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Removal of toxic metals from sewage sludge by EDTA in a closed-loop washing process

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Problem

- More than 50,000 wastewater treatment plants are operating in the European Union, producing more than 10 million tons of dry solids per year.
- Nitrogen and P are abundant in sewage sludge, reaching concentrations ranging from 1.5 to 6.0% and from 0.8 to 11.0% of total solids, respectively.

- Micro-organisms
- Undigested organics
- Inert inorganic material
- Metals: Cr, Mn, Fe, Pb, Zn, Hg, Co, etc.

Wastewater treatment plant in Slovenia

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Current sludge treatments techniques

Physical

Heat (300-400 C),
Electroremediation

+	-
Short time	Loss of nutrients
Elimination of potential organic pollutants	Some authors suggest the use of low pH for Electroremediation

Biological

Vermicomposting, Bioleaching,
Biosurfactant application .

+	-
Low risk of seconday pollution	Long time
Efficient	Efficiency changes according substrate composition

Chemical treatment

Acidification, Ion Exchange,
Chelating, etc.

+	-
Short time	Could change properties
Simple	Could be expensive
Efficient	

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Chemical treatment

Why EDTA?

- Can be recycled
- Economically feasible
- Efficient
- Not harmful in low concentrations
- Simultaneous metals removal

Resoil

Soil EDTA+ Oxalic acid+ Dithionite washing

- 60 % As removal
- 53% Cd removal
- 29 % Zn removal
- 76 % Pb removal

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How does EDTA washing process works?

Organic matter

Residual

Exchangeable

Toxic metals in Sewage Sludge (SS)

Carbonates

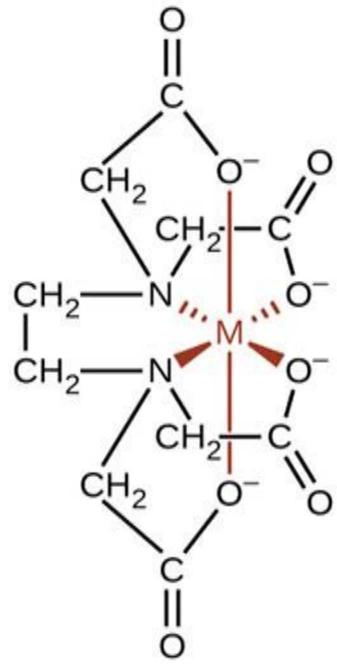
Fe and Mn oxides

SS EDTA washing

Rinsing 1

Rinsing 2

Rinsing 3



Washed SS

Used washing and rinsing solutions

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Solutions recycle

Used washing and rinsing solutions (RS1, RS3) + Lime (CaO) solid = Treated washing solutions + Metals hydroxides (solid)

$$Me\text{-}EDTA + Ca^{2+} + 2(OH)^{-} \leftrightarrow Ca\text{-}EDTA + Me(OH)_2$$

RS1 + H_2SO_4 = Acid rinsing solution (pH2) + Acidic EDTA (solid) to be recycled for next batch

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Pre-experiments

SS coming from WTP of Slovenia metals concentration (mg kg^{-1})

Pb 102 | Zn 968 | Cu 267 | Mn 222 | Cr 101 | Fe 8374

Pre-experiments

Treatment	EDTA	Oxalic Acid (mM)	Dithionite (mM)	H_2SO_4 (mM)	Ratio (w/V)	Time (h)	Pb rem. (%)	Zn rem (%)	Fe rem. (%)	Cu rem. (%)	Mn rem. (%)	Cr rem. (%)
Resoil	100	100	50		1:10	1	65	85	43	0	72	23
1	100	100	/		1:10	21	63	77	31	41	66	20
2	100	/	/	100	1:10	21	53	76	5	57	56	11
3	50	/	/	/	1:7	1	4	45	0	51	7	13
4	/	/	/	50	1:7	1	0	0	0	0	0	4
5	50	/	/	50	1:7	1	37	64	0	64	30	15

Process

Sludge conditioning

- Drying
- Grinding

Sludge washing

- 1 h
- EDTA and H_2SO_4

Sludge rinsing

- Fresh water
- 3 times

Treatment of Procesing solutions

- CaO
- RS1 EDTA

Sludge washing

- 68% of EDTA are recovered

Products

- EDTA washing solution
- 3 Rinsing solutions
- Washed sludge

Removal efficiency

Batch number	Removal efficiency (%) Pb	Zn	Cu	Cr	Mn	Fe
1	42	62	62	22	30	7
2	41	61	61	15	28	7
3	42	61	61	16	26	7
4	43	64	61	19	35	1
5*	/	56	60	17	/	0
6	40	60	62	15	25	0
7	33	56	57	23	20	0
8	34	58	58	18	21	4
9	34	57	59	20	24	2
10	34	57	58	25	23	0

*SS washed in batch 5 was externally contaminated with Pb and Mn after grinding/sieving.

Table 2: The efficiency of removal of toxic metals from sewage sludge in a series of 10 consecutive washing batches.

Used and treated washing solutions

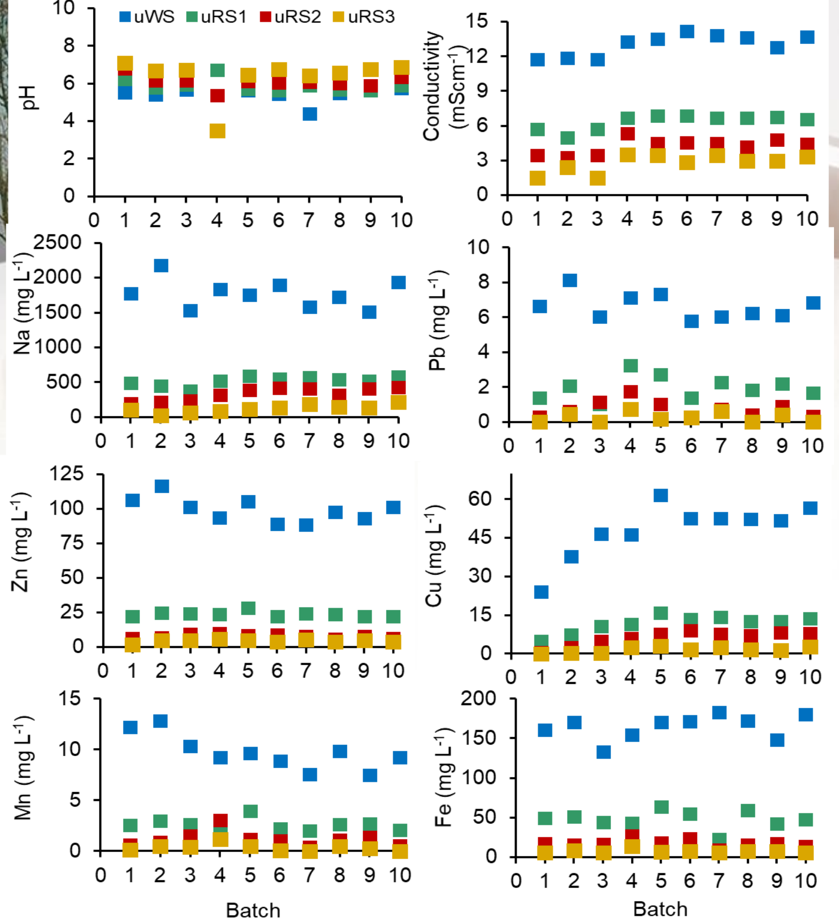

Fig. 2. The properties of used washing, first, second and third rinsing solution (uWS, uRS1, uRS2, and uRS3, respectively) over the 10 consecutive remediation batches.

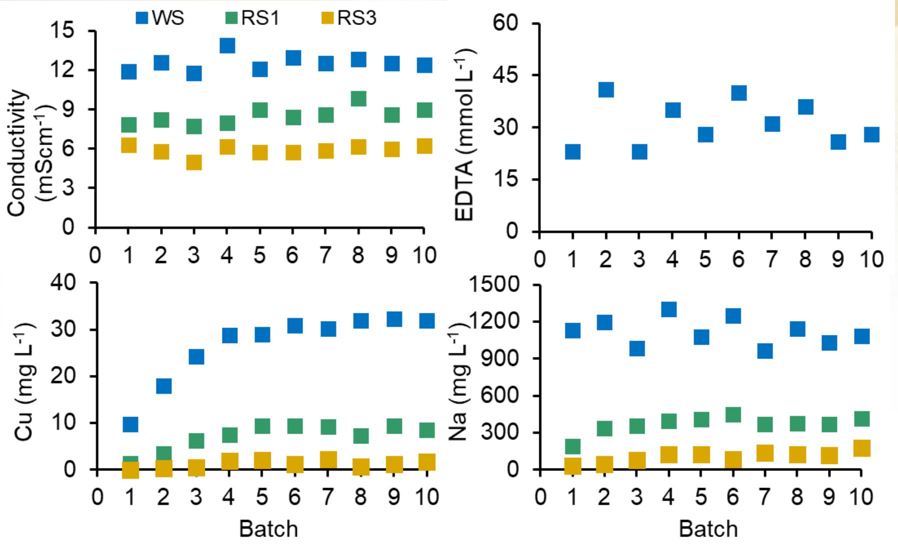

Fig. 3. The properties of the recycled washing, first and third rinse solutions (WS, RS1, and RS3, respectively) over the 10 consecutive remediation batches.

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Sequential extraction

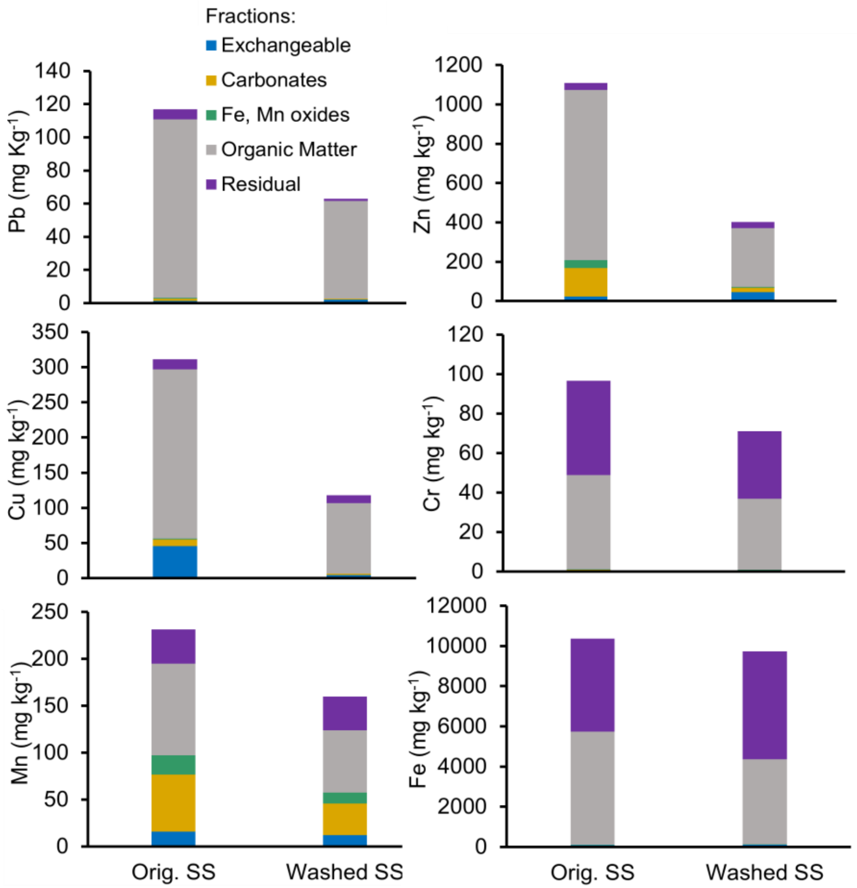

Fig. 4. Fractionation of Pb, Zn, Cu, Mn, Cr, and Fe in original and washed SS. Data are given as averages of 3 subsamples obtained from the homogenized bulk of orig. SS and a combined sample of washed SS from batches 1-10 (except batch 5, which was excluded due to external contamination with Pb and Mn).

Metal leachability

Metals (mg kg^{-1})	Orig. SS	Washed SS	DIN 3814-S4*
Pb	0.63 ± 0.04^b	1.59 ± 0.05^a	10
Zn	11.50 ± 0.02^b	43.73 ± 0.07^a	50
Cu	41.02 ± 0.47^a	3.05 ± 0.05^b	50
Cr	0.59 ± 0.02^a	0.17 ± 0.01^b	10
Mn	1.67 ± 0.05^b	3.25 ± 0.05^a	/
Fe	34.52 ± 0.53^b	54.43 ± 1.02^a	/

*Concentrations stipulated as hazardous (DIN 38414-S4, Council Decision 2003/33/EC)

Table 3. Leaching of metals from original and washed SS. Data are given as average ± SD of 3 subsamples taken from the homogenized bulk of orig. SS and from a combined sample of washed SS from batches 1-10 (except batch 5, which was excluded due to external contamination with Pb and Mn). Different letters indicate significant differences between treatments according to Duncan's test ($P < 0.05$).

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Chemical properties

	Orig. SS	Washed SS
Metals (mg kg^{-1})		
Pb	102 ± 1.16	63
Zn	968 ± 7.67	391
Cu	267 ± 1.19	107
Cr	101 ± 1.86	82
Mn	222 ± 1.96	165
Fe	8374 ± 11.95	8295
Properties		
pH	6.97	6.15
EC (mS cm^{-1})	2.81	3.37
TP (%)	1.85	1.73
P_2O_5 (mg 100 g^{-1})	1806.3	1377.3
TN (%)	5.31	4.78
TOC (%)	30.00	30.51
TC (%)	31.64	31.71
TK (%)	0.22	0.12
K_2O (mg 100 g^{-1})	132.1	41.1
$CaCO_3$ (%)	13.65	9.45

Table 1. Metal concentrations and properties of original and washed SS. Data for metal concentrations in orig. SS are given as average ± SD of 3 subsamples taken from the homogenized bulk, and for washed SS as the calculated average from batches 1-10 (except for batch 5, which was excluded because of external contamination with Pb and Mn). The properties of orig. SS refer to the homogenized bulk, and washed SS of the combined sample from batches 1-10, batch 5 was excluded.

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Acknowledgements
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Process scheme

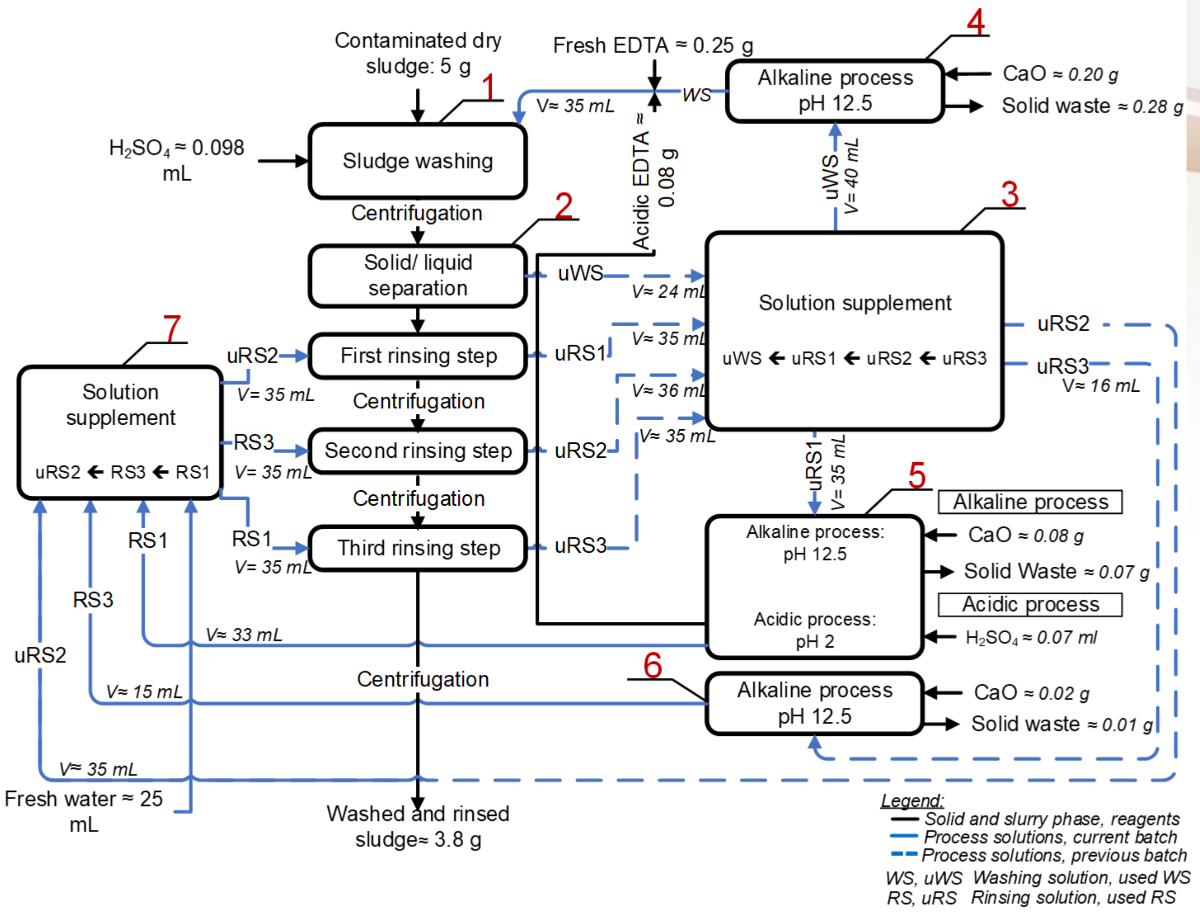

Fig. 1. The flowchart of the process with material balance. Process steps: (1) SS washing, (2) solid-liquid separation and SS rinsing, (3) compensation of water losses, (4) alkalization of uWS, (5) alkalization/acidification of uRS1, (6) alkalization of uRS3. (7) Addition of other solutions and fresh water to each of the process solutions to reach the final volume. WS, uWS denotes washing and used washing solution, RS1 and uRS1 represent first rinsing and used rinsing solution, RS2 and uRS2 represent second rinsing and used rinsing solution, RS3 and uRS3 third rinsing and used rinsing solution. Blue lines denote flow of solutions, dashed blue lines denote flow of solutions from previous batch, black lines denote flow of solids.