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1. Introduction

Manganese oxides are important natural oxidising agents that can sorb metals, facilitate the breakdown of organic contaminants and potentially enhance humification of natural organic matter. However, the competitive sorption effects when both metals and organics are present at the Mn oxide surface are not yet well understood. This study aims to characterise the sorption and oxidation processes in systems containing Mn oxide, metals (Pb or As) and organic contaminants (anthracene).

2. Background

Brownfield land remediation

Low-value brownfield sites are an under-used resource in the UK, and would benefit greatly from the development of low-cost, sustainable remediation solutions.



Figure 1: Brownfield site in Newcastle upon Tyne, UK.

Sustainable remediation

Mn oxides are available as industrial by-products from the water treatment industry (Mn-oxide coated sand) and the Mn mining industry (Mn-rich tailings). The overall objective of this study is to assess the ability of these waste Mn oxides to remediate 'cocktail' contaminated sites.



Figure 2: Tailings dump at Hotazel, South Africa.

3. Soil experiments

•9- month lysimeter trials are currently being undertaken to test the effectiveness of Mn oxide sand as an soil amendment product;

•Contaminated soil was collected from a UK site that had hosted both tar and leadworks.

•Four different soil types are used:

- High metals (Pb, Zn, As);
- High PAHs (anthracene);
- High metals + high PAH combined;
- Clean soil from neighbouring location.

•Leachate and CO₂ are sampled throughout, and soil is analysed at the start and end of the trials;

•Bioaccessibility testing (British Geological Survey BARGE UBM method) indicates that As and Pb bioaccessibility are significantly lower following Mn oxide treatment (Table 1).

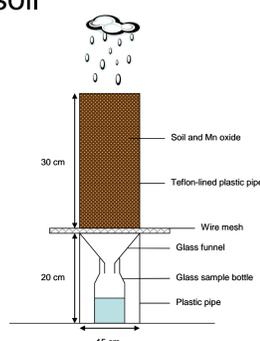


Figure 3: Lysimeter design.

Sample (high metals soil)	Arsenic		Lead	
	Bioaccessible fraction (%)	Bioaccessible fraction (%)	Bioaccessible fraction (%)	Bioaccessible fraction (%)
No Mn oxide- A	27.3		46.9	
No Mn oxide- B	26.6		38.9	
No Mn oxide- C	27.6		45.4	
10% Mn oxide- A	20.8		37.1	
10% Mn oxide- B	20.9		39	
10% Mn oxide- C	21		33.5	

Table 1: Bioaccessibility results for lysimeter trial 1, high metals soil.

4. Pb and anthracene adsorption experiments

Approach

- Batch sorption experiments are undertaken in order to characterise the Pb and anthracene sorption mechanisms;
- Experimental systems include Mn oxide (1 gL⁻¹), Pb (10ppm) and anthracene (0.75 mgL⁻¹), and are equilibrated for 8 hrs;
- Pb is analysed by AAS, and anthracene by HPLC.

Mn oxides

- The 'waste' Mn oxides are highly heterogeneous, and the Mn oxide sand also contains significant quantities of organic matter (Figure 4);
- Parallel experiments are undertaken using synthetic Mn oxides to facilitate characterisation of the reaction mechanisms.

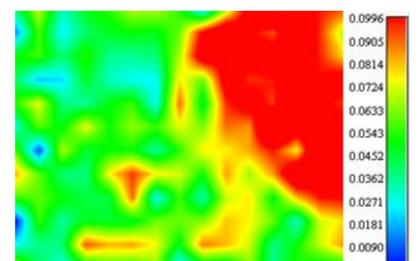


Figure 4: Reflectance micro-FTIR spectroscopy for the study of Mn oxide sand. False-colour image showing the location of molecules with absorption bands intrinsic of stretching C-H (3000-2800 cm⁻¹). Relative absorbance scale (a.u.) for the vC-H peaks is shown on the right.

Results

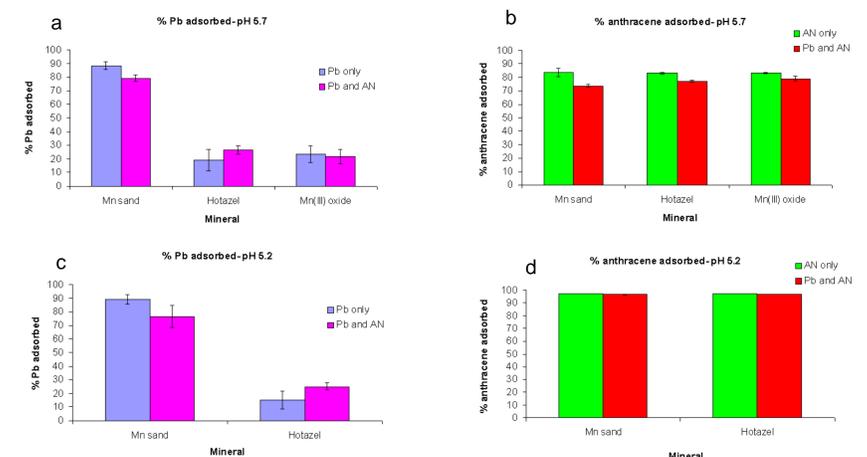


Figure 5: Adsorption experiment results: (a) Pb adsorption, pH 5.7; (b) anthracene adsorption, pH 5.7; (c) Pb adsorption, pH 5.2; (d) anthracene adsorption, pH 5.2.

- Initial results show that the presence of anthracene leads to reduced Pb adsorption to the Mn oxide sand, but increased Pb adsorption to the Hotazel tailings;
- The percentage of anthracene adsorbed decreases slightly when Pb is present at pH 5.7, but does not change significantly at pH 5.2;
- Results indicate that adsorption mechanisms may differ between the Mn oxide sand and the Hotazel tailings;
- The organic matter present in the Mn oxide sand may play an important role in Pb and anthracene adsorption;
- Spectroscopic (EXAFS) analysis will investigate whether sorption is primarily to the organic or mineral fraction of the Mn oxide sand;
- Further work will include study of As sorption and oxidation in the presence of anthracene;
- Findings could have implications for adsorption behaviour to biogenic Mn oxide minerals in the environment.

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