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Application of XRF, AAS and BCR-Sequential Extraction Procedure for Characterization and Assessment of Metals in Sewage Sludges from Two Treatment Plants in Jordan

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Abstract

This study was performed to characterize and determine the heavy metal contents in sewage sludge from two different wastewater treatment plants in Jordan using three stage BCR(Community Bearue of reference) sequential extraction procedure. The extracts were analyzed for determining Cd, Co, Cr, Fe, Mn, Ni, Pb, and Zn using flame atomic absorption spectrometry. Microwave digestion procedure was used to investigate the total contents of heavy metals. The obtained results showed a good recovery percentage of the studied metals. The results from the partitioning study indicated that the oxidisable fraction was dominated for Cr, Cd, Fe, Pb and Zn while Mn is the greatest easily mobilized forms in acid exchangeable. X-ray fluorescence method was also used in this study in order to evaluate some of other elements such as V and Sc, which indicated an a relatively high concentration levels in both sludges.

Keywords: XRF; Toxic metals; Sewage sludge; Sequential extraction.

Introduction

Sewage sludge is the essential consequence of treating wastewater and contains most of the pollutants which otherwise would contaminate water courses and water supplies, therefore, the introduction of sewage treatment represents a major development in public health The accumulation of sludge is considered an environmental problem world wide, for example the accumulation of sludge in China is expected to exceed four million tons/day of dry matter [1,2]. A solutions for this problem is the using of sewage sludge on lands, especially on agricultural lands. Sewage sludge is high in organic content and plant nutrients particularly phosphorous and nitrogen; therefore it is a good fertilizer. The availability of nitrogen is more dependent on sludge treatment, while the untreated liquid sludge and dewatered treated sludge are releasing nitrogen slowly which reflect more benefits to crops than being released over a relatively long period[3,4]. Additionally, heavy metals such, Fe, Mn, Cu, and Ni in low level are important micronutrients for plants [5,6]. But, there is a concern of the presence of toxic heavy metals and other contaminants that may accumulate in soil, by sorption and precipitation [7-10]. Consequently land-based waste disposal must be carefully controlled because of potential hazards associated with application of wastes, include pathogens, toxic heavy metals and organic by-products, as reviewed by [11]. Therefore, information is needed to provide data on the quality of sludge used for agriculture practices.

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The accurate determination of heavy metals in sewage sludge goes on to be of a large value in environmental monitoring, not only because of their total amount, but more critically their offered forms in environment will decide their toxicity, mobility and bioavailability [12], thus, different simple and sequential extraction methods have been widely applied to differentiate the chemical forms in which trace metals are present in soils, sediments and sledges [13,14], In this study a three stage sequential extraction procedure suggested by the Community Bureau of References (BCR) had been used for the determination of Fe, Cu, Pb, Mn, Zn, Cd, Cr and Ni. The used procedure improved the comparability between results, and had been widely used by others [15,16].

The aim of this study was to evaluate the content of heavy metals and their concentrations from the different steps of BCR (Community Bearue of reference) sequential extraction procedure in sewage sludge from two wastewater treatment plants in south and north Jordan. Mutah University MUWWTP) and in north Jordan Irbid city (IRWWTP).

Materials and Methods

Sludge samples and its preparation

All the sewage sledge samples were taken from the catchments areas of wastewater treatment plant in Irbid city and from wastewater treatment plant in Mutah University Karak, Jordan. The sampling was carried out periodically at summer season 2008. To insure that the collected samples were representative, each sewage sample was collected by taking subsamples from different points in sampling sites (about 3 kg sewage). Polypropylene shovels were used in collecting the samples subsequently then were transferred to a clean nylon bags, and finally were carried to the laboratory. The sludge samples were spread onto nylon sheet in the fumehood and allowed to dry at room temperature for about one week. Each mixed samples were grind with a clean mortar and pestle, then sieved to obtain a fraction of less than 200 μm. The resulting material was labeled and stored in polyethylene bottles in the Frigidaire at $5^{o}C$ until the time of analysis. For the determination of pseudo-total concentration of metals using X-ray fluorescence, 5 g of homogenized samples were used. Each sample was pressed into stable pellets with diameter of 30 mm using 50 ton press. Three replicate sewage sludge samples were prepared for each analysis.

Reagents

All used reagents used in the procedure were of analytical reagent grade. Double–distilled deionized water was used for preparing all needed solutions for the analysis of the standard solutions of heavy metals Fe, Mn, Pb, Ni, Zn, Co, Cd and Cr. They were prepared by dilution of 1000 ppm certified standard solutions (Buchs, Switzerland) of corresponding metal ions .The certified reference material Soil-7 from the National Institute of Standards and Technology (NIST), was used to asses the accuracy of the procedure. All glassware and plastic materials were rinsed with deionized water. The 50 ml washed polyethylene centrifuge tubes were used for extraction, while 50 ml polyethylene vessels were used for storage of extractants.

Instrumentation

Atomic absorption flame emission spectrophotometer (model AA-6200 Shimadzu) with an air-acetylene flame was used for the determination of metal contents in each step of sequential extraction and for pseudo-total. Hollow cathode lamps with resonance lines at 228.8, 240.7, 357.9, 248.3, 279.6, 232.0, 283.3 and 213.9 nm were used as radiation source for determination of Cd, Co, Cr, Fe, Mn, Ni, Pb, and Zn, respectively. Lamp intensity and band pass were used according to the manual instruction recommendations. For the evaluation of other heavy metal contents such Sc, As, Ca, K,V and Si , X-ray fluorescence (XRF) type EDX 800 HS, 230 VCE spectrometer was used. All measurements were carried out under the vacuum conditions while the Rh tube was equipped with a liquid-nitrogen-cooled detector. In order to maximize the XRF sensitivities for wide range of elements in interests, different combinations of XRF parameters (voltage, current and X-ray filters were employed for different elements. In general the applied voltage was increased in general with the required Kα or K_β or Lα line energies. The current was adjusted to maintain similar portions of detection time. The X-ray filters were used for particular line energies to reduce the relevant background signals. Standard reference material (IAEA SL-1) was run in order to assign the accuracy of the method. Microwave laboratory station Milestone Terminal 240 was used for the digestion of sludge samples for pseudo-total determination of heavy metal contents.

The BC R Sequential Extraction Procedure

Exchangeable metals

Forty milliliters of 0.11 M acetic acid were added to 1.00 g of dry sludge sample in a 50-ml polypropylene tube. The mixture was shaken for 16 hr at 25 °C at 400 rpm. The extract was separated from the solid phase by centrifuging at 3800 rpm for 20 min. the supernatant liquid was decanted into a 100-ml beaker and then covered with a watch glass. The residue was washed by adding 20 ml of double–distilled water, shacked for 15 min, and then centrifuged. The second supernatant liquid was discarded without any loss of residue.

Metals bound to iron and manganese oxides

Metals bound to iron and manganese oxides were extracted by adding 40 ml of 0.1 M hydroxyl ammonium chloride (adjusted to pH 2 with 2 M nitric acid) onto the residue from the first step. After shaking the mixture for 16 h at 22 ± 3°C, it was centrifuged for 15 min, and then decanted in to a beaker. Using 20 ml of distilled water, the residue was washed, centrifuged, and the supernatant discarded.

Metals bound to organic matter and sulphides

Ten milliliters of 8.8 M hydrogen peroxide were carefully added in small aliquots to the residue in the centrifuge tube. The tube ingredients were digested at room temperature for 1 hr with occasional manual shaking. The procedure was continued for 1 hr at 85 °C and the volume reduced to a few milliliters by further heating in a water bath. A second aliquot of 10 mL of hydrogen peroxide was added to the residue and the digestion procedure was repeated. The solution was heated to near dryness, and 50 mL of 1.0 M ammonium acetate solution (adjusted to pH 2 with nitric acid) were added to the moist residue. The sample solution was shaken and centrifuge, and the extract was separated.

Residual

The analysis of the residue was performed using aqua regia for metals insoluble in the previous steps .For this purpose, first 6mL of double-distilled water and then aqua regia solution in a sequence of 15 and 10 mL were added to the remaining residue and heated until near dryness. Then the extract then was filtered through filter paper by adding 5% HNO_3 solution, and suitable doubled distilled H_2O was added up to the mark.

The determinations of Cr, Cd, Mn, Fe, Ni, Pb, Zn and Co in the extracts were performed by FAAS.

Physicochemical characterization of sludge

Replicate samples of each studied sludge samples were analyzed for physicochemical parameters pH, conductivity, Moisture content, Organic matter content, Total Kjeldahl Nitrogen (TKN). pH and conductivity values of each characterized sample were determined using a ratio of wastewater sludge to ultra pure water [17]. The organic matter content was obtained by ashing each studied sample in muffle furnace at 550 ^{o}C for 6 hours and repeated until constant weight [18]. The total nitrogen content was determined by the Kjeldahl method [19]. The content of various elements such as: Ca, Sc, As, Ba, Na, and V was obtained by XRF method; results are shown in table 1.

Table 1: Physicochemical characteristics of the sludges

Parameter	**IRWWTP, Mean±S.D**	**MUWWTP, Mean±S.D**
pH	7.4 ±0.1	6.5±0.1
Conductivity (mS/cm)	2.16±0.03	3.11±0.06
Dry matter %	85.1 ± 0.8	87.8 ± 0.7
Organic matter (%)	28.78±0.61	23.05 ±1.06
Total N (%)	2.01 ±0.15	5.23±1.09
Ca $mg.kg^{-1}$	23379 ±4241	13775 ± 2319
K $mg.kg^{-1}$	282 ± 48	1097±291
Ba $mg.kg^{-1}$	3241 ± 105	3193 ± 112
Silica $mg.kg^{-1}$	N.D	656±54
Sc $mg.kg^{-1}$	5495 ± 60	2383± 45
V $mg.kg^{-1}$	247± 23	175±28
As $mg.kg^{-1}$	12.5±3.7	232±62

Digestion method for pseudototal metal contents

The microwave technique was applied to the dissolution of total heavy metals from different matrixes within very low time period as compared to conventional methods [20]. In this work, the pseudo-total metal contents of the sludge samples were determined using a microwave-assisted acid digestion with aqua regia: 65% high pure HNO_3 (2 ml), 6 ml of 37% HCl and 1 ml of HF acid were added to 0.2 g of powdered sample in 25 ml Teflon vial. The mixture was left to stand for 5 hr at room temperature. Then it was heated in a microwave oven following a one-stage digestion program: (250 W, 25 min). After cooling, sample digests were filtered through a Whatman 42 filter paper in a 25 ml Teflon vial and double distilled H_2O was added to the mark. The accuracy of the procedure for total metal determinations was checked using the Soil-7 standard reference material under the same conditions. Analysis of these reference materials in three replicates showed satisfactory accuracy, with the recoveries for all metals in soil-7 between 91.2% and 104.9%.

Results and Discussion

Sludge characteristics

The different physical and chemical parameters during the characterization of the studied sludges are shown in table 1. The values of pH are 7.4 for IRWWTP and 6.5 for MUWWTP. At low pH, the leaching of heavy metals and their mobility increases; this can be noticed from the increase in the total heavy metals of Mutah sludge comparing with Irbid sludge. The organic matter is an important component because it tends to either form soluble or insoluble material with the heavy metals, as a result it can be migrate or retained in the soil [21]. Table 1 shows a high percentage of total nitrogen (2.01%-5.63%) and organic matters (28.78%-23.05%), these amounts highlight the benefits of using the sludges as agricultural fertilizer. As regards to the composition of Ca, K, Na, Ba, Sc, V and As, it was found that Ca is the most abundant, followed by Sc, Ba, K, Na, V and As.

Total metal content

Total content of Cr, Cd, Mn, Fe, Ni, Pb, Zn, and Co in IRWWTP and MUWWTP sludges are represented in table 2. All data are expressed as mean values in $mg.kg^{-1}$ of three determinations. The use of sewage sludges from treatment plants as fertilizers depends on their heavy metal contents; high level of sludge-borne metals might cause adverse effects on soil, organism, and plants on nitrogen fixation [22,23]. By the comparison of the allowable concentrations of various metals in sewage sludge in different countries (Table 3), United States has the most wide range for metals among developed countries at pH>6. From data in table 3, there is no general agreement concerning the maximum allowable concentrations of various metals in sewage sludge, each country has its own rules in consideration of the permeable levels of heavy metals amended to soil for agricultural use. According to table 2 most metal concentration for Cd, Cr, Ni and Pb, and Zn in the two sludges were within the permitted levels for agricultural use (Table 3). These findings are also confirmed in other world wide sludges analysis [24]. The level of Zn in IRWWTP and MUWWTP were higher than the American standard. However the total contents of other heavy metals found in Mutah University sludge were higher than in Irbid city sludge, despite that the later is a large city comparing with the former. This can be explained by the nature of the discharged effluent into sewers. In Irbid city, the sewerage system with mainly domestic discharges, but in Mutah University the sewerage system discharged from different department sources such as: laboratories of chemistry, biological, engineering, medical center and military wing at the university. Co, Ni and Fe of both sludges were rather immobile. One important notification is that, the concentrations of scandium in both sludges were presented in a large level; 5495 mg.kg^{-1}for Irbid sludge and 2383 mg.kg^{-1} for Mutah, these findings can be attributed to the ground water in Jordan [25]**.** The high level of Sc focused our attention for the need of a further study of the possible sources of Sc element. The presence of such toxic elements could cause phytotoxicity [24].

Table 2: Total, heavy metal content of each sludge in mg.kg^{-1}

Element	IWWTP, Mean±S.D.	MUWWTP, Mean±S.D.
Cr	12.41±0.43	82.4±11.7
Cd	ND*	1.44±0.03
Mn	130.5±7.5	394.5± 35.7
Fe	7465±37	17207±67
Ni	67.5±5.3	77.12± 21.2
Pb	56.00±2.18	104.2±26.6
Zn	1956.3±108.	4878.4±710.8
Co	309.3±15. 7	758.7±20.8

N.D.-not detected

Table 3: Allowable concentration in ppm of various metals in sewage sludge in someCountries

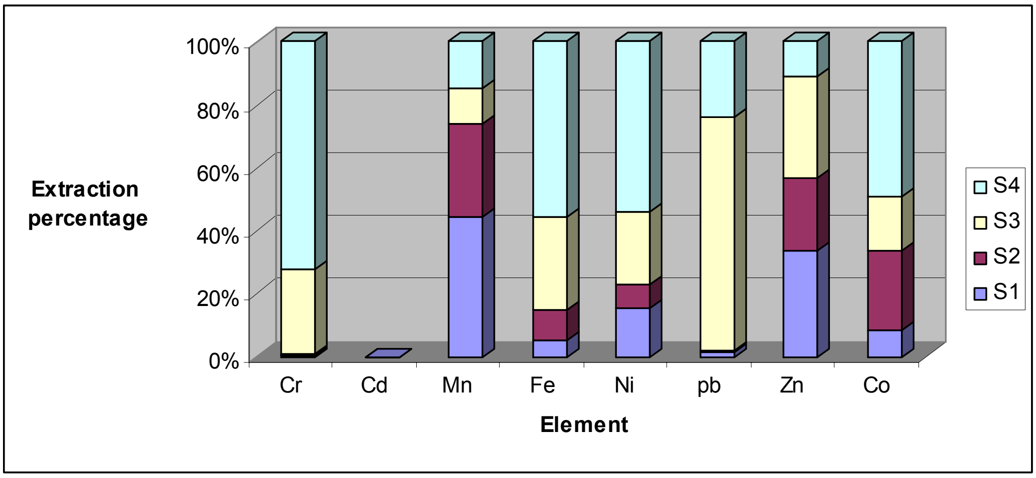
Country	Elements						Reference
	Cd	Cu	Cr	Ni	Pb	Zn	
European Community	1-3	50-140	100-150	30-75	50-300	150-300	30
Germany	1.5	60	100	50	100	200	31
United Kingdom	3	135	400	75	300	1200	32
United States	20	750	1500	210	150	1400	33

Application of BCR scheme

Using BCR sequential extraction method allows us to predict the mobility of heavy metals in the sample. The results of application the BCR sequential extraction to the studied samples are shown in table 4. As reported by Fuentes et al. [26]. Cr has low mobility. From figures 1 and 2 the concentrations of chromium that was found confirm the above reported results from others [26]. The high concentration was mainly found in the fourth step (residual) and third step (oxidisable). Chromium is more likely to be found in the organic fraction or considered as insoluble sulfide, this also was confirmed by Fuentes et al. [26].The large amount of Co in both locations was mainly extracted from the forth and second steps. About 56% of the total Co content is associated with the residual fraction and 20% is associated with the reducible fraction. In the oxidisable fraction it is probably present as CoS see step 3 in figures 1 and 2, while iron was mainly associated with fourth step (residual), because it is immobile and this was confirmed by Fuentes et al., Zufiaurre et al and Staelens et al. [7,26, 27]. The high fraction of Mn and Zn, were extracted mainly from the first, second and third steps. The sum of their percentages were ranged 78-79% and 83-95% for Mn and Zn respectively, these findings were confirmed by both Wong et al. and Scancar et al [24,28]. The extractable contents of Ni and Pb contents of studied sludges were presents at high percentages in oxidisable and residual fractions, reflecting that Ni and Pb were more mobile in the sewage sludge samples. With regard to Pb, both studied sludge samples have a similar distribution pattern. As shown from figures 1 and 2, most of the Pb is present in the oxidisable fraction, followed by the residual fraction. These findings showed that organic matter is important scavengers of Pb in sewage sludge. Of the elements studied Cd at highest relative level in the oxidisable fraction (48% and 55% for samples in MUWWTP this is due to the content of organic matter presents in the sludges. In contrast a relative amount of Cd was present in the acid-soluble fraction (from 10% to 14%). These results are in agreement consistent with the reported values [29]. In IRWWTP the Cd was not detected.

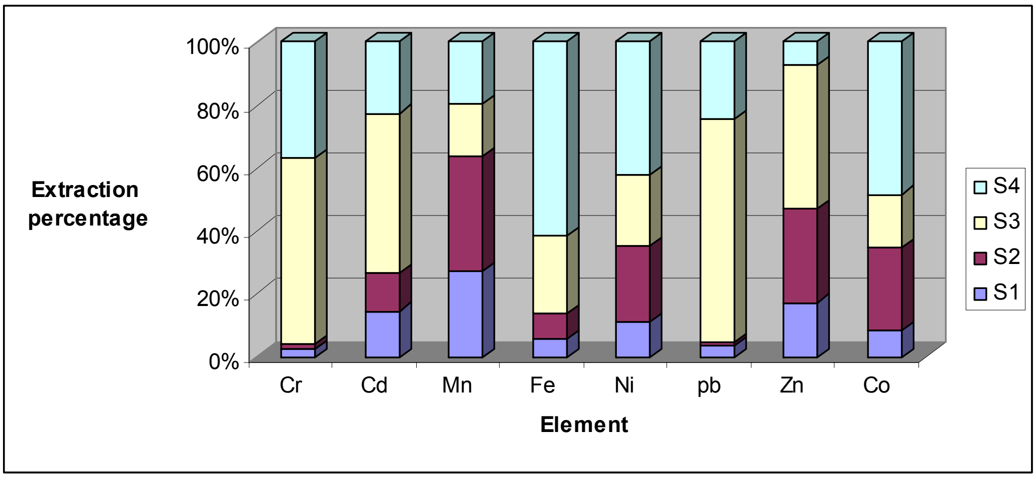
Table 4: Concentrations of heavy metals from the different steps of BCR scheme

Metal	**Step 1**	**Step 2**	**Step 3**	Step 4	**Sum**	**%Recovered**
IWWTP						
Cr	0.03±0.01	0.06±0.03	3.05±0.05	8.12±0.47	11.26	90.7
Cd	ND	-	-	-	-	-
Mn	57.67±1.03	38.44±2.04	14.38±1.61	19.22±0.92	129.71	96.5
Fe	352.92±69.32	678.16±123.65	2048.32±148.72	3840.6±219.46	6920	92.7
Ni	10.09±0.41	5.01±0.07	15.10±0.61	31.22±5.03	61.42	91.0
Pb	0.92±0.04	0.25± 0.03	42.55±1.72	13.80±0.91	57.52	102.7
Zn	592.24±57.03	405.40±21.12	564.04±43.02	197.41±7.14	1759.01	89.9
Co	25.03±0.98	74.80±7.32	49.77±5.37	145.78±36.22	295.38	95.5
MUWWTP						
Cr	2.11±0.26	1.27±0.24	41.43±6.70	28.32±2.43	77.13	88.9
Cd	0.20±0.05	0.16±0.03	0.69±0.11	0.31±0.02	1.36	94.4
Mn	104.71±9.05	139.62±21.03	64.82±7.01	74.80±10.03	384	97.3
Fe	923.1±87.4	1376.4±111.0	3997.4± 179.5	10167.5±67.4	16464.5	95.7
Ni	7450±231	16.51±1.04	15.01±0.76	28.77±3.47	67.79	87.9
Pb	3.67±0.1 3	1.09±0.21	69.93±12.13	24.30±8.70	98.99	95.0
Zn	745.11±112.8	1290.94±187.0	1974.53±243.7	320.57±17.0	4331.1	88.8
Co	64.62±9.20	198.72±34.23	129.16±29.08	367.72±54.11	760.22	100.2



S1: Exchangeable; S2: Reducible; S3: Oxidisable; S4: Residual

Figure 1: Percentage of determined in each step of the sequential extraction procedure applied for sewage sludge at IRWWTP



S1: Exchangeable S2: Reducible; S3: Oxidisable; S4: Residual

Figure 2: Percentage of determined in each step of the sequential extraction procedure applied for sewage sludge at MUWWTP.

Conclusion

The results of this study provide a comprehensive overview on the heavy metals content in both types of sludge. They results showed high concentrations of various toxic metals particularly Sc, which needs further investigation to determine its source.

Based on the data obtained from the analyzed total metal contents with microwave digestion technique and using three steps BCR sequential extraction procedure, it can be concluded that the digestion with microwave technique can be useful in determination of total metal contents.

The results obtained from fractionation indicate that Pb in both types of sludge were most abundant in the organic phase, while Co most abundant in residual fraction. Comparing the results of the two types of sludge, MUWWTP showed higher concentration of toxic metals which is due to the use of different educational laboratories.

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