Assessment Of The Efficacy Of Superabsorbent Polymers In The Treatment Of Metal Mining Effluents

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Abstract

Several techniques are commonly employed to treat AMD, including raising the pH by adding alkaline materials, precipitating dissolved metals by introducing sulfide reagents, and using biological processes. Superabsorbent polymers (SAPs), known for their high water absorption and retention capacity, offer a promising alternative for treating mining effluents due to their unique properties. In this study, synthetic metal solutions were used to assess the effectiveness of SAPs in effluent treatment using artificial solution. Investigation results demonstrate the effectiveness of SAPs in sequestering metal ions. The sequestration capacity of metals is influenced by pH, the ionic radius of the element, and the availability of binding sites in the SAPs.

To better understand the relationship between absorption rates, metal and metalloid sequestration and these chemical factors, equations have been proposed that consider both ionic radii and the concentrations of the elements analyzed. These equations provide highly accurate predictions of the metallic ion absorption rate.

Keywords: Superabsorbent polymers, water absorption, metal sequestration .

Introduction

Acid Mine Drainage (AMD), which results from mine wastes, is one of the most challenging environmental problems currently faced by the mining industry. Mining operations generate large amounts of waste, such as waste rock and tailings, which must be properly managed to protect the environment. Special attention is required when these wastes contain sulfidic minerals, such as pyrite and pyrrhotite. The oxidation of sulfides exposed to atmospheric conditions tends to acidify water, making it more prone to the mobilization of metals contained in the rock. These processes generate an acidic leachate known as acid mine drainage (AMD) or Acid Rock Drainage (ARD) (e.g., Aubertin *et al.*, 2002). AMD is characterized by high levels of sulfate and metals at low pH, and if not properly managed, it can negatively affect surrounding soils, surface water, and groundwater (Maqsoud *et al.*, 2016).

Acid mine drainage generally requires treatment before being discharged into the natural environment (Ben Ali *et al.*, 2019; USEPA, 2014). This treatment primarily involves increasing the pH (when applicable) and alkalinity, along with removing metals and sulfates. Several active and passive treatment technologies are well known and have been successfully applied to achieve these objectives (Wolkersdorfer, 2022; Skousen *et al.*, 2017; USEPA, 2014; Genty, 2012; Ben Ali *et al.*, 2019). The selection of a treatment technology is site-specific and must account for various parameters, including flow rate and water quality, while also considering economic, environmental, regulatory, and social factors.

Another technique that can be used in effluent treatment is the application of superabsorbent polymers (SAP). These polymers have high water retention as well as metal and metalloid sequestration capacities

(Ismi *et al.*, 2015; Addi *et al.*, 2019; Rifi *et al.*, 2005; Kanny-Diallo *et al.*, 2024). The sequestration of chemical elements is also linked to the water retention capacity of the polymers. This property could be utilized in the management of mine tailings (tailings densification) to enhance the geotechnical stabilization of mine tailings (Sahi *et al.* 2019).

This paper aims to assess the absorption rate and sequestration capacity of SAP for metals and metalloids and to establish a relationship between metal ion absorption rates and various chemical factors. To achieve this, an experimental study was conducted using an artificial solution and recycled superabsorbent polymers (SAP).

Materials and Methods

Materials

The superabsorbent polymers (SAPs) used in this study are based on sodium polyacrylates (PaNa). They are sourced from the recovery of defective diapers by Recyc PHP Inc. in Drummondville, Quebec, Canada. For these SAPs, the point of zero charge (PZC) was evaluated to determine the optimal pH for SAP sorption. This parameter was assessed using the salt addition method (Belviso *et al.*, 2014). The pH_{pzc} is the point where there are equal amounts of positive and negative charges. As shown in Fig. 1, the point of zero-charge corresponds to 5.83 for PANa coming from diapers. At this pH, SAPs would be more appropriate to capture cations, and this optimal pH was used for all tests performed.

Adsorption and sequestration tests

Salt solutions of different concentrations were prepared separately in deionized water. A volume of 200 ml of each saline solution was used, into which 0.50 g of hydrogel (dry PA-Na) was placed for 1 hour.

After this contact time, hydrogels containing trapped metal ions and water were separated from the saline solution by vacuum filtration. The resulting hydrogel was then weighed to determine the mass of the SAP at equilibrium swelling ($M_{SAP\text{-}eq}$).

From this, the absorption rate (Q^{eq}) can be calculated using equation (1) (see Sahi *et al.* 2019):

$$Q_{eq} = \frac{M_{SAPeq-}\,M_{SAPDry}}{M_{SAP-Dry}} = \frac{M_{water-absorbed}}{M_{SAP-Dry}} \quad (1)$$

Where MSAPeq corresponds to the mass of the SAP at equilibrium swelling.

Also, the concentrations of salt ions in the solution (after absorption) were evaluated using ICP-AES. By the initial concentrations measured in the solution, including the

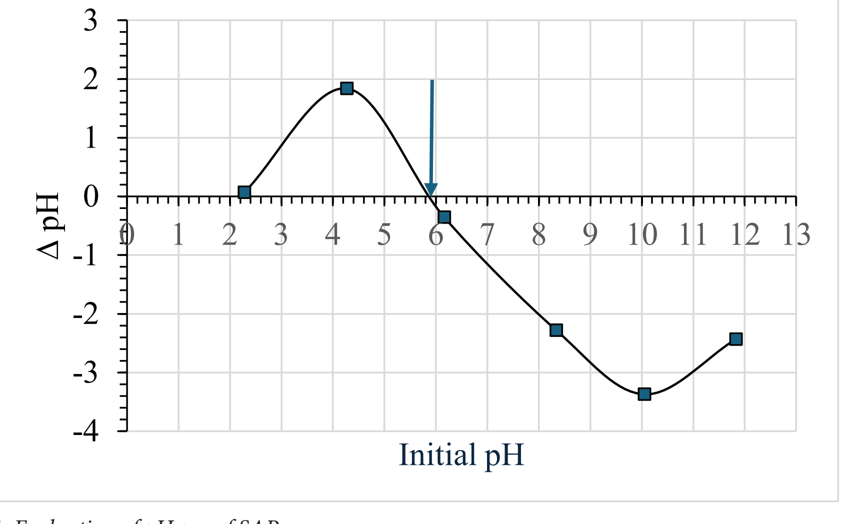


Figure 1 *Evaluation of pH pzc of SAP.*

volume used in each test, the initial mass ($M_{0\text{-ion}}$) for each element was defined. After the absorption test, final mass ($M_{f\text{-ion}}$) was determined using the same technique.

$$SP\ (\%) = \frac{M_{0-ion} - M_{f-ion}}{M_0 - ion} \times 100 \qquad (2)$$

These masses were used to evaluate the ion sequestration potential using the following equation:

Implications for Risk Assessment and Mitigation:

The detailed characterization of the fault system has important implications for risk assessment and mitigation related to the TSF. Understanding the fault's geometry and hydraulic properties allows for a more accurate assessment of the potential for contaminant migration along the fault. The finding that the fault acts as a hydraulic barrier suggests that infiltration from the TSF may be preferentially channelled along the fault zone, potentially affecting specific areas. This information can be used to inform the design and placement of monitoring wells and to develop targeted mitigation strategies to prevent groundwater contamination.

Results

In this section, we present the results related to the absorption and sequestration capacity of metals and metalloids by SPA.

Absorption rate (Q_{eq})

Absorption rates of Zinc, Arsenic, Lead, Nickel, Copper, Cadmium, Iron, and Cobalt are presented in Fig.2. This figure shows that for the tested element one can observe a decrease of Qeq by comparison to absorption in the deionised water. Also, one can observe that the absorption rate is also affected by the increase in the concentration

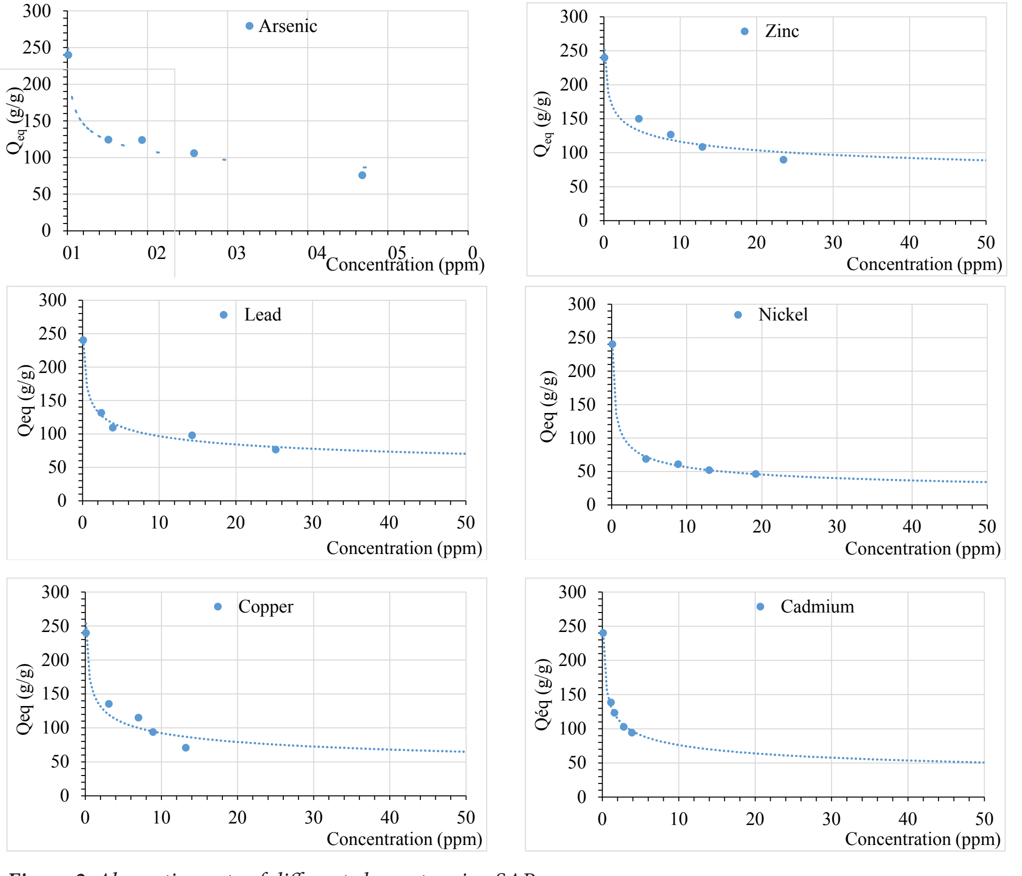


Figure 2 *Absorption rate of different elements using SAP*

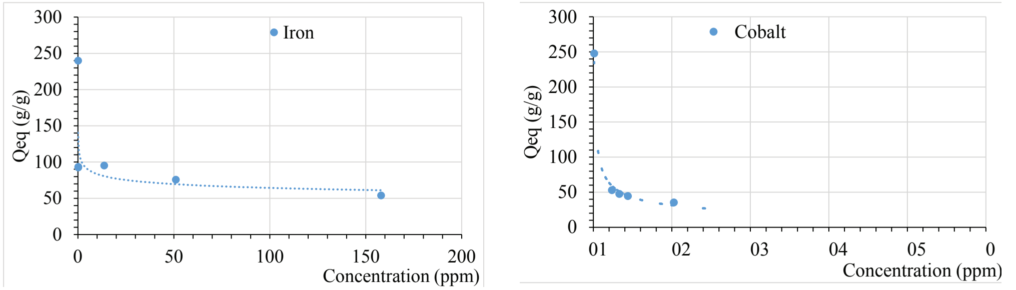


Figure 2 Absorption rate of different elements using SAP (continued)

of the analysed elements. This reduction is included between 146 and 205 g/g for cadmium and Cobalt respectively. This reduction in Qeq can probably be explained by the occupation of sites by metal ions or even by the closure of polymeric meshes, thus preventing absorption.

For the different elements, adjustments were made to the measured values, and all the elements analysed fit adequately using a power model.

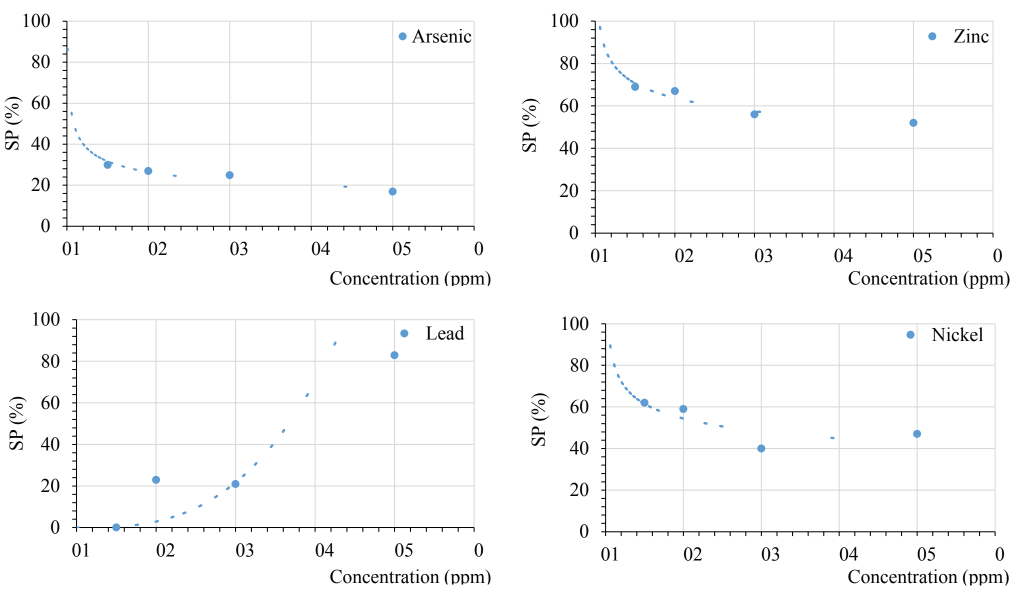
Sequestration potential (SP)

The sequestering potential by PSAs of chemical elements depends on the ionization degree of SAPs, pH, chemical concentration, ionic and charge state of the element, and the molar amount (Taouil, 2014). The metal and metalloid sequestration potential was calculated using Formula 2, and the results are shown in Fig. 3. This last figure shows that the sequestration potential ranges from 33 to 40% for Co, 11 to 16% for Cu, 0 to 83% for Pb, 52 to 69% for Zn, 17 to 30% for As, 48 to 69 % for Cd, and 47 to 62 % for Ni.

The sequestration potential exhibits two types of behavior:

- An increase in concentrations is accompanied by a decrease in SP. This behavior is observed for arsenic, zinc, nickel, and cadmium.
- An increase in solution concentrations is accompanied by an increase in SP. This behavior is observed for copper, lead, and cobalt.

The sequestration capacity of PA-Na is due to the forces of diffusion and electrostatic attraction between the carboxyl groups



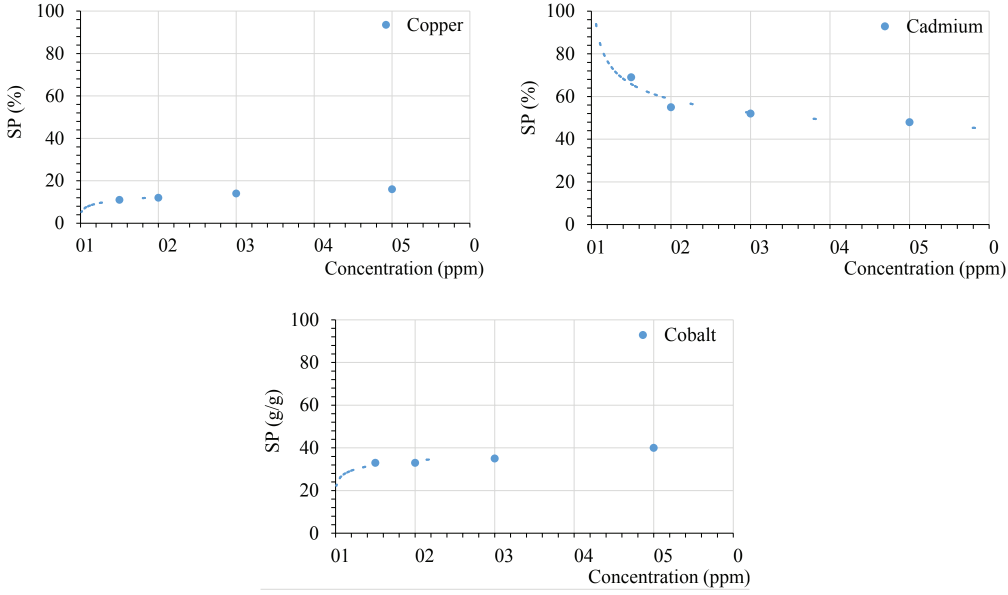


Figure 3 *Sequestration potential of metal and metalloids by SAP*

(COO-) and the metal ions, which favors the penetration of metal ions into the hydrogel network.

Discussion

The presence of metal ions reduces the absorption rate (see Fig. 2), as inter-chain reactions with carboxylate groups restrict the expansion of the polymer network.

Also, the evolution of sequestration potential as a function of metal ion concentration primarily depends on the pH of the medium, the ionic radius of the element, and the available sites in the polymer.

To illustrate the relationship between the absorption rate (Q^{eq}) and the corresponding chemical elements, an equation has been proposed that incorporates both the ionic radii (r) and the initial concentrations (C_i) used in the analysis:

$$Q_{eq} = K_1 \times r + (K_2/r^3) + K3 \times C_i + (K4 \times \ln(C_i^3)) \quad (3)$$

With K_1 =96.84, K_2 = 14.22 and K_3 =0.3116 et K4 =-1.023.

The proposed equation was used to calculate Q^{eq} for all the analyzed elements, and the results are presented in Fig. 4a. This figure compares the measured and predicted Q^{eq} values. As indicated by the coefficient of determination R^2 (R^2 = 0.98), the predictions are highly accurate, leading to the conclusion that the proposed equation allows for a highly precise calculation of the absorption rate. However, to generalize this equation, it is necessary to validate it using additional data that were not included in the development of Equation 3.

Also, to illustrate the relationship between the absorption rate (Qeq), the initial mass ($M_{0\text{-ion}}$) and final mass ($M_{f\text{-ion}}$) (both used for the calculation of SP), an equation has been proposed:

$$M_{f-ion} = AM_{0-ion} + BQ_{eq}^2 \quad (4)$$

Where A = 0.84 and B = $-0.2E^{-4}$

The proposed equation was used to calculate the final mass for all the analyzed elements, and the results are presented in Fig. 4b. This figure compares the measured and predicted values of final mass of metal and metalloid. As indicated by the coefficient of determination R2 (R2 = 0.9978), the predictions are highly accurate, leading to the conclusion that the proposed equation allows for a highly precise calculation of the final mass used for the calculation of the SP.

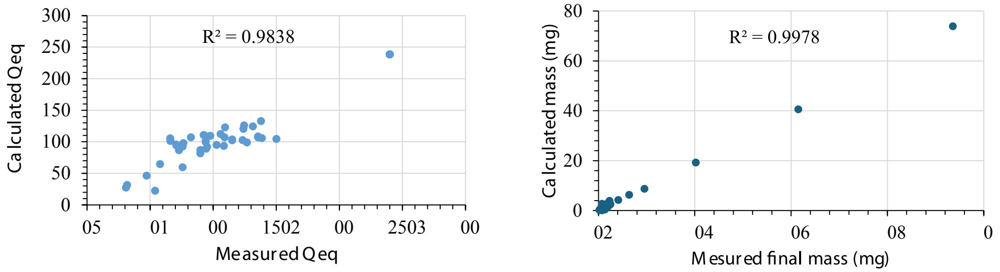


***Figure 4** Measured and calculated values: a) Absorption rate (Qeq) b) final metal and metalloid mass*

Conclusions

Investigation results demonstrate the effectiveness of SAPs in the absorption water and the sequestering of metal and metalloid. The sequestration capacity of metals is influenced by the ionic radius of the element, and the availability of binding sites in the SAPs and the initial concentration of element.

To better understand the relationship between absorption rates, (Qeq), the potential sequestration (SP) and these chemical factors, equations have been proposed that considers both ionic radii and the concentrations of the elements analyzed. These equations provide highly accurate predictions of absorption rate and sequestration potential of metal and metalloid. However, further validation using data not included in the equation's development is required to generalize their applicability

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