Assessment of metals speciation in sewage sludge and stabilized sludge from different Wastewater Treatment Plants, Greater Cairo, Egypt

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ABSTRACT

The metals speciation in all sludge samples from the different Wastewater Treatment Plants (WWTPs) indicated that, Mn, Ni and Zn were most abundant in the exchangeable, carbonate and Fe/Mn-oxide forms which are the easily assimilable fractions and showed the greatest degree of their mobility, while Cd, Cu, Cr and Fe were major in the organic and sulfide (exhibit some degree of mobility), and the residual form (inert phase) which, corresponds to the part of the metals which cannot be mobilized.

Cement kiln dust significantly reduced the availability of metals by chemical modification of their chemical speciation into less available forms.

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1. Introduction

Based on the population studies and rates of water consumption, the total wastewater flows generated by all governorates in Egypt, assuming full coverage by wastewater facilities is estimated to be 3.5 billion m³/year. Approximately 1.6 billion m³/year receives treatment. By the year 2017, an additional capacity of treatment plants equivalent to 1.7 billion m³ is targeted [1].

Depending on the treatment technology and increased establishment of sewage treatment plants the amount of sewage sludge for the whole of Egypt can increase to 2 million tons dry solids/year by the year 2020 [2]. With improved control and treatment of connected industrial wastewater, this sludge can be utilized as a valuable fertilizer and soil conditioner. The sludge can also be used for energy production by collecting methane from sludge digestion, which in a secondary step can generate electricity [3].

In Greater Cairo, the sewerage systems serve both industrial and commercial activities, therefore, instances of high levels of toxic substances in wastewater have been reported and mainly accumulated in the sludge. Improper sludge disposal and/or reuse may lead to contamination of surface and ground water [4].

According to the Egyptian regulations (Decree No. 214/1997), levels of Zn, Cu, Ni, Cd, and Cr in sludge permitted to be re-used in agriculture are 2800, 1500, 42039 and 1200 mg/kg, respectively [3].

Sewage sludge has been utilized for agriculture for many years, which represents a good source of nutrients such as N and P for plant growth [5] and organic matter that can improve soil physical properties [6].

From an agricultural point of view, the factor of greatest concern is the high concentrations of heavy metals in sludge, since they are adsorbed and accumulated in soil [7,8].

It is widely recognized that the distribution, mobility and bioavailability of heavy metals in the environment depend not only on their total concentration but also on the association form in the solid phase to which they are bound [9].

During recent decades, a great variety of extraction schemes, both simple and sequential have been developed. Sequential extraction is recognized as the best available method for gaining information on the origin, manner of occurrence, bioavailability, mobilization and transport of heavy metals [10] and also, therefore, for sewage sludge [11–16].

The distribution of metals in sludge and their possible synergic and antagonist effects depend not only on the amount of these elements in sewage sludge but also on the stabilization process applied to the sludge [17].

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Sequential extraction scheme proposed by Tessier et al. [18], one of the most widely applied method, where, heavy metals are associated with the following fractions:

(a) the exchangeable fraction, which is likely to be affected by changes in water ionic composition (e.g., in estuarine waters), as well as sorption–desorption processes;
(b) the carbonate fraction, that is susceptible to changes in pH;
(c) the reducible fraction, that consists of iron and manganese oxides which thermodynamically are unstable under anoxic conditions;
(d) the organic fraction, that can be degraded leading to a release of soluble metals under oxidizing conditions;
(e) the residual fraction, that contains mainly primary and secondary minerals, which may hold metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature.

Recently, heavy metal removal from contaminated sludge for land application was reviewed. A comparative and critical analysis of the application of chemical extraction, bioleaching, electroreclamation, and supercritical fluid extraction (SFE), in removing heavy metals was presented. Acid treatment seemed to effectively remove Cd, attaining as much as 100% removal for some studies, as compared to bioleaching. SFE also gave higher removal efficiency than bioleaching. Cr, Pb and Ni seemed to be also effectively removed by the acid treatment. For the removal of Cu, Mn and Zn, the bioleaching process seemed to be appropriate. Electroreclamation technology is limited by its relatively higher energy consumption and limited application to sludge. The SFE method is limited by the complexity of the process and the cost of ligands suitable for effective metal extraction [19].

Recently, increased attention was paid to the sludge stabilization process aiming to minimize the mobility of heavy metals by using various additives, due to compliance to more stringent regulations issue in USA and European Union [20,21].

According to USEPA [22], stabilization refers to techniques that chemically reduce the hazardous potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms, while solidification refers to techniques that encapsulate the waste, forming a solid material, and does not necessarily involve a chemical interaction between the contaminants and the solidifying additives.

Sewage sludge can be solidified and stabilized in a matrix of Portland cement. Heavy metal compounds bound themselves strongly with ettringite during its formation and were permanently immobilized, therefore, the stabilized matrixes exhibited very high retention of heavy metals and very low leaching concentrations owing to ettringite formation [23].

Several types of interactions may occur simultaneously in the solidified systems. The waste component may react in one or more of the following ways: adsorption, chemisorption, precipitation, ion exchange, passivation, surface complexation, inclusions and chemical incorporation into the cement system [24].

The main objectives of this study are as follows:

1. To evaluate total heavy metal concentrations in the sludge from different Wastewater Treatment Plants.
2. To assess the chemical forms of heavy metals in sludge, in accordance with a sequential extraction method.
3. To evaluate the stabilization potential of heavy metals in contaminated sludge by using cement kiln dust.
4. The information can be used to assess the potential mobility of heavy metals, their bioavailability and related eco-toxicity and

provide evidence on the feasibility of sludge reuse for agronomic application.

2. Materials and methods

2.1. Sludge samples were collected from different WWTPs

1. Secondary Wastewater Treatment Plant of Helwan (A), its capacity is approximately $350,000 \, m^3/day$ which serves municipal industrialized south area of Cairo.
2. Secondary Wastewater Treatment Plant of El-Gabal El-Asfer (B), its capacity is approximately $1,500,000 \, m^3/day$ which serves municipal industrialized east of Cairo.
3. Secondary Wastewater Treatment Plant of 6th of October City (near Cairo) (C), its capacity is approximately $90,000 \, m^3/day$ which serves mainly industrial areas.
4. Secondary Wastewater Treatment Plant of El-Berka (D), its capacity is approximately $600,000 \, m^3/day$ which serves municipal industrialized area of north east Cairo.
5. Secondary Wastewater Treatment Plant of Balaqus (E), its capacity is approximately $600,000 \, m^3/day$ which serves municipal industrialized north of Cairo.

Conventional activated sludge treatment process is employed in all the Wastewater Treatment Plant (WWTP).

To avoid excessive chemical transformations within the sludge samples, which might be produced from prolonged storage, the experiments were initiated within the shortest possible time after obtaining the samples from the Wastewater Treatment Plants. Sludge samples are dried in an oven at 105 °C for 2 days. The dried sludge samples were passed through a 0.2 mm sieve, discarding the fraction >2 mm and eliminating stones, roots and fragments of plastic and metal. The final dried sludge samples were stored in plastic bottles at room temperature until analysis.

All chemicals used are of Analytical Reagent grade from Merck, Fluka or Aldrich Company. Freshly prepared daily-diluted solutions are prepared using deionized water and all glassware and plastic containers were washed with 15% nitric acid solution and rinsed thoroughly with deionized water.

2.2. Metals speciation in sludge

The metals speciation using sequential extraction scheme and procedure proposed by Tessier et al. [18] and modified by Elsokkary and Müller [25] was used to partition the heavy metals into the following five operational steps:

Fraction I (Exchangeable): One gram dry solid sludge sample was shaken for 1 h at room temperature with 8 ml of 1 M magnesium chloride-6 hydrate ($MgCl_2 \cdot 6H_2O$).
Fraction II (Bound to carbonates): The residual solid from exchangeable fraction of metals was shaken for 30 min at room temperature with 8 ml of 1 M sodium acetate anhydrous ($C_2H_3NaO_2$) and adjusted to pH 5.0 with acetic acid (99.83% $C_2H_4O_2$).
Fraction III (Bound to iron and manganese oxides: reducible): The residual solid from carbonate fraction of metals was shaken at 85 °C in water bath for 5 h with 20 ml of 0.04 M hydroxylamine hydrochloride ($H_3NO \cdot HCl$) in 25% acetic acid (99.83% $C_2H_4O_2$) (v/v).
Fraction IV (Bound to organic and sulfide): The residual solid from Fe/Mn-oxide fraction of metals was shaken at 85 °C in a water bath for 2 h with 5 ml of hydrogen peroxide (30% H_2O_2). Nitric acid (0.02 M HNO_3) was added to reach the pH of samples to 2 ± 0.2 pH units. Subsequently, a second addition of 3 ml of 30% H_2O_2 was

added and pH was monitored during the experiments and additional acid was added as required to maintain the pH of the samples within 2 ± 0.2 pH units and shaken again at 85 °C in a water bath for 3 h.

Fraction V (Residual): Finally, the residual solid from the organic and sulfide fraction of metals was digested with a mixture of HNO_3, HF, $HClO_4$, HCl in (4:1:1:1) ratio, respectively, for 3 h in a water-bath. The residue was dissolved and diluted with 50 ml distilled water.

In each operational fraction step the extractions were conducted in centrifuge tubes (50 ml with cap) to minimize losses of solid materials, and centrifuged at 2000 rpm for 30 min. The supernatant was filtered through Whatman No. 4 filter paper and the residue was washed, shaken with 8 ml of deionized water for 30 min and centrifuged, so it was ready for the next step and the washing was combined with the supernatant of each step [26,27]

- The concentrations of heavy metals in all operational fraction steps were determined after digestion according to Standard Methods, 1998 [28].
- The analyses of the sequential extractions procedure and total digestion samples were being replicated three times.
- The percentages of the metal fraction extracted were calculated in relation to the sum of metal fractions, in order to minimize errors and also to control the good reliability of the speciation procedure. The results showed a relatively good agreement within 10% between the sum of the metal fractions and the total analysis. This is in agreement with Han and Banin, 1997 and 1999 [29,30].

The percentage of metal fraction extracted for dry samples was calculated according to Jenkins et al., and Lo and Chen [31,32] and each percentage of extracted metals is expressed as a simple mean $\pm$ standard deviation of triplicate sludge samples in mg/kg of dry solid.

For the dry sludge samples the percentage of extracted metals was calculated referring to the weight of dry solid sludge samples:

$$\text{Percentage of extracted metals} = \left(\frac{V_f F}{DI} \right) \times 100$$

where D: 1 g dry solids sludge; V_f: final volume after dilution to 25 ml; F: concentration of metal in filtrate (mg/l); I: concentration of metal in initial dry solid sample (mg/kg).

2.3. Metal remediation in sludge using stabilization method

- Cement dust pass way which was obtained locally from a cement plant (National Cement Company).

The processing for remediation of heavy metals using stabilization method involved the following steps:

1. From the survey of our study, select the sludge samples which have high metal concentrations.
2. Sludge samples were dried in an oven at 105 °C for 24 h.
3. Furthermore, in order to normalize the variations in grain size distributions, the dried samples and the stabilized materials are grounded to fine particles in an agate mortar and sieved to obtain a fraction of less than 0.2 mm before the stabilization process.
4. Cement dust were mixed manually with the samples in a proportion of 0, 20, 40 and 50% (dry weight basis) by adding distilled water to facilitate curing using a bowl and a rubber spatula.

5. The mixed slurries were poured into plastic cylindrical molds. Air bubbles in the paste were removed by tapping the mold for about 1 min.
6. The cured samples were dried in an oven at 105 °C for 24 h, and then grounded to pass through a 0.2 mm sieve.

Sequential extraction procedure was used in order to further investigate the behavior of metal contaminants after stabilization process for sludge.

3. Results and discussion

3.1. Total heavy metals content

Total heavy metals content and pH of sludge from different Wastewater Treatment Plants of Helwan, 6th of October; Balaks; El-Berka; and El-Gabel El-Asfer (WWTPs) are shown in Table 1. The pH value of sewage sludges varies from 6.3 to 7.4. It can be seen that, the heavy metals content in the sludge samples were within the maximum permitted levels adopted by Egyptian regulations in Decree 214/1997 for sludge permitted to be re-used in agriculture except for zinc in 6th of October WWTPs. However, due to prolonged application of sludge to soil, heavy metals can accumulate in the soil and produce harmful effects on animals and vegetation through the food chain by means of biomagnifications [33]. Therefore, it is necessary to apply speciation techniques to obtain meaningful data on both availability and mobility.

Metal concentration ranges were as follows: Cd (2.3–3.9), Cu (184–1383), Cr (107–1120), Fe (7500–11,642), Mn (77–120), Ni (39–271) and Zn (350–3541).

Sludge composition is also determined by the kind of effluents discharged into sewers. Sewerage systems with industrial discharges will give rise to sludges differing markedly in composition with time depending on the industrial activities, weather and other factors. Heavy metal composition of sludges can be extremely variable [34].

Sommers [35] reported coefficients of variation for metals in sludges from eight U.S. cities to be: Cd, 27–160%; Zn, 26–58%; Cd/Zn ratios, 18–190%; Cu, 18–167%; Ni, 12–144% and Pb, 9–56%.

3.2. Application of sequential extraction scheme

A comprehensive characterization of metals in sewage sludge is important. Depending on their nature metals are associated in a variable manner with different phases making up the sludge. These forms in sludge are studied through sequential extraction which is recognized as the best available method for gaining information on the origin, manner of occurrence, bioavailability, mobilization and transport of heavy metals [10]. An appreciation of the effect of heavy metals in sludge on crops can only be attained from a precise knowledge of heavy metal speciation and the response of the plant to each species [34].

The partitioning pattern of heavy metals in the different sludge samples from the sequential extraction results are shown in Table 1 and Fig. 1. Generally, all the results obtained for metal fractionation (as mg/kg of metal extracted in each step and the percentage of each fraction) were calculated in base on the total amounts of metals determined in each sequential extraction scheme. The results are the mean of three independent determinations.

The percentages of metal concentrations for each extraction step in the sludge samples of Helwan (A), El-Gabel El-Asfer (B), 6th of October (C), El-Berka (D), and Balaqus (E) were represented in Fig. 1. It is clear that the dominant binding phase for cadmium

Table 1
Speciation of metals in sludges from different Wastewater Treatment Plants

WWTPs	Heavy metals	pH	Summed total (mg/kg)	Exchangeable (mg/kg)	Carbonate (mg/kg)	Mn/Fe-oxide (mg/kg)	Organic (mg/kg)	Residual (mg/kg)
Helwan (A)	Cd	6.8	3.02	–	–	1.42 ± 0.07	0.4 ± 0.0014	1.2 ± 0.1
	Cu		197.70	10 ± 1	3.7 ± 0.48	9 ± 1.1	159 ± 0.38	16 ± 0.19
	Cr		107.43	–	0.83 ± 0.18	20.5 ± 0.63	63.5 ± 2	22.6 ± 0.38
	Fe		9029	210 ± 12	76.2 ± 0.37	1724.4 ± 28.4	2168 ± 109.6	4850 ± 188
	Mn		99.28	34.9 ± 0.09	9.94 ± 0.39	26.2 ± 0.31	13.24 ± 0.43	15 ± 0.48
	Ni		39	9.47 ± 0.45	6.084	6.0 ± 0.12	9.3 ± 0.3	8.15 ± 0.47
	Zn		1770.34	229.6 ± 0.85	451.9 ± 10.3	844 ± 76.4	224 ± 12.8	20.84 ± 0.27
El-Gabel El-Asfar (B)	Cd	6.8	2.56	–	0.325 ± 0.08	1.05 ± 0.05	0.58 ± 0.14	0.6 ± 0.05
	Cu		311.23	3.6 ± 0.15	5.93 ± 1.3	13.7 ± 1.1	262.5 ± 2.8	25.5 ± 2.3
	Cr		1120.42	0.32 ± 0.15	14.8 ± 1.1	41.7 ± 3.3	843 ± 49	220.6 ± 5.2
	Fe		7980	114.4 ± 6	183 ± 23.9	210 ± 36.3	2963 ± 60	4510 ± 60.6
	Mn		120.17	29.4 ± 0.1	28.84 ± 0.6	38 ± 1.3	10.7 ± 0.4	13.23 ± 0.93
	Ni		55.80	17.81 ± 0.4	5.21 ± 0.05	8.075 ± 0.6	16.8 ± 0.6	7.9 ± 0.3
	Zn		515.40	20 ± 0.91	53.2 ± 5.3	217.6 ± 1.7	199.6 ± 5.2	25 ± 0.9
6 of October (C)	Cd	6.3	3.42	0.725 ± 0.025	0.24 ± 0.1	0.75 ± 0.03	0.72 ± 0.12	1 ± 0.18
	Cu		1391.42	59.95 ± 59.95	65.91 ± 2.9	43.89 ± 3.8	1107.67 ± 143	114 ± 10.7
	Cr		234.34	–	0.208 ± 0.09	57.98 ± 1.5	137.4 ± 1.2	38.75 ± 3
	Fe		10,779	38.8 ± 4	18.88 ± 0.53	1800.2 ± 55	3157.92 ± 358	5762.92 ± 339
	Mn		111.25	39.15 ± 0.99	13.36 ± 1.3	35.29 ± 1.3	10.2 ± 0.91	13.25 ± 0.3
	Ni		291.53	78.74 ± 2.8	37.83 ± 2.5	108.88 ± 1	48.51 ± 0.75	17.57 ± 0.94
	Zn		3237.52	821.44 ± 71	817.43 ± 20	1450.83 ± 45	788.75 ± 57	94.2 ± 4.9
El-Berka (D)	Cd	6.8	3.56	–	0.325 ± 0.15	1.77 ± 0.2	0.57 ± 0.07	0.85 ± 0.13
	Cu		200.20	6.84 ± 0.86	5.58 ± 0.45	8.23 ± 0.45	142.25 ± 22	37.3 ± 1.4
	Cr		192.04	–	0.908 ± 0.1	14.94 ± 0.98	149.67 ± 22	26.52 ± 3.2
	Fe		11,643	264.4 ± 38	51.21 ± 1.4	1291.87 ± 119	4071.25 ± 146	5964.17 ± 355
	Mn		137.57	35.625 ± 5.8	21.44 ± 2	45.775 ± 3.2	11.825 ± 0.46	22.9 ± 2.3
	Ni		56.30	18.67 ± 2.7	5.69 ± 1.3	9.7 ± 0.5	12.71 ± 1.2	9.53 ± 0.95
	Zn		1181.62	121.24 ± 5.7	100 ± 8	658.79 ± 65	250.75 ± 6.4	50.84 ± 6.8
Balaqus (E)	Cd	7.4	2.16	–	0.58 ± 0.18	0.517 ± 0.06	0.3083 ± 0.058	0.75 ± 0.058
	Cu		184.88	16.96 ± 2.5	7.85 ± 1.3	5.475 ± 1.2	132.29 ± 3.1	22.3 ± 1
	Cr		361.44	1.192 ± 0.48	2.092 ± 0.51	29.33 ± 4.8	296.3 ± 8.5	32.5 ± 3.3
	Fe		7147	551.58 ± 78	119.13 ± 16	1713.37 ± 76.6	1871.5 ± 75	2891.25 ± 460
	Mn		77.89	24.88 ± 0.17	16.89 ± 0.54	19.69 ± 1.3	5.35 ± 1.2	11.083 ± 1.6
	Ni		36.79	13.61 ± 1.1	6.24 ± 2	5.28 ± 0.66	6.56 ± 0.38	5.1 ± 0.3
	Zn		684.95	135.76 ± 4.4	130.94 ± 20.7	249.7 ± 18.5	137.91 ± 2.6	30.64 ± 1.8

was Fe/Mn-oxide fraction of the sequential extraction scheme in A, B and D, where the percentages for cadmium in the Fe/Mn-oxide fraction were 47.02, 41.1 and 49.76%, respectively. For (C) cadmium was almost equally distributed among the fractions of exchangeable (21.11%), Fe/Mn-oxide (21.83%), organic and sulfide (20.96%) and residual (29.11%). Fuentes et al., and Lombi et al. [15,36] have clearly demonstrated that the fraction of cadmium in sludges is distributed in the various chemical forms without showing a definite pattern.

The dominant binding phase of copper was organic and sulfide fraction in all sludge samples. The percentages of copper in organic and sulfide fraction were 80.42, 84.34, 79.61, 71.05 and 71.56% for A, B, C, D and E, respectively. This may be explained by the fact that the greatest extraction percentage in the organic and sulfide fraction can be attributed to the preference of copper for organic matter which is supported by the high stability constant of copper complexes with organic matter. Such fact is confirmed by several authors [14,17,37–40].

In the case of chromium, more than 80% of its compounds are distributed in the last two fractions, organic and sulfide, and residual fractions. Chromium is more likely to be found in the organic and sulfide fraction or considered as insoluble sulfide form compared with the residual fraction [15,39,41]. Furthermore, chromium did not exceed 1.33% in the first two fractions (exchangeable and carbonate fraction) in any sludge. This is an evidence for low mobility and availability of chromium as has been stated by Fuentes et al. [15].

Iron was mainly associated with residual fraction; which is confirmed by several authors [14,15,37]. This fraction, named "inert phase", corresponds to the part of the metal which cannot be mobilized consequently; its mobility and availability in the initial fractions are very low.

The high proportion of manganese species are in the first three fractions, the sum of their percentages were 71.55, 80.09, 78.9, 74.77 and 78.92% for A, B, C, D and E, respectively, a result that reflects the studies conducted by the findings of several authors [14,38,42].

Nickel is extracted in large quantities during the first three extraction steps. The percentage sum of exchangeable, carbonate and Fe/Mn-oxide fractions were 55.35, 55.73, 77.34, 60.5 and 68.3% for A, B, C, D and E, respectively. Our results substantiated by the finding of several authors [14,42–45].

Zinc is extracted mainly from the first three fractions, the sum of the first three fraction percentages of Zinc were 86.17, 56.43, 77.78, 74.49 and 75.4% for A, B, C, D and E, respectively, where Fe/Mn-oxide fraction has the highest percentage. This finding is also confirmed by many authors [14,37,39] who mentioned that the greatest part of zinc was mainly associated with the most mobile forms.

One of the limiting factors for land application of sewage sludge to soil is heavy metal content. Concern for heavy metals is due to its non-biodegradability, toxicity and consequent persistence. Reduction of heavy metals in sewage sludge can be achieved either by source control of industrial and domestic dis-
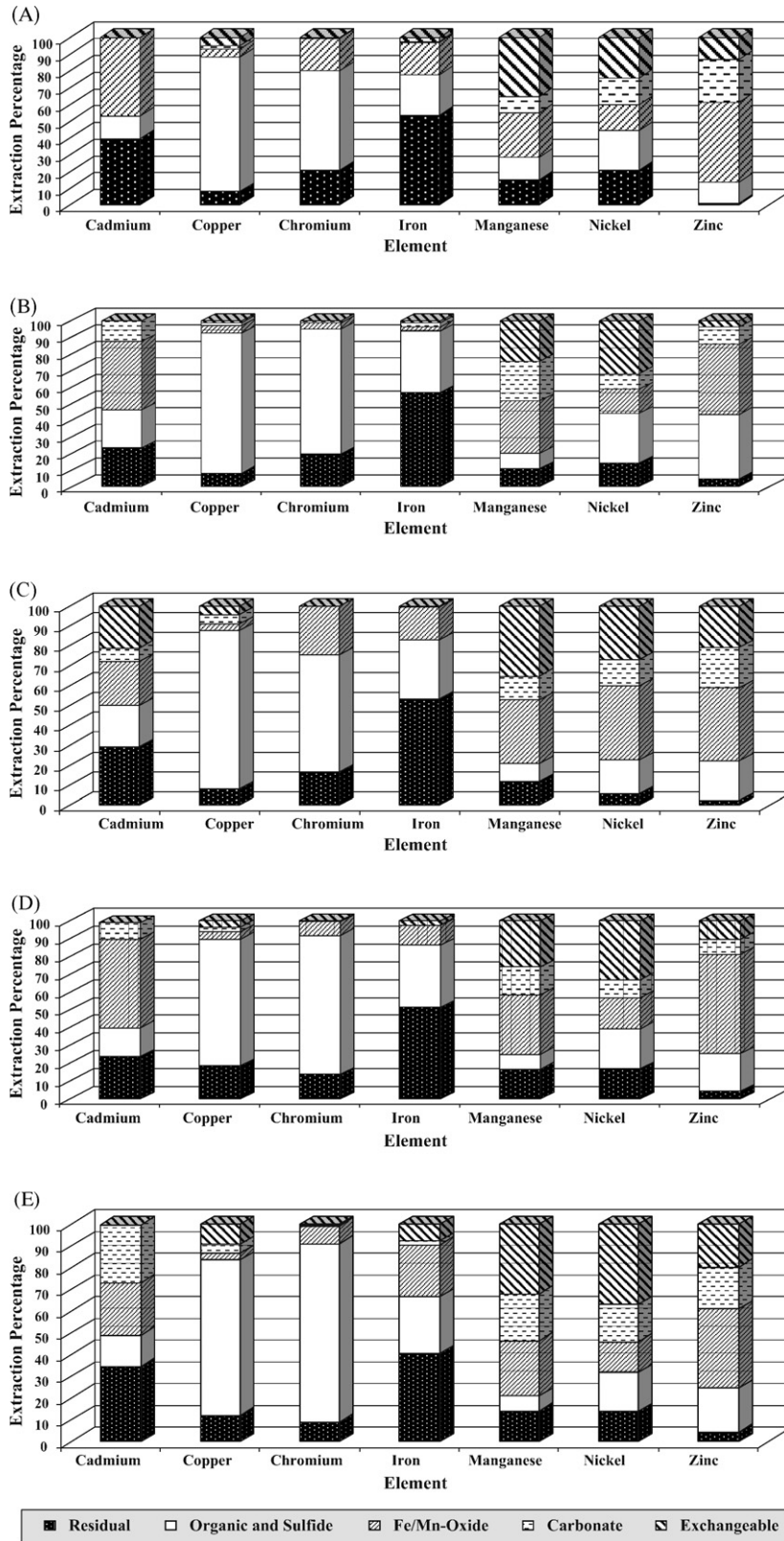
Fig. 1. Speciation of heavy metals in sludges from different Wastewater Treatment Plants.

charges to the sewer systems or by extractive removal of metals from the sludge. Source control includes control of the processes and materials used in production at the industries; removal and controlled disposal of hazardous constituents before they reach the waste stream; separation of highly contaminated industrial wastewater from the domestic wastewater; and pretreatment of the wastes before discharge to the municipal collection system [19].
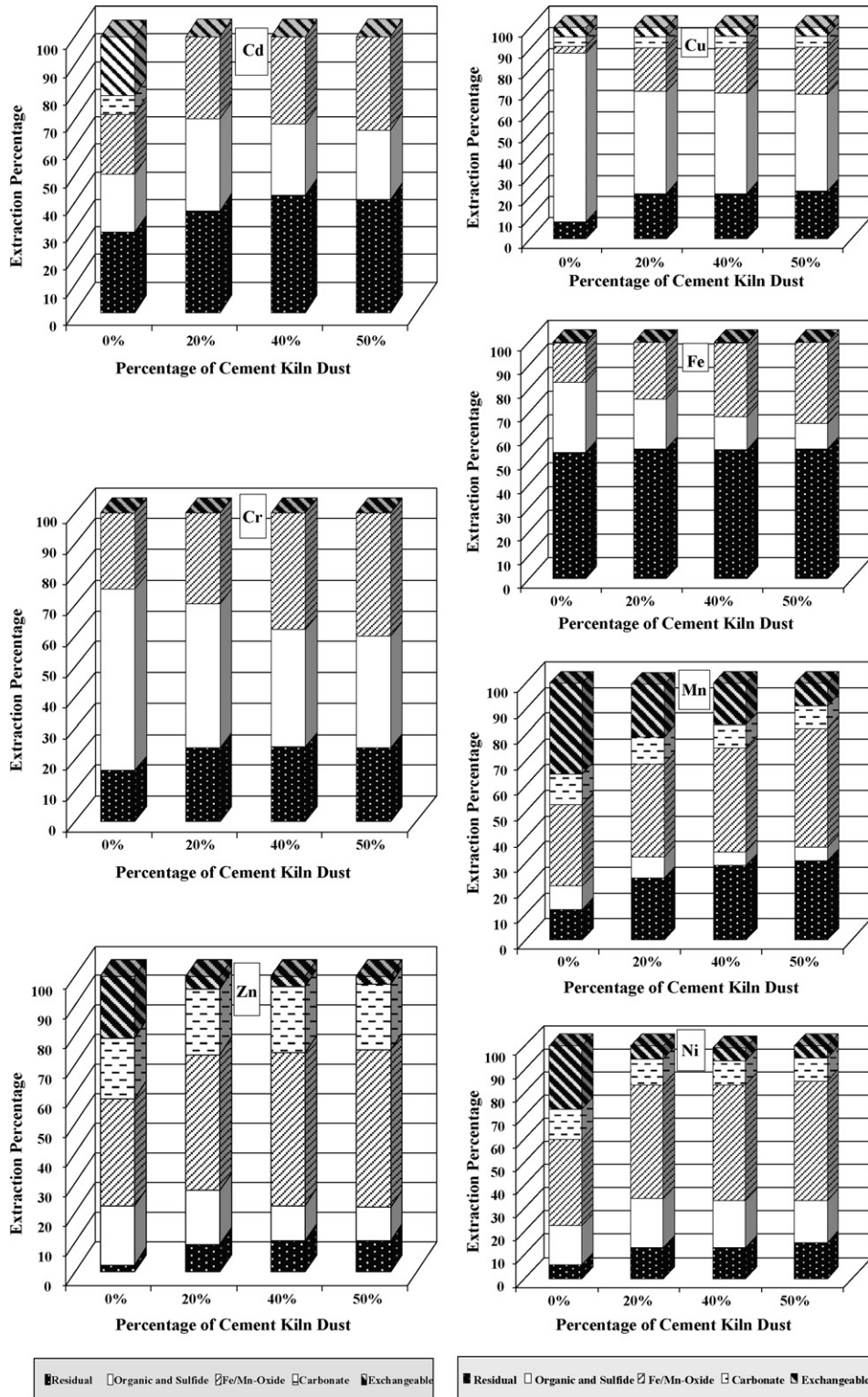
Fig. 2. Speciation of metals in stabilized sludges of 6th of October using different percentages of cement kiln dust.

Recently, the presence of heavy metals in municipal sludge from middle-south region of China was evaluated taking into consideration both the speciation of metals and local environmental characteristics. The sequential extraction results showed that Cu and Zn were principally distributed in the oxidizable fraction and the distribution of Cd showed no obvious characteristic [46].

Finally, on examining the results of metals speciation in all sludge samples from the different WWTPs we can conclude that, (i) Mn, Ni and Zn were the most abundant in the exchangeable, carbonate and Fe/Mn-oxide forms which are the easily assimilable fractions, (ii) Cd, Cu, Cr, and Fe were major in the organic and the sulfide, and, (iii) the residual form. This conclusion agrees to some extent with observations, which have been achieved by [14,15,39].
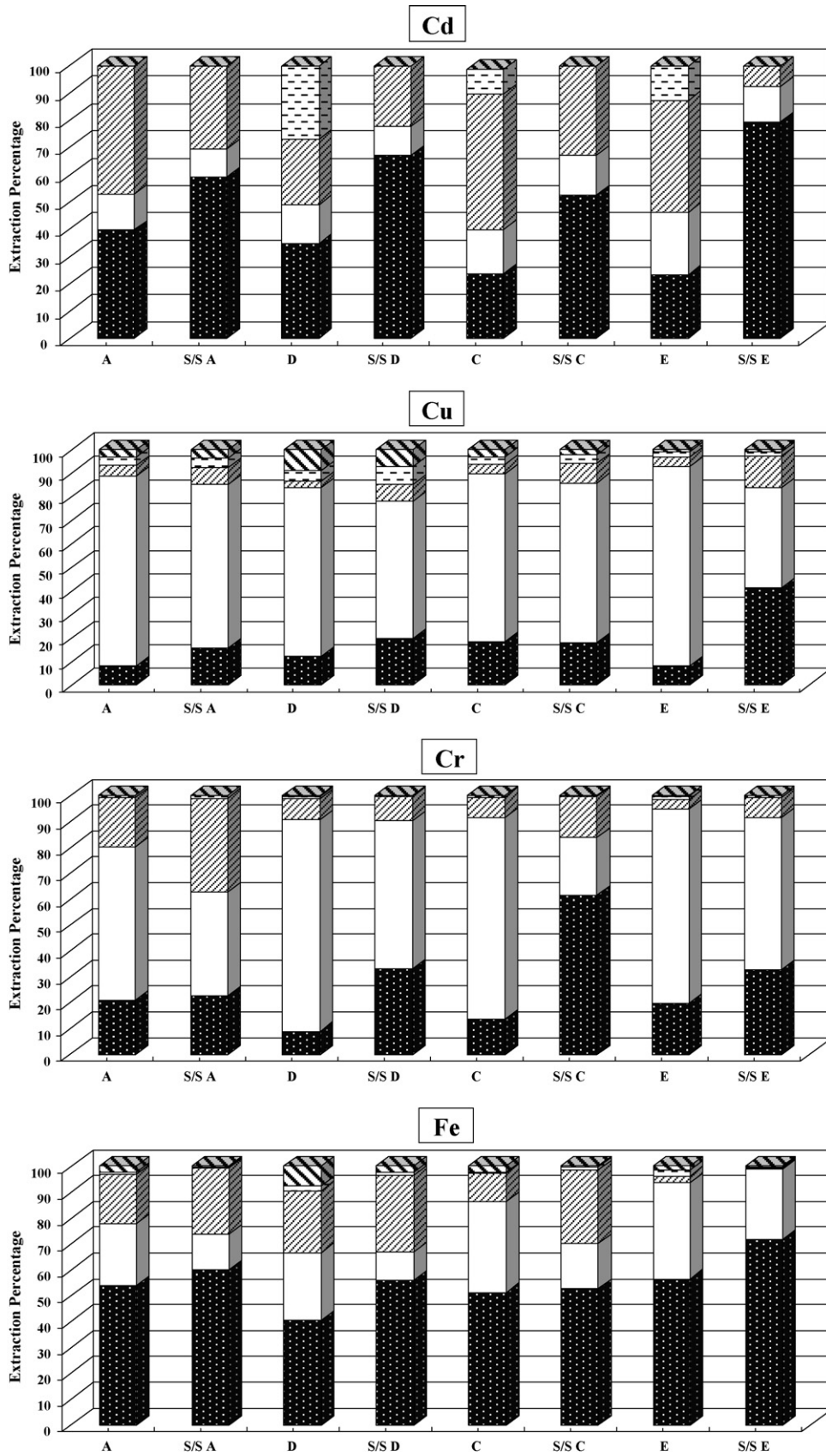
Fig. 3. Percentage of cadmium, copper, chromium and iron speciation in stabilized sludges from different Wastewater Treatment Plants using 50% of cement kiln dust.
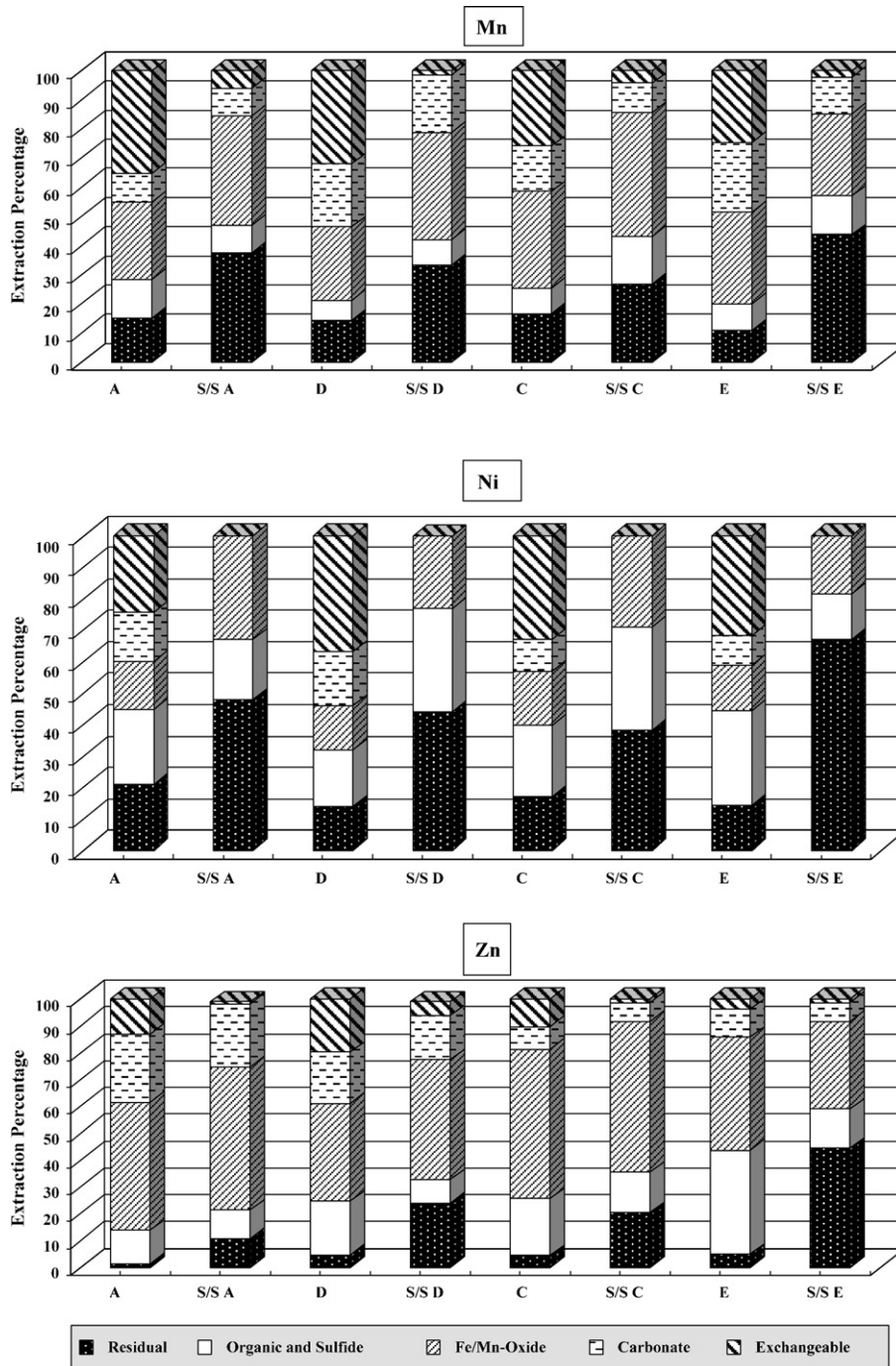
Fig. 4. Percentage of lead, manganese, nickel and zinc speciation in stabilized sludges from different Wastewater Treatment Plants using 50% of cement kiln dust.

3.3. Stabilization for metals in sludge

Immobilization refers to process of retaining substances absorbed or trapped within a sludge matrix. Stabilization refers to the technique that reduces the hazardous behavior of metals by means of chemical reaction [47,48].

Cement kiln dust was commonly used as sludge stabilizer, liming agent, and materials additive, where its absorptive capacity and its alkaline properties can reduce the availability of heavy metals enriched in sludge. The dry samples under investigation were mixed with different percentages of cement kiln dust (0, 20, 40 and 50%).

By increasing percentages of cement kiln dust increased the pH of stabilized samples from 6.3 to 10.5. These results were matching to some extent with the findings of several authors [24,49,50] who mentioned that, the highly alkaline condition of stabilized samples due to high content of CaO, MgO and calcium silicate hydroxide phase in stabilized materials.

Fig. 2 shows the transformations in the chemical forms of heavy metals in stabilized sludge samples of 6th of October (C) at different percentages of cement kiln dust. The results showed that, as the percentages of cement kiln dust increased from 0 to 50%, the percentage of metal forms in Fe/Mn-oxide and residual forms increased. The sum of the percentages for the immobilized forms

of metals in the stabilized sludge sample of (C) WWTP were 100% of Cd, 90.65% of Cu, 99.86% of Cr, 99.74% of Fe, 82.58% of Mn, 85.15% of Ni and 75.17% of Zn.

The results demonstrated a very good stabilization of heavy metals in sludge samples and the mobility of heavy metals reduced by increasing the percentage of their presence in Fe/Mn-oxide and residual fractions. This conclusion agrees to some extent with observations, which have been achieved by several authors [24,51–53].

When the percentage of cement kiln dust increased from 40 to 50%, the percentages of immobilization of all metals slightly increased. Therefore, 50% of cement kiln dust was selected for the subsequent studies, owing to the cementitious properties of cement kiln dust for binding of contaminant heavy metals as proposed by several authors [24,55,54].

To evaluate the efficiency of stabilization methods for heavy metals in sludges, the speciation pattern of heavy metals was used as an indicator for the availability and mobility of heavy metals in stabilized sludge samples. Figs. 3 and 4 represent metal speciation for un-stabilized and stabilized sludge with 50% of cement kiln dust as stabilizer material to identify the changes associated with the metal speciation and the transformations in the chemical forms of heavy metals in stabilized sludge samples of A, B, C, D and E. The degree of fixing or binding of contaminant heavy metals by 50% of cement kiln dust is very efficient. This conclusion agrees to some extent with observations, which have been achieved by many authors [24,52,53].

The chemical speciation of Cd changed when sludge was stabilized with cement kiln dust. For Helwan sludge (A), the percentage of Cd in the residual fraction increased from 23.44 to 79.42 and that in the organic and sulfide decreased from 22.66 to 12.86. Similarly, for Balaqus (E) percentage of Cd in the carbonate fraction decreased from 26.85 to zero and that in the residual fraction increased from 23.44 to 79.42.

Similarly, at Helwan, percentage of Cu in the residual fraction increased from 8.19 to 41.37 and that in the organic and sulfide decreased from 84.34 to 42.37. Chromium, iron and nickel showed similar behavior. Zinc was the least effected by cement kiln dust stabilization.

The heavy metals immobilization using cement kiln dust is mainly due to the formation of pozzolanic reaction products such as calcium silicate hydrate and calcium aluminum silicate hydrates [54].

Overall, on examining the results of metals stabilized by cement kiln dust we can conclude that cement kiln dust is uniquely suited for use as stabilizer material for heavy metal contaminants in sludges. Heavy metals are locked in the cement kiln dust depending on its cementitious properties; therefore, it reduces the mobility of heavy metals by increasing the percentages of metal forms in the Fe/Mn-oxide and residual fractions. This conclusion agrees to some extent with observations, which have been achieved by many authors [27,52,53,55].

4. Conclusions

The mobility of heavy metals, their bioavailability and related eco-toxicity to plants, depend strongly on their specific chemical forms or ways of binding. Consequently, these are the parameters that have to be determined, rather than the total element content, in order to assess toxic effects and to study geochemical pathways.

It is clear that, sequential extraction scheme provides valuable information on the mobility of metals in sludge and helps in predicting their behavior if used for soil amendment. In addition, it must be taken into account the chemical forms (speciation) and mobility of heavy metals, than their total concentrations, before disposing of sludge to the soil as a purpose of agricultural processes. Finally, the stabilization method used influenced the metals distribution and lowered their bioavailability since the metals associated mainly with Fe/Mn-oxide and residual fractions.

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