Red mud as mineral additive to reduce the toxicity of marine dredged sediments

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Overview

- Introduction: Sediment pollution, dredging operation, bauxite residue.
- Experiments: Stabilization of marine dredged sediments with cost effective mineral additives.
- Results and discussions
- Conclusions

Introduction : Sediment pollution and dredging

- The contamination of aquatic sediments with heavy metals and organic compounds is a widespread problem. This type of pollution is a source of health-related, environmental and social problems[1].
- Recent studies reported an elevated level of metals (As, Cu, Cd, Zn, Ni and Mo)[2-4] , organic compounds (PAHs and PCBs)[5] and organotins in Mediterranean port sediments [6].
- Dredging activities on ports and harbors are carried out to maintain the maritime navigation. This activity generates huge volume of sediments.

[1] Forstner ,U. Contaminated sediments: lectures on environmental aspects of particle associated chemicals in aquatic systems. Berlin: Springer-Verlag; 1989. p. 107-109.
[2] Caplat, C., Texier, H., Barillier, D., Lelievre, C., 2005. Heavy metals mobility in harbour contaminated sediments: the case of Port-en-Bessin. Mar. Pollut. Bull. 50, 504–511.
[3] Schintu, M., Marras, B., Maccioni, A., Puddu, D., Meloni, P., Contu, A., 2009. Monitoring of trace metals in coastal sediments from sites around Sardinia, Western Mediterranean. Mar. Pollut. Bull. 58, 1577–1583.
[4] Risso-de Faverney. C., Guibbolini-Sabatier M.E., Francour, P., 2010. An ecotoxicological approach with transplanted mussels (Mytilus galloprovincialis) for assessing the impact of tyre reefs immersed along the NW Mediterranean Sea. Mar. Environ. Res. 70(1), 87-94.
[5] Andral, B., Stanisiere, J.Y., Sauzade, D., Damier, E., Thebault, H., Galgani, F., Boissery, P., 2004. Monitoring chemical contamination levels in the Mediterranean based on the use of mussel caging. Mar. Pollut. Bull. 49, 704-712.
[6] Díez, S., Ábalos, M., Bayona, J.M., 2002. Organotin contamination in sediments from the Western Mediterranean enclosures following 10 years of TBT regulation. Water Res. 36, 905-918.

French legislation for dredged materials

Dredging = Excavation of sediment

In France marine dredged sediments =50 Million m^3 annually [7]

Regulations for dredged materials: OSPAR (1992) and London convention (1972)

Thus in France, within the framework for management of dredged sediments, two levels (N1 and N2) were fixed for metals and PCBs.

Immersion — Metal concentrations < N1

Landfill — Metal concentrations >N2

French Sediment Quality Guidelines

	N1 (mg/kg)	N2
As	25	50
Cd	1.2	2.4
Cr	90	180
Cu	45	90
Ni	37	74
Pb	100	200
Zn	276	552

(Alzieu et al., 1999)

Metal Concentration between N1 and N2

Toxicity test are recommended along with the chemical analysis

Direct Landfall of highly polluted sediment is problematic, therefore sediment should be treated prior to disposal.

Treatment method: Metal immobilization by mineral additives.

[7] Alzieu, C., Michel, P., Chiffoleau, P., Boutier, B., Abarnou, A., 1999. Dragages et environnement marin: Etat des Connaissances. IFREMER, Nantes, France

Bauxite residue and its uses

- Bauxite residue commonly known as red mud is the by-product which is generated during caustic digestion of bauxite for aluminium production.
- Parallel to sediment management, the management of bauxite residue (red mud) is also a serious and challenging problem that alumina refineries are facing all over the world due to its caustic nature. 90 million tonnes of red are produced each year globally.
- Its main composition is (Al_2O_3, SiO_2, Fe_2O_3, TiO_2, CaO) and has high pH (10-11).
- Red mud has a great potential to remove pollutants (arsenic, cadmium, copper, lead and phosphates) from various environmental media (water, wastewater, acid mine drainage, soil)[8].
- Red mud is low cost material but high pH of material limits its application.

[8] Liu, Y., Naidu.,R., Ming., H. 2011. Red mud as an amendment for pollutants in solid and liquid phases. Geoderma. 163, 1-12.

Aim of the study

- To investigate the efficiency of gypsum neutralized red mud (neutralized with 5% plaster) to stabilize the trace elements in marine dredged sediments.
- To test the different amendment rates suitable for effective stabilization of pollutants.
- To reduce the toxicity of sediment.

Materials and methods

- Sediment sample was collected from a French Navy harbor area and composted for 4 months by port authorities .

- Red mud samples were provided by **ALTEO** and Gypsum neutralized red mudwas provided by **INERIS.**
- pH and electrical conductivities were determined in (100g/L) suspension.
- CEC, Specific surface areas was measured by standard methods.
- Sediment and red mud samples were digested according to USEPA method 3050B using DigiPREP HT.
- Leached metals concentrations were measured by ICP-OES (Optima 2000, Perkin Elmer).
- Rotoxkit (microbiotest Inc., Belgium) was used for toxicity test.

Physicochemical properties

Parameters	Units	Sediment	Red mud	Neutralized red mud	N1	N2
pH		8.18±0.01	10.57±0.02	9±0.02		
EC	(mS/cm)	7.44	0.9153	3.69		
CEC	(meq/Kg)	105.3±0.08	61.8±0.09	40±0.12		
Specific surface area	(m^2/g)	3.5	23.06±0.15	19.1±0.2		
As	(mg/kg)	150±3.2	<DL	-	25	50
Cd	(mg/kg)	4.69±0.12	0.689±0.3	-	1.2	2.4
Cu	(mg/kg)	1721±42	20.23±4	-	45	90
Mo	(mg/kg)	9.08±0.22	<DL	-	-	-
Ni	(mg/kg)	27.36±0.63	7±0.11	-	37	74
Zn	(mg/kg)	1869±49	13.04±3.7	-	276	552
Cr	(mg/kg)	59.11±2.15	1864±25	-	90	180

Experiments

Fig.1 Experimental setup

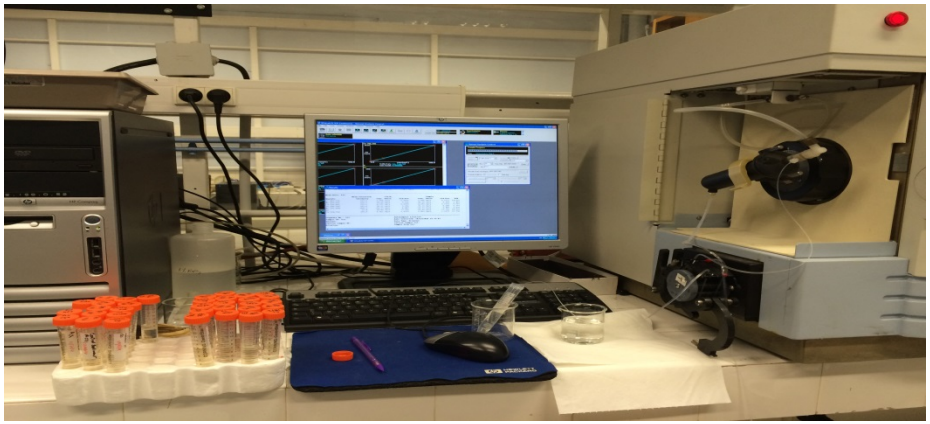
- **Box Size:** (D40×W40 ×H20 cm) which contain a square plastic mesh at the bottom in order to allow collection of leachates. The boxes were also coated with geotextile material to avoid the loss of particles.
- **Amount of sediment in each box:** 6 Kg
- **The duration of the experiment:** 3 months (April 2014-July 2014)
- **Amount of tap water:** 2 L

Leachate analyses

Leachates were collected after 1 hour of drainage
- pH and EC were measure

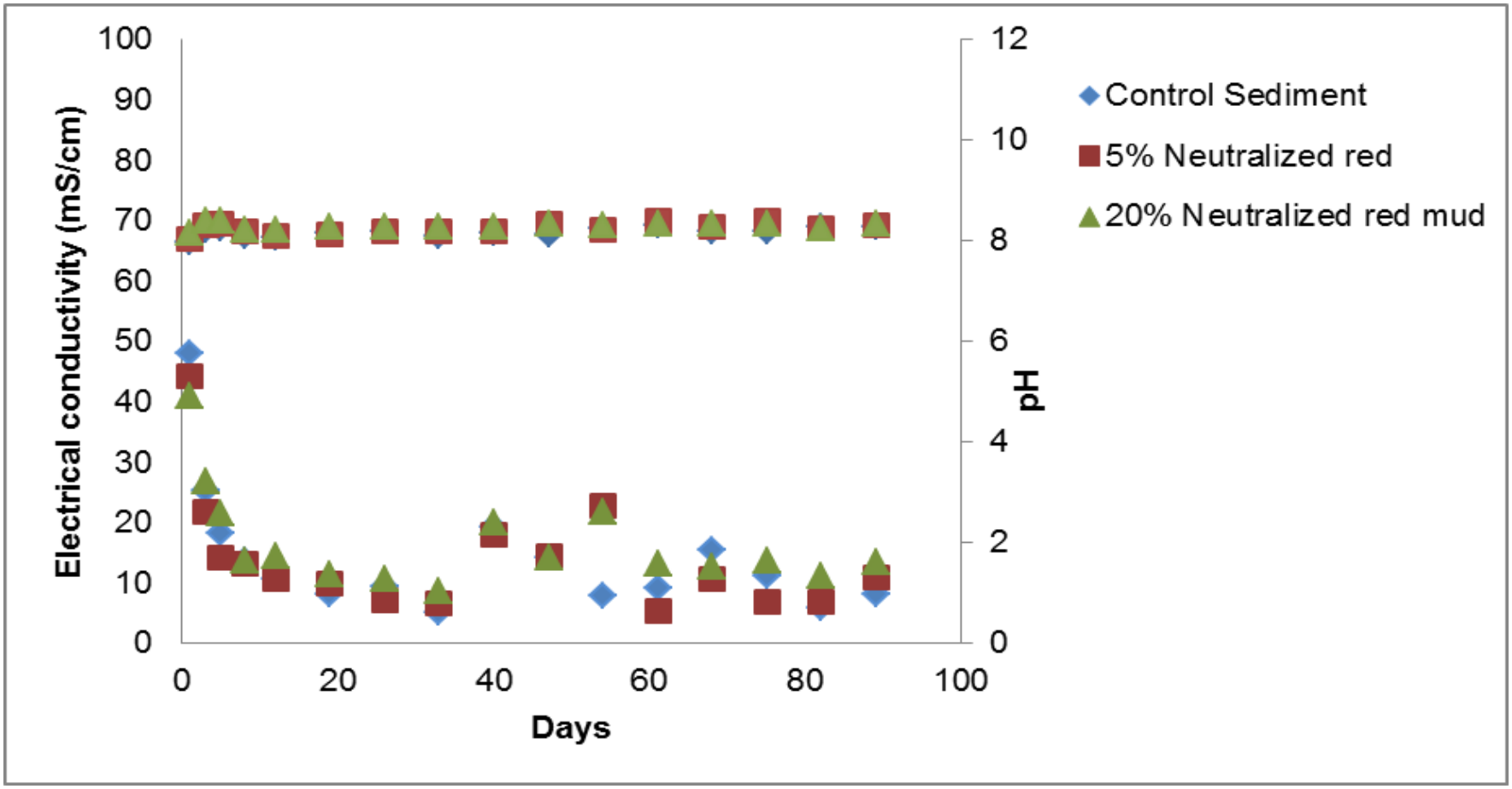
Leachates were centifuged, filtered (a 0.45 µm), and acidified 1% with HNO_3 to measure dissolved (As, Cd, Cu, Zn, Mo, and Cr) for analysis on ICP-OES (Optima 2000, Perkin Elmer)

Toxicity of leachates was tested using Rotoxkit against *(Brachinous plicatilis)* which is purchased from microbiotest Inc., Belgium.

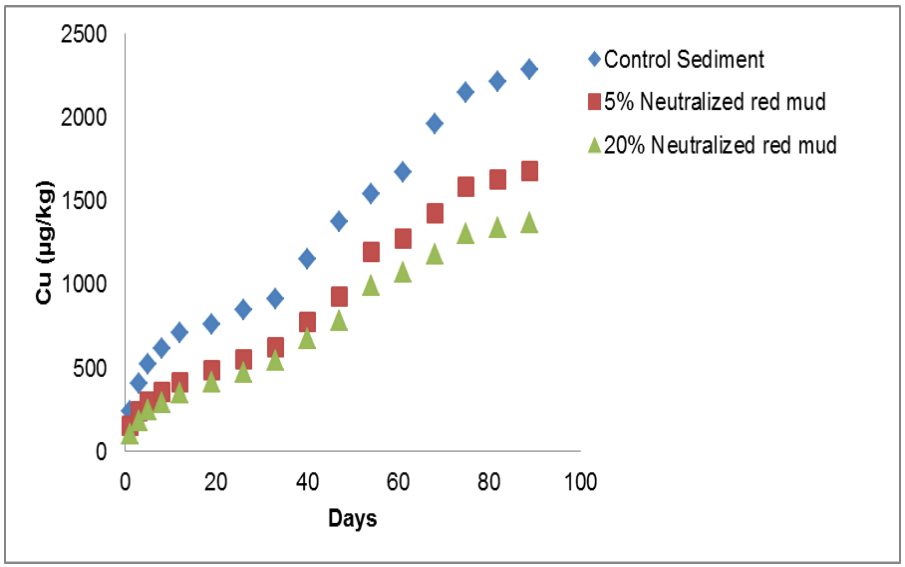


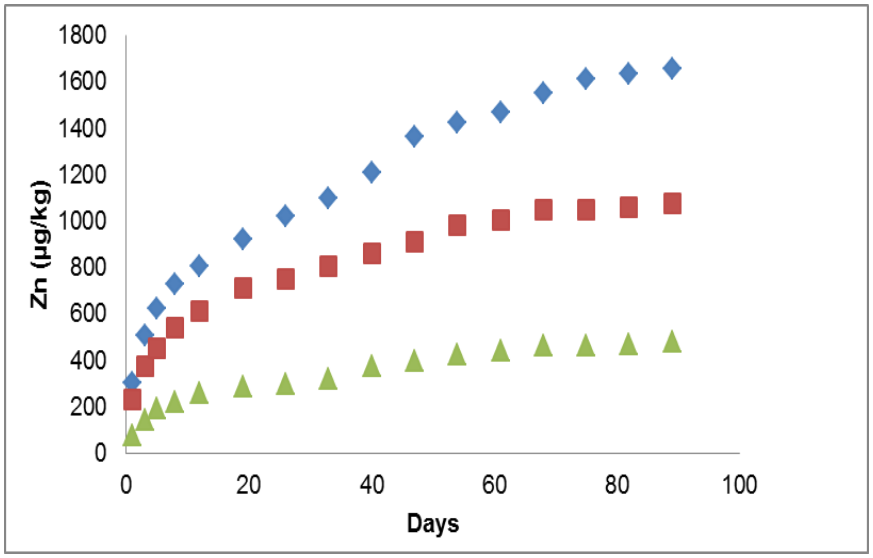
Results and Discussions

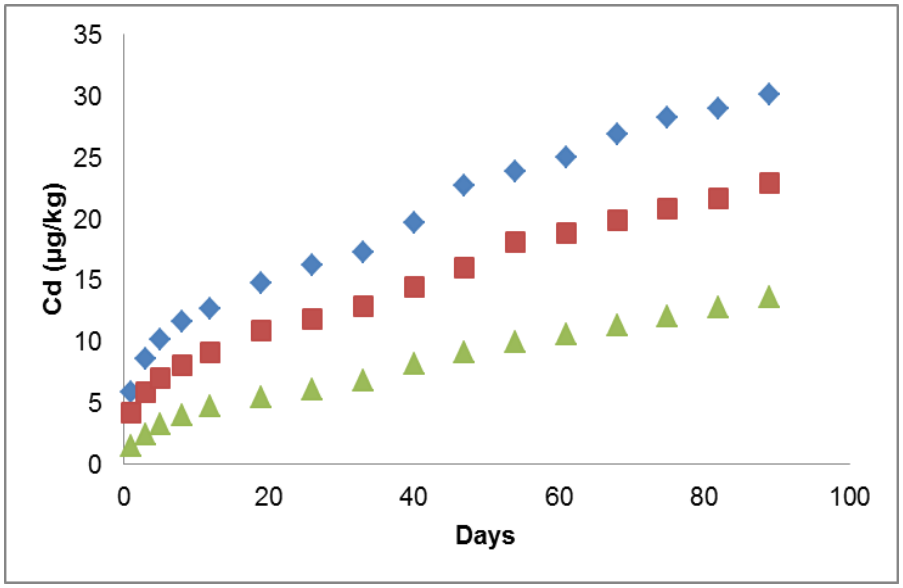
pH and EC of leachates



Amount of trace elements released from control and stabilized sediments during 3 months



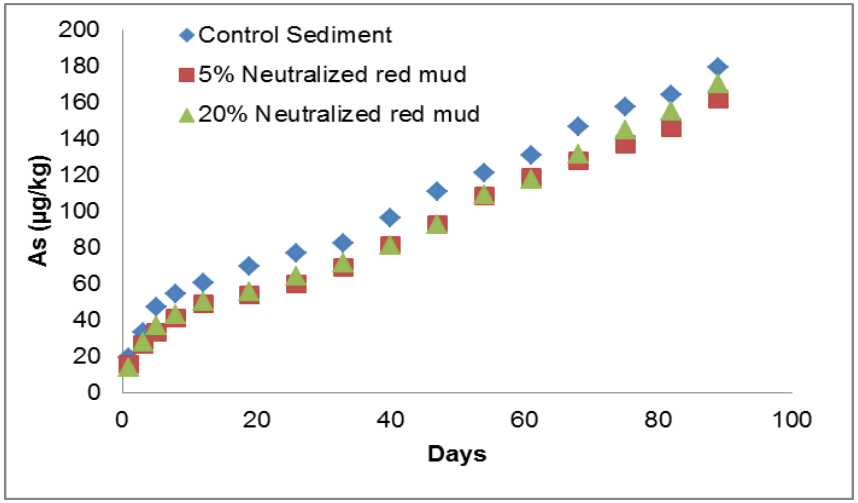


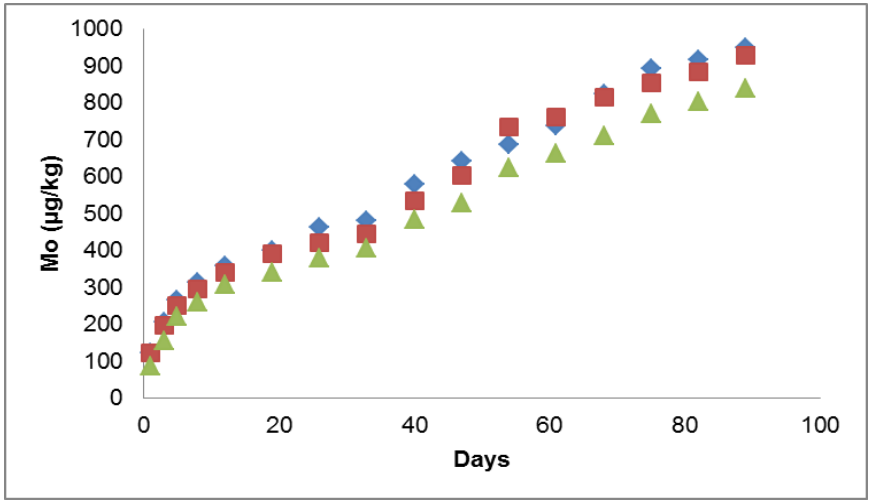


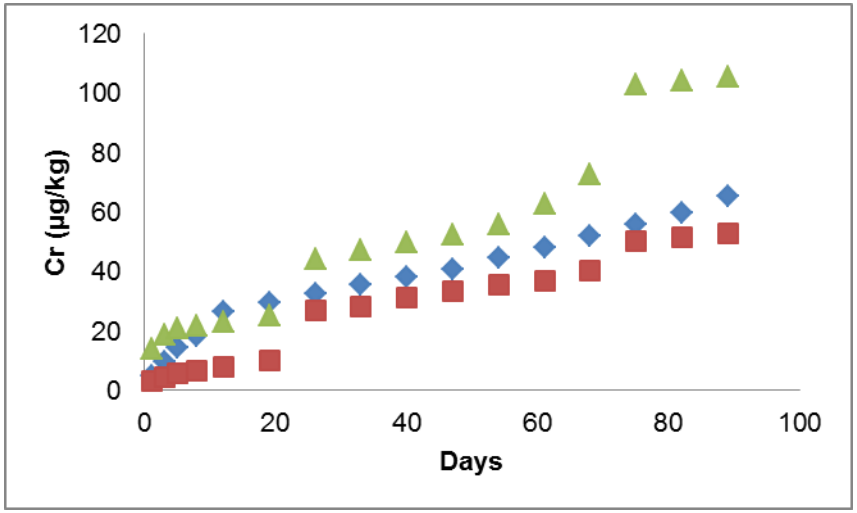
5% mineral additive:
reduced the leaching of pollutants 26.5%, 35%, and 24% for Cu, Zn and Cd respectively.

20 % mineral additive:
Significant stabilization of pollutants was observed as compared to control. Cu 40%, Zn 71.2%, Cd 55%

Amount of trace elements released from control and stabilized sediments during 3 months







As, Mo and Cr were not significantly immobilized. Arsenic is retained only up to 9.6% and 5.2% .

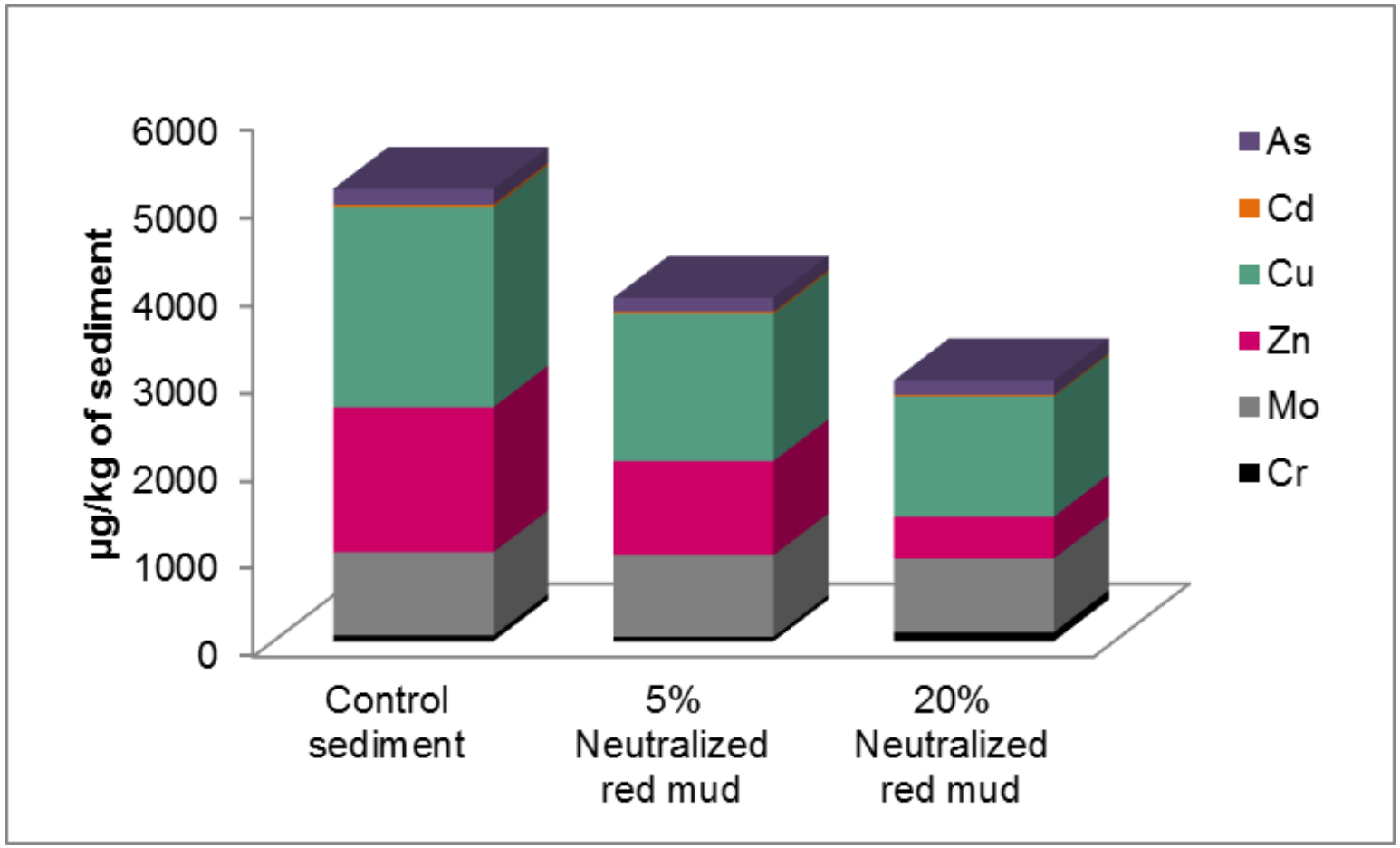
In case of Mo rate the is only up to 2.2% to 11.7% while Cr leaching is reduced 19% as compared to control sediment.

Comparison of trace elements concentrations (As, Cd, Cu, Mo, Cr and Zn) measured in leachates from sediment samples with regulatory levels defined for inert waste at liquid to solid ratio of 2L/Kg.

	Regulatory levels	Units	Control Sediment	5% Neutralized red mud	20% Neutralized red mud
As	100	µg/kg	69.7	54.2	55.5
Cd	30	µg/kg	14.8	10.9	5.4
Cu	900	µg/kg	762.8	486	417
Mo	300	µg/kg	401	392	341
Cr	200	µg/kg	29.4	10	25
Zn	2000	µg/kg	921.1	707.8	286.5

European Council, Council decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of Annex II to Directive 1999/31/EC(2003/33/EC). OJEC L11/27 [16.1.2003]. 2002.

Cumulative quantity of pollutants released from control and stabilized sediments



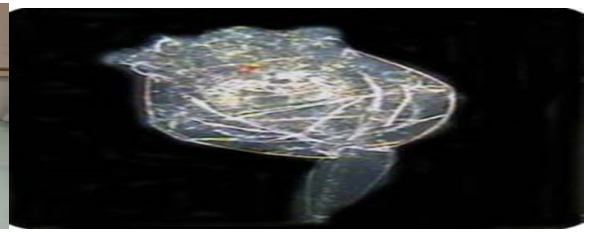
Sediment treatment with two amendments have reduced the total amount of pollutants from sediments

Red mud as additive: decreased the toxicity of sediment

- Toxicity test was performed on leachates collected during experiment against marine rotifers *(Brachionus plicatilis).*

Mortality (%)	Standard Seawater	Control Sediment	5% Neutralized red mud	20% Neutralized red mud
After 24H	0	0	0	0
After 48H	0	73	49	36

Average toxicity of all leachates


Conclusions

pH and EC:

No effect on pH.

EC conductivity decreased due to successive leaching.

Cu, Zn, Cd:

Significant stabilization of cationic pollutants with the 20% rate of amendment as compared to untreated sediment.

As, Mo, Cr:

The amendments rates were not effective

Toxicity:

Application of red mud at the rate of 20% reduced the toxicity of sediment.

Red mud can serve as low cost material for the treatment of sediments polluted with cationic elements.

Thank you

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