USE OF RED MUD IN SOIL REMEDIATION: REVIEW OF APPLICATIONS AND CHALLENGES

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Abstract

Despite the fact that red mud is often contaminated with heavy metals and metalloids, its use in environmental remediation has widely been investigated and applied from laboratory to field scale. Red mud is efficient for the removal of various aquatic pollutants, especially arsenic and phosphate, from waste waters, but the practical utility of these adsorbents on a commercial scale still needs more investigation. Another application of red mud that receives less attention, is its use in soil remediation. In the present paper, the application potential of red mud as a soil amendment for contaminant immobilisation, was critically reviewed.

Introduction

In view of the challenges of increasing resource efficiency, by-products of industrial processes are increasingly used to replace virgin resources in numerous applications. In some cases, industrial symbiosis is even possible: for example, red mud and caustic water, both by-products of alumina production, can be used as a raw material for the production of a gel like coagulant, which on its turn can be used for the purification of industrial waste waters.[1] In the environmental remediation of contaminated soils, sediments and water, numerous types of "waste materials" have showed to effectively immobilise heavy metals (e.g.[2]). In accordance with the European Waste Framework Directive, several European countries and regions already allow the beneficial use of certain waste materials as a secondary resource.

The insoluble product generated In the Bayer process, after bauxite digestion with sodium hydroxide at elevated temperature and pressure, is known as "red mud‘ or "bauxite residue". Despite the fact that red mud (RM) is often contaminated with heavy metals and metalloids, its use in environmental remediation has widely been investigated and applied from laboratory to field scale. For the removal of contaminants from waste water, several literature surveys between 2003 and 2011 (e.g.[3,4]) indicated that that RM is efficient for the removal of various aquatic pollutants, especially arsenic and phosphate, from waste waters but there is still a need to investigate the practical utility of these adsorbents on a commercial scale. Compared to waste water treatment, the use of RM as an amendment to immobilise potentially toxic elements (PTEs) in soil received less attention, but research concerning this application is increasing. The present paper wants to critically review the existing literature dealing with the use of RM to immobilise PTEs in soils. Based on the review, challenges and perspectives for future research are highlighted.

Methodology

The review includes papers on the application potential of RM as a soil amendment for contaminant immobilisation, as well as accidental RM spills on soils. A first selection of papers was made considering all publications registered in Scopus and Web of Science, retrieved using ‘red mud AND soil’, or ‘bauxite residue AND soil’ as search terms. Based on the abstracts of the papers, a second selection of relevant publications was made, where after the full text of the finally selected articles was collected for more detailed analysis. The focus will be on 24 articles published in international peer reviewed journals between January 2002 and April 2015. Papers dealing with the isation of RM only, without investigation of its use as an amendment to soil were not included. Mine tailings in which RM was used to immobilise PTEs were taken into account because of similarities in PTE immobilisation mechanisms and because the majority of the papers deal with soils contaminated by mining and smelting activities. Moreover, because RM is highly alkaline, it has been used to neutralise acid mine drainage.

Results and Discussion

Investigation of PTEs in RM-amended soils

Whereas most studies investigate the addition of RM to contaminated soil samples,[5-18,19-24,27-28] some papers[20,25-26] address the effect (mobility, (bio)availability, toxicity) of adding RM to uncontaminated soil. Most investigations rely on laboratory studies, including leaching tests, microbiological, and ecotoxicology tests and pot experiments. Although the focus of these laboratory investigations is mainly on short-term effects and/or a more operationally defined ‘speciation’[5,17], some articles report on medium-term batch microcosm experiments (100-120) days[26] or pot experiments (up to 12 months)[18]. Only one study (e.g.[14]) was found to address the long-term effects (5 years) of combining phytoremediation with immobilisation with RM. For solid-phase characterisation of RM amended/contaminated soils geochemical methods prevail, while in some cases also XRD and SEM-EDX[22,28] are used. More sophisticated solid-phase characterisation techniques such as XANES,[25] EXAFS and FEG-EPMA have rarely been used until now in the context of RM contaminated/amended soils, whereas this could offer valuable information on PTE speciation and elemental associations in these soils.

Influence of RM addition on PTE occurrence and mobility in soils

RM application to soil results in a pH increase, which decreases the mobility of heavy metals such as Zn, Cd, Ni and Cu. However, the fixation mechanism in RM-treated soils could also be due to specific chemisorption and metal diffusion into the lattice of Fe and Al oxides.[5, 28]

Therefore, amendment with RM may result in a more durable reduction in metal mobility than liming, and also a smaller risk of metal re-mobilisation in the case of decreasing soil pH.[5] Moreover, plant growth, microbial activity and biomass are enhanced as a result of RM application to a contaminated soil.[6] Cucci et al.[7] found that that relatively small additions of RM to the contaminated soils drastically reduces the heavy metal content in the effluent of a column leaching test. Possible drawbacks of the use of RM as a soil amendment include the occurrence of indigenous contaminants such As, V and Cr. In that case, or when the treated soil contains As, Cr or V, the application potential of RM as a soil amendment may be limited, because of the mobilisation of these elements upon an increase of pH. Soil-water systems affected by RM addition may show an increased As mobility under both aerobic and anaerobic conditions.[25] Mixing of RM into organic rich soils can potentially mobilise Cu and Ni as organically bound complexes, especially under anaerobic conditions.[26]

RM is effective at reducing the “mobile” form of Pb, Cd and Zn and at promoting bacterial abundance and soil enzyme activity, but caused a dramatic shift of the cultivable bacterial population from Gram positive to Gram negative forms.[13]
The use of RM is most promising in the remediation of contaminated soils with a near-neutral or subalkaline pH,[22] but Fe_2O_3, Fe-water treatment residues and Al-OH could represent more effective alternatives to RM in the reduction of labile metal(loid)s in circumneutral and/or alkaline soils.[22] RM can be used as soil amendments to develop a cost-effective and efficient in situ remediation technology for mildly contaminated (calcareous) soils.[27] Moreover, the efficiency of RM could be increased by milling the RM to nano-particles to increase its specific surface area.[27]

Table 1: Selected articles investigating the mobility of PTE in RM affected soils

Ref	Soils investigated	Tests
5	Two soils polluted with heavy metals due to past sewage sludge application or Zn smelter activity	Porewater analysis, DGT, pot experiment, Tessier (1979) Sequential extraction
6	Two soils polluted with heavy metals due to past sewage sludge application or Zn smelter activity	biological tests to evaluate the efficiency of treatment with RM
7	Volcanic brown soil contaminated by reddish flotation tailings and gravity processing waste	Column leaching test
8	Soil collected in the vicinity of a former Pb-Zn smelter	Greenhouse study; ammonium nitrate (1 M) extraction
9	Soils spiked with Cd, Zn, Cu, Ni and V and two industrially polluted soils	ammonium nitrate (1 M) extraction
10	Contaminated waters and soils	Serial batch test, Microtox^{TM} test, ASTM microalgae toxicity test, sea urchin embryo toxicity test
11	Sample from the tailings pond of a flotation plant	Column leaching test, batch leaching tests in the pH range 7–11
12	Soil contaminated by emissions from a Zn/Pb smelter	Cultivation of plants (pot experiment) ammonium nitrate (1 M) extraction physiological based extraction test (PBET)
13	Soil in the vicinity of an old mining area (ZnS and PbS).	Determination of soil microbial communities (16S rDNA gene amplification and partial sequencing) + enzymatic activity
14	Soil contaminated by Pb/Zn smelter	5 years field experiment with crops + pot experiment
15	Soil contaminated with Zn, Pb, Cd, As and Cu by metal deposition from Pb/Zn smelter activities.	Combining immobilising amendments with phytoextraction
16	farmland polluted by heavy metals due to a tailings dam collapse	Pot experiments with Maize, Single extraction with $CaCl_2$
17	As-rich gold mine tailings	Enzymatic activity, sequential extraction
18	Sandy, alkaline (pH=8.1) soil contaminated with Pb and Zn by airborne particles from a Pb/Zn smelter	Single extractions with $CaCl_2$, CH_3COOH , HCl and EDTA, Greenhouse experiment with Rhodes grass (12 months)
19	Uncontaminated Hungarian soil samples	Batch and column experiments
20	10 cm thick RM layer that was placed on the top of the soil column	Column test, microbiological and ecotoxicology tests
21	Cd contaminated soils treated with RM	Pot experiment with pakchoi, Na-EDTA extraction
22	As contaminated soil	XRD, sequential extraction, 16S rRNA PCR-TTGE
23	As contaminated soils treated with RM	Leaching test, simplified bioaccessibility extraction test (SBRC), pot trials with *Lolium perenne*
24	Calcareous soils amended with RM, rape straw, and corn straw and zinc fertiliser	Field experiment with different vegetables, sequential extraction
25	Agricultural and wetland soils amended with RM	(An)aerobic batch leaching tests, XANES, HPLC-ICP-MS
26	Agricultural and wetland soils amended with RM	Long term batch microcosm experiments, SPE
27	Calcareous soils amended with RM, and rape straw	Single and sequential extractions, pot experiment with cucumber
28	mine tailings containing Pb, Zn and Cd	TCLP, Sequential extractions, XRD, SEM-EDX

Conclusions

Soils are complex environmental media, in which long term effects, including the fate of heavy metals, are still not always fully understood. Therefore, the long-term efficiency of RM to immobilise PTEs, merits particular attention. Many investigations rely on laboratory leaching and extraction tests, typically operating at conditions that are far away from in situ conditions. Although this is interesting for a general characterisation of the effect of RM addition to soil, the use of more sophisticated analytical techniques (to clarify the reaction mechanisms responsible for (im)mobilisation), in combination with the execution of long term field studies, is necessary.

Despite the fact that RM application has been shown to effectively immobilise heavy metals in soil, long term effects have to be investigated in more detail in order to properly assess the feasibility and effectiveness of RM in environmental remediation. The efficiency of RM as a soil amendment is a complex function of soil conditions, source of contamination, but also the envisaged remediation goals.

Besides extractions and leaching tests, more attention should go to the bio-availability of PTEs in red-mud treated soils. The alkaline pH of these soils is particularly interesting, because alkaline soils are often considered a ‘safe sink’ for heavy metals, with a limited translocation to plants and groundwater. However, metalloids such as Cr, Mo, As etc. are likely to be mobilised upon RM addition. Additionally, the exposure of contaminated soil to strongly acidic conditions, for example upon ingestion of soil particles by animals or human beings represents a risk that cannot be neglected.

References

1. V. Orescanin, K. Nad, L. Mikelic, N. Mikulic and S. Lulic, “Utilisation of Bauxite Slag for the Purification of Industrial Wastewaters”, *Process Saf. Environ. Prot.*, **84** (B4) 265-269 (2006).
2. Y. W. Chiang, R. Santos, K. Ghyselbrecht, V. Cappuyns, J. Martens, R. Swennen, T. Van Gerven and B. Meesschaert, “Strategic Selection of an Optimal Sorbent Mixture for In-Situ Remediation of Heavy Metal Contaminated Sediments: Framework and Case Study”, *J. Environ. Manag.*, **105** 1-11 (2012).
3. S. Babel and T. A. Kurniawan, “Low-Cost Adsorbents for Heavy Metals Uptake from Contaminated Water: A Review”, *J. Hazard. Mat.*, **97** (1-3) 219-243 (2003).
4. A. Bhatnagar, V. J. P. Vilar, C. M. S. Botelho and R. A. R. Bonaventura, “A Review of the Use of RM as Adsorbent for the Removal of Toxic Pollutants from Water and Wastewater”, *Environ.Technol.,* **32** (3) 231-249 (2011).
5. E. Lombi, F. J. Zhao, G. Y. Zhang, B. Sun, W. Fitz, H. Zhang and S. P. McGrath, “In Situ Fixation of Metals in Soils Using Bauxite Residue: Chemical Assessment”, *Environ. Pollut.*, **118** (3) 435-443 (2002).

6. E. Lombi, F. J. Zhao, G. Wieshammer, G. Y. Zhang, and S. P. McGrath, “In Situ Fixation of Metals in Soils Using Bauxite Residue: Biological Effects”, *Environ. Pollut*., **118** (3) 445-452 (2002).
7. R. Ciccu, M. Ghiani, A. Serci, S. Fadda, R. Peretti and A. Zucca, “Heavy Metal Immobilisation in the Mining-Contaminated Soils Using Various Industrial Wastes”, *Miner. Eng.,* **16** (3) 187-192 (2003).
8. W. Friesl, O. Horak and W.W. Wenzel. “Immobilisation of Heavy Metals in Soils by the Application of Bauxite Residues: Pot Experiments under Field Conditions”, *J. Plant Nutr. Soil Sci.* **167** (1) 54-59 (2004).
9. W. Friesl, E. Lombi, O. Horak, and W. W. Wenzel. “Immobilisation of Heavy Metals in Soils Using Inorganic Amendments in a Greenhouse Study”, *J. Plant Nutr. Soil Sci.* **166** (2) 191-196 (2003).
10. C. Brunori, C. Cremisini, L.D'Annibale, P. Massanisso and V. Pinto, “A Kinetic Study of Trace Element Leachability from Abandoned-Mine-Polluted Soil Treated with Ss-Msw Compost and RM. Comparison with Results from Sequential Extraction'”, *Anal. Bioanal. Chem*., 381 (7) 1347-1354 (2005).
11. A. F. Bertocchi, M. Ghiani, R. Peretti, and A. Zucca, “Red Mud and Fly Ash for Remediation of Mine Sites Contaminated with as, Cd, Cu, Pb and Zn', *J. Hazard. Mat.*, **134** (1-3) 112-119 (2006).
12. C. W. Gray, S. J. Dunham, P. G. Dennis, F. J. Zhao and S. P. McGrath, “Field Evaluation of in Situ Remediation of a Heavy Metal Contaminated Soil Using Lime and Red-Mud”, *Environ. Pollut.,* **142** (3) 530-539 (2006).
13. G. Garau, P. Castaldi, L. Santona, Pi.Deiana and P. Melis, “Influence of Red mud, Zeolite and Lime on Heavy Metal Immobilisation, Culturable Heterotrophic Microbial Populations and Enzyme Activities in a Contaminated Soil”, *Geoderma,* **142** (1–2) 47-57 (2007).
14. W. Friesl-Hanl, K. Platzer, O. Horak, and M. H. Gerzabek. “Immobilising of Cd, Pb, and Zn Contaminated Arable Soils Close to a Former Pb/Zn Smelter: A Field Study in Austria over 5 Years”, *Environ. Geochem. Health*, **31** (5) 581-594 (2009).
15. M. Iqbal, M. Puschenreiter, E. Oburger, J. Santner and W.W. Wenzel. “Sulfur-Aided Phytoextraction of Cd and Zn by Salix Smithiana Combined with in Situ Metal Immobilisation by Gravel Sludge and Red mud”, *Environ. Pollut.,* **170** 222-231 (2012).
16. Y.Z. Huang and X. W. Hao, “Effect of RM Addition on the Fractionation and Bio-Accessibility of Pb, Zn and as in Combined Contaminated Soil”, *Chem. Ecol.,* **28** (1) 37-48 (2012).
17. N. Koo, L. Sang-Hwan Lee and K. Jeong-Gyu, “Arsenic Mobility in the Amended Mine Tailings and Its Impact on Soil Enzyme Activity”, *Environ. Geochem. Health,* **34** (3) 337-348 (2012).
18. Y. F. Zhou, R. J. Haynes and R. Naidu, “Use of Inorganic and Organic Wastes for in Situ Immobilisation of Pb and Zn in a Contaminated Alkaline Soil”, *Environ. Sci. Pollut. Res*., **19** (4) 1260-1270 (2012).
19. A. P. Lehoux, C. L. Lockwood, W. M. Mayes, D. I. Stewart, R. J. G. Mortimer, K. Gruiz and I. T. Burke, “Gypsum Addition to Soils Contaminated by RM: Implications for Aluminium, Arsenic, Molybdenum and Vanadium Solubility”, *Environ. Geochem. Health,* **35** 643–656 (2013).
20. M. Rékási , V. Feigl , N. Uzinger , K. Gruiz , A. Makó and A. Anton, “Effects of Leaching from Alkaline RM on Soil Biota: Modelling the Conditions After the Hungarian Red Mud Disaster”, *Chem. Ecol.,* **29** (8) (2013).
21. R. Feng, W. Qiu, F. Lian, Z. Yu, Y. Yang and Z. Song, “Field Evaluation of in Situ Remediation of Cd-Contaminated Soil Using Four Additives, Two Foliar Fertilisers and Two Varieties of Pakchoi”, *J. Environ. Manag*., **124** 17-24 (2013).
22. G. Garau, M. Silvetti, P. Castaldi, E. Mele, P. Deiana and S. Deiana, “Stabilising Metal(Loid)S in Soil with Iron and Aluminium-Based Products: Microbial, Biochemical and Plant Growth Impact”, *J. Environ. Manag.,* **139** 146-153 (2014).
23. M. Silvetti, P. Castaldi, P.E. Holm, S. Deiana and E. Lombi, “Leachability, Bioaccessibility and Plant Availability of Trace Elements in Contaminated Soils Treated with Industrial By-Products and Subjected to Oxidative/Reductive Conditions”, *Geoderma,* **214–215** 204–212 (2014).

24. B. Li, J. Yang, D. Wei, S. Chen, J. Li and Y. Ma, “Field Evidence of Cadmium Phytoavailability Decreased Effectively by Rape Straw and/or Red Mud with Zinc Sulphate in a Cd-Contaminated Calcareous Soil”, *PLoS ONE,* **9** (10) e109967 (2014).
25. C. L. Lockwood, R. J. G. Mortimer, D. I. Stewart, W. M. Mayes, C. L. Peacock, D. A. Polya, P. R. Lythgoe, A. P. Lehoux, K. Gruiz and I. T. Burke, “Mobilisation of Arsenic from Bauxite Residue (RM) Affected Soils: Effect of Ph and Redox Conditions”, *Appl. Geochem.,* **51** 268–277 (2014).
26. C. L. Lockwood, D. I. Stewart, R. J. G. Mortimer, W. M. Mayes, A. P. Jarvis, K. Gruiz and I. T. Burke, “Leaching of Copper and Nickel in Soil-Water Systems Contaminated by Bauxite Residue (Red Mud) from Ajka, Hungary: The Importance of Soil Organic Matter”, *Environ. Sci. Pollut. Res*., DOI 10.1007/s11356-015-4282-4 (2015).
27. J. Yang, L. Wang, J. Li, D. Wei, S. Chen, Q. Guo and Y. Ma, “Effects of Rape Straw and RM on Extractability and Bioavailability of Cadmium in a Calcareous Soil”, *Front. Environ. Sci. Eng*., **9** (3) 419-428 (2015).
28. J. Y Ahn, S. H. Kang, K. Y. Hwang, H. S. Kim, J. G. Kim, H. Song and I. Hwang, “Evaluation of Phosphate Fertilizers and RM in Reducing Plant Availability of Cd, Pb, And Zn in Mine Tailings”, *Environ. Earth Sci.,* doi 10.1007/s12665-015-4286-x (2015).