ADSORPTION OF ACIDIC GOLD-THIOUREA COMPLEX ONTO A STRONG CATION EXCHANGE RESIN.

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Abstract The adsorption of gold-thiourea complex onto a cation exchange resin, Amberlite 252, has been evaluated in a batch stirred reactor. The observed non equilibrium saturation capacity was 3.20 meg Au/g dry resin (620 kg/t) whereas the equilibrium ion exchange capacity was only 0.53 meq/g (103 kg/t). The enthalpy of adsorption was 4 - 25 kJ/mole under equilibrium conditions and increased to 20-200 kJ/mole under non equilibrium conditions. Under non equilibrium conditions, the adsorption capacity of the resin decreased with increasing temperature and increasing thiourea concentration and increased with increasing gold concentration. This dependence of adsorption capacity on thiourea concentration and temperature may be a useful tool for elution of gold from the loaded resin. Scanning electron microscopy revealed evidence of deposition of elemental gold on the loaded resin under non equilibrium conditions. The proposed mechanism for "adsorption" of gold-thiourea complex onto this cation exchange resin consists of an ion exchange reaction followed by a reduction of the exchanged gold complex to elemental gold on the surface of the resin.

Introduction

Cyanidation is the most effective and economical process for treating a wide range of gold-bearing ores. However, some characteristics and disadvantages of the cyanidation process demand the development of an alternative extraction process, and the thiourea process may be a viable alternative.

The major concerns with cyanidation are the health and environmental problems associated with it. These include the possible formation of deadly hydrogen cyanide gas, the ingestion or adsorption through the skin of cyanide salts, the formation of free forms of cyanide in effluent water, and formation of complexes with organic and inorganic substances that are difficult to destroy with conventional destruction methods. Increased environmental and health concerns about the toxicity of cyanide may lead to even stiffer environmental laws and regulations that may be difficult to meet with the present destruction techniques. Federal regulations and guidelines currently specify the limit for discharge from mines and treatment plant effluents at a maximum of 0.02 mg/L total cyanide per day and not to exceed an average daily value of 0.01 mg/L for thirty (30) consecutive days.

Thiourea, on the other hand, is not restricted by the same toxicity factors as cyanide. Toxicity data on thiourea indicate that it has a high threshold limit for mammals and a lethal dose of 10 g/kg for humans. Thiourea has been used for years in the treatment of thyroid diseases in humans and is currently considered non-carcinogenic to humans. However, some studies have shown thiourea to be carcinogenic to rats and trout. Therefore, the State of California, in 1989 (Chemical Engineering, 1989) added thiourea to their list of carcinogenic substances. After several years of investigation (20 years) a major manufacturer (SKW Trostberg, 1985) of thiourea have concluded that thiourea is a product with low acute toxic effect. According to the classification by Toxicology of Drugs and Chemicals (Academic Press 1969), thiourea is considered as slightly toxic upon dermal administration. Therefore, by observing normal safety practice, thiourea can be considered much safer than cyanide.

Another disadvantage of cyanidation is the slower kinetics of dissolution of gold species by cyanide. Theoretical considerations indicate that this disadvantage cannot be overcome easily without considerable increases in consumption of reagents and operation costs. The kinetics of thiourea dissolution of gold is several times faster than those of cyanide.

Yet another disadvantage of cyanidation is the inhibition of the dissolution of gold caused by the presence of some ionic species. Species such as Cu, Fe, Ni, Co, Zn, Cd, As, Sb tend to form ionic complexes with cyanide and reduce the availability of cyanide for gold dissolution. The presence of these species affects thiourea leach process to a much lesser degree.

The main disadvantage of the thiourea process is the higher cost of the reagent and the consumption. In spite of this disadvantage, the thiourea process can be used for special materials where the grade will warrant the higher cost of the overall process. The thiourea process has the potential application in the treatment of refractory sulfide and carbonaceous gold ores. These ores are currently pretreated by roasting, pressure oxidation or bioxidation before cyanidation for gold recovery. These pretreatment techniques all result in the production of acid solutions that require neutralization prior to cyanide leach. Use of acidic thiourea instead of cyanide would allow for immediate leaching of gold without neutralization and result in considerable savings through the elimination of the neutralization step.

For the thiourea process to compete industrially with cyanidation, it is essential to develop efficient process(es) to recover the gold from solution. Research on the leaching of gold by thiourea has been reported extensively in the literature (Plaskin, 1941; Groenewald, 1977; Becker, 1983; Bolten, 1984; Charley, 1984; Bilston, 1984; Gabra, 1984; and Hisson, 1984), but research on the recovery of gold from leach solutions has not been well documented. Some methods for recovering gold-thiourea complex reported in the current literature include electrochemical, activated carbon adsorption, ion-exchange adsorption, precipitation by metal powders and reduction by sulfur dioxide gas (Maslii, 1970; Bek, 1971; Becker, 1983; Varentsov, 1983; Zamyati, 1983; Charley, 1984; Simpson, 1984; Schulze, 1984; Hiskey, 1984; Yen, 1985; Deschenes, 1986, and Lodeishikov, 1986). A review of the current literature reveals that there is no clear consensus among researchers concerning the methods for the recovery of gold from thiourea solutions. It was also obvious from the literature that the maximum loading capacity of ion exchange resins for gold-thiourea complex was not higher than 100 kg/t.

The data presented in this paper are from a detailed adsorption study conducted at the University of Minnesota to evaluate the adsorption characteristics of a cation exchange resin (Amberlite 252) for gold-thiourea complex. We achieved loading capacity values greater

than 200 kg/t of gold for Amberlite 252. The apparent saturation capacity for the resin ranged from 220 to 650 kg/t (1.3 to 3.2 meq/g) whereas the equilibrium ion exchange capacity was only 103±2.3 kg/t (0.526±0.012 meq/g). The adsorption capacity of Amberlite 252 for gold-thiourea complex decreased with increasing concentration of thiourea and increasing temperature. The adsorption capacity increased with increasing concentration of gold. The dependence of the adsorption capacity on temperature and thiourea concentration may be a useful tool for the elution of the loaded gold-complex from the resin. The loaded resin may be eluted using higher concentration of thiourea at elevated temperatures.

Examination of the loaded resin by scanning electron microscope, revealed deposits of elemental gold on the surface of the resin. The presence of elemental gold on the surface of the resin was unexpected and could not be explained at the time of the study. However, other researchers have since reported the presence of elemental gold on the surface of carbon after the latter have been used to adsorb gold-thiourea complex. The presence of elemental gold on the surface of adsorbents suggests some reduction mechanism accompanying the adsorption of gold-thiourea complex.

The proposed mechanism of adsorption of gold-thiourea complex consists of an ion exchange between the cationic gold complex and the positive functional groups on the resin. This adsorbed gold complex is later reduced to elemental gold on the surface of the resin.

Experimental

1. Gold-thiourea Stock Solution.

A synthetic gold-thiourea solution was prepared with reagent grade gold powder (325 mesh, 99.99% Au). The gold powder was dried at about 100° C for twenty-four hours in a desiccator. An acidic thiourea solution was prepared by dissolving 19.0 g of previously dried reagent grade thiourea and 6.3 g of ferric sulfate in approximately 1000 mL of acidified water (1.5 pH). Mixing the solid thiourea and ferric sulfate thoroughly before adding the mixture to the acidified water is important. Two and half grams of cysteine was dissolved in the thiourea solution before adding 1.0 g of previously dried gold powder. The mixture was digested until all the gold was completely dissolved (about 60 minutes leaching time). A stock solution containing about 1000 mg/L gold in 0.25 M thiourea and 2.5 g/L cysteine was thus prepared. The concentration of gold in the stock solution was 995.0 mg/L by atomic adsorption spectrophotometer (AAS). The gold-thiourea solution for the adsorption capacity tests was prepared as needed by diluting this stock solution to the desired concentration with acidified water and cysteine. The typical diluted solution contained 0.025 M thiourea, 0.55 g/L ferric sulfate, 0.45 g/L cysteine at 1.5 pH and 250 mV Eh (vs. SCE).

2. Cationic Resin, Amberlite 252.

Amberlite 252 is a synthetic, high capacity, macro reticular cation exchange resin supplied as insoluble black, spherical particles. The matrix is styrene/divinylbenzene, highly crossed linked with fixed sulfonic SO_3^- ionic groups. Amberlite 252 is manufactured by Rhom and Hass of Philadelphia, PA with a reported minimum total exchange capacity of 4.4 meq/gram resin. The resin is supplied in sodium (Na^+) form and conditioned according to the procedure described later in the text. The as-received resin was first wet screened to determine the size distribution and to provide monosized fractions for the capacity tests. The physical characteristics and the size distribution of Amberlite 252 are listed in Table 1 and Table 2. The adsorption capacity tests used 20 x 28 mesh monosized fraction.

2a. Resin Conditioning.

The resin was conditioned according to the accepted standard procedure described below (Dowex Ion exchange Manual, Dow Chemical Company). The procedure involves converting the cation resin in sodium (Na^+) form to hydrogen (H^+) form and back to sodium (Na^+) form by successively conditioning with HCl and NaOH. The standard procedure for conditioning consisted of the following steps:

1. Transfer the resin into a vertical column (about 20 cc. of resin).
2. Backwash resin in the column with double distilled water to remove entrained air bubbles and classify resin particles (use a masterflex peristaltic pump). Use flow rates to just fluidize the resin particles without overflowing.
3. Stop backwash and allow resin to settle.
4. Drain water from the top of the settled resin bed.
5. Fill resin bed with approximately 2 bed volumes of 1 - 2.0 N HCl using a peristaltic pump at very slow flow rates (< 2.0 cc/min.).
6. Wash acid through the resin bed with 10-15 bed volumes of double distilled water for 30 minutes.
7. Repeat step No. 4
8. Repeat step No. 5 with 2 bed volumes of 1 - 1.5 N NaOH.
9. Wash alkali NaOH through resin bed with 8 - 10 bed volumes of distilled water per hour for 30 minutes.
10. Drain water from resin bed, empty resin and save in fully swollen form until ready to use.

3. Determination of Resin Weight (dry basis).

Since the resin was kept in wet swollen form without drying, it was necessary to determine the dry weight of the resin from the measured weight of the wet resin. The swollen resin was centrifuged in a laboratory centrifuge at 5000 rpm for 20 minutes in a specially designed centrifuge tube with fritted glass bottom to remove maximum amount of moisture. The centrifuged resin was transferred into a beaker, mixed thoroughly and the required amount was weighed out. The moisture content of the as-recieved resin (supplied by manufacturer) was used as an estimate of the moisture content of the

conditioned resin. This moisture content value was used to calculate the weight of the wet settled resin needed for each test. A sample of the resin was taken before and after weighing of the test sample and used to determine the actual moisture content of the conditioned resin. This moisture content was used to calculate the actual weight of the resin (dry basis) used for each test.

4. Adsorption Capacity Test Procedure.

Figure 1 shows the schematic diagram of the apparatus used for the adsorption capacity test. The apparatus consisted of a specially designed twelve multi mixer unit that was set over a hot water bath to maintain constant temperature of reaction. Since each capacity test was ran in sets of six, it was convenient to perform two capacity tests simultaneously. Agitation of the reactants was provided by a 3-blade polyethylene impeller (1¾" diameter) with a motor at specified constant rpm. The procedure consisted of contacting six (6) varying weights (dry basis) of resin with 400 mL. of gold-thiourea solution in six (6) 600-mL. tall beakers. The initial pH and Eh of the gold solution were measured and adjusted where necessary. The beakers were set in the hot water bath, heated to the desired constant temperature and agitated at constant impeller speed for a specified time (until equilibrium is achieved). The time allowed to achieve equilibrium adsorption was decided by analyzing the concentration of gold in the bulk solution at various times.

Equilibrium was considered attained when the concentration of the bulk solution remained approximately constant after two consecutive sampling intervals. At the end of the test, the resin was separated from the bulk solution by filtration and the solution was analyzed for gold content using the atomic absorption spectrophotometer. The procedure for determination of gold in thiourea solutions with AAS has been described elsewhere (Mensah-Biney, 1994). The adsorption capacity in mg Au per g of resin was determined from solution assays only.

The initial tests used small amounts of resin to achieve higher capacity levels. These tests are referred in this paper as those with high level of resin utilization. Other additional tests were performed with excessive amounts of resin to increase the rate of adsorption and to attain equilibrium adsorption within the times investigated. Those tests are referred to as tests with low level of resin utilization

Results and Discussion.

The dissolution of gold by thiourea involves the formation of a single cationic species of gold by thiourea in an acidic medium according to the reaction

$$Au_0 + 2CS(NH_2)_2 = Au[CS(NH_2)_2]_2^+ + e^- \quad [1]$$

During the ion exchange process this single cationic gold species (gold-thiourea complex) is exchanged for the cationic groups on the resin. The general ion exchange reaction is represented as:

$$RN.H^+ + Au[CS(NH_2)_2]_2^+ \leftrightharpoons RN.Au[CS(NH_2)_2]_2^+ + H^+ \quad [2]$$

In theory this reaction can be reversed and driven in the opposite direction with acids to elute the gold from the loaded resin. However, in practice, strong acid cation exchange resins adsorb the gold-thiourea complex so strongly that complete elution of gold from the resins has been difficult even with high concentration of acids. The present study was not designed to evaluate the reversal of the equilibrium reaction. All the tests were performed to evaluate the forward reaction involving the exchange of the gold-thiourea complex for the cationic groups on the resin.

The adsorption capacity of the resin was calculated from the concentration of gold in the initial and final solution as mg of gold adsorbed per g of resin used. These values were converted to meq Au per g of resin or kg Au per tonne of resin. The influence of the following variables on the adsorption capacity was evaluated:

1. Time.

Under normal ion exchange equilibrium studies, the contact time to reach equilibrium is usually on the order of several hours. However, our previous experience with gold adsorption revealed that we could not attain equilibrium loading even after several days of contact. Therefore, we investigated the influence of time on the attainment of equilibrium adsorption. Two sets of tests were performed at 48 hours and 144 hours. Table 3 lists the adsorption capacity data at varying initial gold concentrations. The change in adsorption capacity as a function of time is also included in the table as ΔQ (Q_2/Q_1) where Q_1 is the capacity at time t_1 and Q_2 is the capacity at time t_2 ($t_2 > t_1$). Figure 2 shows a typical adsorption isotherm for Amberlite 252 demonstrating the influence of time. The adsorption capacity increased by 10 - 14% when the contact time was increased from 48 to 144 hours. The data did not demonstrate clearly attainment of equilibrium adsorption in 144 hours. Moreover, the adsorption equilibrium was complicated by the evidence of reduced gold on the surface of the loaded resin. Thefore, we cannot describe the mechanism for adsorption as solely by simple ion exchange equilibria due to the reduction reaction revealed by the scanning electron microscope. However, some of the data indicated that at low levels of resin utilization equilibrium adsorption may be attained within the times investigated.

Another series of capacity tests were performed using increased amounts of resin to decrease the level of resin utilization. The data generated from these tests are listed in Table 3a and the isotherms are also presented in Figure 2. The results clearly showed that the adsorption capacity remained constant when the contact time was increased from 48 hours to 96 hours. The results from these tests have shown that equilibrium adsorption was attainable within 48 to 96 hours of contact time. Therefore, under conditions of low level of resin utilization, represented by the use of excessive amounts of resin, equilibrium adsorption may be achieved within several hours and not several days. We did not perform elution studies to determine whether the equilibrium reaction could be reversed.

2. Gold Concentration.

The effect of gold concentration on the adsorption capacity was evaluated using three levels of initial concentration, 31.0, 58.0 and 96.0 mg/L Au. The adsorption capacity values for the isotherm in kg/t are tabulated in Table 4, and the isotherms are shown in Figure 3. The adsorption capacity of Amberlite 252 for gold-thiourea complex ranged from 132 to 514 kg/t in 48 hours when using 31 mg/L of gold and increased with increasing initial concentration of gold. The adsorption capacity increased by 15% when the initial concentration of gold was increased from 31 mg/L to 58 mg/L. Increasing the initial concentration from 31 mg/L to 96 mg/L Au increased the adsorption capacity by 40%. This increase in capacity as a function of increasing concentration is not consistent with typical ion exchange adsorption behavior and may be due to the possible reduction reaction. The correlation between the change in capacity and gold concentration is given by equation [3] below and is shown in Figure 4:

$$\Delta Q = 0.0062[Au]_0 + 0.8 \qquad [3]$$

where $[Au]_0$ is the initial gold concentration in mg/L, ΔQ (Q_2/Q_1) is the change in average adsorption capacity, Q_2 is the average capacity from a solution with any given initial gold concentration and Q_1 is the average capacity from a 31 mg/L gold solution. This equation predicts that the adsorption capacity of Amberlite 252 will decrease by 17% (110 to 427 kg/t) when using 5.0 mg/L gold solution which is a typical mill solution.

The data from the tests with low level of resin utilization (equilibrium adsorption), in Table 4a, showed that increasing the initial gold concentration from 24 mg/L to 40 mg/L resulted in only marginal change (3% reduction) in the adsorption capacity. Thus, the concentration of gold did not significantly affect on the adsorption capacity which is consistent with ion exchange systems. This supports our proposition that equilibrium adsorption by ion exchange mechanism was attained with low levels of resin utilization.

3. Temperature.

Our previous work with other ion exchange systems for the recovery of gold has shown that temperature affects the adsorption capcity of resins. We investigated the influence of temperature on the adsorption of gold-thoiurea onto Amberlite 252. Adsorption capacity measurements were made at three different temperatures, 30, 40 and 50° C. The results are tabulated as isotherm data in Table 5, and represented as isotherms in Figure 5. The adsorption capacity of Amberlite 252 from a 55 mg/L gold solution in 48 hours ranged from 170 to 238 kg/t and decreased with increasing temperature. The adsorption capacity decreased by 35±3% when the temperature was increased from 30° to 40° C whereas increasing the temperature from 30° to 50° C decreased the capacity by 53±3%. The tests with low level of resin utilization (equilibrium adsorption) showed 35±2% decrease in capacity when the temperature was increased from 30° to 50° C. This is consistent with ion exchange equilibria.

The influence of temperature on adsorption capacity is in agreement with the adsorption of gold-cyanide by activated carbon and may be useful for elution of loaded resins. The correlation between the change in capacity and temperature was represented by equation [4] and shown in Figure 6:

$$\Delta Q = 152.7T^{-1.479} \qquad [4]$$

where ΔQ is the change in capacity (Q_T/Q_{30}), Q_T is the capacity at any temperature T, and Q_{30} is the capacity at 30° C. Using this equation we can predict a reduction in the adsorption capacity of 87% at a temperature of 120° C. Thus, it is possible to elute 87% of the loaded gold on the resin by increasing the temperature from 30° to 120° C. We did not generate data to support this prediction, but it is interesting to note that this is the temperature range where elution of gold from the cyanide system is performed. Conversely, the equation predicts that decreasing the temperature from 30° to 22° C will result in an increase in the capacity by 58%.

3a. The Enthalpy of Adsorption.

The adsorption capacity as a function of temperature was used to estimate the enthalpy of adsorption. The enthalpy of adsorption is defined as the enthalpy change accompanying the adsorption of one mole of adsorbate at constant surface coverage. This is a thermodynamic quantity derived from the Vant' Hoff equation. The integrated form of the equation for the enthalpy of adsorption is represented as:

$$\ln C_e = \frac{-\Delta H^{ads}}{RT} + k \qquad [5]$$

where C_e is the equilibrium concentration at a constant loading and particular temperature
T is the absolute temperature in °Kelvin,
R is the universal gas constant
ΔH^{ads} is the enthalpy of adsorption.
k is a constant

Since equilibrium adsorption was attained at low levels of resin utilization, the data from these tests, tabulated in Table 5a, were used to determine the enthalpy of adsorption. The Freundlich equilibrium isotherm equation was used to model the data at 30° C and 50° C. The Freundlich model equations generated from the data at the two temperatures were:

at 30° C $\ln Q_e = 0.5695 \ln C_e + 0.1602$ [6]

at 50° C $\ln Q_e = 0.6165 \ln C_e - 0.186$ [7]

The variation of enthalpy of adsorption with surface coverage (θ) was determined using the data generated from the Freundlich equilibrium equations. The surface coverage ($Q_e/Q_.$) was calculated as a fraction of the equilibrium capacity $Q_.$ determined from the model equations. The variation of enthalpy of adsorption with

surface coverage is tabulated in Table 6 and shown in Figure 7. The enthalpy of adsorption was low, 4-25 kJ/mole, and decreased with increasing surface coverage. This low value for the enthalpy of adsorption suggests physical adsorption. This is in agreement with our proposition that equilibrium adsorption was attained at low levels of resin utilization, through a physical adsorption type of mechanism such as ion exchange.

Although, non equilibrium conditions prevailed for the capacity measurements with high level of resin utilization, the data were used to determine the enthalpy of adsorption. The Freundlich model equations used for calculating the enthalpy of adsorption were :

at 30° C $\ln Q_e = 0.9875 \ln C_e + 1.6145$ [8]

at 50° C $\ln Q_e = 3.49 \ln C_e + 4.3967$ [9]

The variation of enthalpy of adsorption with surface coverage was also determined and is shown in Figure 7. The enthalpy of adsorption was high, 70 to 250 kJ/mole, and decreased with increasing surface coverage. This high value for the enthalpy of adsorption suggests chemical adsorption and supports our proposition that the adsorption mechanism at high levels of resin utilization includes a chemical reaction step and probably resulted in the reduction of ionic gold species to elemental gold.

4. Thiourea Concentration.

The effect of thiourea concentration on the adsorption capacity of Amberlite 252 for gold-thiourea complex was also evaluated. Three levels of initial thiourea concentration were evaluated, 0.025M, 0.125M and 0.25 M. The adsorption capacity data are tabulated in Table 7 and the isotherms are shown in Figure 8. The adsorption capacity of Amberlite 252 from a 0.025M thiourea solution in 48 hours ranged from 132 to 541 kg/t and decreased with increasing thiourea concentration. The adsorption capacity decreased by about 65% when the initial thourea concentration was increased from 0.025M to 0.125M. Further increase in the initial thiourea concentration to 0.25M resulted in the decrease in the adsorption capacity value by 85%. This relation between thiourea concentration and adsprption capacity may be useful for eluting the loaded resin.

The correlation between the change in adsorption capacity and thiourea concentration was represented by equation [10] and is shown in Figure 9:

$$\Delta Q = - 0.376 \ln[TU] - 0.4 \qquad [10]$$

where [TU] is the initial thiourea concentration in moles/liter (M), $\Delta Q(Q_2/Q_1)$ is the change in average adsorption capacity, Q_2 is the average capacity from a solution with any given initial thiourea concentration and Q_1 is the average capacity from a 0.025M thiourea solution. We can predict from this equation that increasing the thiourea concentration to 0.3M will achieve a reduction of 95%. Although we do not have experimental data to support this, our previous studies with the gold-bromine system revealed that elution of gold-bromide from loaded resins was possible with more than 0.5M thiourea solution.

5. Adsorption Isotherms.

The raw data from these adsorption tests were represented as isotherms that correlated the adsorption capacity in meq/g or kg Au/t with the bulk solution concentration in meq/L or mg Au/L. We have established that under the conditions of high level of resin utilization, the ion exchange reaction is accompanied by a possible reduction reaction. Therefore, these isotherms could not be regarded as equilibrium isotherms and the use of the term equilibrium adsorption capacity was not valid. A new term *apparent saturation capacity* (Mensah-Biney, 1991) was introduced to represent the apparent "equilibrium" adsorption capacity. The shape of the isotherms showed that more than one level of apparent saturation capacity was attainable on an isotherm. The level of apparent saturation capacity was dependent upon several variables encountered during the test. Some of the variables known to affect the level of apparent saturation capacity include resin utilization capacity, temperature, time and initial solution concentration. The isotherms in Figures 2 & 3 show two levels, a lower apparent saturation capacity at a low level of resin utilization and a higher apparent saturation capacity at a higher level of resin utilization.

The Freundlich equilibrium isotherms generated from the data are shown in Figure 10. Although the data fitted the Freundlich model fairly well (correlation coefficients of fit 0.950- 0.995), the isotherm constants derived from the data were not consistent with accepted theories of adsorption. This was expected since we have established that the mechanism for adsorption was not by ion exchange alone, but included possibly a reduction reaction.

The results of additional tests conducted with excessive amounts of resin representing a low level of resin utilization, are listed in Table 3a & 4a and presented as isotherms in Figure 2 & 3. The results clearly show that equilibrium adsorption was attained at this low level of resin utilization, with the capacity remaining virtually constant for the two contact times investigated. Scanning electron microscopy of the loaded resin did not show any evidence of reduced gold on the surface. The data were fitted to the Freundlich and Langmuir isotherm models as shown in Figures 11 and 12. The equilibrium constants based on the Freundlich and Langmuir equations are tabulated in Table 8. The data fitted both models very well, and the isotherm constants derived from both models were consistent with equilibrium adsorption behavior. The calculated equilibrium capacity by the Lamgmuir model was 0.526±0.012 meq/g (103±2.3 kg/t) whereas the equilibrium capacity calculated by the Freundlich model was 1.217±0.122 meq/g (239.8±24 kg/t). The Langmuir constants showed the least variation and the calculated equilibrium capacity value was closer in value to the measured capacity. Therefore, the isotherm obeyed the Langmuir model better than the Freundlich model.

These results have shown that at low levels of resin

utilization, the apparent saturation capacity represents the equilibrium ion exchange capacity whereas at higher levels of resin utilization, the saturation capacity does not represent the ion exchange capacity. The apparent saturation capacity at higher levels of resin utilization may include a contribution from the reduction reaction.

6. Scanning Electron Microscope (SEM) Examination of the Loaded Resin.

Our previous research with gold loading from bromine solutions using resins revealed deposition of elemental gold on the loaded resin. Samples of the loaded resin from the tests with high level of resin utilization were examined with a scanning electron microscope to observe the nature of the adsorbed gold species on the resin. Figure 13 shows a SEM micrograph of a loaded resin from one of the loading tests. The micrograph showed deposition of elemental gold (determined by energy dispersive x-ray analysis, EDAX) on the surface of the resin. The gold deposition was not substantial and the gold was deposited as separate crystalline particles on specific sites on the resin. The particle size of the deposited gold crystal ranged from 0.6 to 3.1 μm. There was no evidence of degradation of the resin as was the case with the loaded resin from the bromine system. The deposition of elemental gold on the resin was unexpected and could not be explained at the time of the tests. However, other researchers have since reported the same observed deposition of elemental gold on loaded activated carbon from the thiourea system. We are proposing that the deposition of elemental gold was due to a reduction reaction accompanying the ion exchange process. The gold-thiourea complex was adsorbed onto the resin by an ion exchange mechanism after which the complex was reduced to elemental gold. The reduction of the gold complex is possible through an electron exchange mechanism. The redox potential of the gold-thiourea complex (- 0.38 volts) is probably higher than the redox potential of the electron exchanger (cross linked hydrocarbon matrix), and the reduction of $Au[CS(NH_2)_2]_2^+$ to elemental gold Au^0 is therefore theoretically possible.

Summary and Conclusion

This study has demonstrated that adsorption of gold from acidic thiourea solution by a cationic ion exchange resin is feasible. Capacity values greater than 100 kg/t were achieved within 48 hours of contact time and values greater than 400 kg/t were achieved after 144 hours of contact. Equilibrium adsorption could not be attained within the contact times investigated due to the proposed reduction reaction accompanying the ion exchange process. These high adsorption capacity values and the phenomenon of gold reduction on the resin were observed under conditions of high level of resin utilization. The apparent saturation capacity of the resin under these non equilibrium conditions was several times higher than the ion exchange capacity due to the contribution from the reduction reaction. The reduction reaction resulting in the deposition of gold on the resin is possible through electron exchange reaction between the resin matrix and the gold-thiourea complex. Evidence of the deposition of gold on the resin was revealed by scanning electron microscopy with EDAX. Adsorption isotherms generated from the raw data revealed that several levels of apparent saturation capacity can occur on each isotherm.

Under non equilibrium conditions, the adsorption capacity increased with increasing gold concentration and decreased with increasing temperature and thiourea concentration. The influence of these variables on the adsorption capacity was not consistent with equilibrium adsorption behavior. The influence of temperature and thiourea concentration on the adsorption capacity may be useful for elution of the loaded resin. The correlation between adsorption capacity, temperature and thiourea concentration predicted that loaded resins could be eluted with a high concentration of thiourea and at high temperatures (≥ 0.3 M thiourea at 120° C).

Equilibrium adsorption was attained when the level of resin utilization was low. The equilibrium adsorption capacity was lower than the values obtained under the non equilibrium conditions (103±10 kg/t versus 400 kg/t). Under equilibrium conditions, temperature and gold concentration only slightly affected the adsorption capacity. This was consistent with ion exchange adsorption equilibria. Scanning electron microscopy with EDAX did not reveal any deposition of gold under equilibrium adsorption conditions.

The proposed uptake of gold from thiourea solution onto the cation exchange resin, Amberlite 252, consists of an ion exchange process followed possibly by the reduction of the adsorbed gold species to elemental gold through electron exchange reaction.

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Table 1. Physical Characteristics of Amberlite 252.

Total Capacity (meq/g dry resin)	4.4
Shape	Black spherical beads
Wet Screen Grading (mesh)	16 to 50
Effective size (mm)	0.50
Moisture Content (%)	49.0
Density (g/L)	768 to 832

Table 2. Size Distribution of Amberlite 252 (as-received).

Size, mesh	Weight Retained (dry), g	Weight Retained %
20	4.94	35.2
28	6.48	48.7
35	1.92	13.7
48	0.26	1.8
Pan (-48)	0.08	0.6

Table 3. The Change in Adsorption Capacity as a function of Time for Amberlite 252 (varying gold concentrations) at 30° C. High Level of Resin Utilization.

Adsorption Capacity Data for the Isotherm, kg Au/t resin.								
31.0 mg/L $[Au]_o$			56.9 mg/L $[Au]_o$			95.7 mg/L $[Au]_o$		
48 hrs (Q_1)	144 hrs (Q_2)	$\Delta Q (Q_2/Q_1)$	48 hrs (Q_1)	144 hrs (Q_2)	$\Delta Q (Q_2/Q_1)$	48 hrs (Q_1)	144 hrs (Q_2)	$\Delta Q (Q_2/Q_1)$
514.1	657.9	1.28	222.6	415.6	1.87[1]	460.9	619.9	1.35
244.2	303.3	1.24	238.3	250.2	1.05	340.8	387.5	1.14
185.2	212.7	1.15	208.8	246.2	1.18	267.9	300.8	1.12
167.4	165.4	0.99	195.0	220.6	1.13	232.4	253.3	1.09
141.8	151.7	1.07	169.4	189.1	1.12	189.1	207.0	1.09
132.0	149.7	1.13	169.4	177.3	1.05	191.1	201.1	1.05
Average		1.14			1.10			1.14
Standard Deviation		0.11			0.06			0.10

1. This value was excluded from calculation of average and standard deviation.

Table 3a. The Change in Adsorption Capacity as a function of Time for Amberlite 252 (varying gold concentrations) at 30° C. Low level of Resin Utilization.

Adsorption Capacity Data for the Isotherms, kg Au/t resin.					
24.6 mg/L $[Au]_o$			40.2 mg/L $[Au]_o$		
48 hrs (Q_1)	96 hrs (Q_2)	$\Delta Q (Q_2/Q_1)$	48 hrs (Q_1)	96 hrs (Q_2)	$\Delta Q (Q_2/Q_1)$
58.1	54.6	0.94	68.5	70.2	1.02
48.6	54.4	1.12	53.3	49.5	0.93
45.0	45.4	1.01	39.4	40.2	1.02
37.4	38.7	1.04	32.7	33.9	1.04
31.8	32.2	1.01	28.8	29.0	1.01
27.9	28.3	1.01	25.1	25.2	1.00
Average		1.02			1.00
Standard Deviation		0.06			0.04

Table 4. The Change in Adsorption Capacity as a function of Gold Concentration for Amberlite 252 at 30° C. High Level of Resin Utilization.

Adsorption Capacity Data for the Isotherms, kg/t									
48 hour contact time					144 hour contact time				
31 mg/L (Q_1)	57 mg/L (Q_2)	96 mg/L (Q_3)	$\Delta Q (Q_2/Q_1)$	$\Delta Q (Q_3/Q_1)$	31 mg/L (Q_1)	57 mg/L (Q_2)	96 mg/L (Q_3)	$\Delta Q (Q_2/Q_1)$	$\Delta Q (Q_3/Q_1)$
514.1	222.6	460.9	0.43	0.90	657.9	415.6	619.9	0.63	0.94
244.2	238.3	340.8	0.98	1.40	303.3	250.2	387.5	0.82	1.28
185.2	208.8	267.9	1.13	1.45	212.7	246.2	300.8	1.16	1.41
167.4	195.0	232.4	1.16	1.39	165.4	220.6	253.3	1.33	1.53
141.8	169.4	189.1	1.19	1.33	151.7	189.1	207.0	1.25	1.36
132.0	169.4	191.1	1.28	1.45	149.7	177.3	201.1	1.18	1.34
Average			1.15	1.40	Average			1.15	1.39
Standard Deviation			0.11	0.05	Standard Deviation			0.19	0.09

Table 4a. The Change in Adsorption Capacity as a function of Gold Concentration for Amberlite 252 at 30° C. Low level of Resin Utilization

Adsorption Capacity Data for the Isotherms, kg Au t resin.					
48 hrs			96 hrs		
24.6 mg/L (Q_1)	40.2 mg/L (Q_2)	$\Delta Q (Q_2/Q_1)$	24.6 mg/L(Q_1)	40.2 mg/L (Q_2)	$\Delta Q (Q_2/Q_1)$
58.1	68.5	1.18	54.6	70.2	1.28
48.6	53.3	1.10	54.4	49.5	0.91
45.0	39.4	0.88	45.4	40.2	0.88
37.4	32.7	0.87	38.7	33.9	0.88
31.8	28.8	0.91	32.2	29.0	0.90
27.9	25.1	0.90	28.3	25.2	0.89
Average		0.97			0.96
Standard Deviation		0.13			0.16

Table 5. The Change in Adsorption Capacity as a function of temperature for Amberlite 252, 50 ppm $[Au]_0$. High level of Resin Utilization

Adsorption Capacity Data for the Isotherms, kg Au t resin.									
48 hours					144 hours				
30° C (Q_1)	40° C (Q_2)	$\Delta Q (Q_2/Q_1)$	50° C (Q_3)	$\Delta Q (Q_3/Q_1)$	30° C (Q_1)	40° C (Q_2)	$\Delta Q (Q_2/Q_1)$	50° C (Q_3)	$\Delta Q (Q_3/Q_1)$
222.6	372.3	1.67	169.4	0.76[1]	415.6	805.6	1.94[1]	431.4	1.04
238.3	155.6	0.65	124.1	0.52	250.2	82.7	0.33	57.1	0.23
208.8	133.9	0.64	94.5	0.45	246.2	173.3	0.70	47.3	0.19
195.0	133.9	0.69	84.7	0.43	220.6	82.7	0.38	78.8	0.36
169.4	114.2	0.67	82.7	0.49	189.1	110.3	0.58	59.1	0.31
169.4	102.4	0.60	76.8	0.45	177.3	92.6	0.52	78.8	0.44
Average		0.65		0.47			0.50		0.31
Standard Deviation		0.03		0.03			0.15		0.10

1. These values were excluded from the calculation of the average and standard deviation.

Table 5a. The Change in Adsorption Capacity as a function of Temperature for Amberlite 252, 25 ppm $[Au]_o$, 48 hour. Low level of Resin Utilization.

Adsorption Capacity Data for the Isotherms, kg Au/t resin.		
30° C (Q_1)	50° C (Q_2)	ΔQ (Q_2/Q_1)
58.1	37.8	0.65
48.6	33.4	0.69
45.0	29.6	0.66
37.4	26.6	0.71
31.8	21.5	0.68
27.9	19.6	0.70
Average		0.68
Standard Deviation		0.02

Table 6. Enthalpy of Adsorption for gold-thiourea on Amberlite 252.

Surface Coverage (θ), %	Enthalpy of Adsorption (ΔH), kJ/mole	
	Equilibrium Condition	Non Equilibrium Condition
1.0	25.1	171.4
2.0	21.4	115.6
5.0	16.4	88.5
10.0	12.6	68.0
12.5	11.4	61.4
25.0	7.6	41.0
50.0	3.8	20.5

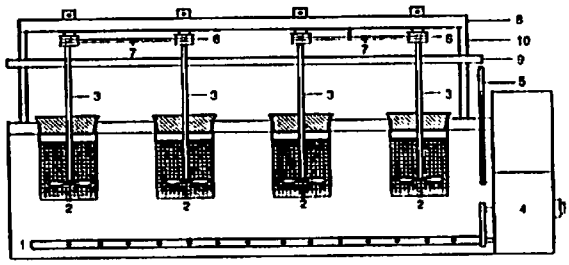
Table 7. The Change in Adsorption Capacity as a function of Thiourea Concentration for Amberlite 252, 25 ppm Au, 30° C. High level of Resin Utilization.

Adsorption Capacity Data for the Isotherms, kg Au/t resin.					
0.025M TU (Q_1)	0.125 MTU(Q_2)	ΔQ (Q_2/Q_1)	0.025M TU (Q_1)	0.25 M TU (Q_2)	ΔQ (Q_2/Q_1)
514.1	73.9	0.14[1]	514.1	50.5	0.10
244.2	103.6	0.42	244.2	18.8	0.08
185.2	41.1	0.22	185.2	13.9	0.08
167.4	51.7	0.31	167.4	30.0	0.18
141.8	54.9	0.39	141.8	33.1	0.23
132.0	49.3	0.37	132.0	28.4	0.22
Average		0.34			0.15
Standard Deviation		0.08			0.07

1. This value was excluded from the calculation of the average and standard deviation.

Table 8. Freundlich and Langmuir Equilibrium Isotherm Constants of Amberlite 252 for Acidic Gold-thiourea Complex.

$[Au]_o$	Time	Freundlich Isotherm Equation			Langmuir Isotherm Equation		
		Intensity	Equilibrium Capacity		Constant	Equilibrium Capacity	
mg/L	hours	(1/n)	meq/g	kg/t	(K)	meq/g	kg/t
24.6	48	0.5694	1.1737	231.2	14.3	0.5237	103.2
24.6	96	0.5378	1.0984	216.4	14.6	0.5352	105.4
40.2	48	0.6756	1.3860	273.0	10.8	0.5348	105.3
40.2	96	0.6289	1.2123	238.8	11.8	0.5109	100.6
Average			1.2176	239.8		0.5262	103.6
Standard Deviation			0.1218	24.0		0.0115	2.3



Schematic Diagram of the Apparatus for the Loading Capacity Tests.

1. Water Bath
2. Reactors (Tall Form Beakers)
3. 3-blade Impeller
4. Temperature Controller
5. Thermometer
6. Pulley
7. Flexible Belt
8. Al. Bracket for Motor
9. Plexiglass Protective Shield
10. Aluminum Support

Figure 1 Schematic diagram of the apparatus for the loading capacity tests.

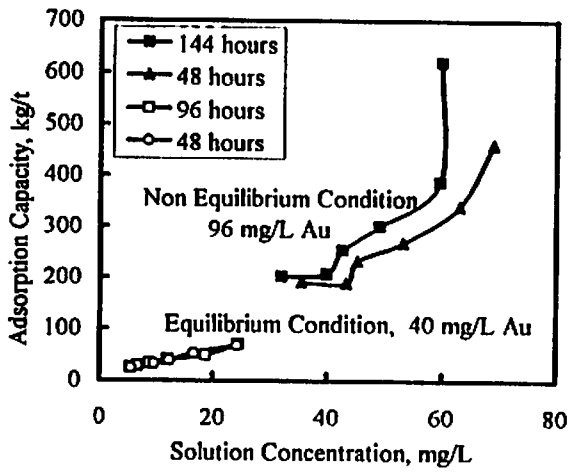


Figure 2. Effect of Time on the Adsorption Capacity of Amberlite 252, 30 deg. C.

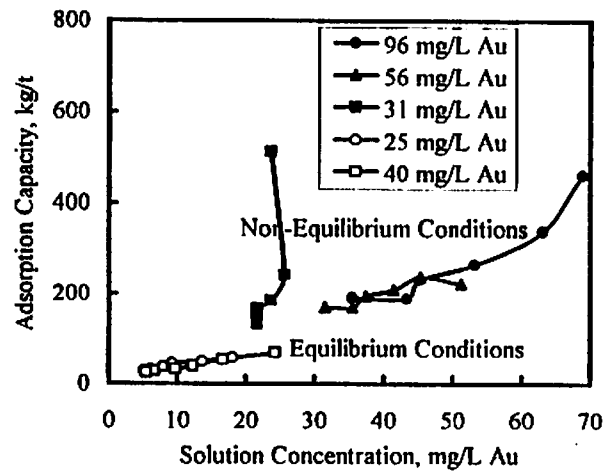


Figure 3. Effect of Gold Concentration on the Adsorption Capacity of Amberlite 252, 30 deg. C, 48 hours.

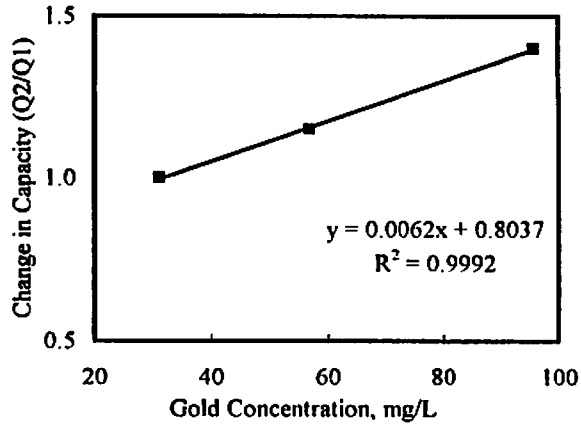


Figure 4. Influence of Gold Concentration on the Capacity of Amberlite 252, 30 deg. C.

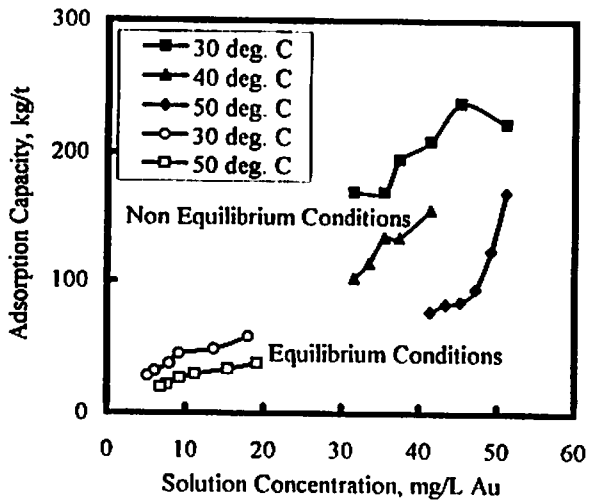


Figure 5. Effect of Temperature on the Adsorption Capacity of Amberlite 252, 56 mg/L Au, 48 hrs.

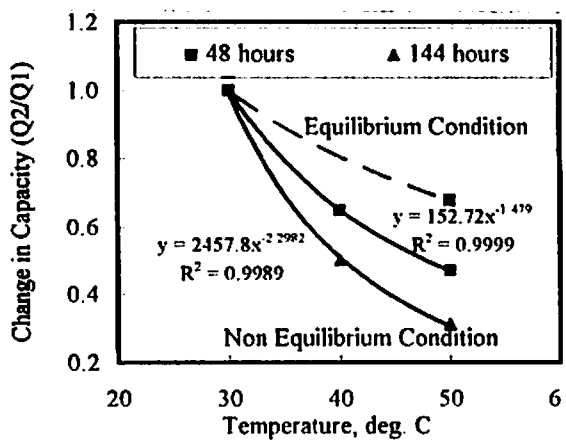


Figure 6. Influence of Temperature on the Adsorption Capacity of Amberlite 252.

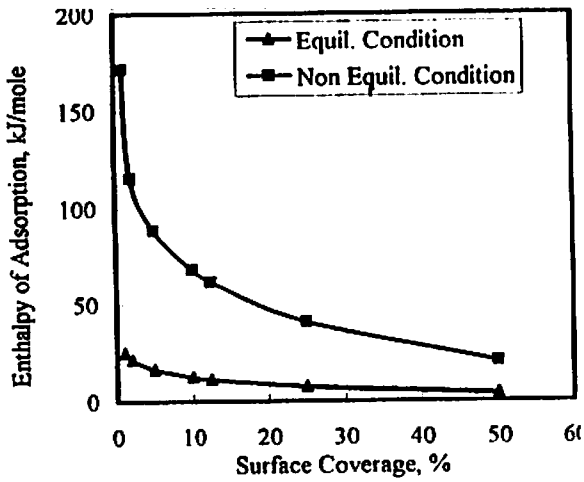


Figure 7. Variation of Enthalpy of Adsorption with Surface Coverage for Amberlite 252.

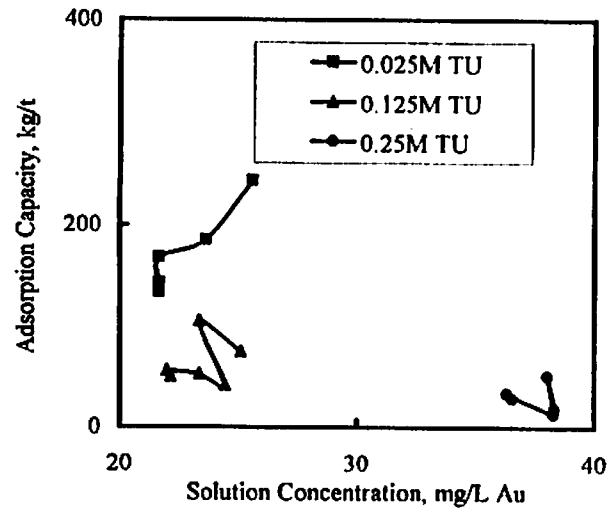


Figure 8. Effect of Thiourea Concentration on the Capacity of Amberlite 252, 30 deg. C, 48 hr.

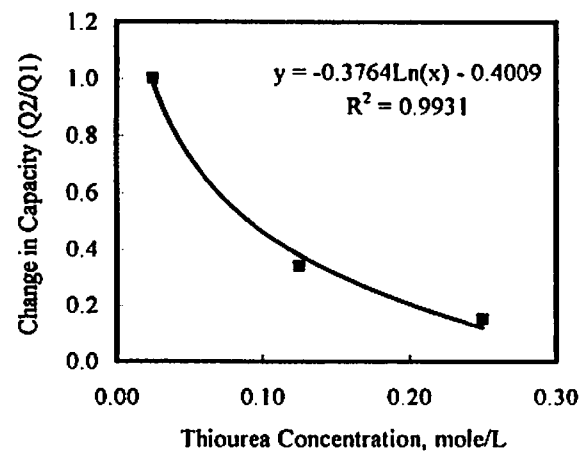


Figure 9. Influence of Thiourea Concentration on Capacity of Amberlite 252, 30 deg. C, 48 hr.

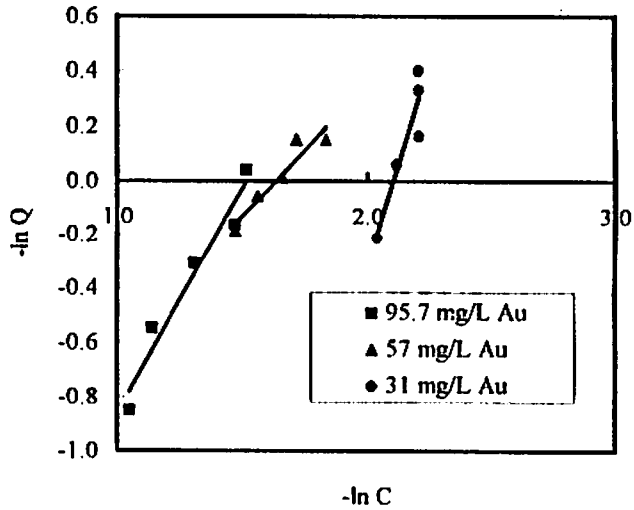


Fig. 10. Freundlich Isotherms showing influence of Au Concentration, 48 hr. Non Equilibriun Conditions.

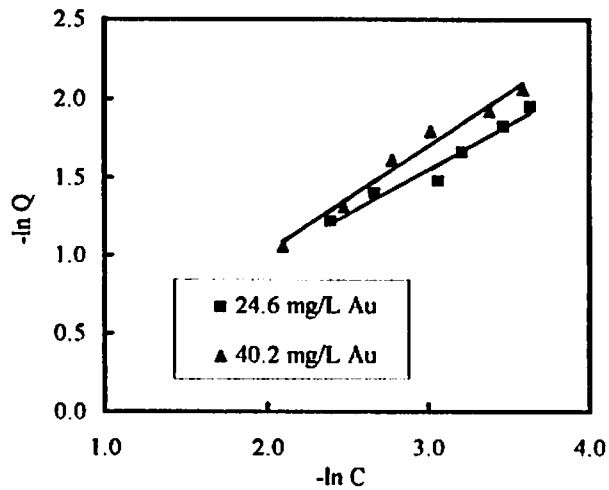


Fig. 11. Freundlich Equilibrium Isotherms showing the effect of Gold Concentration, 48 hr.

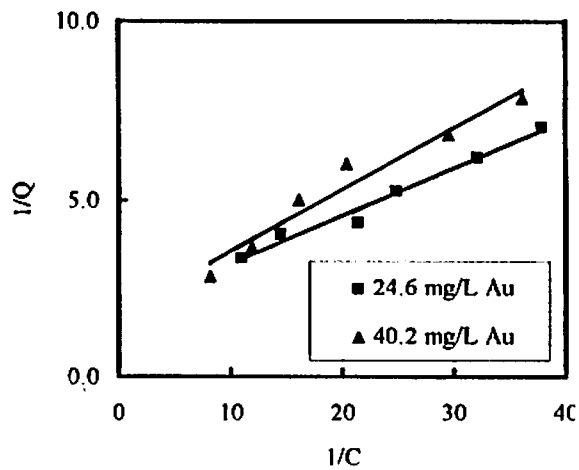


Fig. 12. Langmuir Equilibrium Isotherm showing the effect of Gold Concentration, 30 deg. C, 48 hr.

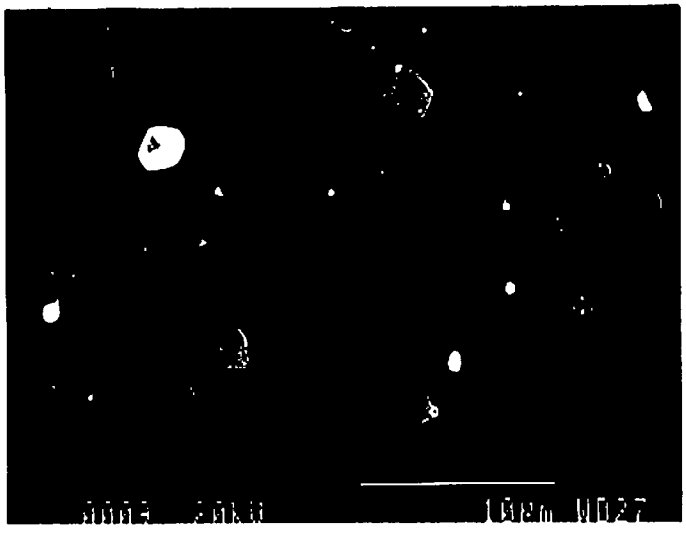


Figure 13. SEM Micrograph of Loaded Amberlite 252, 30° C, and144 hr. contact time. High Resin Utilization.