Application of silica polyamine composites for the removal of metals from mine wastewaters

H. Tutu[1], S. Dlamini[1], E. Bakatula[1], E. Rosenberg[2], V. Kailasam[2], E. M. Cukrowska[1]

[1]*University of the Witwatersrand, School of Chemistry, P. Bag X3, WITS 2050, Johannesburg, South Africa*
[2]*University of Montana, Department of Chemistry and Biology, Missoula, MT 59812, USA*

Abstract Batch sorption studies were conducted to assess the potential of a phosphonated silica polyamine composite to remove metals (Co, Cu, Fe, Mg, Mn, Ni, U and Zn) from mine waters. The metals showed a good Langmuir isotherm fit. Ni and Fe fitted both the Freundlich and Langmuir isotherms. The activation energies (Ea) of Co, Mg and Ni ranged between 5 and 40 kJ mol^{-1}, signifying physisorption while U showed a chemisorption type of reaction (with Ea > 50 kJ mol^{-1}). Cu and Fe on the other hand gave negative Ea values, indicating their preference to bind to low energy sites. Adsorption was almost constant over a wide pH regime and increased with time. It increased with concentration of the metals with the exception of Co, Fe and Ni which displayed about 40% drop at a concentration of 200 mgl^{-1}. Desorption experimental data gave poor results except for the desorption of uranium which showed 99.9 % desorption.

Key Words silica polyamine composites, acid mine drainage, sorption

Introduction

Mining of certain minerals, including gold, copper, and nickel, is associated with acid mine drainage (AMD) problems that cause long-term impairment to waterways and biodiversity (Akcil and Koldas 2005). There are several existing methods for the treatment of AMD, depending upon the volume of effluent; the type and concentration of contaminants present (Chander and Mohan 2001). These include chemical treatment (e.g. oxidation and neutralisation by lime); phytoremediation (i.e. phytoextraction, phytovolatilization and phytostabilization); ion exchange (e.g. use of activated carbon), polymers and biosorption among others. There are some drawbacks associated with most of these methods e.g. neutralisation leads to the formation of metal-containing solid waste that poses disposal problems; slow rates of biomass production in phytoremediation (Jiang et al. 2009); and polymer adsorbents tend to have low selectivity of the metals and often swell and shrink due to their elastic nature.

This study presents a silica-based polyamine composite, namely BPAP as an alternative material for the abstraction of metals from acidic mine leachates and wastewaters. Generally, silica-based composites have polyamine chelating ligands which are bound to the silica gel layer covalently. The polyamine chelating ligands can be further modified with metal selective functional groups, which is an advantage for these composites. These materials do not shrink or swell, can be used at high temperatures (up to 110°C), have improved stability with regard to radiolytic decomposition and have an elongated usable lifetime than their polymer counterparts (Rosenberg et al. 1999). The polar nature of their surfaces also makes for better mass-transfer kinetics in aqueous solutions. These surfaces can be further modified with metal selective functional groups in ways similar to their polymer counterparts.

Methods

A phosphonated silica polyamine composite (BPAP) was used as an adsorbent (Fig. 1). Reagents used for the sorption studies were of analytical reagent grade. The metal ion solutions (Co, Cu, Fe, Mg, Mn, Ni, U and Zn) were prepared by serial dilution of 1000 mg L^{-1}stock solutions. Adsorption was done using a solid:solution ratio of 1:50. The effect of pH on adsorption was assessed over the range 2 – 10 and the thermodynamic dependence was assessed at 18 and 30°C.

The effects of metal concentrations were assessed in the range 10 – 200 mg L^{-1} while contact time was in the range 0 – 180 min. Desorption of metals (regeneration of BPAP) was conducted using H_2SO_4, ethylene diamine tetraacetic acid (EDTA) and Na_2CO_3 of concentrations in the range 0.1 – 3.0 M. The metal ion concentrations were measured using a Genesis Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; Spectro, Kleve, Germany).

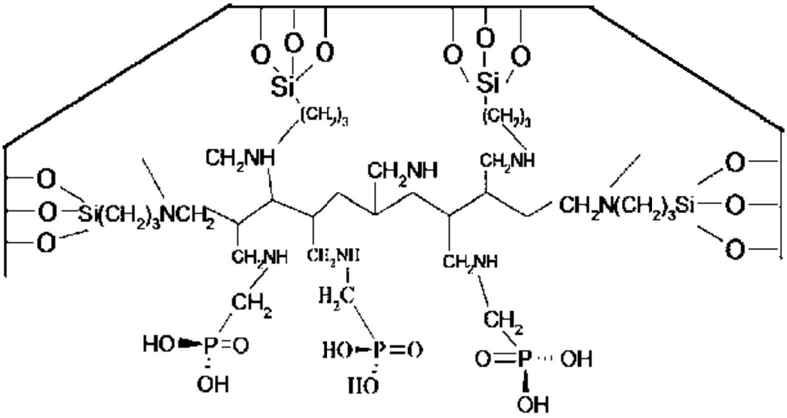

Figure 1 Structure of the BPAP silica polyamine composite

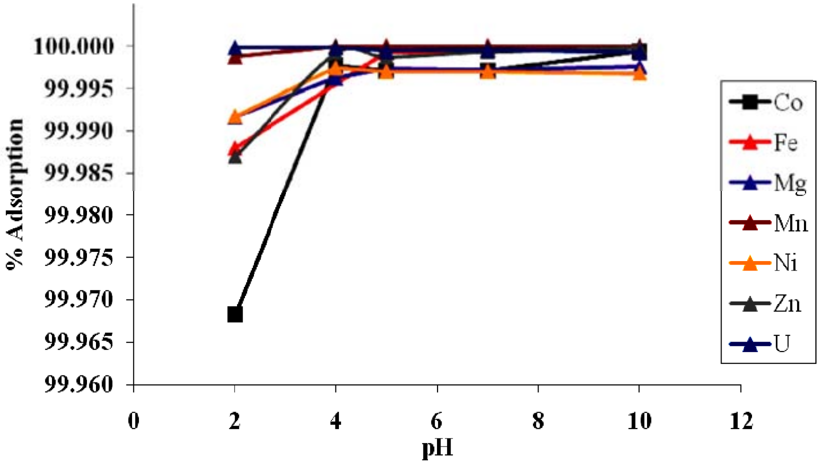

Figure 2 Metal ion adsorption dependence on pH

Results and Discussion

Effect of pH

The results for the effect of pH on metal adsorption are shown in Fig. 2. Adsorption was based on a solution containing 5 mg l^{-1} of each metal. Adsorption was performed for 2 hours.

The adsorption for all the metals was in the range 99.9 – 100%. The elevated adsorption at low pH regimes shows that this adsorbent is effective in the remediation of AMD.

Effect of time

The rates of reaction for the different times studied in this experiment are given in Table 1. The following formulae were used for the pseudo-first order and pseudo-second order reactions:

$$q_t = q_e(1 - 10^{-\frac{k_1 \cdot t}{2.303}}) \quad (1)$$

$$\ln k_2 = \ln A_0 - \frac{E_a}{RT} \quad (2)$$

Table 1 *Reaction rates for different times for metal ions adsorbing on BPAP*

Time (min)	Rate (mg l^{-1}.min)						
	Co	Fe	Mg	Mn	Ni	Zn	U
0	0	0	0	0	0	0	0
10	5.12	4.44	0.222	0.007	2.35	4.42	4.92
30	1.205	0.995	0.037	0.005	0.372	1.695	2.286
60	0.293	0.54	0.003	0.003	0.341	0.3	0.09
120	0.092	0.145	0.005	0.002	0.087	0.06	0.009
180	0.007	0.087	0.004	0.001	0.029	0.008	0.002

where: q_t is adsorption capacity at a particular time; q_e is equilibrium adsorption capacity; t is time and k_1 is the rate constant for the pseudo-first order; k_2 is the rate constant for the pseudo-second order; A_o is the initial concentration; E_a is the activation energy; R is the universal gas constant and T is the absolute temperature.

All the metals were observed to adsorb fast within 10 minutes (kinetic control), with a decrease beyond that time zone (equilibrium control). This is largely attributed to the availability of active reaction sites that depresses with time.

Effect of concentration

The results for the dependence of adsorption on metal ion concentration are presented in Fig. 3. During these experiments, pH was kept constant at 2.5. Cu, Mg, Mn, U and Zn showed a constant maximum adsorption as concentration of each metal increased from 10 mg L^{-1} to 200 mg l^{-1}. Co and Ni on the other hand showed a decrease in adsorption beyond 60 mg L^{-1} while Fe showed a decrease beyond 90 mg L^{-1}. The trend is correlated to the activation energies obtained. Ni had an Ea value of 0.76 kJ mol^{-1} (defining a diffusion mechanism) while Fe and Co had negative Ea values of -90.51 and -2.61 kJ mol^{-1}, respectively. The negative values depict preference for low energy sites during adsorption, which could have been exhausted at 60 mg L^{-1}. The rest of the other metals showed a physisorption type of adsorption while U showed a chemisorptions type with an Ea value of 54.61 kJ mol^{-1}.

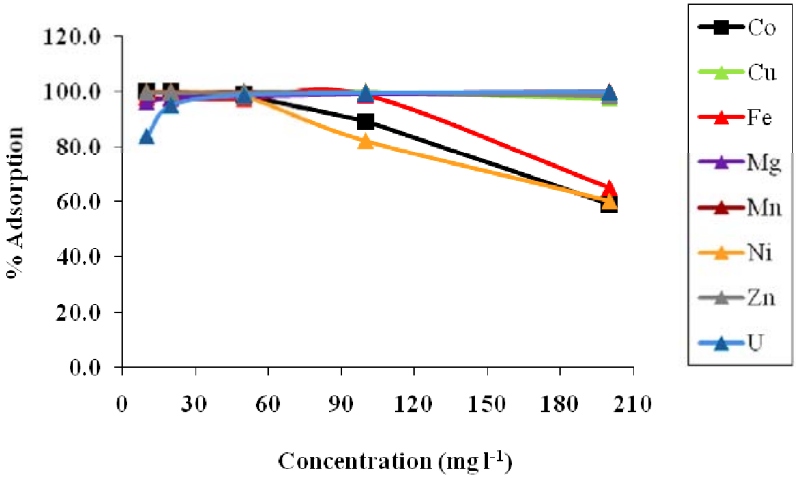

Figure 3 *Metal ion adsorption dependence on concentration*

The activation energies were calculated based on the equation:

$$\ln k_1/k_2 = (Ea/R)(1/T_1 - 1/T_2) \quad (3)$$

where k_1 and k_2 are rate constants at the first and second temperature, respectively; T_1 and T_2 are the first and second temperature, respectively and Ea is activation energy.

Desorption studies

The results for the desorption of U essentially showed that optimum desorption was at about 0.8 M Na_2CO_3 concentration. This is expected as U tends to form strong complexes with carbonates. The other metals were not released with this solution.

Optimum desorption was achieved at 1 M EDTA concentration. 75% of Fe was desorbed while 30% and 10% of Cu and Mg were desorbed, respectively. The other metals had <5% desorption. At 1 M H_2SO_4 concentration, 45% of Cu and 20% of Mg were desorbed while the rest of the metals had <5% desorption.

Conclusions

The BPAP silica polyamine composite has been shown to be effective as an adsorbent in the removal of metals from AMD. Adsorption kinetics are important in establishing the time zones and effective lifetime of adsorbents and shed information on the need for regeneration. Thermodynamic results are essential in determining the surface-metal reaction mechanisms. While desorption results for U were commendable, those for other metals were not high enough thus necessitating further exploitation of other desorbents.

Acknowledgements

The authors would like to thank the Carnegie Foundation and Friedel Sellschop Foundation for the financial support.

References

Akcil A, Koldas S (2005) Journal of Cleaner Production 14: 1140—1142.
Chander S, Mohan D (2001) Single component and multi-component adsorption of metal ions by activated carbons. Colloids and Surfaces, 177, 183.
Jiang J, Wu L, Li N, Luo Y, Liu L, Zhao Q, Zhang L, Christie P (2009) European Journal of Soil Biology 46: 18.
Rosenberg E, Hagers DL, Fischer RJ, Beatty ST (1999) Ind. Eng. Chem. Res. 38: 4402.