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Kinetics and Equilibrium Models for the Adsorption of Thiosulfate and Polyhtionates onto Strong Base Anion Exchange Resin in Batch System

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Abstract:

Kinetic and equilibrium models for the isotherm adsorption of thiosulfate and polyhionate on resin have been developed using mechanistic approach. The models can be used to predict amount of species adsorbed on resin over time and at the equilibrium. Experimental work has been done, and the results are used to validate the models. Lagergren, Ho and Freundlich models are addressed in the results to challenge the developed models. As the results, parameters needed for the isotherm adsorption model are established. Overall, the model-based results are in a good agreement with the experimental results.

Keywords: adsorption, equilibrium, kinetics, modelling, thiosulfate, polythionates
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1. INTRODUCTION

Alternative reagents have been evaluated in recent studies since there are increasing environmental concerns over the use of cyanide as reagent in the gold recovery, Possibly, thiosulfate leaching appears to be one of the most promising alternatives to cyanidation. And not surprisingly many studies on thiosulfate leaching using different oxidants have been published in the last decade (Langhans et al., 1992, Abbruzzese et al., 1995, Jeffrey, 2001, Breuer and Jeffrey, 2002, Breuer and Jeffrey, 2003).

Activated carbon that's successfully used in the cyanidation as carbon in pulp (CIP) and carbon in leach (CIL) processes is ineffective for the adsorption of gold thiosulfate. The reason for this weakness is the poor capacity of carbon adsorbents for gold thiosulfate due to the less affinity of the gold thiosulfate complex than the aurocyanide anion for carbon (Kononova et al., 2001). In contrast, ion-exchange resin adsorbents are more acceptable because of its selectivity for a particular ion or complex including gold thiosulfate. Ion-exchange resins have abundant functional groups of like charge which concentrate the thiosulfate complex of opposite charge (counter-ions), and activated carbon adsorbs the aurocyanide ions between optimally spaced uncharged graphitic layers of the matrix (Grosse et al., 2003).

Lagergren equation (Lagergren, 1989, Vázquez et al., 2007) and Ho equation (Ho et al., 1996) are commonly employed to present adsorption kinetic and to obtain the rate constant based on experimental data. Freundlich model is normally used to present the over-all adsorption capacity and intensity (Faust and Aly, 1998). Yet, the adsorption models of thiosulfate and polythionates onto resin are still limited in the previous studies. Therefore, the main objective of this study would

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be to develop mathematical model for thiosulfate and polythionates adsorbed on strong anion exchange resins in batch system, and the specific objectives would be to develop the isotherm adsorption kinetic model and the equilibrium adsorption isotherm model. The models will be also utilised to predict the amount of species adsorbed on resins based on both liquid and solid phases, and to obtain the overall adsorption capacity and intensity.

2. METHODOLOGY

2.1. Model Development

The adsorption kinetic of an ion exchange reaction could be similar with homogeneous chemical reaction with the assumption that all the available exchange sites are in contact with the solution over time. Therefore the rate of thiosulfate and polythionates adsorbed on resin in batch system is proportional to the species lost in the solution can be expressed as:

$$\frac{d}{dt}X_R(t) = k\frac{\left(X_S(t) - X_S(\infty)\right)V_S}{V_R} \tag{1}$$

where,

k = the rate constant of species adsorbed on resin (min^{-1})
t = the adsorption time (min)
V_R = the resin volume (L)
V_S = the solution volume (L)
$X_R(t)$ = the species concentration on resins at time t (M)
$X_S(t)$ = the species concentration in solution at time t (M)
$X_S(\infty)$ = the species concentration in solution at the equilibrium condition (M)

Meanwhile the overall mass balance of species is:

$$V_R X_R(t) + V_S X_S(t) = V_S X_S(0) \tag{2}$$

Substituting Eq. (2) into Eq. (1), factoring k, and simplification give the equations bellow:

$$\frac{d}{dt}X_R(t) = k\left(-X_R(t) + \delta\right) \tag{3}$$

where

$$\delta = \left(\frac{X_S(0)}{V_R} - \frac{X_S(\infty)}{V_R}\right)V_S \tag{3b}$$

Integrating Eq. (3) results:

$$X_R(t) = \delta - e^{-kt} - C \tag{4}$$

where C as an integration constant. When $t = 0$, $C = \delta$, then the concentration of species adsorbed over time could be predicted using Eq. (5):

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$$X_R(t) = \delta\left(1 - e^{-kt}\right) \tag{5}$$

The adsorption of species on resin at time t, $Q(t)$ (mg/g) can be expressed as Eq (6):

$$Q(t) = \frac{\dfrac{\left(X_S(0) - X_S(\infty)\right)}{m_R}}{V_S MW \left(1 - e^{-kt}\right)} \tag{6}$$

where m_R represents the mass of dry resin (g) and MW is molecular weight of species (g mol^{-1}). Since Eqs. (5) and (6) consist of the equilibrium constant of species, $X_S(\infty)$ it is badly needed to derive a model, so that the concentration of species adsorbed on resin could be predicted at any time before reaching the equilibrium condition. Because $X_S(\infty)$ also represents the concentration of species in the solution, the species concentration on resins at any time t, $X_S(t)$ is worthy to obtain. By substituting Eq. (5) into Eq. (2) for $X_R(t)$, gives:

$$X_s(t) = \left(X_S(0) - X_S(\infty)\right)e^{-kt} + X_S(\infty) \tag{7}$$

While the species concentration at the time t such the adsorption equilibrium condition is being reached, $X_s(t)$ value is equal to $X_S(\infty)$ value. In modelling the equilibrium concentration of species, the deviation between $X_s(0)$ and $X_S(\infty)$ values denoted as AE is consequently applied and give the mathematical expression as below:

$$X_S(\infty) = \frac{\left|X_S(0)e^{-kt_e} - AEe^{-kt_e}\right|}{e^{-kt_e}} \tag{8}$$

where t_e is the time (s) when the adsorption equilibrium condition is being reached, which can be obtained from the batch test. The AE value is obtained from the experimental and simulated results of batch experiments. The absolute value is need to be taken into account in Eq. (8) because AE can be presented as $X_s(0) - X_s(\infty)$ or $X_s(\infty) - X_s(0)$, and there should be a deviation between experimental-based $X_s(\infty)$ and model-based $X_s(\infty)$. Substituting Eq. (8) into Eq. (6) results;

$$Q(t) = \frac{\left(X_S(0) - \dfrac{\left|X_S(0)e^{-kt_e} - AEe^{-kt_e}\right|}{e^{-kt_e}}\right)}{\dfrac{m_R}{V_S MW \left(1 - e^{-kt}\right)}} \tag{9}$$

Then, the equilibrium exchange relationship between the liquid and solid phases can be represented by:

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$$Q_e = \frac{\left(X_S(0) - \dfrac{\left| X_S(0)e^{-kt_e} - AEe^{-kt_e} \right|}{e^{-kt_e}} \right)}{\dfrac{m_R}{V_S MW \left(1 - e^{-kt_e} \right)}} \tag{10}$$

where Q_e denoted as the adsorption of species on resin at the equilibrium time (mg/g). It is also worthy to model the isotherm adsorption kinetics based on the initial concentration of liquid phase, so the equilibrium concentration of species in liquid and on solid phase can be predicted before the equilibrium condition reached. In addition, manipulating the initial concentration of liquid phase is also needed when optimization and control approach is required. Hence, Eqs. (9) and (10) would be modified to expand the AE such as a function of initial concentration of species in solution. Because resin capacity, CP_R (eq/L) is fixed in batch system, the total of available charge surface sites on resin, S_R (eq) is also constant. The constant value is dependent on the resin volume, V_R (L); $S_R = CP_R V_R$. As the consequence, the AE value attains maxima when S_R is filled by charge species, S_S (eq), and the AE trend should be;

$$AE\left(X_S(0)\right) = AE_{\max}\left(1 - e^{-\frac{X_S(0)}{C_A}} \right) \tag{11}$$

where C_A is denotes as a correction factor, which is can be obtained from experimental and model simulation; $X_S(0)/C_A$, and $AE_{\max}$ is maximum AE where the value can be determined using experimental data at the maximum initial concentration of species by which it is assumed that all species in solution filled all the available charge surface sites on resin. Instead of using $AE_{\max}$ term, M term is presented to adopt the step response of a first-order process (Seborg et al., 2004), Eq. (11) can be expressed as;

$$AE\left(X_S(0)\right) = M\left(1 - e^{-\frac{X_S(0)}{C_A}} \right), \quad X_S(0) \subseteq X_{R-S\max}(0) \tag{12}$$

where M is the magnitude of the response; $M = S_S = S_R/V_S$, and $X_{R-S\max}(0)$ is the maximum concentration of species in solution based on resin calculation; $X_{R-S\max}(0) = S_R c_R / c_S$. The $c_R(e)$ is the charge on each site on resin when 1 mol of resin exchange centre being released from resin, and $c_S(e)$ corresponds to the charge of 1 mol species. When $X_S(0) > X_{R-S\max}(0)$, Eq. (12) becomes;

$$AE\left(X_S(0)\right) = M\left(1 - e^{-\frac{X_{R-S\max}(0)}{C_A}} \right) \tag{13}$$

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To compare our modelling result on the adsorption kinetics studies using resin and species adsorbed on resin, the Lagergren equation (Lagergren, 1989, Vázquez et al., 2007) representing the pseudo-first-order model shown by Eq. (14) and Ho equation (Ho et al., 1996) as the pseudo-second-order model shown by Eq. (15) are taken into account and the equations can be presented as;

$$\frac{d}{dt}Q(t) = k_L \left(Q_e - Q(t) \right) \tag{14}$$

$$\frac{d}{dt}Q(t) = k_H \left(Q_e - Q(t) \right)^2 \tag{15}$$

where k_L (min^{-1}) and k_H (g mg^{-1} min^{-1}) are rate constants of adsorption based on Lagergren and Ho, respectively. Freundlich isotherm model, Eq. (16) is also taken into account to highlight the equilibrium isotherm for the adsorption of species. The models can be presented as;

$$Q_e = K_F C_e^{1/n} \tag{16}$$

where C_e (M) is the sorbent concentration in solution at the equilibrium condition ($C_e = X_S(\infty)$), K_F (mg/g) is the Freundlich over-all adsorption capacity, and n indicates the adsorption intensity.

3. RESULTS AND DISCUSSION

The commercial strong based anion exchange resin of Purolite A500/2788 is used in the experimental work and modelling (PUROLITE, 2008). The exchange centre of the resin is the chloride electron. The resin (0.333 g wet) used in the experiments and modelling has parameters as listed in Table 1. As shown in Table 1. m_R value based on experiment is varied but it is still acceptable and much closed to model-based one. For instance, experiment-based m_R are approximately 0.2004, 0.2003, 0.1993, 0.2006 and 0.1998 g for 5 batches.

Table 1. Resin parameters for experiments and modelling

Parameter	Experiments	Modelling
CP_R (eq/L)	1.3	1.3
$c_R(e)$	-1	-1
m_R (g)	~ 0.2	0.2
V_R (L)	~ 0.0005	0.0005
S_R (eq)	~ 0.65	0.65

3.1 Adsorption thiosulfate and polythionates

The adsorption kinetics studies were started by conducting experiment of the thiosulfate Resin-Solution Batch (RSB) system with the initial concentration of 3 mM, the solution volume of 200 mL and 0.333 g of wet resin. The adsorption of species on resin at time *t* until approaching

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equilibrium was calculated based on experiment and modelling in which the equilibrium time for Muslim model, t_e is assumed to be 300 mins, and the result is shown in Figure 1.a. The rate constant for thiosulfate adsorption was worked out using Muslim equations (Eqs. (6) and (12)), Lagergren and Ho equations. Levenberg-Marquardt method (Williams et al., 2002) was used to obtain the rate constant of species adsorption. The same conditions were applied to conduct the experiments of trithionate and tetrathionate RSB systems.
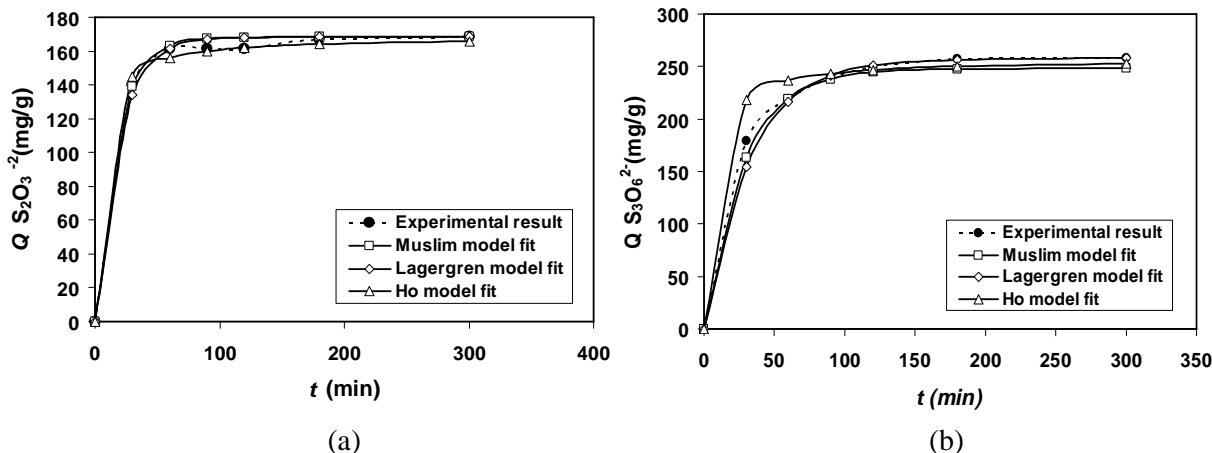

Figure 1. Adsorption kinetics of thiosulfate (a) and trithionate (b) at 25 ^{0}C.

As shown in by the experimental result (dash-dot curve) in Figure 1.a, thiosulfate adsorbed on resin sharply increase from 0 to about 140.136 mg/g with an increasing of time from 0 to 30 mins. It is approximately 138,739 133.785 and 144.825 mg/g based on Muslim, Lagergren and Ho at the adsorption time of 30 mins. Then, it slowly increases with time following first-order model until reaching the equilibrium which is approximately 168.317, 168.297, 168.317 and 165.6299 mg/g based on experiment, Muslim, Lagergren and Ho, respectively at about 300 mins. Not surprisingly, Muslim-based result on thiosulfate adsorbed on resin has better agreement with the experiment-based one compared to the one based on Lagergren and Ho, and the correlation coefficient, R^2 is approximately 0.998, 0.995 and 0.997, respectively using the data shown in Figure 1.a. Meanwhile, the rate constant of thiosulfate adsorption, k, k_L and k_H is approximately 0.0579, 0.0528 and 0.0012 min^{-1}, respectively.

Figure 1.b shows the profile of trithionate adsorbed on resin versus the adsorption time. The rate constant of trithionate adsorption, k, k_L and k_H is approximately 0.0359, 0.0304 and 0.0007 min^{-1}, respectively. As revealed in Figure 1.b, Muslim-based result still has the same trend with the one by experiment, Lagergren and Ho. The equilibrium of trithionate adsorbed on resin based on Lagergren is almost the same as the experiment-based one, which are 257.921 and 257.950 mg/g, respectively. Meanwhile it is lower for the others which are approximately 248.078 and 253.402 mg/g based on Muslim and Ho, respectively. Muslim, Lagergren and Ho based result on trithionate adsorbed on resin has better agreement with the experiment-based result with the R^2 is approximately 0.996, 0.996 and 0.968, respectively. Similarly, Muslim-based modelling result on tetrathionate fits well with the experiment-based result with the R^2 being approximately 0.991 which is the same value with the R^2 of Lagergren-based result. The rate constant of tetrathionate adsorption based on Muslim, Lagergren and Ho, k, k_L and k_H is approximately 0.0199, 0.0205 and 0.0001 min^{-1}, respectively.

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3.2 Equilibrium adsorption thiosulfate and polythionates

Thiosulfate, trithionate and tetrathionate at the concentration range of 1-3 mM were applied in the experiment and modelling work of equilibrium adsorption. Using the k value of each species in the previous results, the data shown in Table 1, and the Levenberg-Marquardt-based optimised C_A value for thiosulfate, trithionate and tetrathionate being 1.0081, 1.3007 and 1.2500 respectively, Freundlich isotherm of the species was worked out using Muslim model, Eqs. (8), (10) and (13). The results are compared with the ones by experiments. Figure 2 shows one of the results by which Muslim model gives closed isotherm adsorption profile to one by the experiment.
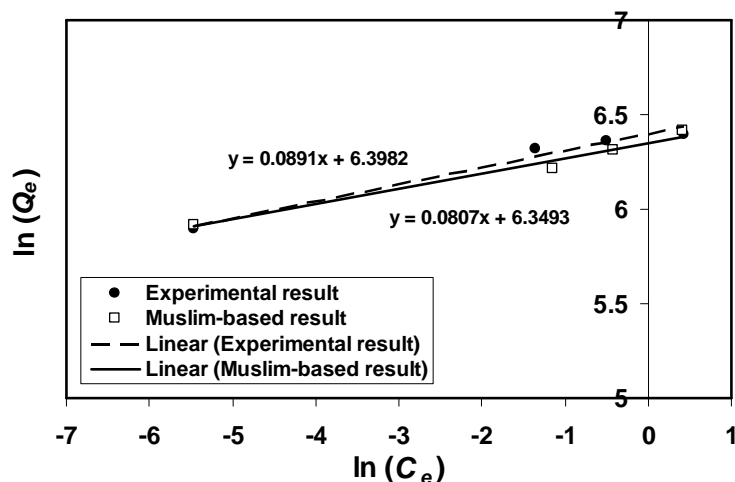

Figure 2. Freundlich isotherm of thiosulfate based on experiment and Muslim model.

As shown by the fitting equations in Figure 2 with R^2 being approximately 0.977 (experimental result) and 0.981 (Muslim-based result), and as written in Table 2, the Freundlich over-all adsorption capacity, K_F is approximately 0.803 (mg/g) based on Muslim model, and it is about 0.806 (mg/g) based on the experiment. The adsorption intensity, n is approximately 12.392 based on Muslim model, and it is about 11.223 based on the experiment. Meanwhile, the K_F value for trithionate and tetrathionate is approximately 0.808 and 0.807 (mg/g), respectively based Muslim model with the fitting R^2 being 0.993 and 0.997, respectively. These are almost the same as the thiosulfate K_F. From the n values, it is clearly shown that trithionate is stronger adsorbed on resin. Overall, the model-based results are in a good agreement with the experimental results as shown by the deviation (D) numbers listed in Table 2.

Table 2. Isotherm adsorption parameter based on experiment and Muslim model

Species	Experiment		Model		K_F-D (%)	n-D (%)
	K_F	n	K_F	n		
Thiosulfate	0.806	11.223	0.803	12.392	0.413	10.409
Trithionate	0.811	14.347	0.808	16.639	0.360	15.973
Tetrationate	0.810	13.351	0.807	14.347	0.324	7.461

Currently, this model is being development for gold thiosulfate, single component and multiple components in batch systems. The details of this model will be reported in a future publication.

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4. CONCLUSION

Models presenting the isotherm adsorption kinetic and equilibrium of thiosulfate and polythionate on resin have been developed. Experimental works were conducted in batch with thiosulfate, trithionate and tetrathionate in solution and commercial strong based anion exchange resin of Purolite A500/2788. As a result on the kinetic model, the rate constants were obtained by which the model-based result is compared with Lagergren and Ho-based results. It fits well with the experimental result, and the correlation coefficient, R^2 is approximately 0.998, 0.996 and 0.991 for thiosulfate, trithionate and tetrathionate, respectively. Using the rate constants and the proposed equilibrium model, parameters in the Freundlich equilibrium isotherm for the adsorption of all species on resin were obtained with the average R^2 being approximately 0.991. The average model-based adsorption capacity, K_F is approximately 0.806 mg/g which is very close to the one by experiment, being 0.809 mg/g. Overall, trithionate is stronger adsorbed on resin as indicated by the adsorption intensity number.

5. ACKNOWLEDGMENT

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