

MINE WATER TREATMENT USING HIGH DENSITY SLUDGE: a computational and experimental approach

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Introduction

Water pollution from gold mines is mainly associated with the leaching of trace metals from mine wastes. This has a bearing on the composition of water in abandoned mine shafts and voids. As part of the intention to repurpose high density sludge (HDS), it was necessary to assess the capability of hydrous ferric oxide (Hfo, represented chemically as $\equiv\text{FeOH}$) to adsorb trace elements from acid mine drainage (AMD) that is found in such mine shafts and voids. For this purpose, the PHREEQC geochemical modelling code was used for experimental design and to build a platform to understand the interaction between AMD and HDS. The approach involved using surface complexation models based on the Dzombak and Morel assumption of two surface sites (strong and weak sites) having densities of 0.005 and 0.2 (mol Fe)⁻¹.

Aim

To repurpose the high density sludge (HDS) produced in AMD treatment plants by using it for in situ conditioning and pre-treatment of AMD

Methods

Geochemical modelling approach

- PHREEQC interactive code was used and the Minteq.v4.dat database was selected in all simulations. Different pH values, a varying mass of Hfo and different Hfo surface areas (strong and weak sites) were considered to assess the optimal conditions of adsorption of trace metals.
- Generalised surface complexation with calculated log k value of individual potentially toxic trace metals were assessed to look at the effect of pH to find out if adsorption of potentially toxic trace metals onto Hfo is through physisorption (adsorption) or surface complexation (chemisorption).

```
TITLE RAW AMD
SOLUTION 1
  temp      25
  pH        5.03
  pe        4
  redox     pe
  units     mg/l
  density   1
  Al        23.7
  Alkalinity 0
  Ca        509
  Co        5.1
  Cu        7.6
  Fe       1888
  K         2.1
  Li         1.1
  Mg        301
  Mn        67.8
  Na        186
  Ni        19.7
  Pb         6.9
  S(6)      7434
  Zn         8.8
  -water   1 # kg
```

```
SURFACE_MASTER_SPECIES
Hfo_s  Hfo_sOH
Hfo_w  Hfo_wOH
```

```
SURFACE_SPECIES
Hfo_sOH + Pb+2 = Hfo_sOPb+ + H+
log_k  4.65

Hfo_sOH + Cu+2 = Hfo_sOCu+ + H+
log_k  2.89

Hfo_sOH + Zn+2 = Hfo_sOZn+ + H+
log_k  0.99

Hfo_sOH + Ni+2 = Hfo_sONi+ + H+
log_k  0.37

Hfo_sOH + Co+2 = Hfo_sOCo+ + H+
log_k  0.41
```

```
SURFACE 1 #HFO surface
-equilibrate with solution 1
Hfo_s .0611400000
Hfo_w .0061140000
-no_edl
```

```
SELECTED_OUTPUT 1
-file
-high precision
-reset
-solution
-inverse_modeling
-active
-user_punch
```

```
selected.xls
true
false
true
false
true
true
```

END

PHREEQC input script for trace metals adsorption onto Hfo

Experimental Approach

- Batch adsorption studies were conducted in triplicate to determine the effect of HDS dosage on the adsorption of trace metals. Different masses (10, 20, 50, 100 and 500 mg) of HDS were contacted with 10 ml of raw AMD at room temperature.
- The effects of varying pH of the solution, adsorbent dosage, concentration, and contact time were studied. The volume of the solution (10 ml) was kept constant throughout.
- The centrifuge tubes were shaken using an elliptical benchtop shaker (Labcon, South Africa) at a constant rate of 150 rpm, allowing enough time for adsorption and equilibrium to be reached. The filtrates were analysed using ICP-OES.



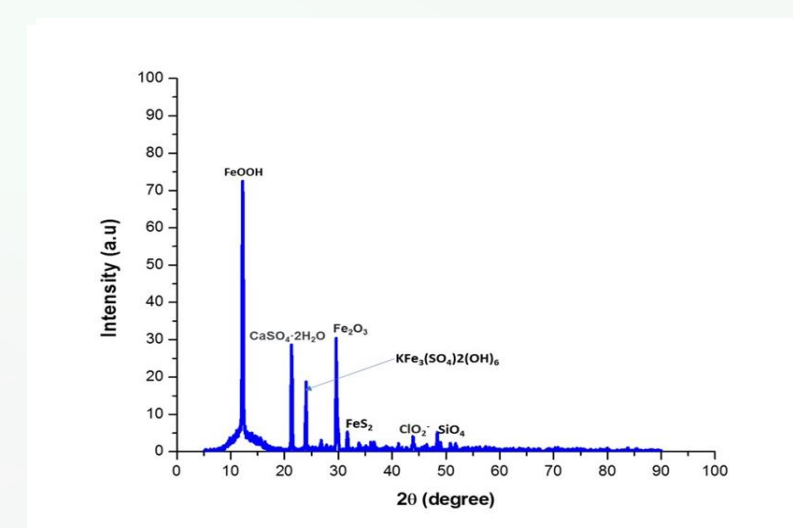
Sludge drying
FTIR, XRF, SEM and PXRD:
functional groups, elemental
composition, surface morphology
and mineralogy respectively.

Microwave digestion
ICP-OES: Elemental composition

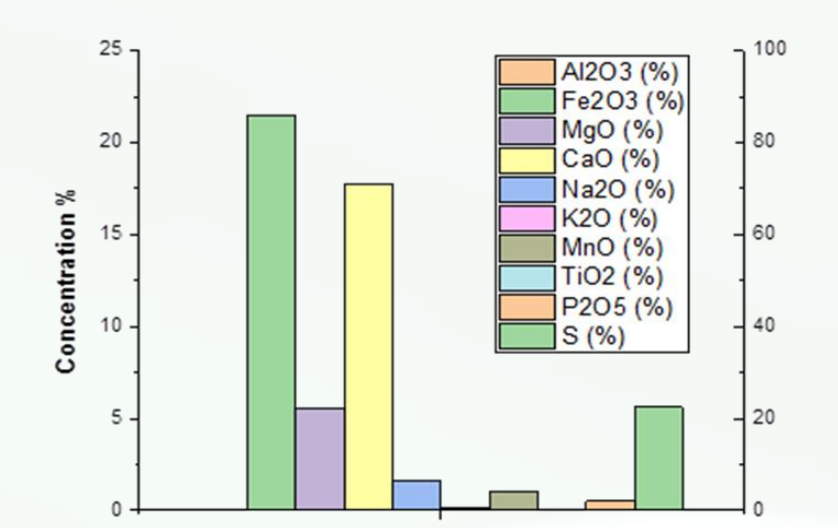
Batch Experiments :
Mass: 10, 20, 50, 100, and 500mg.
pH: 2.5, 3.5, 4.5, 5.5, 6.5, 7.5, 8.5,
9.5 and 10.5.
Contact time: 1, 5, 10, 30, 60,
180, 360, 540, 1080, and 1440
min.
Initial conc.: 1,2,3,4 and 5 mg l⁻¹



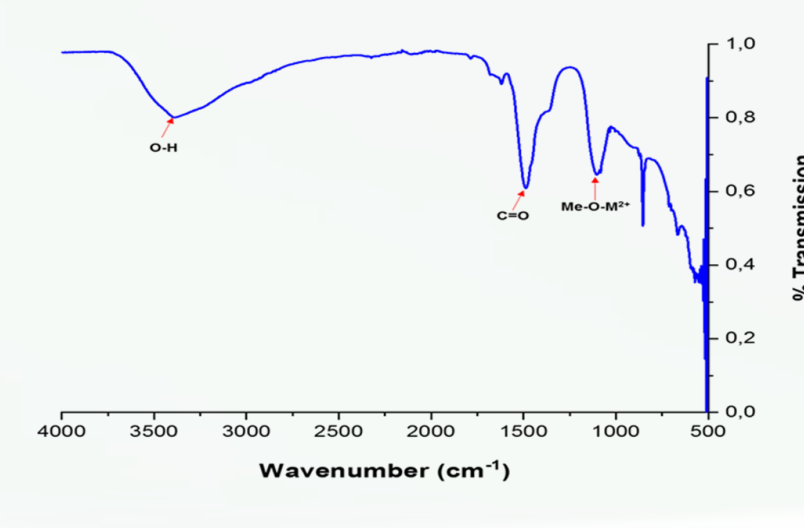
Results



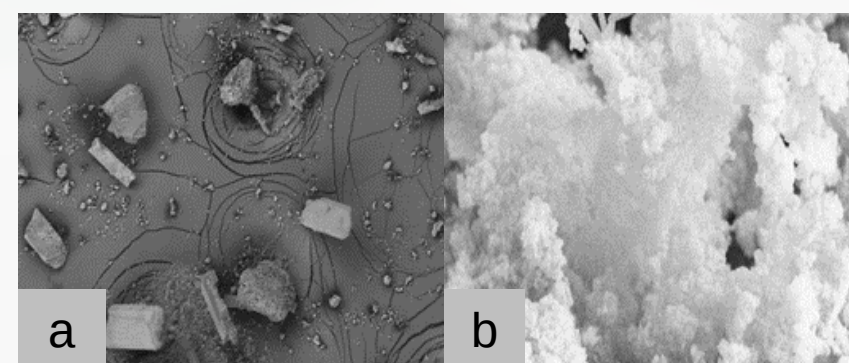
PXRD analysis to determine the mineral composition of HDS



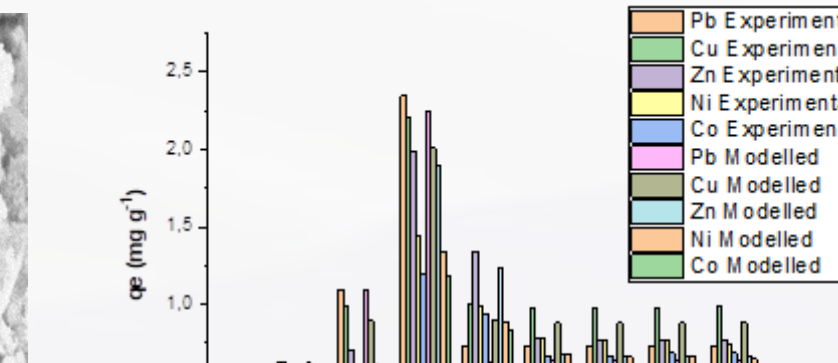
XRF analysis to determine the elemental composition of HDS



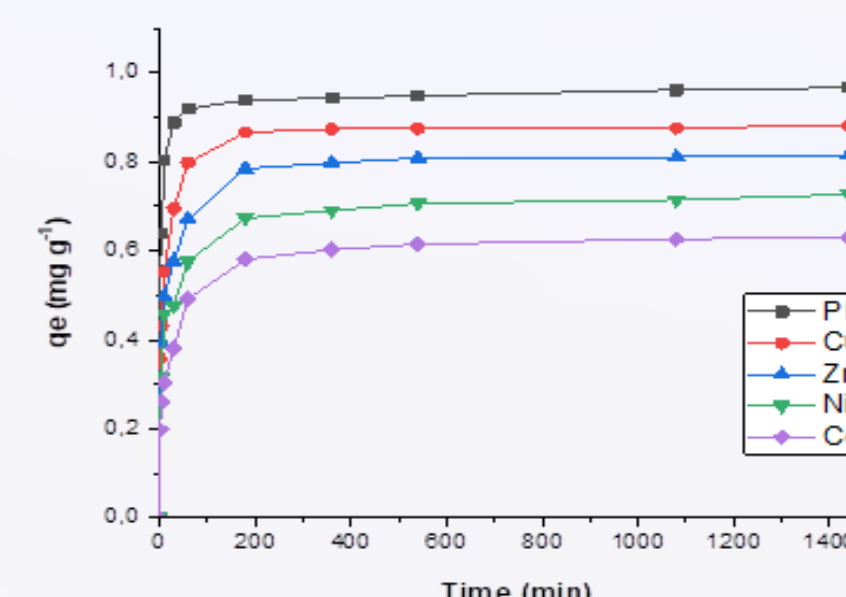
FTIR analysis to determine the functional groups in HDS matrix



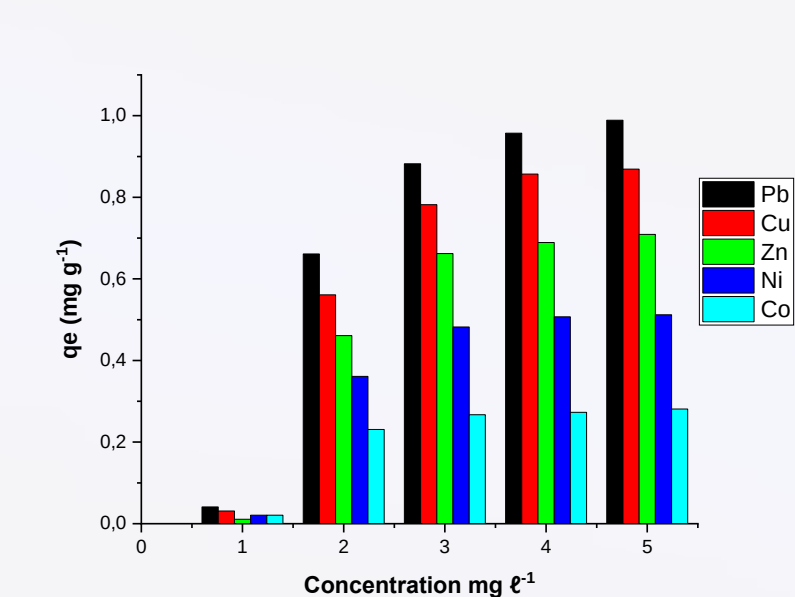
SEM analysis to determine the surface morphology (a) HDS before adsorption (b) HDS after adsorption



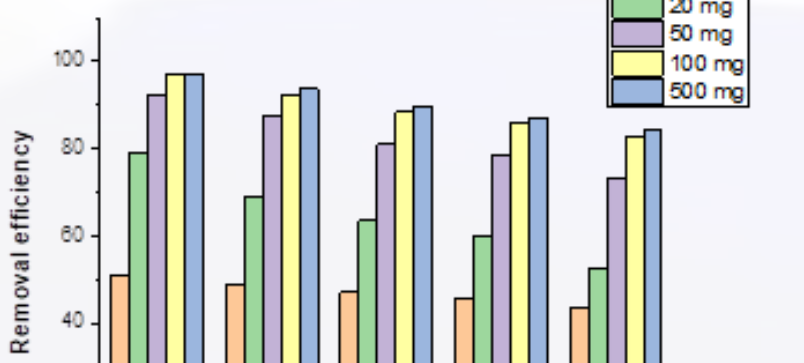
Generalised surface complexation for metals sorption with PHREEQC coupled with PEST



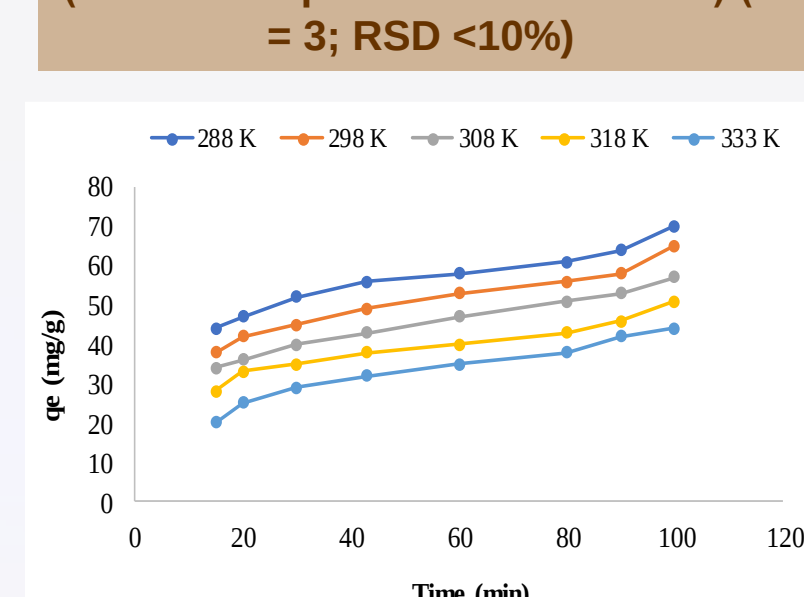
Effect of contact time on the adsorption of trace metals onto HDS for a pH = 5.5; metal concentration of 5 mg l⁻¹ (solid:liquid ratio of 1 g:10 ml) (n = 3; RSD <10%).



Effect of concentration on adsorption of trace metals onto HDS for a pH = 5.5; (solid:liquid ratio of 1 g:10 ml); for 24 h (n = 3; RSD <10%).



Effect of mass on the adsorption of trace metals onto HDS for a pH = 5.5; metal concentration of 5 mg l⁻¹ (constant liquid volume of 10 ml) (n = 3; RSD <10%)



Effect of temperature on the adsorption of trace metals onto HDS

Isotherms	Metal ion	Estimated isotherms parameters		
		q _{max} (mg g ⁻¹)	K _L (L mg ⁻¹)	R ²
Langmuir	Pb	0.555	0.0624	0.997
	Cu	0.347	0.0613	0.998
	Zn	0.278	0.0312	0.996
	Ni	0.205	0.0210	0.999
	Co	0.144	0.0123	0.997
Freundlich	Metal ion	n	K _r (mg g ⁻¹) (mol L ⁻¹) ^{1/n}	R ²
	Pb	2.340	3.457	0.991
	Cu	2.234	1.016	0.995
	Zn	1.931	2.706	0.995
	Ni	1.750	1.231	0.997
Dubinin-Radushkevich	Metal ion	X _m (mol g ⁻¹)	E _i (kJ mol ⁻¹)	R ²
	Pb	4.89	22.36	0.988
	Cu	3.92	11.18	0.993
	Zn	3.64	10.00	0.994
	Ni	3.45	7.905	0.996
Temkin	Metal ion	a _r (L kg ⁻¹)	b _r (kJ mol ⁻¹)	R ²
	Pb	4.39	21.36	0.968
	Cu	3.52	12.13	0.943
	Zn	3.25	11.55	0.894
	Ni	3.35	8.815	0.796
	Co	3.41	7.344	0.934

Isotherms parameters of adsorption of trace metals onto HDS (pH = 5.5; solid:liquid ratio of 1 g:10 ml; shaking for 24 h; temp = 25 °C) (n = 3; RSD <10%)

Kinetics	Metal ion	Estimated kinetic parameters		
		Q _{eq} (mg g ⁻¹)	K _i (min ⁻¹)	Q _{cal} (mg g ⁻¹)
Pseudo first-order	Pb	0.519	0.003	0.802
	Cu	0.798	0.004	0.695
	Zn	0.672	0.004	0.564
	Ni	0.576	0.003	0.373
	Co	0.492	0.005	0.387
Pseudo second-order	Metal ion	Q _{eq} (mg g ⁻¹)	K _i (mg g ⁻¹ min)	R ²
	Pb	0.902	0.102	0.999
	Cu	0.795	0.302	0.999
	Zn	0.667	0.345	0.999
	Ni	0.573	0.321	0.999
Elovich	Metal ion	a (kg mol ⁻¹ min ⁻¹)	b (kg mol ⁻¹ min ⁻¹)	R ²
	Pb	0.003	0.802	0.851
	Cu	0.004	0.695	0.823
	Zn	0.004	0.564	0.872
	Ni	0.003	0.373	0.858
Intraparticle Diffusion model	Metal ion	Ip	Kp	R ²
	Pb	0.003	0.802	0.951
	Cu	0.004	0.695	0.723
	Zn	0.004	0.564	0.872
	Ni	0.003	0.373	0.658
Film diffusion model	Metal ion	Γ _∞	K _f	R ²
	Pb	0.003	0.802	0.751
	Cu	0.004	0.695	0.823
	Zn	0.004	0.564	0.972
	Ni	0.003	0.373	0.858

Kinetic parameters of trace metals removal onto HDS (pH = 5.5; concentration = 5 mg l⁻¹; solid:liquid ratio of 1 g:10 ml; temp = 25 °C) (n = 3; RSD <10%)

Conclusions

- HDS was successfully characterised and the adsorption capacity of Pb and Cu were observed to be higher.
- The selectivity followed this order: Pb>Cu>Zn>Ni>Co for both strong sites (Hfo_sOH) and weak sites (Hfo_wOH).
- An increase in adsorbent amount and concentration of trace metals resulted in increased adsorption.
- An increase in adsorbent amount and concentration of metals resulted in increased adsorption. pH was found to result in the peaking of adsorption at 5.5.
- The Langmuir isotherm best fitted the adsorption data while the pseudo second-order model, implying that the mechanism was chemisorptive, best described the kinetics of adsorption.
- Overall, the trend in adsorption onto HDS resembles that observed for Hfo. However, the effect of components such as the polyacrylate polymer within the HDS structure was also studied.
- Generalised surface complexation model was useful in achieving this based on the results obtained. The findings showed that simulations could be successfully used where limited experimental data was available

References

- Parkhurst D.L., and Appelo C.A.J. (2013). Description of Input and Examples for PHREEQC Version 3 – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geol. Surv. Tech. Methods, 6, 1-497.
- Mosai, A.K., Bakatula, E.N., and Tutu, H. (2017). Adsorption of cadmium, copper, and chromium by an agricultural soil impacted by mining activities, Water Air Soil Pollut., 228, 287.