

Application of silica polyamine composites for the removal of heavy metals from acid mine drainage

H. Tutu¹, S. Dlamini¹, E. Bakatula¹, E. Rosenberg², V. Kailasam² and E.M. Cukrowska¹

¹School of Chemistry, University of the Witwatersrand, South Africa
²Dept of Chemistry, University of Montana, Missoula, USA



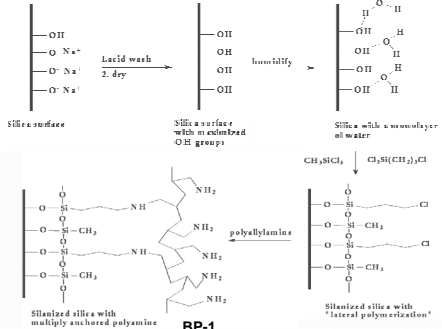
Presentation Outline

- Introduction
 - Treatment and remediation of AMD
 - Silica polyamine composites (BPAP)
- Methodology
- Results and Discussion
- Conclusion
- Outlook
- Acknowledgements

Treatment and remediation strategies

- Neutralization by lime/limestone
- Phytoremediation – phytoextraction, phytostabilisation, phytovolatilisation
- Bioremediation e.g fungal and algal biomass, bacteria
- Zeolite, activated silica, clay, activated carbon, nanomaterials
- Wood shavings, chitosan, shells, sewage sludge, peat, tea bags
- Fly ash, cement kiln dust, recycled concrete
- Ion exchange (chelator) resins
- **Amorphous silica polyamines**

Silica Polyamine Composites



Modifiers for composites

Amino-acetate (WP-2)

NC(=O)COP(=O)(O)O

Ethylenediaminetetraacetic acid (BPED)

CC(=O)N(CC(=O)O)CCN(CC(=O)O)CC(=O)O

Q quaternary amine (BPQA)

C[N+](C)(C)COP(=O)(O)O

Amino-phosphonate (BPAP)

NC(=O)COP(=O)(O)O

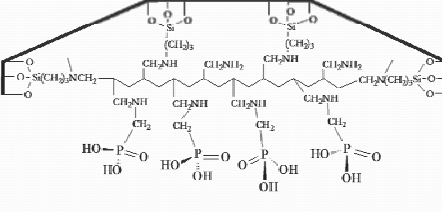
8-Hydroxyquinoline (WP4)

Oc1ccc2ncncc12

Formation of BPAP

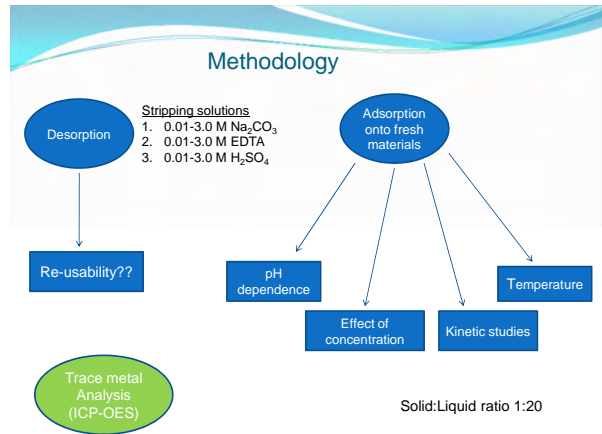
BP-1 + CH₂O + H₃PO₃

Mannich Reaction $\xrightarrow{H^+}$



Objectives of Project

- Main objective: Assess capability of SPCs in heavy metal removal from AMD and reusability (regeneration)
- Specific tasks:
 - Desorption of heavy metals
 - Previously used BPAP material
 - Different extractant solutions
 - Batch adsorption
 - Adsorption edges/isotherms
 - Assessing effects of pH, time and concentration on adsorption
 - Adsorption energies

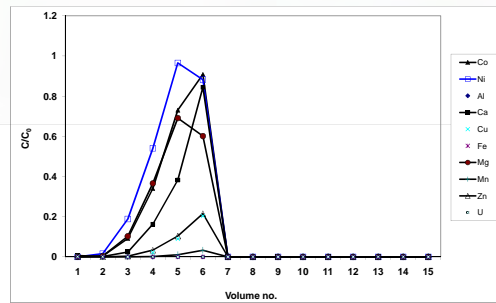


Results and Discussion

- Preceding work: involved adsorption of heavy metals in a synthetic AMD solution (pH = 2.5) onto BPAP through use of columns

Metal load in synthetic solution (mg l ⁻¹)									
Al	Ca	Co	Cu	Fe	Mg	Mn	Ni	Zn	U
383.6	340.1	17.45	12.33	66.05	144.8	57.2	52.01	130.2	70.23

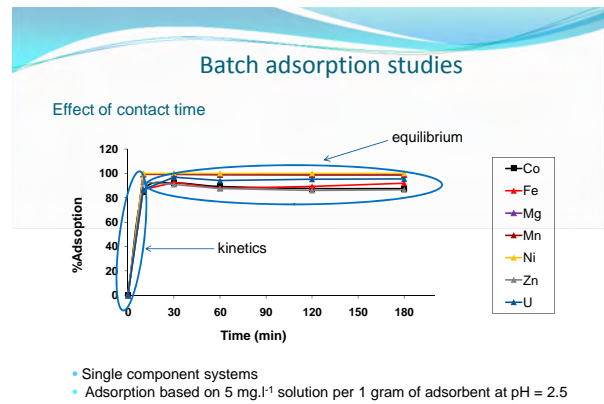
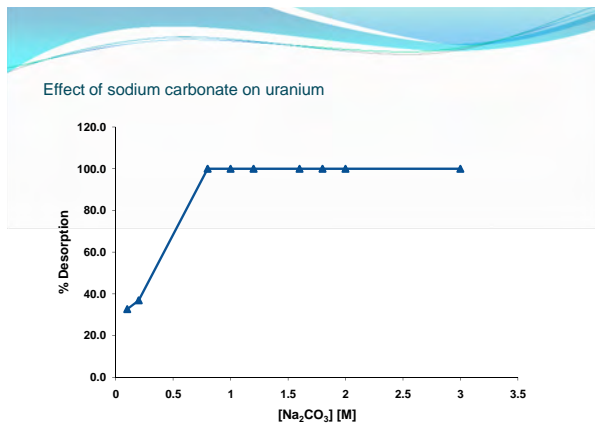
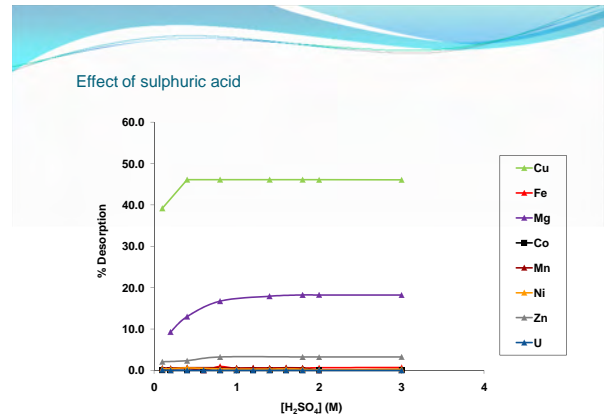
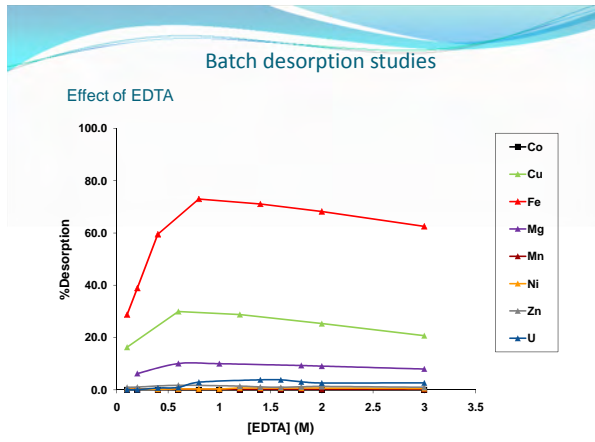
Breakthrough curves in column experiments



- Heavy metals adsorbed onto BPAP
- Stripping/desorption (using 0.1 M solutions)
 - NaF- only Al, Ca and a little Si removed
 - Na₃PO₄ – only Ca removed
 - EDTA- removed mainly Fe and a bit of Cu and U
 - H₂SO₄ - removed U, Fe, Ni, Zn, Co, Mg

Retained metals

Metals adsorbed on BPAP (mg/g)							
Co	Cu	Fe	Mg	Mn	Ni	Zn	U
7.86	4.13	54.56	63.76	24.44	27.34	73.68	62.09



Pseudo first order reaction

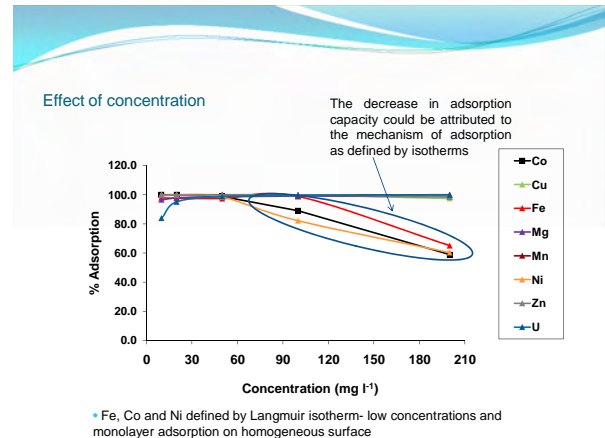
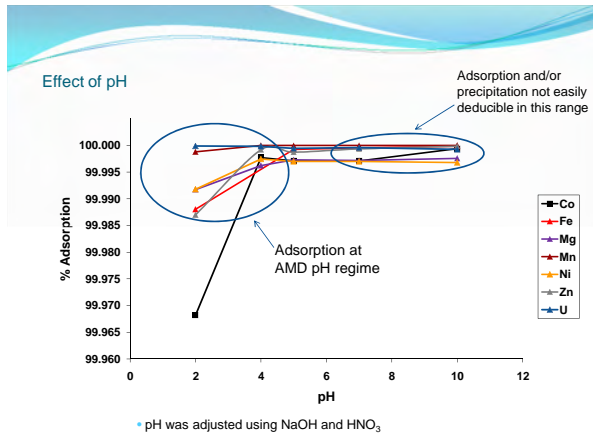
$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$

Pseudo second order reaction

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t$$

q_e – adsorption at equilibrium
 q_t – adsorption at time t

	Pseudo 1 st order		Pseudo 2 nd order	
	k	R ²	k	R ²
Co	0.145	0.691	0.105	0.970
Fe	0.220	0.541	0.141	0.984
Mg	1.903	0.401	0.862	0.754
Mn	1.182	0.0006	1.004	0.967
Ni	0.187	0.004	0.125	0.285
Zn	0.208	0.559	0.186	0.287
U	0.386	0.637	0.321	0.965



Effect of temperature

Metals	Ea kJ.mol ⁻¹	ΔG		Type of adsorption
		kJ.mol ⁻¹		
		18 °C	30 °C	
Co	14.78	-13.06	-1.5	Physisorption
Cu	-2.613	-13.06	-13.42	-
Fe	-90.51	-10.14	-22.44	-
Mg	5.104	-28.65	-27.95	Physisorption
Mn	19.792	-52.48	-49.79	Physisorption
Ni	0.757	-2.98	-2.87	Diffusion
Zn	16.04	-15.39	-37.19	Physisorption
U	54.61	-66.4	-58.97	Chemisorption

•Chemisorption: Ea= 40-800 kJ. mol⁻¹
 •Physisorption: Ea= 5-40 kJ.mol⁻¹

$\Delta G = -RT \ln K_d$
 $K_d = q_e/C_e$
 $\ln \frac{A_1}{A_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

- ### Conclusion
- SPCs have been shown to be effective in abstracting metals from AMD
 - Sodium carbonate has been shown to be effective for the desorption of uranium
 - The effect of concentration on adsorption is important in establishing the effective life time of the adsorbent material, e.g. in determining time for desorption
 - The thermodynamic results are important in establishing the surface-metal reactions

- ### Outlook
- Further work on kinetics
 - Exploring more desorption solutions – selective desorption
 - Application to the recovery of metal complexes (e.g. cyanide complexes) and metalloids (e.g. As)
 - Exploring cheaper sources of silica e.g. fly ash, zeolites, liquid glass

- ### Acknowledgements
- Friedel Sellschop Foundation
 - National Research Foundation
 - Carnegie Corporation