Competitive Equilibrium Adsorption of Metal Cyanides on Activated Carbon

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Abstract

Adsorption equilibria in aqueous solutions of metal cyanides are imperative in the description of the adsorption behavior of carbon-in-pulp plants. The transfer of oxygen into the liquid phase was found to have a critical influence on adsorption equilibria of both gold and silver cyanides on activated carbon. Freundlich isotherm expressions described the equilibria of adsorption of single metal cyanides on carbon adequately over a wide range of concentrations. These expressions were used, together with competition coefficients estimated from binary systems of metal cyanides, to yield Freundlich-type multicomponent isotherms for the competitive adsorption of gold and silver cyanides on activated carbon. It was shown that the ideal adsorbed solution model is not applicable to the adsorption of gold and silver cyanides on activated carbon.

INTRODUCTION

Cyanide has been the main lixiviant for most of the primary gold and for a significant proportion of the primary silver produced in the world. Gold and silver can be recovered from these pulps or solutions using adsorption on activated carbon in combination with zinc dust cementation or electrowinning.

The availability of granules of hard activated carbon, developed in the Second World War, made it possible to use carbon directly in the

cyanided pulp so as to avoid the costly filtration step. In 1952 Zadra et al. (*1*) developed a technique for the effective elution of both gold and silver from loaded carbon by the use of a hot sodium hydroxide–sodium cyanide solution. By 1973 the carbon-in-pulp (CIP) process had been introduced at the Homestake Mine in South Dakota for the treatment of 2,050 tons/d of cyanided slime (*2*). This operation has changed the image of the CIP process from an experimental process into an economically viable process for the treatment of high tonnage flows.

Six of the 10 largest mines in the United States are currently employing CIP technology for the recovery of gold and silver (*3, 4*). Menne (*5*) predicted that CIP plants with a total capacity of 4.7 million tons per month will be operational in South Africa by the end of 1985.

Although much work has been published on the mechanism by which activated carbon loads inorganic species, these theories still remain a matter of controversy. Tsuchida et al. (*6*) provided experimental evidence that gold and silver cyanides are adsorbed on activated carbon as neutral species. These species were believed to be the salts of the cyanide complex, with the cation and anion at separate nearby sites. The $Au(CN)_2^-$ or $Ag(CN)_2^-$ may be oxidized by adsorbed oxygen to AuCN or AgCN at some of the active sites. Both Dixon et al. (*7*) and Davidson et al. (*8*) observed lower equilibrium gold loadings when nitrogen instead of oxygen or air was bubbled through a solution of gold cyanide.

Jevtitch and Bhattacharyya (*9*) showed that the adsorption of various cadmium chelates on activated carbon obeyed the Freundlich isotherm. This isotherm has also been used by various authors to describe the adsorption of gold cyanide on carbon from synthetic solutions (*10, 11*). Tsuchida et al. (*6*) showed that not only gold, but also silver and mercury cyanides follow the Freundlich isotherm during adsorption on activated carbon. As mentioned by Peel (*12*), some systems which fit a Langmuir model have also been shown to fit the Freundlich model. Therefore, mechanistic significance should not be attached to the coefficients of the isotherms, which instead should be regarded as empirical curve-fitting procedures.

Despite the fact that most CIP plants treat pulps containing both gold and silver cyanides, no research has been published on any aspect of the competitive adsorption of two or more metal complexes on activated carbon. Multicomponent equilibrium expressions are imperative in the modeling of CIP plant dynamics. This paper is concerned with the application of existing multicomponent isotherms to the competitive equilibrium adsorption of gold and silver cyanides on activated carbon.

EXISTING MULTICOMPONENT ISOTHERMS

Fritz and Schlünder (13) proposed a general empirical equation for calculating the adsorption equilibria of organic solutes in aqueous solution:

$$q_l = \frac{A_l C_l^{n_{l,0}}}{D_l + \sum_{k=1}^{N} B_{l,k} C_k^{n_{l,k}}} \qquad (1)$$

For $n_{l,0} = n_{l,k} = D_l = 1$, this expression becomes the Langmuir model for multisolute systems (14). With $N = 1$ and $D_l = 0$, the Freundlich equation can be obtained from Eq. (1). In this equation the number of parameters which have to be estimated in order to describe the interaction between solutes increases rapidly with the number of adsorbates.

A simpler multicomponent isotherm which is also based on the Freundlich isotherm was derived by Sheindorf et al. (15). It is assumed that the coverage by each sorbate at each energy level is given by the competitive Langmuir isotherm. The preexponential coefficient A_l and the exponent n_l in the single solute Freundlich equation

$$q_l = A_l C_l^{n_l} \qquad (2)$$

are parameters of this multicomponent isotherm:

$$q_l = A_l C_l \left(C_l + \sum_{\substack{k=1 \\ k \neq l}}^{N} B_{l,k} C_k \right)^{n_l - 1} \qquad (3)$$

where $l = 1, 2, 3, \ldots, N$.

The isotherm for each component in an N-component system employs $N - 1$ competition coefficients $B_{l,k}$ which should be determined experimentally or from thermodynamic data. Although Sheindorf et al. (15) showed this isotherm to correlate well with binary equilibrium data for various organics, this isotherm has not been cited in other publications on multicomponent adsorption. Parameter estimation in this isotherm is much simpler than that for the isotherm in Eq. (1). For a binary system, Eq. (3) can be written as:

$$q_1 = A_1 C_1 (C_1 + B_{1,2} C_2)^{n_1 - 1} \qquad (4)$$

and

$$q_2 = A_2 C_2 (C_2 + B_{2,1} C_1)^{n_2 - 1} \tag{5}$$

These equations can be written in the form:

$$f(C_1) = \left\{ \left(\frac{A_1 C_1}{q_1} \right)^{1/(1 - n_1)} - C_1 \right\} = B_{1,2} C_2 \tag{6}$$

and

$$f(C_2) = \left\{ \left(\frac{A_2 C_2}{q_2} \right)^{1/(1 - n_2)} - C_2 \right\} = B_{2,1} C_1 \tag{7}$$

Sheindorf et al. (15) plotted the terms $(A_1 C_1 / q_1)^{1/(1 - n_1)}$ and $(A_2 C_2 / q_2)^{1/(1 - n_2)}$ versus C_2 and C_1 at constant values of C_1 and C_2, respectively. This involves tedious experimental work, as a constant equilibrium concentration of one component is not obtained easily when different equilibrium concentrations for the other component have to be established in order to cover a wide range of experimental points on such plots. In this paper the left-hand sides of Eq. (6) and (7) are plotted versus C_2 and C_1, respectively, and the competition coefficients $B_{1,2}$ and $B_{2,1}$ estimated from the slopes of these plots.

One of the more significant developments in multicomponent adsorption studies in recent years is the formulation of the ideal adsorbed solution (IAS) theory (16), which predicts multisolute equilibria from the single species isotherms of the respective adsorbates. A practical concern in applying this model is its increasing mathematical complexity as the number of components increases, regardless of the simplicity of the single solute isotherm equation. The IAS theory defines adsorption equilibrium by the following set of equations:

$$C_i = x_i C_i^0 \tag{8}$$

$$q_i = x_i q_T \tag{9}$$

$$q_T = \left[\sum_{l=1}^{N} \frac{x_l}{q_l^0} \right]^{-1} \tag{10}$$

$$\sum_{l=1}^{N} x_l = 1 \tag{11}$$

$$\Pi_i = \frac{RT}{A_p} \int_0^{C_i^0} q_i^0 \frac{dC_i^0}{C_i^0} \tag{12}$$

Since single solute concentrations C_i^0 are defined at the same spreading pressure as that of the mixture,

$$\Pi_l = \Pi_{k \neq l} \tag{13}$$

The relationship between q_l^0 and C_l^0 is given by the single solute isotherm for component l, which is a Freundlich isotherm in this paper. The equilibrium loadings q_l can be calculated from the IAS theory for a specified set of C_l values by solving Eq. (8) to (13) simultaneously with the single solute isotherms.

Although the IAS model has been applied successfully to the competitive adsorption of various organics on activated carbon (*17, 18*), no attempt has been made to apply this model to inorganic or ionic systems. According to Fritz et al. (*17*), deviations from the IAS model can be found in mixtures where the solutes are partially dissociated, or when there is a great difference in the sizes of the molecules of the individual solutes.

EXPERIMENTAL

Potassium aurocyanide, $KAu(CN)_2$, and potassium argentocyanide, $KAg(CN)_2$, were used as adsorbates. The potassium aurocyanide was obtained as a pure crystalline salt from Barry Colne & Co. The potassium silver cyanide was prepared by dissolving silver cyanide, AgCN, in a potassium cyanide solution and reducing the level of free cyanide in solution by the addition of hydrochloric acid. Glass distilled deionized water was used in all experiments.

Le Carbone G210 AS coconut shell charcoal, obtained from Gencor Group Laboratories (East), was used in all experiments. The carbon used was in the sieve size fraction 1.4 to 1.7 mm and had an apparent density of 980 kg/m^3. All samples of carbon were dried at 100°C for 3 days before being weighed for use in experiments.

A pH of 8.5 was maintained in all experiments by adding small amounts of KOH solution or dilute HCl. The liquid phase temperature was regulated between 18 and 20°C. Atomic absorption spectrophotometry was used in all experiments to measure the concentration of gold and silver in solution. The equilibrium loadings of gold and silver on carbon were calculated by mass balance. At the end of each experiment the samples of carbon were analyzed for gold and silver by x-ray fluorescence spectrometry. These assays were conducted by the Council for Mineral Technology, using the method described by Balaes (*19*).

Different amounts of carbon were added to 1.0 L of solution at different initial concentrations of gold and silver in solution. Initially, these mixtures were rolled in sealed plastic bottles in such a way that the carbon granules were kept in suspension. One bottle containing gold cyanide and one containing silver cyanide were rolled without carbon to serve as a blank. Small samples of solution were taken intermittently and analyzed for gold and silver until attainment of equilibrium was assured after about 4 months. Some of these mixtures were agitated in stirred tanks which were open to the atmosphere. Owing to evaporation, the level of liquid in these tanks had to be maintained by the addition of distilled water. In this case, equilibrium was attained after about 2 weeks.

RESULTS AND DISCUSSION

The equilibrium data obtained in this study consist of the single species isotherm data of gold cyanide and silver cyanide, and equilibrium concentrations involving the simultaneous adsorption of these cyanides.

Figures 1 and 2 show typical single species isotherm curves obtained for gold and silver cyanides in closed bottles after 4 months of agitation on rollers. When these closed bottles were opened to the atmosphere and left without further agitation, the concentrations of both gold and silver in solution decreased significantly. When the contents of these bottles were transferred to open agitated vessels, loadings of silver and gold on the carbon increased rapidly. It appears as if sufficient oxygen should be present in solution for the attainment of a true equilibrium. This is in agreement with the findings by Dixon et al. (7) and Davidson et al. (8), who concluded that the exclusion of oxygen from the system reduced the number of active sites available. When the bottles were opened and agitated by hand once a day, the increase in gold and silver loadings on the carbon was much slower. However, the equilibria achieved eventually were the same as those obtained in open agitated vessels. These equilibria obtained in open vessels are also shown in Figs. 1 and 2. This effect of oxygen is usually not discussed in work on the adsorption of organics on activated carbon, and many authors do not mention whether open or closed vessels are considered.

Although some authors have found it necessary to use segmented Freundlich isotherm expressions for the adsorption of organics on activated carbon (17, 18), the isotherms presented in Figs. 1 and 2 may be described adequately by simple Freundlich expressions. The following isotherm expressions have been estimated by least-squares regression of
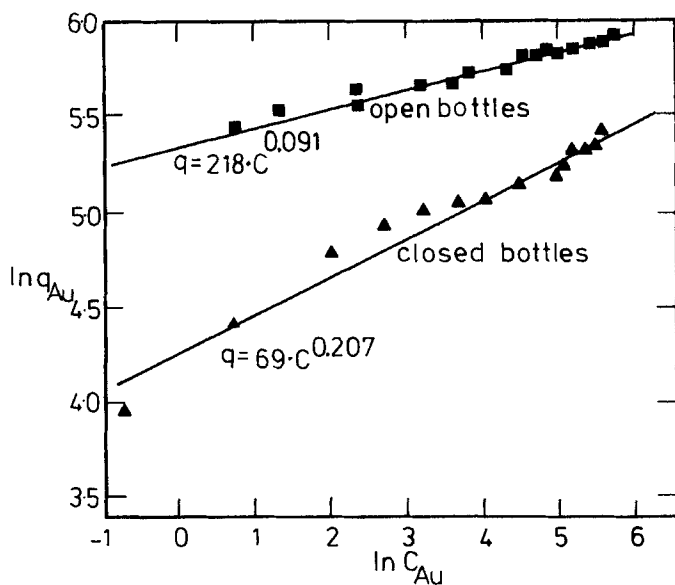
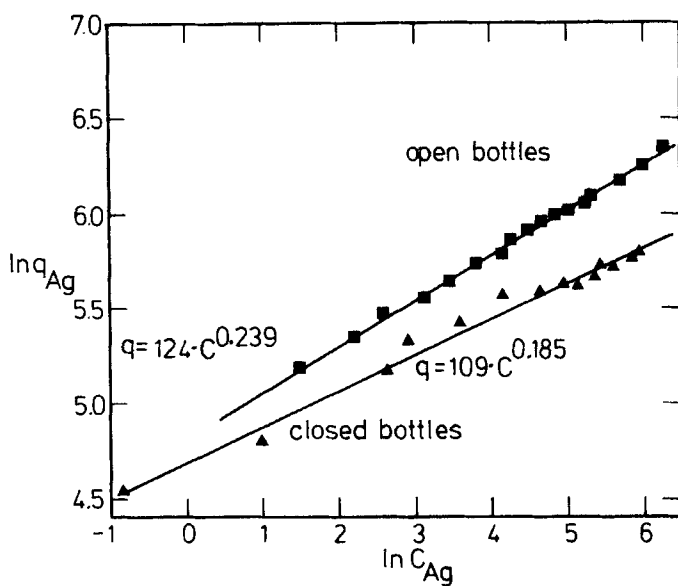FIG. 1. Equilibrium adsorption of gold cyanide on granular carbon.

FIG. 2. Equilibrium adsorption of silver cyanide on granular carbon.

TABLE 1

Comparison of Experimental and Predicted Values for the Competitive Equilibrium Adsorption of Gold and Silver Cyanides on Activated Carbon

					Predictions			
				Freundlich-type model		IAS theory		
Experimental data				q_{Au} pred	q_{Ag} pred	q_{Au} pred	q_{Ag} pred	
C_{Au} (μmol/L)	C_{Ag} (μmol/L)	q_{Au} (μmol/L)	q_{Ag} (μmol/L)	q_{Au} exp	q_{Ag} exp	q_{Au} exp	q_{Ag} exp
1	9	135	141	0.601	1.089	1.520	0.029
3	19	149	135	0.975	0.975	1.584	0.038
5	28	163	159	1.052	0.805	1.543	0.040
10	83	179	154	0.882	1.292	1.485	0.101
15	93	193	148	0.948	1.206	1.428	0.103
25	111	200	159	1.059	1.002	1.443	0.100
30	139	216	142	0.985	1.207	1.353	0.133
41	176	227	148	0.977	1.189	1.320	0.149
46	185	241	143	0.948	1.208	1.258	0.157
61	195	243	164	1.019	0.932	1.279	0.132
76	204	254	160	1.032	0.870	1.252	0.133
102	269	270	148	0.998	0.998	1.203	0.174
162	343	296	142	0.988	0.963	1.144	0.203
198	352	304	134	1.003	0.918	1.135	0.208
279	399	322	136	1.003	0.808	1.105	0.210

equilibrium data obtained in open containers, and will be used in the prediction of competitive adsorption:

$$\text{Gold cyanide: } q_{Au} = 218C_{Au}^{0.091} \tag{14}$$

$$\text{Silver cyanide: } q_{Ag} = 124C_{Ag}^{0.239} \tag{15}$$

Table 1 shows equilibrium concentrations in solution and loadings on the carbon measured during the competitive adsorption of gold and silver cyanide on activated carbon. The functions $f(C_{Au})$ and $f(C_{Ag})$ were calculated from these data and the parameters given in Eqs. (14) and (15).

Figure 3 shows a linear relationship between $f(C_{Au})$ and C_{Ag}. The slope of the line was determined by least-squares regression to be 0.098. The equilibrium loading of gold during the competitive adsorption of gold and silver cyanides is then given by

$$q_{Au} = \frac{218C_{Au}}{(C_{Au} + 0.098C_{Ag})^{0.909}} \tag{16}$$

The competition coefficient of 9.561 estimated from the slope of the linear relationship between $f(C_{Ag})$ and C_{Au}, depicted in Fig. 4, yields the following expression for the equilibrium loading of silver during the competitive adsorption of gold and silver cyanides on carbon:

$$q_{Ag} = \frac{124C_{Ag}}{(C_{Ag} + 9.561C_{Au})^{0.761}} \tag{17}$$

The ratios of predicted versus experimental values given in Table 1, rather than Figs. 3 and 4, should be used to assess how well the Freundlich-type multicomponent isotherm fits experimental data. Table 1 shows that this isotherm gives sufficiently accurate predictions of the equilibrium gold and silver loadings. In this case the agreement between prediction and experiment is of the same degree as that obtained by Larson and Tien (18) between the IAS theory and experiment.

The IAS theory was used to predict equilibrium loading of gold and silver from the single-species isotherms, Eqs. (14) and (15), for each of the sets of values of C_{Au} and C_{Ag} given in Table 1. The results, given in Table 1, show that the agreement between prediction and experiment is completely unacceptable. Jossens et al. (20) observed that organics which are partially dissociated exhibit large deviations from the IAS theory, and suggested that discrepancies are caused by dissociation effects rather than nonidealities in the adsorbed phase. Furthermore, Tsuchida et al.
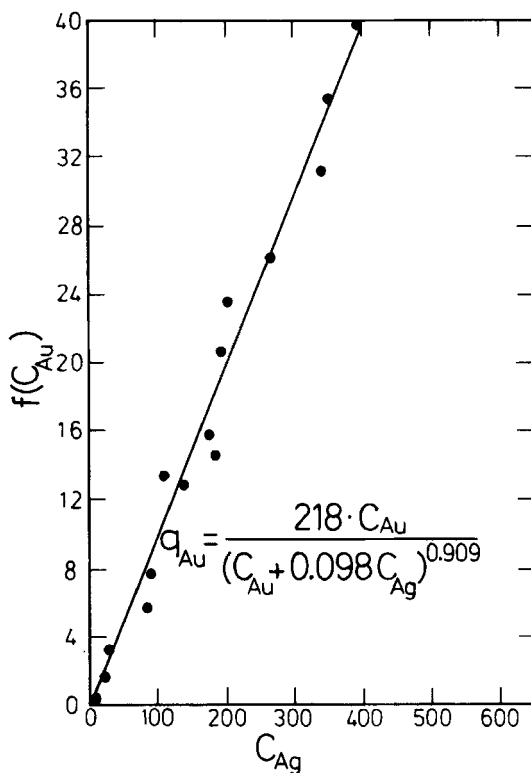
FIG. 3. Competitive adsorption of gold and silver cyanides on carbon, presented in the linear form of the Freundlich-type multicomponent isotherm: estimation of the competition coefficient $B_{Au, Ag}$.

(6) suggested that the salts of cyanide complexes adsorb on activated carbon as dissociated cations and anions at separate nearby sites. This could explain the inability of the IAS theory to simulate the competitive equilibrium adsorption of gold and silver cyanides on carbon.

CONCLUSIONS

The transfer of oxygen into the liquid phase was found to have a significant influence on the adsorption of gold and silver cyanides on activated carbon. A Freundlich-type multicomponent isotherm describes the competitive equilibrium adsorption of these cyanides adequately. The IAS theory is not applicable to the system studied.

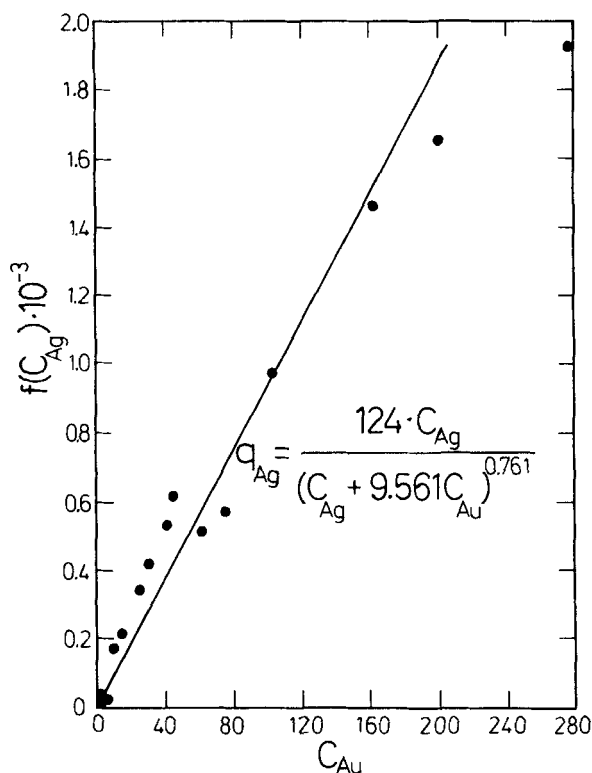$$q_{Ag} = \frac{124 \cdot C_{Ag}}{(C_{Ag} + 9.561 C_{Au})^{0.761}}$$

FIG. 4. Competitive adsorption of gold and silver cyanides on carbon, presented in the linear form of the Freundlich-type multicomponent isotherm: estimation of the competition coefficient $B_{Ag, Au}$.

This paper presents a first approach to the modeling of the competitive adsorption of metal cyanide on activated carbon. Much more work should be done before the dynamics of the simultaneous adsorption of precious metal cyanides and other contaminants in a carbon-in-pulp system can be modeled.

SYMBOLS

A_l Freundlich isotherm coefficient for component l

A_p surface area per unit mass of carbon (m^2/g)

$B_{l, k}$ competition coefficient in multicomponent isotherms

C_l solution phase concentration of component l at equilibrium ($\mu mol/L$)

C_l^0 solution phase concentration of component l in its single-species state at equilibrium (μmol/L)

D_l empirical constant in Eq. (1)

f function defined in Eqs. (6) and (7)

n_l Freundlich isotherm exponent for component l

q_l loading of component l on carbon at equilibrium (μmol/g)

q_l^0 loading of component l in its single-species state on carbon at equilibrium (μmol/g)

q_T total loading on carbon at equilibrium (μmol/g)

R ideal gas law constant (J/(μmol $\cdot$ K))

T absolute temperature (K)

x_l molar fraction of component l on the carbon

Greek

Π_l Spreading pressure of component l, which is the lowering of surface tension at the carbon–solution interface

Acknowledgments

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