ADSORPTION OF POLYTHIONATES AND THIOSULFATE ON STRONG BASE ANION EXCHANGE RESINS

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ABSTRACT

Thiosulfate leaching is an alternative process to cyanidation for recovering gold from ores. Resin in pulp has been suggested as a possible operation for the recovery of gold from the thiosulfate leach solutions. The aim of this work is to investigate the adsorption of polythionates and thiosulfate on strong based anion exchange resins, as they are the competing species for the adsorption of gold. The kinetics of thiosulfate, trithionate and tetrathionate load is first order, approaching equilibrium. The equilibrium constants for the adsorption reactions were obtained using the experimental data. The use of the rate constants and equilibrium constants for adsorption allows the resin in pulp process to be effectively modelled.

INTRODUCTION

The cyanidation process relies on the fact that gold dissolves in aerated cyanide solution to produce the gold cyanide complex (MacArthur, 1988). Due to its high efficiency, it has been the most important extraction process of gold and silver for over 100 years (MacArthur, 1988, Marsden and House, 1992, Logsdon et al., 1999, Young, 2001). However, its use in certain environments has been restricted owing to the acute toxicity of cyanide (Korte and Coulston, 1995, Moran, 1998, Miller and Pritsos, 2001). In order to improve the process, additional treatments can be adapted when processing refractory ores such as pressure oxidation, ultra-fine grinding, roasting and biological oxidation (Koslides and Ciminelli, 1992, La Brooy et al., 1994, Mosher and Figueroa, 1996, Linge and Welham, 1997). Among the alternatives to cyanide (Hilson and Monhemius, 2006), thiosulfate is the most promising because it is environmentally friendly and a relatively cheap reagent (Muir and Aylmore, 2004).

There has been a number of extensive studies on the leaching of gold with thiosulfate ($S_2O_3^{2-}$), and the presence of ammonia and copper ions with copper(II) being the oxidant (Gong et al., 1993, Abbruzzese et al., 1995, Jeffrey, 2001, Breuer and Jeffrey, 2002). During leaching, the oxidation of thiosulfate by copper(II) (Tozawa et al., 1981, Langhans et al., 1992, Li et al., 1995, Breuer and Jeffrey, 2003), consumes thiosulfate leading to the generation of polythionates including tetrathionate (Wan, 1997). The presence of polythionates affects the gold recovery using ion exchange resins (Nicol

and O'Malley, 2002). Therefore the aim of this work is to investigate the adsorption of polythionates, thiosulfate and gold on using anion exchange resins, and to obtain the equilibrium constants for the adsorption reactions.

MATERIALS AND METHODS

Apparatus and Chemicals

For the analysis of polythionates and thiosulfate, a Waters 2695 HPLC separation module was used with the separation being effected using a Dionex IonPac AS16 ion exchange column equipped with an IonPac AG16 guard column. The species detection was via a Waters 2996 Photodiode Array Detector. A pump with the flow rate of 1 mL min^{-1} was used, and the column temperature was 25 °C. Empower software was used for the calculation of peak area (Waters, 2002). The wavelength of peak UV adsorption, and the peak retention time is described in the literature (Jeffrey and Brunt, 2007). Solutions were prepared from either analytical grade or synthesized reagents and Millipore water was used in the all experiments. Sodium trithionate was prepared using the methods outlined in the literature (Kelly and Wood, 1994).

Adsorption Experiments

Resin-solution system equilibrium without gold

Identical volumetric flasks (200 mL) were filled with synthetic loading solution containing various concentrations of sodium trithionate ($Na_2S_3O_6$), sodium tetrathionate ($Na_2S_4O_6.2H_2O$) and sodium thiosulfate ($Na_2S_2O_3$) at natural pH. Before placing 0.333 g of wet Purolite A500/2788 strong base anion exchange resin in the flasks, 1 mL of the loading solution was taken as a sample at t = 0 h. Then, the flasks were stirred at 100 rpm with an overhead IKA stirrer. After 5 h loading, 1 mL sample was taken for HPLC analysis. The resins were decanted and washed 4 times and then 2 batches of 50 mL sodium perchlorate (0.5 M) were added to strip the resin. Following the strip, the resins were washed and finally dried.

Resin-solution equilibrium system with gold

Gold loading was accomplished by mixing sodium gold thiosulfate with 210 mL of 5 mM sodium thiosulfate and 5 mM sodium trithionate. The loading solution sample of 10 mL at t = 0 h for analysis with an inductively coupled plasma-optical emission spectrometer (ICP-OES) followed by a 1 mL sample for HPLC. The same anion exchange resin was used with a mass of 0.5 g. After 5 h loading, a 10 mL sample and a 1 mL sample were taken for ICP-OES and HPLC, respectively. A similar strip procedure was used for the gold loaded resin, with a 10 sample and a 1 mL sample taken for ICP-OES and HPLC, respectively, for each of the strip batches. The experiment was repeated for various initial gold concentrations in the range 0.2-9.5 mg/L.

RESULTS AND DISCUSSIONS

Kinetics of adsorption of a single component onto anion exchange resins

Thiosulfate and polythionates adsorb onto available strong base ion exchange sites on

the resin simultaneously with gold, and the adsorption of each species is represented by Equations [1], [2], [3] and [4] where R represents the resin functional group;

$$2R\text{-}Cl_{(s)} + S_2O_3{}^{2-}{}_{(aq)} <=> R_2S_2O_{3(s)} + 2Cl^-{}_{(aq)} \qquad [1]$$

$$2R\text{-}Cl_{(s)} + S_3O_6{}^{2-}{}_{(aq)} <=> R_2S_3O_{6(s)} + 2Cl^-{}_{(aq)} \qquad [2]$$

$$2R\text{-}Cl_{(s)} + S_4O_6{}^{2-}{}_{(aq)} <=> R_2S_4O_{6(s)} + 2Cl^-{}_{(aq)} \qquad [3]$$

$$2R\text{-}Cl_{(s)} + S_5O_6{}^{2-}{}_{(aq)} <=> R_2S_5O_{6(s)} + 2Cl^-{}_{(aq)} \qquad [4]$$
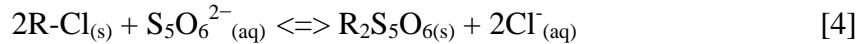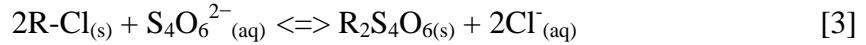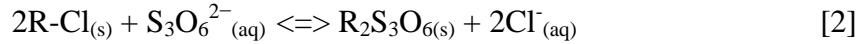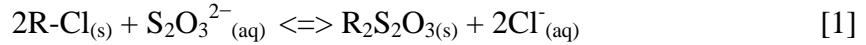
The adsorption onto the ion exchange resin is a heterogeneous process, with the rate of adsorption being limited by the mass transfer (diffusional resistance) of the anionic species to the ion exchange sites. Since mass transfer is most often a first order process, and also the adsorption of each species approaches an equilibrium, the kinetics of loading can be represent by Equation [5],

$$\left[S_xO_y{}^{2-} \right]_t = \left(\left[S_xO_y{}^{2-} \right]_0 - \left[S_xO_y{}^{2-} \right]_{EQ} \right) \exp\left(-kt\right) + \left[S_xO_y{}^{2-} \right]_{EQ} \qquad [5]$$

where k is the rate constant (s^{-1}); $[S_xO_y{}^{2-}]_t$ is the species aqueous concentration (M) at time t (s); $[S_xO_y{}^{2-}]_0$ denotes as the initial species aqueous concentration (M); and $[S_xO_y{}^{2-}]_{EQ}$ is the species concentration (M) in the solution at equilibrium.
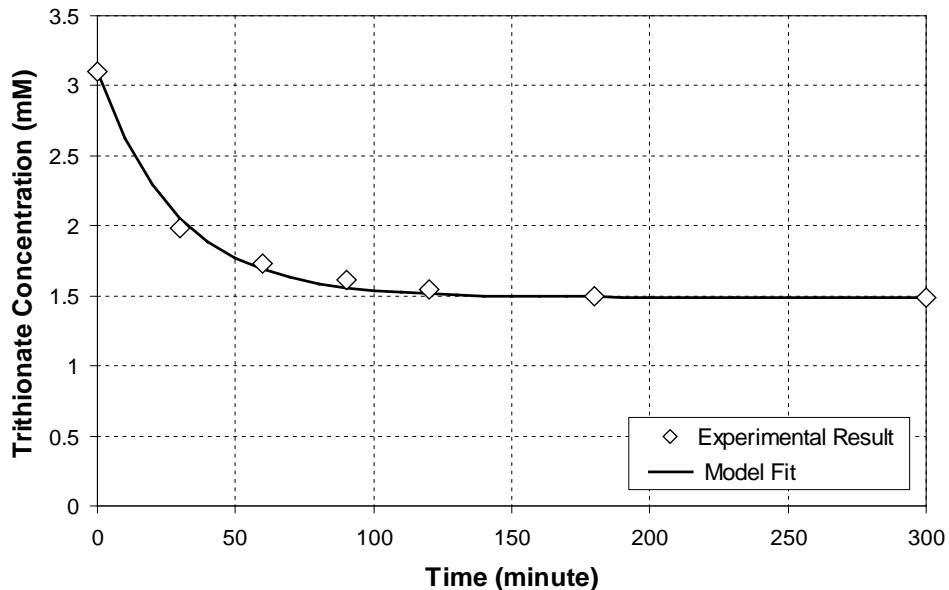

Fig. 1: The experimental trithionate concentrations in solution vs. time for the loading onto the anion exchange resin.

Figure 1 shows the kinetics of trithionate loading on the resin, from which it is seen that the trithionate equilibrium concentration is 1.49 mM at 300 minutes. Using the model of Equation [5], the experimental data, and Levenberg-Marquardt method (Williams et al., 2002) to minimize the sum of weighted deviation square between the model and experiment-based results, the rate constant is obtained, which is approximately 0.035 min^{-1}. Using the same method, the rate constants for thiosulfate and tetrathionate

loading were calculated to be 0.058 min^{-1} and 0.019 min^{-1}, respectively.

Equilibrium adsorption on the resin

In order to investigate the competition between species for loading, experiments with two components were conducted. For instance with solutions containing trithionate and tetrathionate, as shown in Figure 2, the trithionate concentration on the resin increases with the increase in concentration in solution. Similarly, as the tetrathionate concentration was increased, the trithionate loading decreased.
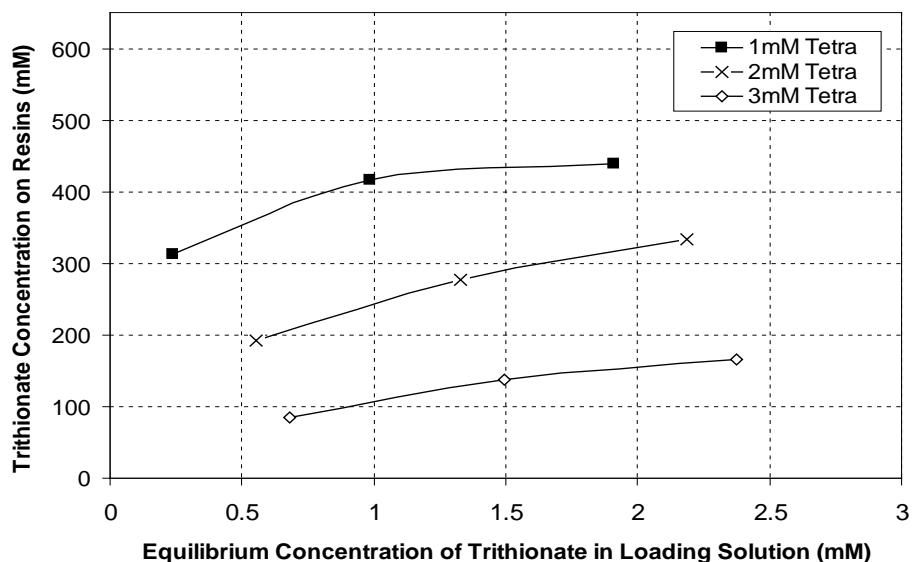

Fig. 2: The equilibrium loading of trithionate plotted as an isotherm for three tetrathionate concentrations.

During the competitive adsorption of thiosulfate and polythionates, the chloride initially present on the resin is almost completely desorbed, since it is weakly adsorbed compared to thiosulfate and the polythionates. Thus in the absence of high concentrations of chloride, Equations 1-4 can be rearranged to give the following equilibrium equations 6-8. Equation 9 can be written for hexathionate as well;

$$[R_2S_2O_3][S_3O_6^{2-}]K_{3/2} = [R_2S_3O_6][S_2O_3^{2-}] \qquad [6]$$

$$[R_2S_3O_6][S_4O_6^{2-}]K_{4/3} = [R_2S_4O_6][S_3O_6^{2-}] \qquad [7]$$

$$[R_2S_4O_6][S_5O_6^{2-}]K_{5/4} = [R_2S_5O_6][S_4O_6^{2-}] \qquad [8]$$

$$[R_2S_5O_6][S_6O_6^{2-}]K_{6/5} = [R_2S_6O_6][S_5O_6^{2-}] \qquad [9]$$
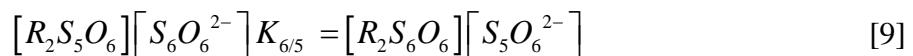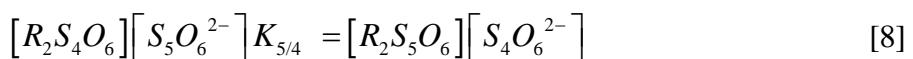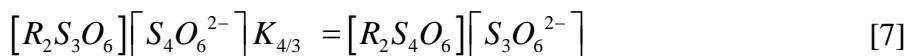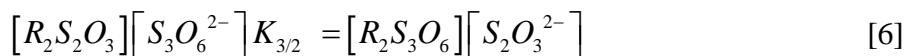
where $K_{3/2}$ represents the equilibrium constant for the reaction of thiosulfate on resins + trithionate in solution; $K_{4/3}$ is the equilibrium constant for the reaction of trithionate on resins + tetrathionate in solution; $K_{5/4}$ is the equilibrium constant for the reaction of

tetrathionate on resins + pentathionate in solutions; and $K_{6/5}$ is the equilibrium constant for the reaction of pentathionate on resins + hexathionate in solution. Therefore in the case of the system containing trithionate and tetrathionte, a plot of $\left[R_2 S_4 O_6 \right] / \left[S_4 O_6^{2-} \right]$ vs. $\left[R_2 S_3 O_6^{2-} \right] / \left[S_3 O_6^{2-} \right]$, should yield a straight line with the slope being the equilibrium constant, $K_{4/3}$.
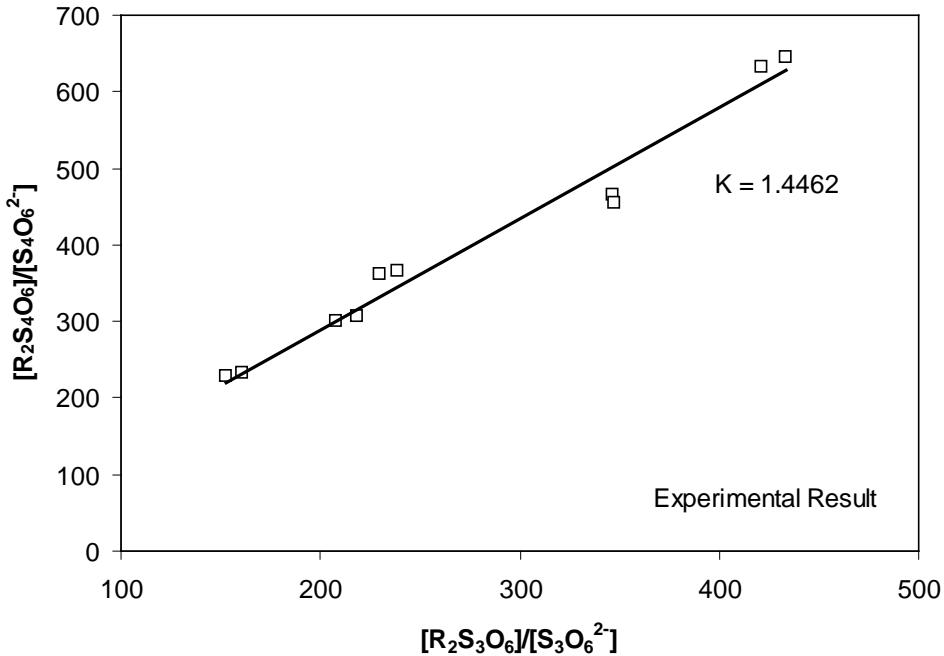

Fig. 3: The graphical representation of the equilibrium constant for tetrathionate loading over trithionate. The slope of the plot is the equilibrium constant.

Figure 3 shows the loading affinity of tetrathionate versus the loading affinity of trithionate. As can be seen, the loading affinity of tetrathionate linearly increases with the increase in the loading affinity of trithionate, and the equilibrium constant for the loading of tetrathionate over trithionate is 1.446. Since this value is above 1, the tetrathionate loads more strongly than the trithionate.
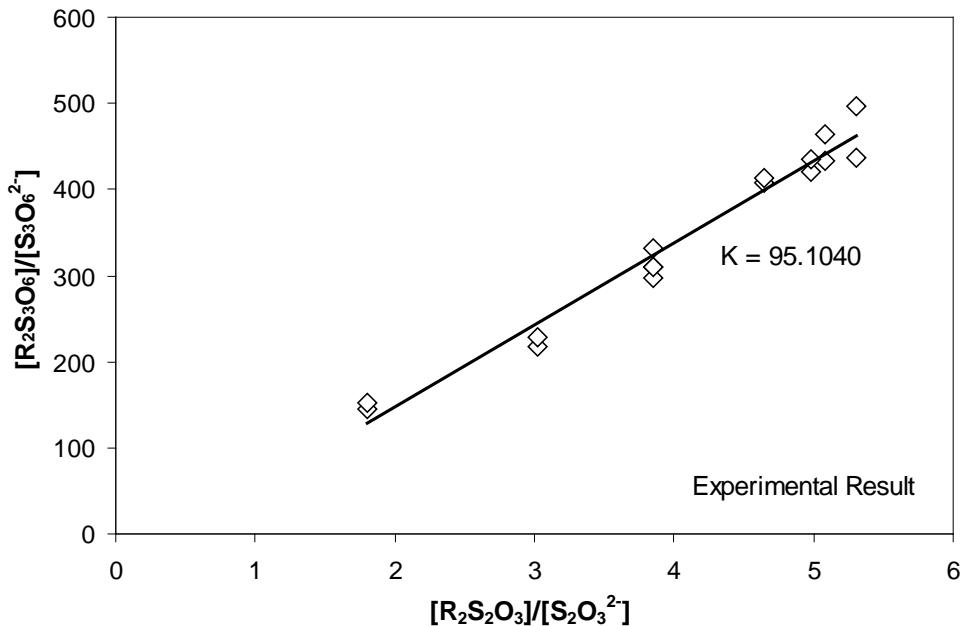
Fig. 4: The graphical representation of the equilibrium constant for trithionate loading over thiosulfate. The slope of the plot is the equilibrium constant.

The equilibrium constant for the system of thiosulfate + trithionate shown in Equation [6] is determined from the slope of linear correlation between the loading affinities of thiosulfate and trithionate, as can be seen in Figure 4. From the value of equilibrium constant, 95.104, it is clear that trithionate is much more strongly loaded that thiosulfate.

Tab. 1: The equilibrium loading of thiosulfate, trithionate, tetrathionate and pentathionate on resin. Also shown is the calculated equilibrium constant for pentathionate loading over tetrathionate.

Experiment	1	2	3	4	5
Thiosulfate					
Init Concentration (mM)	1.5785	1.5766	1.5406	1.5492	1.5305
Equil Concentration in Sol. (mM)	1.4575	1.4632	1.3695	1.3972	1.4155
Equil Concentration on Resins (mM)	32.2067	30.7177	46.5032	40.9472	30.8798
Trithionate					
Init Concentration (mM)	1.3138	1.3053	1.3003	1.2974	1.2978
Equil Concentration in Sol. (mM)	0.7646	0.7678	0.7630	0.7580	0.7547
Equil Concentration on Resins (mM)	146.2642	145.6324	146.0513	145.2690	145.8587
Tetrathionate					
Init Concentration (mM)	2.5189	2.5157	2.5416	2.5466	2.5413
Equil Concentration in Sol. (mM)	1.3785	1.3902	1.3970	1.3880	1.3923
Equil Concentration on Resins (mM)	303.6956	304.9122	311.1059	311.9876	308.6092
Pentathionate					
Init Concentration (mM)	0.9588	0.9571	0.8806	0.8816	0.8776
Equil Concentration in Sol. (mM)	0.4172	0.4199	0.3815	0.3805	0.3809
Equil Concentration on Resins (mM)	144.2083	145.5191	135.6649	134.9596	133.3965
K Tetrathionate-R + Pentathionate = Pentathionate-R + Tetrathionate	**1.5688**	**1.5799**	**1.5968**	**1.5781**	**1.5800**

Since pentathionate is also adsorbed on resins, we needed to also obtain the equilibrium

constant between tetrathionate and pentathionate. However, since pentathionate cannot be purchased in pure form, a synthetic polythionates mixture was prepared by mixing thiosulfate with tetrathionate, and allowing the rearrangement to occur (Steudel and Holdt, 1986). The solution which was generated contained thiosulfate, trithionate, tetrathionate and pentathionate at a concentration of ca. 1.5 mM, 1.3 mM, 2.5 mM, and 1.0 mM, respectively. As shown in Table 1, the equilibrium constant associated with Equation [8] was on average 1.581. This implies that pentathionate has higher affinity for the resin than tetrathionate.

Equilibrium constant for the gold thiosulfate complex

The final species investigated was gold thiosulfate. The equilibrium between this complex and trithionate can be represented by the following equation;

$$3R_2S_3O_{6(s)} + 2Au(S_2O_3)_2{}^{3-}{}_{(aq)} <=> 2R_3Au(S_2O_3)_{2\,(s)} + 3S_3O_6{}^{2-}{}_{(aq)} \qquad [10]$$

The equilibrium constant for this reaction can be represented by;

$$K = \left(\frac{\left[R_3Au(S_2O_3)_2\right]}{\left[Au(S_2O_3)_2{}^{3-}\right]}\right)^2 \times \left(\frac{\left[S_3O_6{}^{2-}\right]}{\left[R_2S_3O_6\right]}\right)^3 \qquad [11]$$

Hence

$$\log K + 3\log\left(\frac{\left[R_2S_3O_6\right]}{\left[S_3O_6{}^{2-}\right]}\right) = 2\log\left(\frac{\left[R_3Au(S_2O_3)_2\right]}{\left[Au(S_2O_3)_2{}^{3-}\right]}\right) \qquad [12]$$

It should thus be clear that if the adsorption follows this model, a plot of log ($[R_3Au(S_2O_3)_2]/[Au(S_2O_3)_2{}^{3-}]$) vs. log ($[R_2S_3O_6]/[S_3O_6{}^{2-}]$) will yield a straight line of slope 1.523, and intercept 0.5 log K. Figure 5 shows that this is the case, and a value of K = 0.53 is calculated from the intercept.
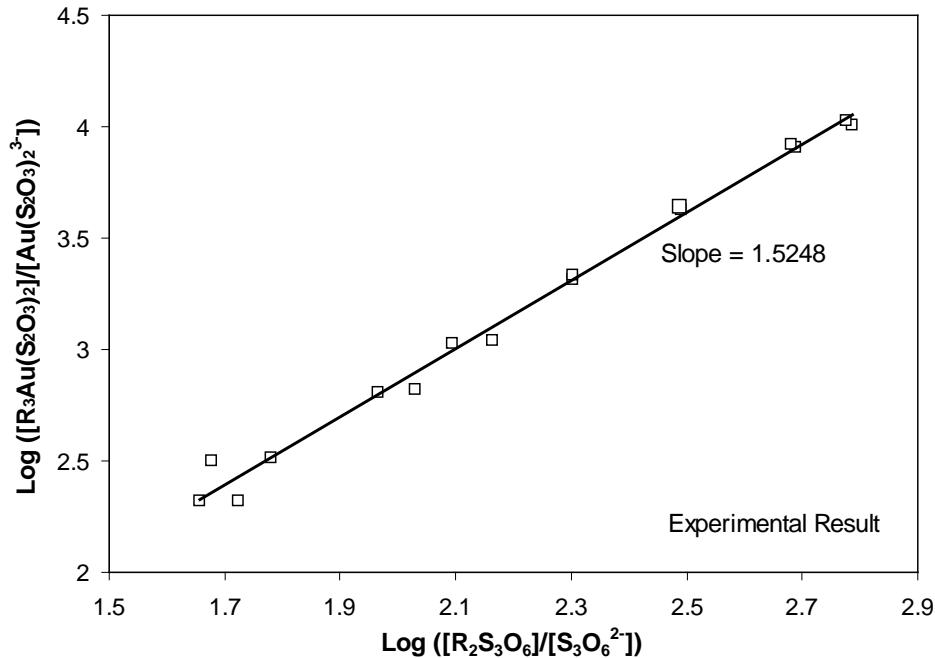
Fig. 5: The graphical representation of the equilibrium constant for gold loading over trithionate. The slope of the plot is the order, and the intercept is 0.5 log K.

Equations utilised for the modelling of the equilibrium resin loading

In order to calculate the equilibrium concentration of thiosulfate, trithionate, tetrathionate, pentathionate and gold thiosulfate in solution and on the resin, 10 equations are required. These are the mass balances for each species (Equations [13]-[17]), the 4 equilibrium equations (Equations [18]-[21]) for which the equilibrium constant is known, and resin charge balance (Equation [22]) where Vs and Vr are the solution and resin volume respectively, as shown below;

$$Vs * [S_2O_3^{2-}]_{total} = Vs * [S_2O_3^{2-}] + Vr *([R_2S_2O_3] + 2[R_3Au(S_2O_3)_2]) \qquad [13]$$

$$Vs * [S_3O_6^{2-}]_{total} = Vs * [S_3O_6^{2-}] + Vr * [R_2S_3O_6] \qquad [14]$$

$$Vs * [S_4O_6^{2-}]_{total} = Vs * [S_4O_6^{2-}] + Vr * [R_2S_4O_6] \qquad [15]$$

$$Vs * [S_5O_6^{2-}]_{total} = Vs * [S_5O_6^{2-}] + Vr * [R_2S_5O_6] \qquad [16]$$

$$Vs * [Au(S_2O_3)_2^{3-}]_{total} = Vs * [Au(S_2O_3)_2^{3-}] + Vr * [R_3Au(S_2O_3)_2] \qquad [17]$$

$$3R_2S_2O_{3(s)} + 2Au(S_2O_3)_2^{3-}{}_{(aq)} <=> 2R_3Au(S_2O_3)_{2 (s)} + 3S_2O_3^{2-}{}_{(aq)} \quad log\ K_{16} = a \quad [18]$$

$$3R_2S_3O_{6(s)} + 2Au(S_2O_3)_2^{3-}{}_{(aq)} <=> 2R_3Au(S_2O_3)_{2 (s)} + 3S_3O_6^{2-}{}_{(aq)} \quad log\ K_{17} = b \quad [19]$$

$$3R_2S_4O_{6(s)} + 2Au(S_2O_3)_2^{3-}{}_{(aq)} <=> 2R_3Au(S_2O_3)_{2 (s)} + 3S_4O_6^{2-}{}_{(aq)} \quad log\ K_{18} = c \quad [20]$$

$$3R_2S_5O_{6(s)} + 2Au(S_2O_3)_2^{3-}{}_{(aq)} <=> 2R_3Au(S_2O_3)_{2 (s)} + 3S_5O_6^{2-}{}_{(aq)} \quad log\ K_{19} = d \quad [21]$$

$$-1300 = -2 * [R_2S_2O_3] + -2 * [R_2S_3O_6] + -2 * [R_2S_3O_6]$$
$$+ -2 * [R_2S_4O_6] + -2 * [R_2S_5O_6] + -3 * [R_3Au(S_2O_3)_2] \qquad [22]$$
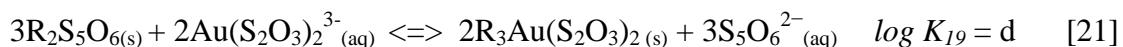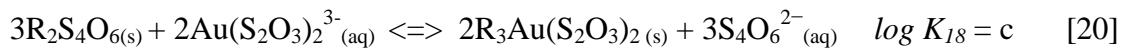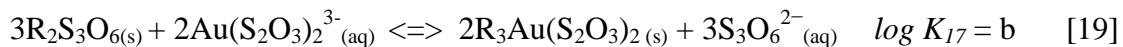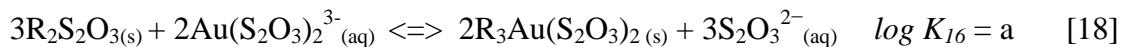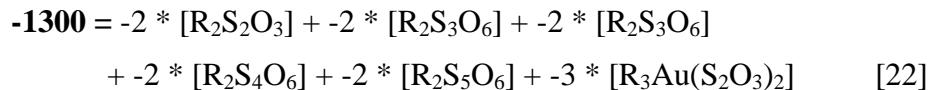
Currently, this model for calculating the equilibrium loading is being incorporated into a more complex model for the semi-batch loading of resin in a resin in pulp circuit. This circuit involves the continuous flow of solution and solids, along with batchwise counter-current transfer of resin. The details of this model will be reported in a future publication.

CONCLUSIONS

The experiments of resin-solution equilibrium (RSE) systems wherein single component, multiple component and mixed polythionates with and without gold applied, have been conducted to study the adsorption of polythionates, thiosulfate and gold on using strong based anion exchange resins. The isotherm kinetics constants for positive exponentially decreasing thiosulfate, trithionate and tetrathionate concentration in loading solution with time were obtained which were approximately be 0.058 min^{-1}, 0.035 min^{-1} and 0.019 min^{-1}, respectively. Meanwhile, the equilibrium constants for the adsorption reactions of thiosulfate-resin + trithionate, trithionate-resin + tetrathionate, and tetrathionate-resin + pentathionate were approximately 95.104, 1.446 and 1.581 on the average obtained using on the model of loading affinities of the species based on the experimental data.

The study on competitive loading of polythionates related to the initial concentration of gold thiosulfate would give the result that trithionate is the most worthy of species on the adsorption of gold thiosulfate on resins. The equilibrium constant of trithionate-resin-gold thiosulfate is approximately 0.53. The rate constants and equilibrium constants for adsorption will be used to effectively model the resin in pulp (RIP) process for further work.

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