Studies of sulfate ions removal by the polyacrylic anion exchange resin Amberlite IRA458: batch and fixed-bed column studies

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Abstract Sulfate uptake by a polyacrylic anion exchange resin (Amberlite IRA458) was studied in batch and fixed-bed experiments. Loading increases with acidity and at pH 2.0, the sulfate loading kinetics is pseudo first order whereas the sorption isotherm can be described by both the Langmuir and Freundlich models. Fixed bed experiments produced high sulfate loading (70 mg SO_4^{2-}/L - resin) at pH 2.0 where HSO_4^- concentration is relevant. Column breakthrough data were fitted to Bohart-Adams, Thomas, Yoon and Nelson and Dose-Response models and all equations could predict the experimental results.

Key Words Sulfate Removal, Adsorption, Ion Exchange, Amberlite IRA458 resin.

Introduction

Acid mine drainage (AMD) is produced during sulfide exposition to water and oxygen and this process is usually catalyzed by bacteria (INAP 2003). AMD is characterized by low pH and high dissolved metals concentrations such as zinc, lead, copper and arsenic (Yanful *et al.* 1997) while sulfate, derived from sulfide oxidation is the main anion in these drainages. Sulfate is also present in effluents of many industries, especially hydrometallurgy due to the widespread use of sulfuric acid in many processes (Feng *et al.* 2000). The anion is associated with equipment corrosion, soil and water acidification (Akcil and Koldas 2006).

Although many countries set no health-based guideline for sulfate in drinking water, it can affect water taste and have laxative effects at above 600 mg/L sulfate. The World Health Organization recommends that health authorities should be notified if sulfate concentrations are above 500 mg/L in drinking water (WHO 2008). Environmental agencies in mining countries set a value varying between 250 and 500 mg/L in mine drainages or effluents while some countries may instead define limits for total dissolved solids, implying that sulfate concentrations must comply with that value (INAP 2003).

Sulfate containing wastewaters or mine drainages are usually treated by a combination of operations including acidity neutralization, lime (or limestone) precipitation, reverse osmosis, electrodialysis and adsorption (Geldenhuys *et al.* 2003). The selection of the treatment process of such effluents is a function of many factors such as chemical availability, local regulations, commercialization of the produced water and process economics (Dry 1998). The eMalahleni Project, for instance applies a sequence of oxidation and precipitation steps before pumping mining water to a membrane system comprising ultrafiltration and reverse osmosis, ultimately producing a <200 mg/L TDS water which is sold as potable water to nearby community after chlorination (Hutton *et al.* 2009).

Some processes have been proposed for AMD treatment applying ion exchange resins. These include a combination of cation and anion exchange resins such as the Sulf-IX™ process commercialized by Bioteq. Ion exchange (IX) is better suited for moderate sulfate concentrations (< 2000mg/L) and is less competitive than lime treatment for higher sulfate concentrations (INAP 2003). Nevertheless, IX can produce very pure water and can also be applied to recovery important elements in the drainages, such as uranium. Despite that, only a few fundamental studies addressing sulfate removal by ion exchange resins have been published (Feng *et al.* 2000; Haghsheno *et al.* 2009; Moret and Rubio 2003; Namasivayam and Sangeetha 2008) and a plethora of different ion exchange resins are available which have different affinities for sulfate. Therefore, this work sought to study sulfate sorption on one of these resins, namely the polyacrylic ion exchange resin Amberlite IRA458, which has not yet been tested for the AMD treatment. Batch and fixed bed experiments were carried out and modeled.

Materials and Methods

It was studied the polyacrylic anion exchange resin Amberlite IRA458, which is a gel type acrylic resin, with 1.25 eq/L exchange capacity and 35°C maximum temperature operation. Prior to the experiments, the resin was kept under water so that swelling could be achieved.

Batch experiments. These experiments aimed to define the optimum conditions for sulfate sorption and the effects of (i) sulfate concentration and (ii) pH on the resin loading were studied. The experiments were performed by mixing 1mL of the resin with 100 mL of a synthetic solution containing sodium sulfate (100 - 1200 mg/L), in an orbital shaker (New Brunswick) at 180 min^{-1}, during 5 hours. When the effect of pH on sulfate loading was assessed, the solution pH was controlled at pH 2, 4, 6, 8, or 10. For the kinetic experiments, 10 mL of the same resin was mixed with 1 liter of a solution containing 800 mg/L sulfate, at 200 min^{-1}, 26±1° C and pH 2. Sampling was performed at different contact times and after chemical analysis the resin loading was determined by mass balance. Following, fitting to pseudo first order, pseudo second order and intraparticle diffusion model was tested. Sorption isotherms were also produced from equilibrium loading experiments. The experimental data were fit to both the Langmuir and Freundlich models. In all batch runs, as the experiment was finished the solution-resin pulp was filtered and the sulfate concentration in the aqueous phase was determined by ICP-OES (Varian, 725).

Elution from the loaded Amberlite IRA458 resin was also studied. To achieve that 1mL of the loaded resin (34.4 mg SO_4^{2-} /mL - resin) was eluted with 100 mL of either sodium chloride (500 mg/L or 1300 mg/L) or sodium hydroxide (pH 10 and 12). The flasks were kept under agitation at 180 min^{-1}, for 24 hours at 34°C. All experiments were done at least twice and the average values are reported.

Fixed-bed experiments. These experiments were carried out in a 13 mm diameter × 142 mm long column, loaded with 10 mL of the Amberlite IRA458 resin (V_{res}) previously conditioned at pH 2 with hydrochloric acid. A 1000 mg/L (C_0) and pH 2 sulfate solution was fed upwards at 10 mL/min (Q) and 26±1° C. Sampling was carried out at every 10 minutes and the sulfate concentration in the column effluent was determined by ICP-OES (Varian). Following, the breakthrough data were modeled. The height of the resin bed was 9 cm, and the upflow velocity (U) was 1.37 cm/min.

Results and discussion

Batch experiments

Effect of pH on sulfate uptake. Fig. 1 depicts sulfate loading by Amberlite IRA458, at different pH and initial sulfate concentrations. Resin loadings increase with initial sulfate concentration in solution up to saturation, which is reached at ≈ 43.6 mg SO_4^{2-}/mL - resin and pH 2. In this pH, HSO_4^- concentration is relevant (≈ 30%, taking $pK_{a,2}$ = 1.54, at 25°C and I = 0.1 mol/L (Martel and Smith 2003)) and contributed for increased sorption. Resin loading is sensibly reduced as pH increases and the maximum loading at pH 10 is only 6 mg SO_4^{2-}/mL - resin. This behavior is typical of weak base resins in which the exchange capacity is function of pH. Nevertheless, as it is aimed to remove sulfate from acid drainage, the resin seems suitable.

Sulfate uptake kinetics was determined at pH 2.0 for a solution containing 800 mg SO_4^{2-}/L and the results are shown in fig. 2. It can be noticed that sulfate loading is fast and levels out within 60 minutes, whereby a loading of 55 mg SO_4^{2-}/L - resin was achieved. The loading kinetics was modeled and from the three equations tested (pseudo first order, pseudo second order and intraparticle diffusion) only the pseudo first order model showed good fit (R^2 = 0.97) with a rate constant (k) value of 0.072 min^{-1}. This suggests that, in the experimental conditions of the present work, film diffusion is likely the controlling step during sulfate uptake by Amberlite IRA458 resin, while pore diffusion is fast.

Following, sulfate elution was studied batchwise applying two different solutions at two different concentrations. As it can be seen in tab. 1, sodium hydroxide showed much better results as compared to sodium chloride solutions. This is be-

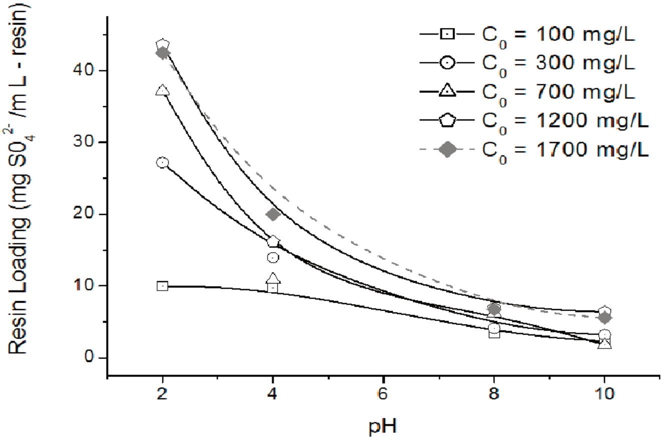

Figure 1 *Sulfate loading in Amberlite IRA458, at different pH values. Experimental conditions: 34±1° C, stirring speed 180 min^{-1}.*

Table 1 *Effect of eluent type and concentration on sulfate elution from Amberlite IRA458 resin. Experimental conditions: 34° C, 180 min^{-1}, sulfate loading: 34.4 mg/mL - resin.*

Eluent solution	Elution efficiency (%)	Eluent solution	Elution efficiency (%)
NaCl (0.5 g Cl^-/L)	3.6	NaOH (pH=10)	41.4
NaCl (1.3 g Cl^-/L)	3.7	NaOH (pH=12)	44.8

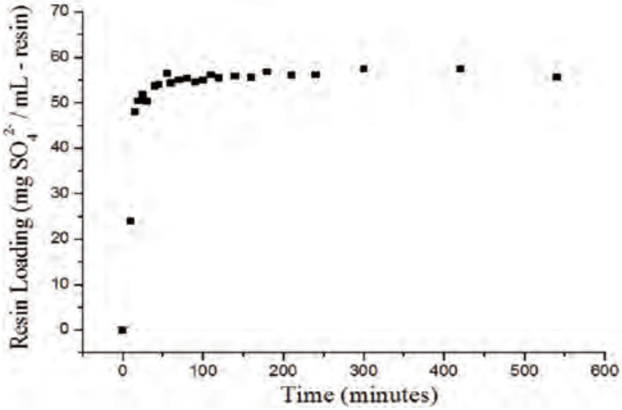

Figure 2 *Resin loading kinetics at pH 2 from 800 mg/L sulfate concentration. Experimental conditions: 26±1° C, stirring speed 200 min^{-1}.*

cause pH has an important effect on sulfate loading on this polyacrylic resin as can be seen in fig. 1. Furthermore, anionic resins have higher affinity for sulfate as compared to chloride because the electrostatic interaction is stronger (Inglezakis and Poulopoulos 2006). Regardless, elution of sulfate loaded Amberlite IRA458 requires further research.

Knowing the time required for equilibrium, sorption experiments were performed at different initial sulfate concentrations followed by data fitting to the Freundlich and Langmuir equations. The loading isotherm is presented in fig. 3 where Qeq represents the equilibrium sulfate loading. It can be observed that both models can represent sulfate uptake by Amberlite IRA458. The Langmuir model showed a somewhat worst fit (R^2 = 0.95) with 41.3 mg SO_4^{2-}/mL – resin maximum loading as compared to that achieved with the Freundlich model (K_f = 12.64 L/mL - resin, n = 6.09, R^2 = 0.98).

Fixed-bed sorption

Fig. 4 depicts the breakthrough curve during sulfate loading on Amberlite IRA458. It can be observed that breakthrough is achieved after 40min whereas saturation is observed after 90 min. In this condition, resin loading was 70 mg SO_4^{2-}/mL - resin. This value is slightly higher than the maximum exchange capacity (1.25 meq/mL - resin) if sulfate is the adsorbing species. As already stated, however, bisulfate concentration is relevant at pH 2.0 and indeed contributed for the high resin loading.

Breakthrough modeling. Four different equations were applied to model the breakthrough curve produced during sulfate sorption on Amberlite IRA458, namely: (i) Bohart-Adams (1920), (ii) Thomas (1944), (iii) Yoon and Nelson (1984), (iv) Dose-response models (Yan *et al.* 2001). The latter is an empirical equation widely used in the pharmaceutical industry, which was also applied in

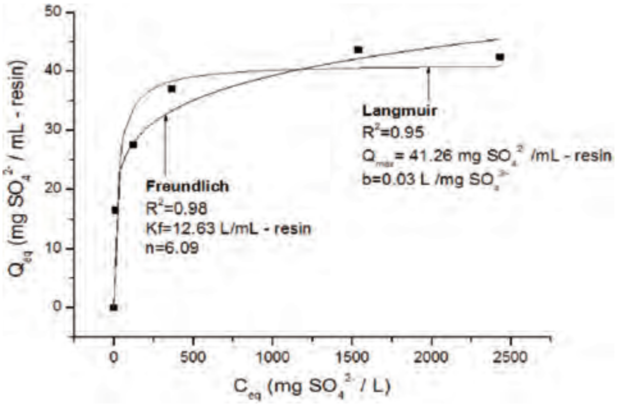

Figure 3 *Loading isotherm for sulfate sorption on Amberlite IRA458. Experimental conditions: pH 2.0, 34°C, stirring speed 200 min^{-1}.*

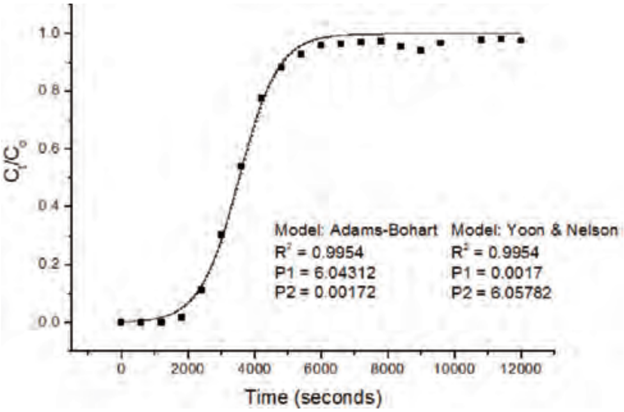

Figure 4 *Breakthrough curve observed during fixed-bed sorption. Experimental conditions: 26±1° C, pH 2.0, upflow velocity 1.37 cm/min.*

biosorption studies (Calero *et al.* 2009; Senthilkumar *et al.* 2006).

Tab. 2 depicts the values achieved by fitting the model equations to the experimental data and good correlation coefficients between the four models and the experimental data can be observed (R^2=0.99). The Bohart-Adams model slightly overestimates whereas the other three models underestimate the resin loading as compared to the experimental result.

Summarizing, all model were found to be suitable for describing the dynamic behavior during sulfate sorption on the anionic polyacrylic ion exchange resin. Further studies are addressing sulfate sorption by other resin types as well as the application of cationic resins so that a process can be devised to treat mine affected waters. This resin shows high sorption capacities in acid solutions similar to that observed with resins containing polystyrene matrixes (Guimarães 2010), but the latter seem more indicated for less acidic drainages.

Conclusions

Anionic polyacrylic resins can be applied for sulfate sorption as the loading process is relatively fast and follows the pseudo-first order model with $k = 0.072\ \text{min}^{-1}$. At pH 2.0, resin loading can reach 41.3 mg SO_4^{2-}/mL - resin, at equilibrium and the isotherm can be described both the Freundlich and Langmuir models. Fixed-bed experiments enables a better utilization of the resin adsorption

Table 2 *Breakthrough parameters achieved with the different models.*

Model	Parameter	Definition	Value
Bohart-Adams $\frac{C}{C_0} = \frac{1}{1+\exp\left(\frac{kN_0}{U}\right) - kC_0 t}$	k_{AB} (L/mg SO_4^{2-}.min)	Bohart-Adams rate constant	$7.61\text{x}10^{-5}$
	N_0 (mg SO_4^{2-}/mL-bed)	Bed sorptive capacity	51.34
	q_0 (mg SO_4^{2-}/mL - resin)	Maximum solid-phase concentration	79.0
	R^2	Correlation coefficient	0.996
Thomas $\frac{C}{C_0} = \frac{1}{1+\exp\left(\frac{kq_0 V_{res}}{Q}\right) - kC_0 t}$	k_{Th} (mL/mg SO_4^{2-}.min)	Thomas rate constant	0.131
	q_0 (mg SO_4^{2-}/mL - resin)	Maximum solid-phase concentration	60.2
	R^2	Correlation coefficient	0.991
Yoon & Nelson $\frac{C}{C_0} = \frac{\exp(k_{yn}t - k_{yn}t_{0.5})}{1+\exp(k_{yn}t - k_{yn}t_{0.5})}$	k_{YN} (min^{-1})	Yoon-Nelson rate constant	0.132
	$t_{0.5}$ (min)	Time to 50% sorbate breakthrough	59.05
	R^2	Correlation coefficient	0.992
Dose-Response $\frac{C}{C_0} = 1 - \frac{1}{1+\left(\frac{VC_0}{V_{res} \cdot q_0}\right)^a}$	A	Dose–Response constant	5.74
	q_0 (mg SO_4^{2-}/mL - resin)	Maximum solid-phase concentration	59.65
	R^2	Correlation coefficient	0.997
Experimental	N_0 (mg SO_4^{2-}/mL - bed)	Bed sorptive capacity	58.47
	q_0 (mg SO_4^{2-}/mL - resin)	Solid-phase conc.	69.85
	$t_{0.5}$ (min)	Time to 50% sorbate breakthrough	58.2

capacity and the selected models can describe the breakthrough curve. The strong effect that increasing pH has on reducing sorption capacity indicates this resin for sulfate removal from AMD only. Sulfate present in neutral drainages should be treated with strong base ion resins such as those containing polystyrene matrixes.

Acknowledgements

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