School of Civil Engineering

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Hexavalent chromium reduction by organic matter

Yorkshire contaminated land forum meeting
Sheffield, 27th February

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The Problem

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- Chromium is widely used in industry.
- Ore processing and industrial use sometimes lead to groundwater contamination.
- Natural processes also lead to Cr(VI) in groundwater
- Cr(VI) contamination is problematic because:
  - Strong oxidizing agent
  - Extremely toxic and potentially carcinogenic
  - Aqueous Cr(VI) species are very mobile in subsurface environments
- Chromium ore processing produces a very alkaline residue. This can produce an alkaline Cr(VI) plume in groundwater which is very difficult to treat.

Chromium ore processing residue, Romania, http://www.srk.com/en/ww-waste-rehabilitation.

Aim

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To investigate the suitability of humic acids extracted from different origins for use to treat chromate contaminated sites over a wide range of pH values.

- ❑ Aldrich humic acid (Coal-derived humic acid).
- ❑ Peat humic acid.
- ❑ Soil humic acid
- ❑ Sludge phyto conditioning residue humic acid (SPCR-HA).

Methodology

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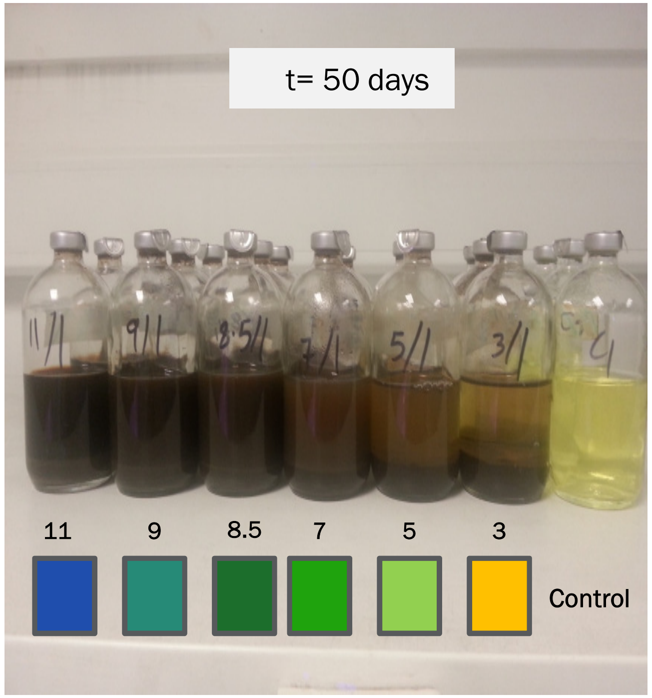
- Humic acids were alkali-extracted from the parent materials and acid precipitated.
- Humic acids were characterised for the main spectroscopic and chemical properties.
- Cr(VI) reduction by the humic acids was tested by preparing suspensions at a wide range of pHs (3-11).
- Aqueous Cr(VI) concentration and pH values were measured periodically over time.
- After equilibrium was reached, the remaining suspensions were separated into aqueous phase and solid phase for total Cr analyses.



Humic acids characteristics

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Test	rAHA	PHA	SHA	SPCR-HA
H/C	1.05	1.11	1.30	1.18
O/C	0.41	0.39	0.56	0.53
N/C	0.03	0.04	0.11	0.08
E_4/E_6	4.9±0.0	4.3±0.2	10.3±0.5	5.4±0.1
Total acidity (meq/g) $Ba(OH)_2$ method	6.4 ± 0.4	6.7 ± 0.1	6.6 ±0.3	6.5±0.2
Carboxyl acidity (meq/g) Ca-acetate method	3.1 ± 0.1	2.6 ± 0.0	2.6 ±0.1	2.9 ±0.2
Phenolic acidity (meq/g)	3.3	4.1	4.0	3.6

Humic acids characteristics

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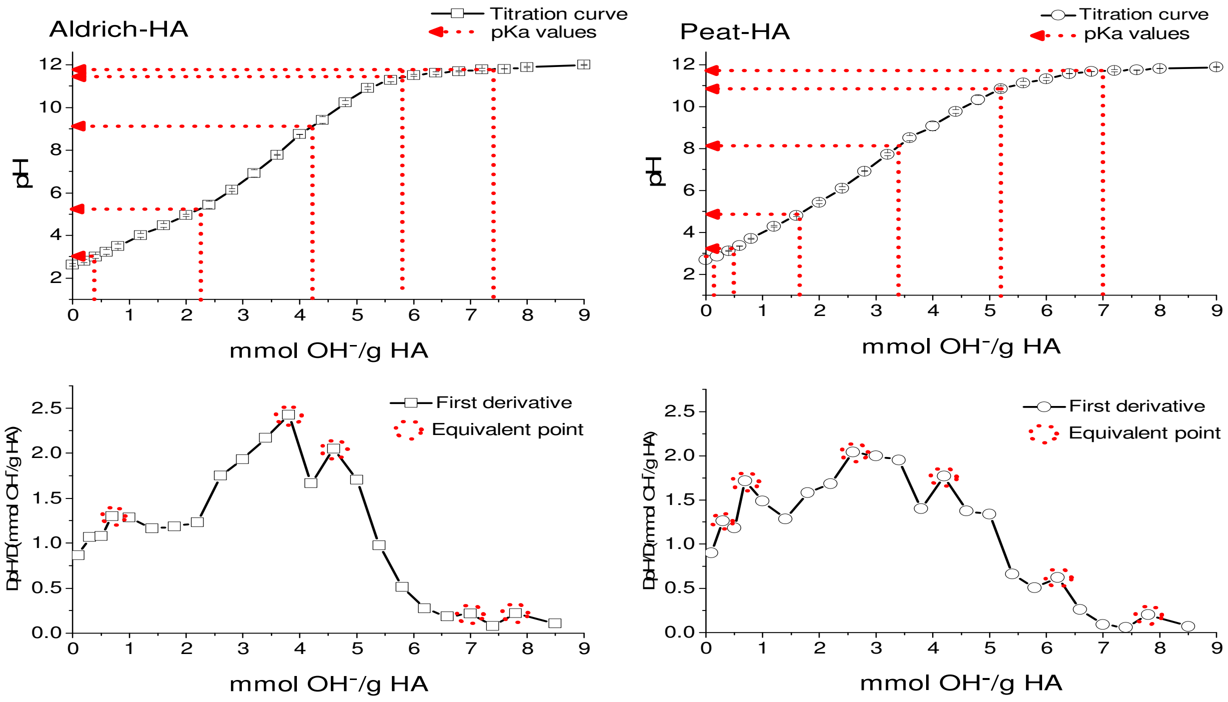
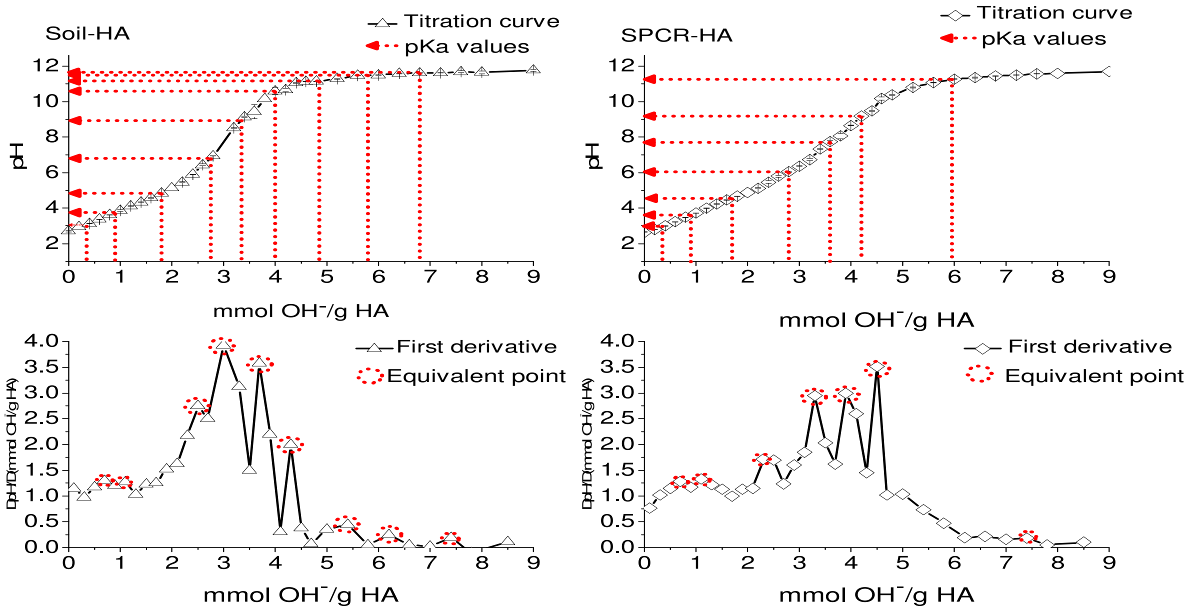


Humic acids characteristics



Cr(VI) Removal with Time

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Reactivity at Different pH values

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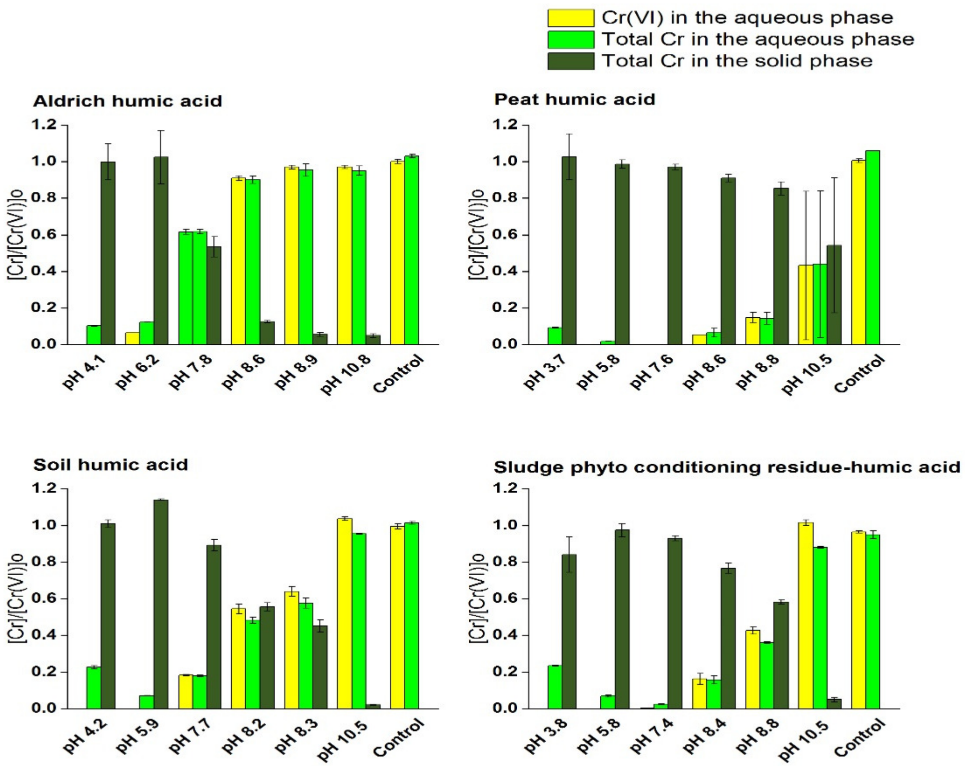

Cr Distribution after ~50 days

- In acidic conditions, most Cr becomes associated with the solid phase, although aqueous Cr(III) is detected at low pH values.
- In neutral and alkaline conditions, peat and sludge phyto conditioning humic acids show a higher percentages of Cr associated to the solid phase comparing to Aldrich and soil humic acids.
- Under hyper alkaline condition, only PHA shows a significant reactivity.

Pseudo First Order Rate Constants

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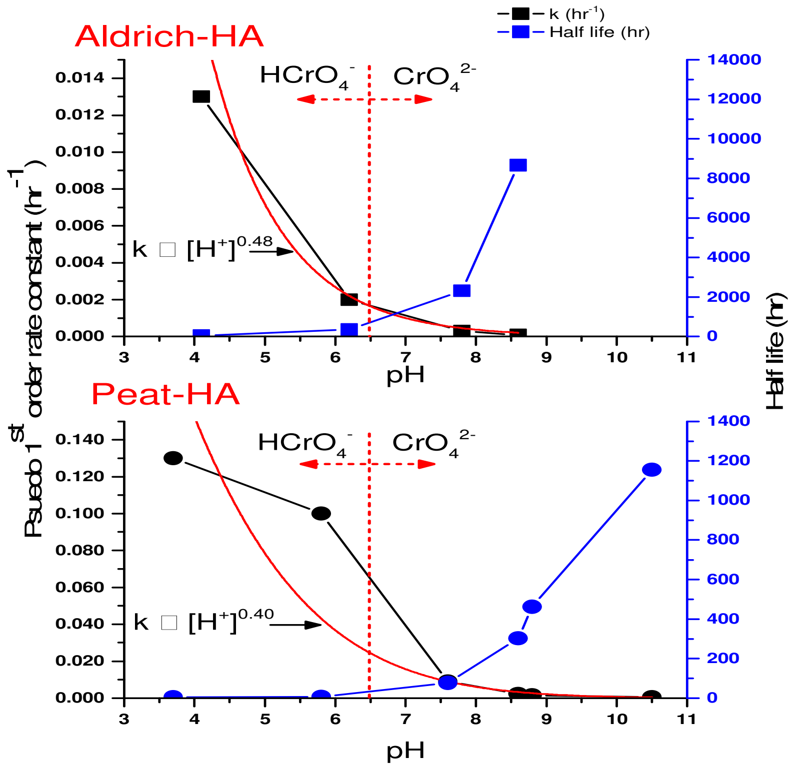

- The reductions rates can be described using pseudo-first-order model with respect to Cr(VI).
- There is an inverse relationship between the rate constants and the pH values.

Comparison between the humic Acids under investigation

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Initial pH	K (day^{-1}) SPCR-HA (Sludge phyto cond i–tioning reside-HA	K (day^{-1}) Soil HA	K (day^{-1}) Peat-HA	K (day^{-1}) Coal-derived H A
3	2.5	0.85	3.1	0.3
7	$1.4*10^{-1}$	$3.2*10^{-2}$	$2.2*10^{-1}$	$7.2 *10^{-3}$
9	$1.2*10^{-2}$	$9*10^{-3}$	$3.6*10^{-2}$	Not determined

Age of humic substances

PHA

SPCR-HA

SHA

AHA

- The rate constant values of humic acids derived from various origins under similar reaction conditions show the environmental significance of humic acids derived from secondary organic matter as peat and SPCR.

Humic Acids Extracted from Lignite and Peat Soil

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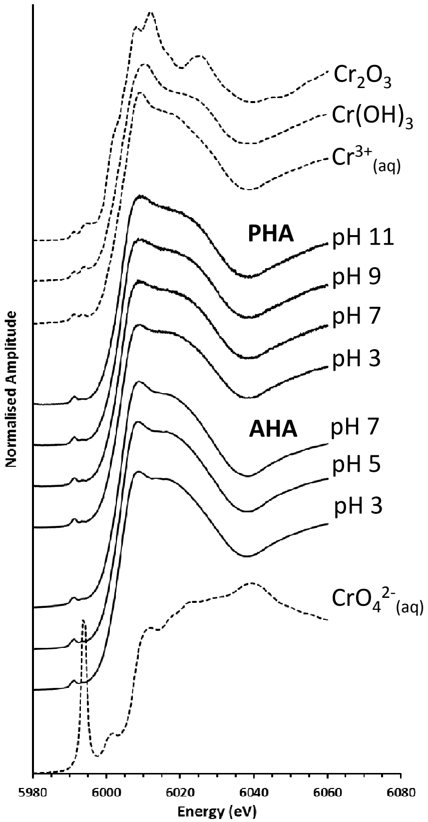
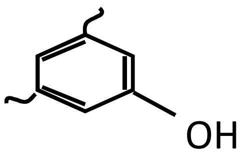
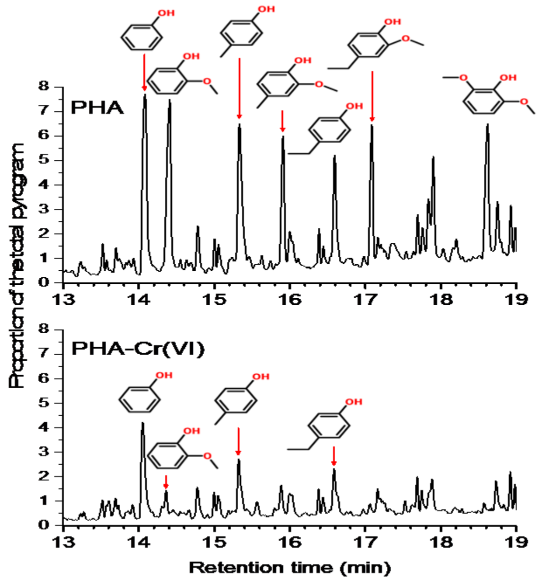


- Aldrich and peat humic acids samples reacted with Cr(VI) at various pH values were analysed by x-ray absorption spectroscopy (XAS).
- Cr K-edge XANES spectra indicate that Cr associated with the humic acid has been reduced to the Cr(III) oxidation state.
- ^{13}C-NMR spectroscopy indicates that reduction of Cr(VI) to Cr(III) results in loss of humic acid aromaticity.
- Our current working hypothesis is that phenolic groups are the reactive site





Probable Reaction Mechanism

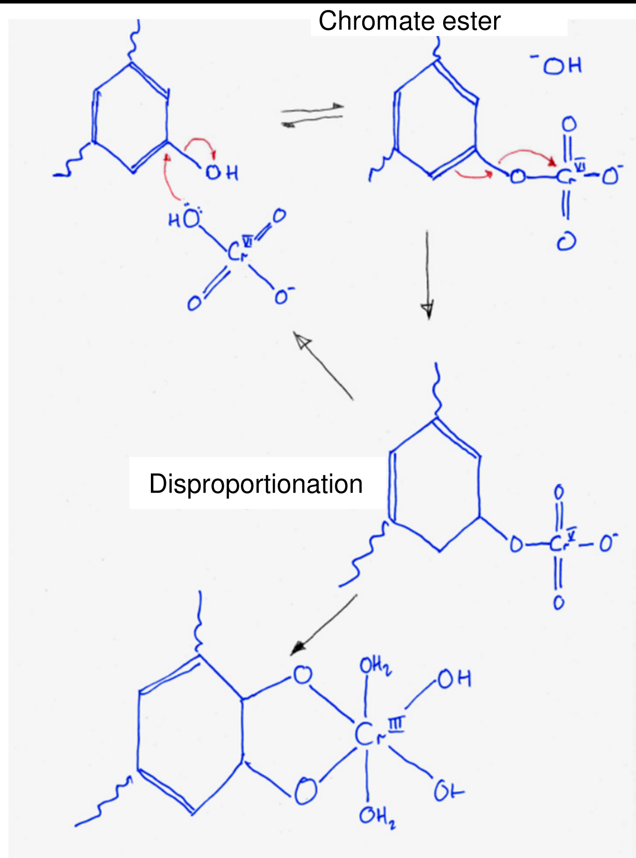
Cr(VI) is reduced by hydroxyl moieties in a two stage reaction:

- ❑ Instantaneous chromate ester formation:

  Bichromate ion attacks the electrophilic carbon centre forming the chromate ester with loss of OH^-.

- ❑ Electron transfer decomposition step (Redox step).

  A chromate - ester decomposes with the transfer of one or two electrons (producing Cr(V) or Cr(IV) intermediates).



Conclusions

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- The rate constant for Cr(VI) reduction by all humic acids decreases with pH increasing.
- Humic acid extracted from the high organic matter secondary materials, such as peat and SPCR can reduce Cr(VI) over a wide range of pH values
- Thus peat and SPCR humic acids may be suitable as a reactive material for treating Cr(VI) contaminated groundwater.
- Residue from chromium ore processing has very high pH, which means that groundwater thus contaminated must be buffered downwards before it is treatable by peat or SPCR.

Suha Aldmour would like to thank Mutah University for her scholarship

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