



Selective adsorption of gold over copper cyanocomplexes on activated carbon



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ABSTRACT

Copper cyanocomplexes have been recognized as competitors for the adsorption sites of activated carbon during gold adsorption. In this paper, the effects of practical parameters (excess free cyanide, calcium ions and aeration conditions) on the selective adsorption of Au over Cu cyanocomplexes on activated carbon samples from different sources are discussed. In addition to the adsorption experiments, the aqueous and solid phases were characterized by Raman spectroscopy in an attempt to elucidate the observed trends. Four solid samples with different structures as regards the relative amount of graphitic planes and density of surface functional groups were selected. The results indicated the highest adsorption of Au and the lowest adsorption of Cu on the sample with the lowest density of surface groups and relative higher crystalline character. In contrast, the highest adsorption of Cu and the lowest adsorption of Au were obtained using the sample with the highest density of surface groups and relative lower crystalline character. These findings support the industrial application of activated carbons with low density of surface functional groups for gold recovery, such as the product obtained from coconut shell, and are consistent with the hypothesis of different preferential sites for the adsorption of Au and Cu. The results also indicate that if there is an excess of free cyanide in the solution, a higher Au/Cu selectivity is observed, but the Au loading on the activated carbon samples declines. In the presence of Ca^{2+} ions in the cyanide solution, positive effects on Au adsorption and negative effects on Cu adsorption were demonstrated for a CN/Cu molar ratio above 4 (i.e., $\text{Cu}(\text{CN})_4^{3-}$ as the predominant species), and these behaviors resulted in a higher Au/Cu selectivity. A previous adsorption of Ca^{2+} ions on the activated carbon surface creates new sites for $\text{Au}(\text{CN})_2^-$ adsorption, in addition to the graphene layers. From aerated solutions, the adsorption experiments revealed a positive effect on Cu adsorption, and negative impact on Au adsorption, thus affecting the Au/Cu selectivity. The aeration of the solution results in a decrease of the cyanide concentration, which reduces the CN/Cu molar ratio. Therefore, the addition of Ca^{2+} ions in the process solution and an optimal concentration of free cyanide, which should take into account the loss of cyanide by oxidation and volatilization, may help to improve Au/Cu selectivity.

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1. Introduction

In nature, gold is generally found in association with other metals, mostly silver, iron, and copper. The occurrence of copper phases in gold deposits may affect the leaching process due to a high and fast solubility of some minerals in the cyanide media (Marden and House, 2006); the exceptions are the less soluble sulfides, such as chalcopyrite and tetrahedrite, and silicates, such as chrysocolla (Hedley and Tabachnick, 1958). This behavior represents an additional cyanide consumption of about 4 kg for each kg of soluble copper contained in the gold concentrate (Maxwell et al., 1997). Furthermore, the treatment of cyanide solutions with a high copper concentration may cause negative impacts on gold adsorption on the activated carbon (Fleming and Nicol, 1984; Marden

and House, 2006; Muir et al., 1989). The copper cyanocomplexes have been recognized as important competitors for the adsorption sites on activated carbon. Thus, a successful application of the traditional routes for treating low-grade, complex gold ores, which include stages such as the Carbon in Pulp (CIP) or Carbon in Leaching (CIL) processes, requires selectivity of gold over copper adsorption. As will be briefly reviewed in the next section, while the adsorption of dicyanoaurate (I) ($\text{Au}(\text{CN})_2^-$) species on the activated carbon has been quite investigated, the adsorption of copper species, such as dicyanocuprate (I) ($\text{Cu}(\text{CN})_2^-$), tricyanocuprate (I) ($\text{Cu}(\text{CN})_3^{2-}$), and tetracyanocuprate (I) ($\text{Cu}(\text{CN})_4^{3-}$), has received less attention, and the effects of practical, operating parameters on the selective adsorption of gold have been overlooked.

In this context, the purpose of the present work was to evaluate the effects of typical, practical parameters on the selective adsorption of Au over Cu on activated carbon samples from different sources. The parameters investigated in the current work are the physicochemical properties of the adsorbent material, excess free cyanide (CN^-) and

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calcium (Ca^{2+}) ions in the solution, and aeration conditions. A better understanding on the effects of relevant properties of the activated carbon will be shown valuable to describe the interactions that occur among the negatively charged cyanocomplexes and the adsorption sites of the activated carbon. The role of Ca^{2+} ions in the preferential adsorption of gold has also practical implication; lime (CaO) is usually added to the industrial solution for pH control. There is evidence of enhanced adsorption of copper on activated carbon when Ca^{2+} cations are available in the cyanide solution (Dai et al., 2010b; Souza et al., 2014). The findings of the present investigation may be helpful for developing gold recovery practices, in which the constraints caused by the presence of copper cyanocomplexes in the cyanidation could be minimized.

2. Background

Activated carbon remains the main industrial adsorbent for gold, and even with the consolidation of the CIP and CIL process, the adsorption mechanism of this metal is not fully understood. Among the proposals, some may be cited: gold adsorption as $[\text{M}^{n+}(\text{Au}(\text{CN})_2)_n]$ species (where $\text{M}^{n+} = \text{Ca}^{2+}, \text{H}^+, \text{Na}^+, \text{and } \text{K}^+$, named “spectator” cations) (Adams and Fleming, 1989; Davidson, 1974); gold adsorption as $[\text{M}^{n+}(\text{Au}(\text{CN})_2)_n]$ species, which decomposes to AuCN and cyanate (CNO^-) ion, followed by the decomposition of the latter to carbonate (CO_3^{2-}) ion and ammonia (NH_3) (Tsuchida and Muir, 1986); gold adsorption as $\text{Au}(\text{CN})_2^-$ species, which decomposes to $\text{Au}(\text{CN})$ or $\text{Au}(\text{CN})_x$ (McDougall et al., 1980); and adsorption of the $\text{Au}(\text{CN})_2^-$ species on the graphitic structure of the activated carbon (Ibrado and Fuerstenau, 1995; Jones et al., 1989; Klauber, 1988; Sibrell and Miller, 1992).

Regarding the adsorption of copper cyanocomplexes on activated carbon, few works focused on this interaction under practical, industrial conditions are available in the literature. It has been assumed that the adsorption is strongly affected by metal speciation, which depends on the pH solution and free cyanide concentration. Results by Fleming and Nicol (1984) at pH 6 and pH 10 indicated that the maximum Cu adsorption occurs at CN/Cu molar ratio about 2, and at higher ratios the metal adsorption decreased. The authors concluded that the $\text{Cu}(\text{CN})_2^-$ species adsorbs well on the material surface, while the $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ complexes do not. Thus, it has been suggested that the $\text{Cu}(\text{CN})_2^-$ species may represent the main competitor for the adsorption sites of the activated carbon. This conclusion possibly took into account the similarities between this species and the $\text{Au}(\text{CN})_2^-$ species, as already pointed out by Klauber (1988). Hence, in practice, the cyanidation conditions are adjusted to high pH values and high free cyanide concentration in order to favor the stability of the $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ complexes, which are claimed as secondary competitors for the adsorption sites of the activated carbon (Fleming and Nicol, 1984). A negative implication is that Au adsorption becomes unfavorable under such conditions, as the CN^- ions also compete for the adsorption sites (Nicol et al., 1984).

Regardless of the contributions that previous works have provided, the effects of pH and free cyanide concentration on the physicochemical properties of the adsorbent material has not been evaluated and, thus, the adsorption mechanism of copper cyanocomplexes has been discussed only on the basis of metal speciation. Souza et al. (2014) demonstrate that copper cyanocomplexes are preferentially adsorbed on activated carbon samples with a high density of surface functional groups, mainly basic groups, and the presence of Ca^{2+} ions in the cyanide solution was found to be beneficial to $\text{Cu}(\text{CN})_3^{2-}$ adsorption. The interaction of Ca^{2+} ions with the acid groups available in the surface of the activated carbon (e.g., carboxyl and phenol) may generate an excess of positive charges, thereby enhancing adsorption of the tri-coordinated copper complex.

In light of the above brief review, it is evident that the efforts to comprehend and improve the selectivity of Au adsorption on activated

carbon from Cu-containing cyanide solutions should take into account not only the effects of operating parameters, but also the effects of these parameters on physicochemical properties of the adsorbent and metal speciation. In this paper, the selectivity of gold adsorption was investigated considering the effects of aeration, excess free cyanide, Ca^{2+} ion concentration, and the type of activated carbon (characterized by specific surface area, ash content, density of surface functional groups, point of zero charge, and also degree of graphitization).

3. Experimental

3.1. Activated carbon samples

In this work, four types of activated carbon from different source materials were used: Samples produced from coconut shell (C), *Eucalyptus* powder (E), wood waste (W); and also bituminous carbon (B). Prior to the adsorption experiments, the samples were thoroughly rinsed and dried according to the procedure described by Souza et al. (2014).

3.2. Characterization of the activated carbon samples

The activated carbon samples were characterized by the following physicochemical properties: specific surface area (SSA); ash content (A); density of surface functional groups (DSFG); and point of zero charge (PZC). The analytical methods and procedures used for determining the above properties are described in previous publication (Souza et al., 2014).

3.3. Adsorption experiments

The adsorption experiments were carried out at 25 ± 1 °C from solutions prepared by dissolving potassium dicyanoaurate (I) ($\text{KAu}(\text{CN})_2$, Aldrich 99%), copper (I) cyanide (CuCN , Aldrich 99%), and potassium cyanide (KCN, Aldrich 96%), in deionized water (Millipore® Milli-Q). The initial gold and copper concentrations were $250 \text{ mg}\cdot\text{L}^{-1}$ Au ($1.26 \text{ mmol}\cdot\text{L}^{-1}$ Au) and $250 \text{ mg}\cdot\text{L}^{-1}$ Cu ($3.93 \text{ mmol}\cdot\text{L}^{-1}$ Cu), respectively. The amount of KCN added to the solutions depended on the CN/Cu molar ratio and free cyanide concentration to be evaluated. In this work, an excess of free cyanide was investigated (i.e., CN/Cu > 4). The pH value was adjusted to 10.5, which represents a typical, industrial condition, by adding the required volumes of 0.1 N potassium hydroxide (KOH, Synth 99%). The effect of calcium was investigated by adding $0.25 \text{ mol}\cdot\text{L}^{-1}$ Ca^{2+} ions in the cyanide solution, as calcium chloride dihydrate ($\text{CaCl}_2\cdot 2\text{H}_2\text{O}$, Synth 99%).

Regarding the experimental procedure, 1 g of solid sample was contacted with 100 mL of solution in Erlenmeyer flasks sealed with a flexible film. The heterogeneous mixture was kept under stirred conditions (200 rpm) in a shaker for 24 h. Air was added to the solution by means of a pump (Whisper 30, flow capacity of $567 \text{ L}\cdot\text{h}^{-1}$) connected to tubing with a fritted glass (1.5 cm diameter \times 3.2 cm height). The adsorption experiments were carried out for 30, 60, 90, 300, 720, and 1140 min. After each interval, the solution was vacuum filtered using a $0.44 \mu\text{m}$ cellulose membrane (Millipore®) and, then, analyzed for gold and copper. The metal concentrations were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) with a Perkin Elmer spectrophotometer (Optima 7300 DV).

The metal adsorption density (AD) on the activated carbon samples, the amount of Au and Cu adsorbed per unit area ($\mu\text{mol}\cdot\text{g}^{-1}$), was determined by mass balance:

$$\text{AD} = ([\text{M}]_i - [\text{M}]_f) \cdot V / (m) \quad (1)$$

where $[\text{M}]_i$ represents the metal concentration in the feed solution ($\mu\text{mol}\cdot\text{L}^{-1}$); $[\text{M}]_f$ the metal concentration in the filtrated solution ($\mu\text{mol}\cdot\text{L}^{-1}$); V the solution volume (L); and m the mass of the solid

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