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Supercritical Carbon Dioxide Elution of Gold—Cyanide Complex from Activated Carbon

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ABSTRACT

The elution of gold from activated carbon using supercritical carbon dioxide is reported. Results of the conditions that maximize recovery of gold are presented. The parameters that were investigated include pressure, solvating agent, ionic strength, and static mode time. Repeating short static time periods followed by dynamic periods (on the same gold-loaded carbon sample) yielded higher recoveries compared to longer static time periods. It is proposed that the desorption process is kinetically controlled. The standard deviation for the recovery process was 7.6% or better.

INTRODUCTION

The increased awareness of environmental and human health effects from pollution has led to such acts as the Toxic Substance Control Act of 1976, and the Clean Air and Water Acts of 1970 and 1977, respectively. Some extractive processes use liquid solvents or solutions which may be toxic to humans, hazardous to the environment, and have high disposal costs. For example, sodium cyanide solutions are used in the extraction of gold from its ores. The United

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States Environmental Protection Agency (USEPA), the World Health Organization, and the National Institute for Occupational Safety and Health (NIOSH) have set rigid guidelines for environmental exposure, water quality, and human exposure to cyanide, respectively. As a result, there is a need to find safe and cost-effective alternatives to cyanide gold extraction metallurgy.

Most of the world's gold is processed using the carbon-in-pulp process wherein gold exists as the dicyanoaurate(I) anion, $Au(CN)_2^-$. Activated carbon is dipped into a series of tanks, countercurrent to the flow of the cyanide leacheate, which enhances the adsorption of gold onto activated carbon. The loaded carbon is then ready for the elution process in which gold is desorbed from its surface.

The elution step uses cyanide solutions of greater concentration than in the adsorption step, depending on the method. In the 1950s, Zadra and coworkers (1) at the US Bureau of Mines develop a desorption process which involves treating a column of loaded carbon at 95–100°C with 1% sodium hydroxide and 0.1% sodium cyanide which is cycled through the carbon and to an electrowinning cell. Usually the process runs at atmospheric pressure and requires 30–48 hours, but increased pressures of 500–600 kPa and temperatures of 135–140°C decrease the time needed to 10–12 hours (2).

In an attempt to reduce the total sodium cyanide usage, a variation of the Zadra process was developed at the Anglo American Research Laboratories (AARL) in South Africa. It involves a static presoak stage of the loaded carbon in a hot 5% sodium cyanide and 1% sodium hydroxide solution for 1 hour, followed by a dynamic stage with pure water at 110°C and under slight pressure. This reduces the elution time to 10–12 hours (2).

Other methods have been reported that entail adding organic solvents to a typical Zadra solution to enhance the desorption and decrease the elution time (3, 4). Espiell et al. (3) reported over 90% desorption in 2 hours with 50% acetone, 1 g/L NaOH at 30°C. The best solvents in decreasing order were found to be acetonitrile > acetone > ethanol > methanol. Though extraction times and percent recovery are highly promising with organic solvents, the method is not favored due to hazards associated with the use of organic solvents in large quantities and the attendant toxicity, flammability, and disposal costs.

Supercritical carbon dioxide ($scCO_2$) has typically been used for the extraction of nonpolar organic compounds. Under the guise of "like dissolves like," it is natural that CO_2, which is nonpolar, should solvate nonpolar organic compounds. Recently, many researchers have been exploring ways to enhance the extraction of polar species like amino acids, phenols (5, 6), and metal ions (e.g., 7–14) by adjusting parameters which include pressure, temperature, and the use of complexing agents or cosolvents. Mooiman and Miller (15) and Miller et al. (16) reported that tributyl phosphate (TBP) is an effective ligand for liquid–liquid extraction of gold from an alkaline cyanide solution. TBP solvates the ion pair $M^{n+} \ldots [Au(CN)_2^-]_n$ (where $M^+ = H^+$, Na^+, K^+, Ca^{2+}, Mg^{2+}) and increases its hydrophobicity.

The novel method using supercritical carbon dioxide to desorb gold from activated carbon had been reported earlier (17). The method can provide fast elution times and quantitative recovery of gold. Additionally, a drastic reduction of the amount of NaCN or potential elimination are salient advantages in favor of this method. The earlier work (17) showed that it is possible to extract gold from activated carbon using $scCO_2$ and TBP as a solvating agent. The present study was aimed at optimizing the methodology with regards to elution time, ionic strength, solvating agent concentration, and pressure. To our knowledge, supercritical fluid elution of gold from activated carbon, using TBP as a chelating agent, has not been investigated elsewhere.

EXPERIMENTAL SECTION

Materials

Type GRC-11 12 × 30 activated carbon was obtained from Calgon Carbon Corporation. Tributyl phosphate, 99%+, was purchased from Aldrich (St. Louis, MO). NaCN, NaOH, NaCl, and ethanol (all ACS grade) were from Fisher Scientific (Chicago, IL). Gold was obtained in the salt form, $K[Au(CN)_2]$, from Johnson Matthey (Ward Hill, MA). High-pressure extraction vessels rated to 10,000 psi were purchased from Keystone Scientific, Inc. (Bellefonte, PA). The depressurizing tubing was a fused silica, 100 μm capillary tube (Polymicro Technologies, Inc., Tucson, AZ). The capillary tubing was threaded through a 18-mm heavy duty TEFLOW silicon septum (Alltech Associates, Inc., Deerfield, IL) which was secured under the top of a 25-mL capacity collection vial.

Procedure

The instrumental design was as previously reported (17). The activated carbon was washed with distilled water to remove fines and dried in an oven overnight at 105°C. After cooling, the carbon was weighed and then soaked in a 200 mL solution containing 250 ppm NaCN (0.025% w/v) and 200 ppm Au for 7 days. The solution was stirred and opened to air daily. After 7 days the solution was decanted, and the wet carbon was stored in a sealed plastic bottle. The decanted solution was analyzed for its gold concentration and subtracted from the original concentration in order to calculate the gold loading.

The extraction vessel was charged with 0.5 g of the wet loaded activated carbon and spiked with 0.1–0.5 mL solvating agent (TBP), NaCN (0–1 mL of 0.2% w/v) to maintain ionic strength, and topped off with distilled water. The effect of the presence of water was not tested, rather water was added to maintain sample consistency, particularly when the effect of ionic strength was examined.

The extraction process was performed in two regimes: the static stage when CO_2 was allowed to equilibrate with the sample, and the dynamic regime, during which the extracted materials are leached out. The static regime has been shown to be more important than the dynamic regime (17). At the end of the dynamic stage the extraction vessel was opened, and either (i) the carbon was removed and weighed for the calculation of percent water content and percent recovery of gold, or (ii) other doses of the elution solutions were added for the "repeated" cycles before finally removing the carbon.

The effects of ionic strength, amount of solvating agent, static regime time, and pressure were investigated to establish optimal conditions for the quantitative recovery of gold. Variables that remained constant included sample size, extraction vessel size, temperature (150°C), and dynamic phase regime time of 20 minutes. Pressure was varied between 2000 to 6000 psi during the static regime. Previous works (17, 18) had indicated 4000 psi to be sufficient for metal complexes extraction. Various reports have shown that gold extraction increases with ionic strength. This was investigated using NaCN in concentrations far smaller than are used by current methods.

The eluted gold was collected in 2–3 mL of ethanol. The depressurized CO_2 and the collection vessel were vented into a fume hood. To avoid contamination between extractions, the capillary tubing was washed between extractions. Also, CO_2 was passed through the whole system with an empty vessel in place. Extractions and analyses were run in duplicates. Extracts were analyzed on the Unicam 969 Solaar Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

The static time profiles shown in Fig. 1 indicate a kinetic and equilibrium region, with the latter occurring at around 65% recovery of gold in 6 hours. To improve the percent recovery, it was worthwhile to work within the kinetic region. Instead of "bulk" static times, short static time durations were performed on a given gold-loaded carbon sample. The elution mixture was replaced between static–dynamic cycles. Figure 1 also shows 25 and 14% increases in gold recovery at 4000 psi when a total of 90 minutes of static time was broken into 15 and 30 minutes repeated cycles, respectively, over a 90-minute bulk static time. The total recovery after the six 15 minutes repeated cycles rose to 82%. Extrapolation of the curves indicate that quantitative recovery would be achieved between 2 $\frac{1}{2}$ to 3 hours, a time frame that is comparable to the fastest elution time of conventional methods.

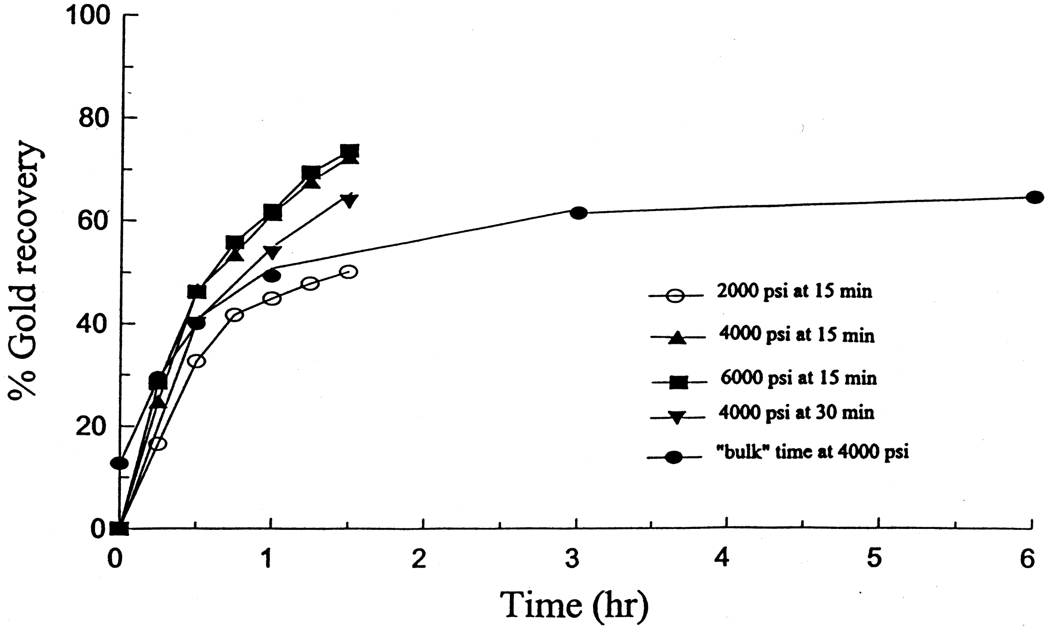

FIG. 1 Effect of pressure and static time on the elution of gold. Conditions: 0.5 g loaded carbon; 0.5 mL TBP; 0.5 M NaCN; 20 minutes dynamic time; 150°C.

The results in Fig. 1 show that a static time of 30 minutes, used in repeated cycles, gave an overall percent yield that was less than that of the 15-minute static time cycles. It is conceivable that repeated static times of less than 15 minutes would achieve quantitative recovery in shorter time. The 15 and 30 minute results suggest that the reversible adsorption of desorbed gold starts to occur quite early. The standard deviation for the recovery was 7.6% or better. This was calculated by combining the results of matching duplicates of the different sets of conditions studied.

Figure 1 also shows the effect of pressure with repeated static–dynamic cycles on the same gold-loaded carbon sample. Cummulative percent gold recovery at 4000 psi was about 30% higher than at 2000 psi. Recoveries at 4000 psi were statistically the same as that at 6000 psi. It seems therefore, that there is no significant advantage operating at pressures higher than 4000 psi, as mentioned above.

Figure 2 shows that the use of TBP as a solvating agent is important for the quantitative recovery of gold. It does also show that the ion pair $Na^+ \ldots [Au(CN)_2^-]$ has some appreciable solubility in $scCO_2$. Elutions at higher pressures may not require the addition of TBP since the density and polarity of CO_2 is expected to increase. There were no statistical differences between percent recoveries at the levels of TBP tested. Therefore, only a minimal amount of TBP needs to be present to enhance the solubility of the ion pair at moderate $scCO_2$ pressures.

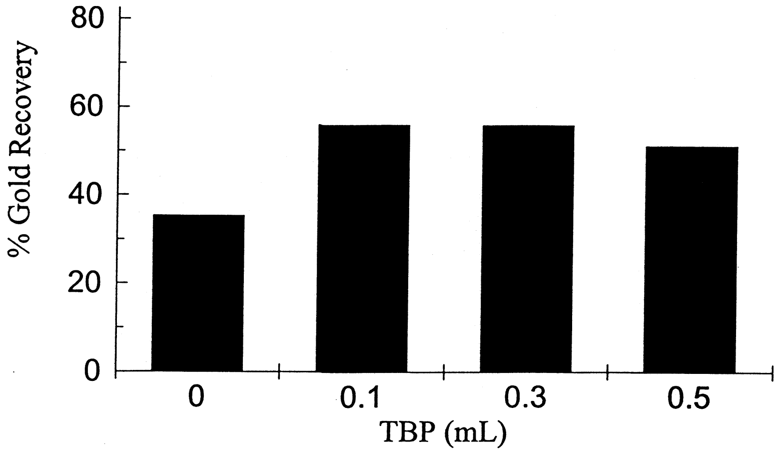

FIG. 2 Effect of tributyl phosphate (TBP) on the elution of gold. Conditions: 0.5 g loaded carbon; 4000 psi; 0.5 mL TBP NaCN; 1 hour static time; 20 minutes dynamic time; 150°C.

Figure 3 confirms that as the ionic strength of the elution mixture increases, the percent recovery of gold increases. Not only does ionic strength increase, but NaCN provides the Na^+ ion for the formation of the ion pair $Na^+ \ldots [Au(CN)_2^-]$, which is then solvated by TBP and mobilized into the supercritical carbon dioxide. An alternative source of the Na^+ ion and maintaining ionic strength would further reduce the amount of NaCN. Figure 4 shows that the recovery of gold decreases in the order NaCN > NaOH > NaCl, suggesting that NaCN is not only important in terms of ionic strength, but also helps to maintain the stability of the ion pair. The recovery order observed for NaCN and NaOH was reported by Adams and Nicol in a Zadra-type elution process

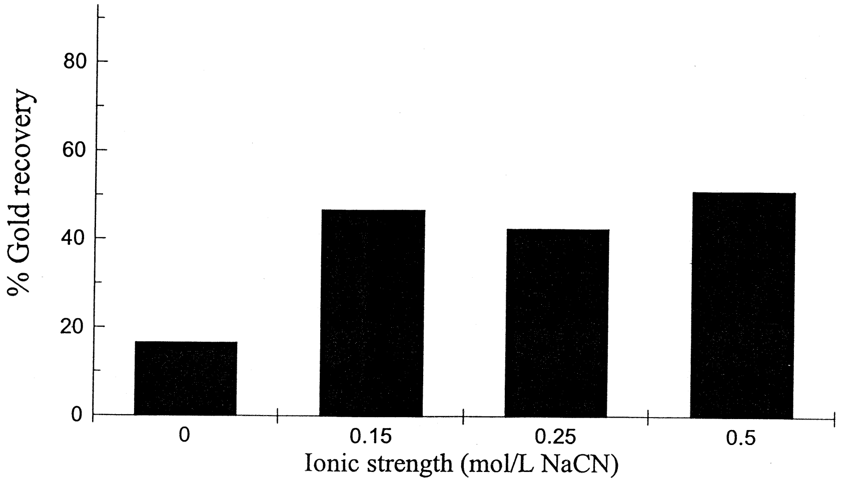

FIG. 3 Effect of ionic strength on the elution of gold. Conditions: 0.5 g loaded carbon; 4000 psi; 0.5 mL TBP; 1 hour static time; 20 minutes dynamic time; 150°C.

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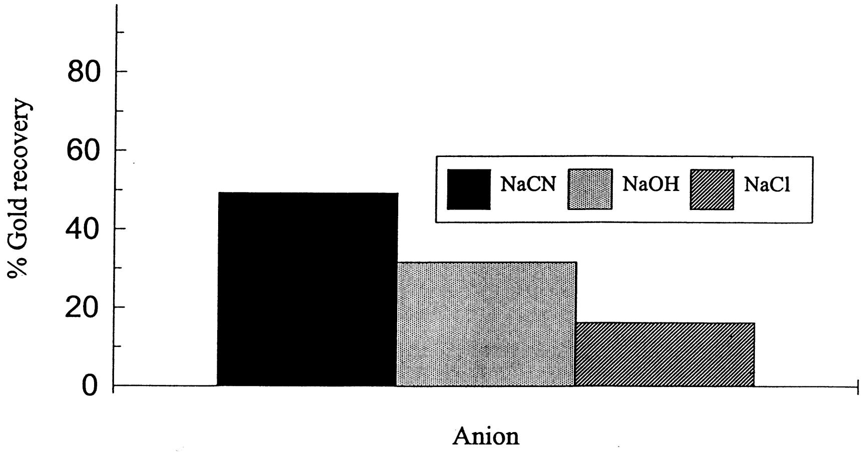

FIG. 4 Effect of anion on the elution of gold. Conditions: 0.5 g loaded carbon; 4000 psi; 0.5 mL TBP; ionic strength = 0.5 M; 1 hour static time; 30 minutes dynamic time; 150°C.

(19). It is known that high pH levels aid the desorption of gold from activated carbon (2, 20). The presence of NaOH results in higher recovery of gold compared to NaCl, in agreement with the previous works cited.

CONCLUSION

The $scCO_2$ method is well suited for elution (or recovery) of gold (and other metals) from loaded columns of activated carbon. NaCN is important for the quantitative recovery of gold from activated carbon. NaCN maintains the ionic strength and integrity of the ion pair $Na^+ \ldots [Au(CN)_2^-]$. The quantity of NaCN required is greatly reduced in the present method, and NaCN might not be needed at all in the elution step of the industrial carbon-in-pulp (CIP) process. From measurements described, 30% of the weight of the "wet" gold-loaded carbon is water. When carbon is brought from the adsorption stage of the CIP process to the elution stage, the "pore" water will likely contain enough NaCN and requisite ionic strength that no additional NaCN needs to be added. A reduction of a toxic chemical, like cyanide, from an industrial process as prevalent as gold processing not only decreases environmental and human health concerns, but will benefit industry as well with reduced disposal costs. If electrowinning will be the method to plate out gold, the conductivity of the bath could be maintained with a salt other than NaCN.

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