Kinetic, equilibrium and thermodynamic modelling of the sorption of metals from aqueous solution by a silica polyamine composite

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ABSTRACT

Batch sorption studies were conducted to assess the potential of a phosphonated silica polyamine composite (BPAP) to remove metals (Co, Cu, Fe, Mg, Mn, Ni, U and Zn) from mine waters. The metal adsorption showed a good Langmuir isotherm fit. Ni and Mn 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 adsorption (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. The pseudo-second-order kinetic model provided the best correlation of the experimental data, except for Mg and Ni for which the pseudo-first-order model and the Elovich model gave a better fit, respectively. Adsorption was almost constant over a wide pH regime and increased with time. Adsorption increased with concentration of the metals with the exception of Co, Fe and Ni which displayed about a 40% drop at a concentration of 200 mg·ℓ⁻¹. Desorption experimental data gave poor results except for U which showed 99.9% desorption.

Keywords: silica polyamine composite, sorption, kinetics, isotherms, desorption

INTRODUCTION

The presence of trace metals in aquatic systems is of concern because of their toxicity and non-biodegradable nature. The sources of metals in the environment include sewage, mining, agricultural and industrial activities, with mining accounting for the larger proportion. 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, 2006). There are several existing methods for the treatment of AMD, depending upon the volume of effluent, and 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, phytovolatilisation and phytostabilisation), 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); 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 adsorption 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 of these composites. In the case of BPAP, the Mannich reaction was

used to convert the polyamine composite to an amino phosphonic acid-functionalised composite which has been used to immobilise high valent metals (Fig. 1) (Rosenberg et al., 2006). 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, unlike their polymer counterparts (Kailasam et al., 2009). The polar nature of their surfaces also makes for better mass-transfer kinetics in aqueous solutions. This study focused on the kinetic, equilibrium and thermodynamic processes related to metal sorption on BPAP, using metals commonly found in AMD.

Kinetics of metal ion sorption governs the rate, which determines the residence time and is one of the important characteristics defining the efficiency of an adsorbent (Kaur et al., 2012). The kinetic models used included the pseudo-first-order model, the pseudo-second-order model, the intraparticle diffusion model and the Elovich model.

The pseudo-first-order equation (Lagergren, 1898) has been widely used by many other researchers to study the kinetics of heavy metal adsorption (Qiu et al., 2009). The model has the following form:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \qquad (1)$$

where:

q_e and q_t are the amount of metal ions adsorbed (mg·g⁻¹) at equilibrium and at any time *t*, respectively
k_1 is the rate constant (min⁻¹) of pseudo-first-order adsorption.

By applying the boundary conditions *t = 0* to *t = t* and $q_t = 0$ to $q_t = q_t$, the integration form is given by the equation below:

$$\log (q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \qquad (2)$$