Effects of surface properties of activated carbon on the adsorption mechanism of copper cyanocomplexes

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ABSTRACT

Copper cyanocomplexes have been recognized as important competitors for the adsorption sites of activated carbons during gold adsorption. In the present paper, an adsorption mechanism of negatively charged Cu cyanocomplexes on available sites of different activated carbons is proposed. The mechanism considers the (i) solution chemistry (e.g., effects of pH, CN/Cu molar ratio, and ionic strength by adding Na^+, K^+, and Ca^{2+} cations); (ii) surface properties of the activated carbon samples (e.g., density of surface functional groups and point of zero charge — PZC); and (iii) copper speciation. The adsorption experiments demonstrated that the enhanced interaction of copper species at pH < PZC and low ionic strength can be ascribed to the net positive charge on the surface of the solid phase. When the basic surface groups are completely deprotonated (i.e., pH > PZC > $pK_{a\ basic\ groups}$), electrostatic repulsion inhibits the adsorption of negatively charged Cu species. It is also proposed that the interaction of Ca^{2+} ions with acid groups generate an excess of locally positive charges on the surface of the activated carbon, and such positive charges enhance the adsorption of negatively charged copper cyanocomplexes, even when the net surface charge is negative. The results from thermodynamic and Raman analyses indicated that under typical, practical conditions of gold adsorption from cyanide solutions (pH > 9 and CN/Cu molar ratio > 4), the main competitor for the adsorption sites of the activated carbon is the $Cu(CN)_3^{2-}$ species and not the $Cu(CN)_2^-$ species.

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1. Introduction

Due to a relatively high solubility in cyanide media, copper minerals typically present in gold ores may affect the extraction of this precious metal. Exceptions are the less soluble chalcopyrite, chrysocolle and tetrahedrite (Hedley and Tabachnick, 1958). It has been estimated a cyanide consumption of approximately 4 kg for each kg of soluble copper contained in the ore (Maxwell et al., 1997). Furthermore, the treatment of a copper concentrated cyanide solution has negative effects on gold adsorption on the activated carbon (Fleming and Nicol, 1984; Muir et al., 1989). The copper cyanocomplexes have been recognized as important competitors for the adsorption sites of this material and, in addition, the presence of these complexes in the solution may affect the loading–elution cycles, by increasing the reagent consumption during elution.

Thus, a successful application of the traditional methods for treating low-grade, complex gold ores, which include stages such as the Carbon in Pulp (CIP) and Carbon in Leaching (CIL) processes, requires a high selectivity of Au adsorption from solutions containing Cu. While the adsorption of the dicyanoaurate (I) ($Au(CN)_2^-$) complex on the activated

carbon has been well described (Adams and Fleming, 1989; Adams et al., 1987; Davidson, 1974; Ibrado and Fuerstenau, 1995; Sibrell and Miller, 1992), the adsorption of the copper cyanocomplexes, such as the dicyanocuprate (I) ($Cu(CN)_2^-$), tricyanocuprate (I) ($Cu(CN)_3^{2-}$) and tetracyanocuprate (I) ($Cu(CN)_4^{3-}$), has received less attention. In spite of the technical constraints that the copper species may cause to the gold production plants, few works deal with the copper adsorption process itself (Dai et al., 2010; Fleming and Nicol, 1984; Liebenberg and Van Deventer, 1997).

The adsorption of copper cyanocomplexes on activated carbon has been suggested to be strongly affected by copper speciation, which depends on the solution pH and free cyanide concentration. Results from Fleming and Nicol (1984) at pH 6 and 10 indicated that the maximum Cu adsorption occurs at CN/Cu molar ratio ~2 and at higher CN/Cu ratios the metal adsorption decreased. The authors concluded that the $Cu(CN)_2^-$ species adsorbs on the material surface, while the $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ complexes did not adsorb significantly. Thus, it has been suggested that the $Cu(CN)_2^-$ species may be the main competitor for the adsorption sites of the activated carbon, but this conclusion possibly took into account the similarities between this species and the $Au(CN)_2^-$ species, as already pointed out by Klauber (1988). Therefore, in practice, the cyanidation conditions are optimized in order to favor the formation and stability of the tri- and tetra-coordinated complexes ($Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$), which are considered less important

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competitors for the adsorption sites. It has been found that these complexes are thermodynamic stable at high pH and free cyanide concentration (Fleming and Nicol, 1984). An undesirable implication is that Au adsorption on activated carbon becomes unfavorable under these conditions, as the cyanide (CN^-) ions also compete for the adsorption sites (Nicol et al., 1984). Hence, the conditions that affect Cu adsorption on activated carbon are relatively well-established, but the mechanisms by which this metal interacts with the material surface are not fully understood. Liebenberg and van Deventer (1997) have ascribed an enhanced Cu adsorption at pH 8.5 to the decomposition of the $Cu(CN)_3^{2-}$ to $Cu(CN)_2^-$ species, with the simultaneous oxidation of CN^-. In the modeling by Dai et al. (2010) it was assumed that in the presence of the activated carbon, the copper cyanide speciation in solution changes according to the adsorption of the copper species.

Regardless of the contributions that such previous works provided, it is important to highlight that the interaction mechanisms among the copper cyanocomplexes and activated carbon remain unclear, and the effects of parameters such as cyanide concentration, pH, and ionic strength on physicochemical properties of the adsorbent material have been overlooked. To date, the adsorption of Cu cyanocomplexes on the activated carbon has been discussed mostly on the basis of metal speciation. In this context, an adsorption mechanism of copper cyanocomplexes is presented in this paper, which takes into account the effects of pH, CN/Cu molar ratio, and ionic strength on copper speciation and on relevant properties of the adsorbent material. The properties of particular interest here are the density of surface functional groups and surface charge.

2. Experimental

2.1. Activated carbon samples

In this work, four types of activated carbon from different source materials were investigated, as follows: Samples produced from coconut shell (C), *Eucalyptus* powder (E) and wood wastes (W); and also bituminous carbon (B). The sample C is used in the industrial adsorption of gold from cyanide solutions. Prior to the adsorption experiments, all the samples were thoroughly rinsed with 0.1 mol·L^{-1} sodium hydroxide (NaOH, Synth 99%) solution in order to withdraw humic acid residues. The S/L (solid/liquid) ratio used in the procedure was 1/100 g·mL^{-1}. Following, the samples were thoroughly rinsed with Milli-Q water (resistivity of 18.2 MΩ·cm, Millipore®) and then dried in a furnace at 60 °C for 24 h.

2.2. Characterization of the activated carbon samples

The activated carbon samples were characterized in this work by the following properties: (i) specific surface area (SSA); (ii) ash content (AC); (iii) density of surface functional groups (DSFG), and (iv) point of zero charge (PZC). The SSA was determined by the Brunauer, Emmett, and Teller (BET) method (Quantachrome, NovaWin2), while the AC value was calculated by the weight loss of the samples, after heating in porcelain crucible at 900 °C for 1 h.

The DSFG of the activated carbon samples, as well as the identification of the corresponding groups, was determined by the Boehm method (Boehm, 1994). Thus, 0.5 g of solid sample was added to 50 mL of 0.05 N NaOH, sodium bicarbonate (NaHCO$_3$, Synth 99.9%), sodium carbonate (Na$_2$CO$_3$, Synth 99.9%), or hydrochloric acid (HCl, FMaia 36%) solutions under nitrogen (N$_2$, 99.999%) atmosphere. The heterogeneous mixture was kept under stirred conditions (200 rpm) in a shaker (New Brunswick Scientific) at 25 ± 1 °C for 24 h. Next, the mixture was vacuum filtered and an aliquot of the solution was back titrated with standard 0.1 N NaOH or HCl solutions in order to quantify the density of acid and basic groups, respectively. By this approach, the acid functional groups available on the surface of the activated carbon samples were determined as follows: the amount of carboxyl groups was estimated by

neutralization with NaHCO$_3$ solution; the amount of lactones was obtained from the difference between the neutralization with Na$_2$CO$_3$ solution and that determined for the NaHCO$_3$ solution; and the amount of phenols was estimated from the difference between the neutralization with NaOH solution and that determined for the Na$_2$CO$_3$ solution. Regarding the basic organic groups, typically amines, pyrones and quinones (Boehm, 1994), these were estimated by neutralization with HCl solutions.

The PZC value of the activated carbon samples was obtained according to the procedure described by Strelko and Malik (2002). Thus, 0.1 g of solid sample was added to 20 mL of 0.1 N sodium chloride (NaCl, Synth 99%) solutions with initial pH ranging from 2 to 11. The pH value was adjusted by adding the required volumes of 0.1 N HCl and NaOH solutions. Next, the heterogeneous mixture was kept under stirred conditions (200 rpm) in a shaker at 25 ± 1 °C for 24 h. The pH value was monitored before and after stirring, and the PZC value determined when the initial and final pH values coincided.

2.2.1. Electrophoretic mobility measurements

For the electrophoretic mobility measurements, the activated carbon samples were initially ground in an agate mortar to fine powder (>0.044 mm). The powder (25 mg) was added to 250 mL of NaCl or CaCl$_2$ electrolyte, and the pH value was adjusted by adding HCl and NaOH solutions (in the case of NaCl electrolyte) or HCl and Ca(OH)$_2$ (in the case of CaCl$_2$ electrolyte). The ionic strength of the electrolyte solutions was kept constant (0.01). The mixture remained under rest conditions for 24 h, and the colloidal particles were collected for zeta potential measurements in a Zeta Meter System 3.0+ (model ZM3-D-G).

2.3. Thermodynamic analysis: Cu–CN–H$_2$O system

The thermodynamic stability of the Cu cyanocomplexes was evaluated with the help of Eh–pH diagrams and speciation curves. The Eh–pH diagrams for the Cu–CN–H$_2$O system were prepared with the software Outotec HSC Chemistry® (v. 6.12). The speciation curves were obtained by calculating the corresponding fraction (α) of the Cu cyanocomplexes, as given by:

$$\alpha_i = \left\{ Cu(CN)_i^{(i-1)-} \right\} / \{Cu\}_T \ \text{ or } \ \alpha_i = \beta_i \{CN^-\}^i / \left(1 + \Sigma \beta_i \{CN^-\}^i\right) \quad (1)$$

where { } represents the activity of the Cu species in the solution, $\{Cu\}_T$ the total activity of the Cu species, β the equilibrium constants, and the subscript i = 2, 3 and 4. A list of the selected species used in the thermodynamic analysis, with their respective standard Gibbs free energy of formation, is provided in Table 1. This thermodynamic data were compiled by Lu et al. (2002).

The speciation curves were obtained assuming ideal and non-ideal systems. For this work, the activity coefficients reported by Dai et al. (2010), for each copper species, were used, assuming ionic strength 1.

Table 1
Thermodynamic analysis: The selected species and their corresponding standard Gibbs free energy of formation, $\Delta G°_f$, in kJ·mol^{-1} (Bard et al., 1985 [1]; Wagman et al., 1982 [2]; Izatt et al.,1967 [3]).

Species	$\Delta G°_f$	Ref.	Species	$\Delta G°_f$	Ref.
H$^+$	0	[1–2]	Cu	50.3	[1–2]
H$_2$	0	[1–2]	Cu^{2+}	65.7	[1–2]
O$_2$	0	[1–2]	Cu$_2$O	−148.1	[1–2]
H$_2$O	237.2	[1–2]	CuO	−134.0	[1–2]
OH$^-$	157.8	[1–2]	Cu(OH)$_2$	−359.5	[1–2]
CN$^-$	172.3	[3]	HCuO$_2^-$	258.9	[1–2]
HCN	119.7	[3]	CuO$_2^{2-}$	183.9	[1–2]
CNO$^-$	−98.7	[3]	CuCN	108.5	[1–3]
HCNO	−12.1	[3]	Cu(CN)$_2^-$	258.0	[1–3]
(CN)$_2$	296.3	[3]	Cu(CN)$_3^{2-}$	400.0	[1–3]
Cu	0	[1–3]	Cu(CN)$_4^{3-}$	564.0	[1–3]