes can provide a valuable tool to distinguish among trace metal fractions of different solubility. These fractions are empirically related to mobility classes in different solid samples. The speciation of metals governs their availability to plants and their potential to contaminate the environment. A comparison with the Tessier's sequential extraction procedure and BCR procedure showed a good correlation between the metals extracted in the corresponding steps.

The results of this study indicated high Ni and Zn mobility in the sludge and hence their potential bioavailability. The mobility is low for Pb, Cr, and Cu. More than half of the amount of Pb was found in the most sparingly soluble fraction. From the results of the total metal concentrations and partitioning analysis it can be concluded that this sewage sludge cannot be used in agriculture primarily due to its high total Ni concentration and its high mobility. For environmentally safe disposal of sewage sludge, immobilization strategies for heavy metals in the sewage sludge will be investigated in further work.

References

1. S. Dudka, W. Miller, J. Environ.; Sci. Health **B 34**, 681–708 (1999).
2. J. Hsu, S. Lo. Environ. Pollut.; **114**, 119–127 (2001).
3. G. Petruzzelli, L. Ottaviani, E. Veschetti. Agrochimica; **38**, 277–284 (1994).
4. A. Tessier, P. Campbell, M. Bisson,. Anal. Chem., **51**, 844–851(1979).
5. A. Ure, P. Quevauviller, H, Muntau, B. Griepink,. Int. J.Environ. Anal. Chem., **51**, 135–151 (1993).
6. P. Quevauviller, G. Rauret, J. Lopez-Sanchez, R, Rubio, A. Ure, H. Muntau; The Science of the Total Environment, **205**, 223-234 (1997).
7. G. Rauret, J. Lopez-Sanchez, A. Sahuquillo, R. Rubio, C. Davidson, A. Ure, P. Quevauviller; J. Environ. Monit., **1**, 57-61 (1999).
8. M. Soumare, F. Tack, M. Verloo, Waste Manage., **23**, 517–522 (2003).
9. L. Mercedes, A. Fuentes, S. Jose, S. Antonio, Chemosphere., **54**, 1039-1047 (2004).
10. T. Hernandez, J. Moreno, F. Costa, Soil Sci. Nutr.; **37** (2), 201–210 (1991).
11. U.S. EPA's Wastewater Regulations Use or Disposal of Sewage Sludge: Land Application (US-EPA-40 CFR 503.13). (2000)

12. European Directive 86/278/CEE Official Journal of European Comity (JOCE) L181/04.07 (1986).
13. P. Van Herck. and C. Vandecasteele; Waste Management, **21**: 685-694 (2001)
14. G. Solis, E. Alonso, P. Riesco; Water, Air, and Soil Pollution, **140**: 139-156. (2002)
15. S. Gupta, I. Mehrotra. O. Singh; Environmental Technology, **11**: 229-238 (1990).
16. M. Marchioretto, H. Bruning, N. Loan, W. Rulkens; Water Science and Technology, **46**(10): 1-8. (2002)
17. S. Dudka, A. Chlopecka; Water Air Soil Pollut.**, 51**, 153–160 (1990).
18. R. Thomas, C. Davidson, S. McVery; Anal. Chim. Acta, **291**, 277– 286 (1994).