

Efficiency of Crude α -Cyclodextrin in Gold Recovery from Electronic Waste and Soil

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Abstract

In this study, the metal coordination ability of alpha-cyclodextrin (α -CD) was employed to complex gold and thus isolate and extract it from different matrices of acid-digests of electronic waste and soil. The crude α -CD used was extracted from cassava and yam starch of the non-edible plant species using *E. coli* α -cyclodextrin glucanotransferase (α -CGTase), with yields $\geq 62\%$. The reaction was monitored progressively by ultraviolet-visible spectroscopy and checked with infrared spectroscopy (IR) for the presence of α -CD. The crude α -CD extract without need for purification was refluxed with gold containing-electronic waste and soil predigested in a mixture of NaBr/HNO₃ for 4 - 7 days. Recoveries of up to 22.9% and 70.8% gold were achieved from electronic waste and soil, respectively using 0.1 M α -CD. This approach is cheap, effective, and environmentally benign.

Keywords

Starch, α -Cyclodextrin, Electronic Waste, Soil, Gold

1. Introduction

Noble metals play a critical role in many gadgets due to their inert nature in mild environments and high electrical conductivity. The depletion of natural resources and the detrimental effects of mining activities on the environment and human seeks intervention. Gold recovery has been a central issue in a wide range of studies as a consequence of its high demand. The existing processes of recovering gold from different matrices are cyanide leaching and mercury amalgamation. These processes have a detrimental effect on human health and the environment if poorly handled.

Gold is particularly useful in solid-state electronics that use small voltages and currents that can be interrupted by minor corruptions. Gold is a naturally occurring metal and can be recovered from its ores in gold mines by both mechanical and chemical processes. The secondary source of gold is recycling and recovery from electronic waste it occurs with other metals such as copper, silver, palladium and many others. Gold recovery during electronic waste recycling and mining activities especially the Artisanal miners employ toxic and pollutive solvents with a detrimental effect on human health and the environment. Cyanides are used by industries and often discarded without proper treatment [1]. The use of mercury in the amalgamation process has been reported in Artisanal gold mines in more than 50 countries [2]. Therefore, there is a need for environmentally benign gold-coordinating systems of which cyclodextrins with numerous hydroxyl functional groups capable of metal coordination offer a better alternative.

Cyclodextrins are oligosaccharides having six to eight glucose units linked by glycosidic bonds at positions 1 and 4 categorized as α , β , or γ with 6, 7 or 8 glucose units, respectively (Figure 1(a)). They have a truncated cone shape with a hydrophilic exterior and a hydrophobic cavity/interior (Figure 1(b)), which can allow both covalent and non-covalent interactions with other species [3] [4] [5]. They can be synthesized by the action of the enzymes in particular CGTase on amylose [6].

Cyclodextrins are capable of forming coordination complexes by the hydroxyl interactions with metals using metal-oxygen bonds with the first α and β -CD metal complexes reported by Matsui *et al.* [7] [8] [9]. They have a versatile application since the hydroxyl groups can be randomly or selectively derivatized to complex metal ions of interest. Amine, carboxylic, ester and thiol derivatives have been employed in the complexation of metals such as copper, zinc and nickel [10] [11] [12]. However, of interest are the precious metals such as gold in components such motherboards, computer processing unit (CPU) and random-access memory (RAM) chips in dead electronic gadgets damped in the environment.

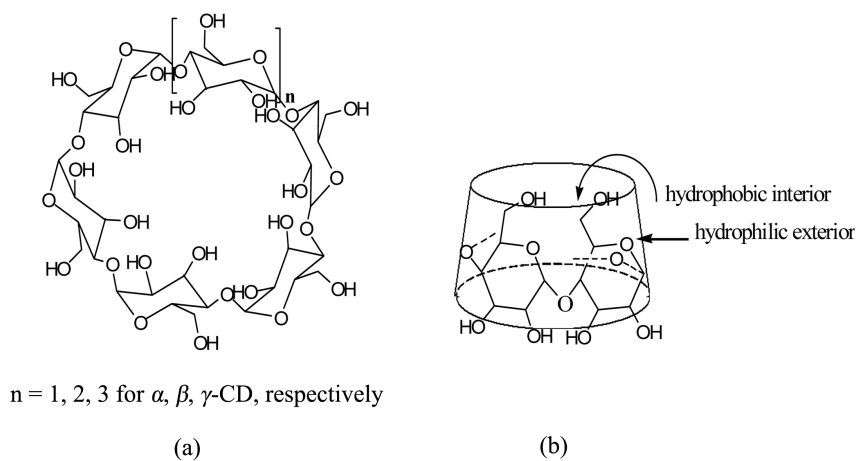


Figure 1. (a) Structure of cyclodextrins. (b) The truncated cone shape of cyclodextrins.

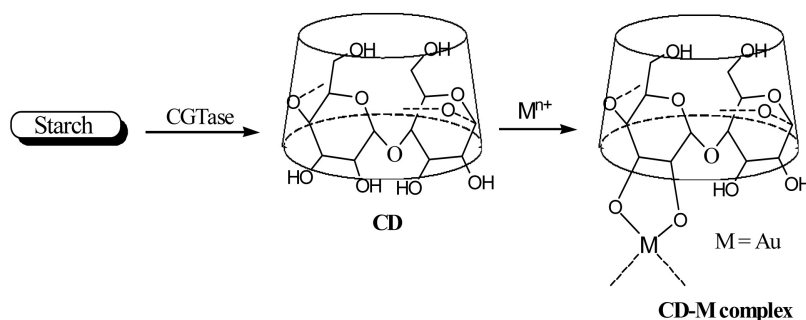
The concept of gold isolation as reported in (Liu *et al.*, 2013 [13]) is a one-dimensional supermolecular complex with extended $\{[K(OH_2)_6][AuBr_4] \subset (\alpha\text{-CD})_2\}_n$ chain superstructure formed during a rapid co-precipitation of $\alpha\text{-CD}$ and $KAuBr_4$ in water [13]. It relies on the self-assembly of complex originated from the mixing of gold-bearing matrices with a mixture of HBr/HNO_3 and $\alpha\text{-CD}$ in an aqueous solution to form a co-precipitate. This forms a 1:2 ratio complex with an extended structure. This co-precipitation gives an advantage to the selectivity of gold salt even in the presence of other metal complexes. According to Liu *et al.*, 2013 the bromide ions are needed in the inclusion process to isolate the gold from different matrices. The square planar $AuBr_4^-$ formed during the digestion of gold is encapsulated with the second-sphere cavity between the primary OH faces of the repeated face-to-face $\alpha\text{-CD}$ pairs stabilized by the hydrogen bonding interactions. A seemingly perfect match between $\alpha\text{-CD}$, K^+ , and $[AuBr_4]^-$ facilitates the specific second sphere coordination involving both $[AuBr_4]^-$ and $[K(OH_2)_6]^+$ ions which interact with each other non-covalently. This combination drives the co-precipitation of the $\{[K(OH_2)_6][AuBr_4] \subset (\alpha\text{-CD})_2\}_n$ complex [14]. This leads to the use of a modified aqua regia (AR) with HBr/HNO_3 (3:1) replacing conventional AR (HCl/HNO_3) to dissolve the gold in the matrices.

Therefore, the use of $\alpha\text{-CD}$ was envisaged in gold recovery from electronic waste by metal coordination reaction (Scheme 1). The $\alpha\text{-CD}$ was synthesized from cassava starch by cleavage and cyclisation of short glucose units using enzyme action of *Escherichia coli* $\alpha\text{-CGTase}$. All subsequent chemical reactions were performed in one pot without isolation of the CD.

2. Materials and Methods

2.1. General Procedure for the Synthesis of $\alpha\text{-CD}$ from Starch

The extraction of $\alpha\text{-CD}$ was performed using the Solvent process described by Li *et al.* [15] where the $\alpha\text{-CGTase}$ breaks and rearranges starch obtained from yams and cassava to $\alpha\text{-CD}$ units. In brief, the recovered starch (5% w/v) was suspended in 100 mL of distilled water. The slurry was heated to 92°C to completely gelatinize the starch. The gelatinized starch solution was then cooled to 50°C and the pH adjusted to 7 - 8 using sodium phosphate dibasic and $NaOH$. The



Scheme 1. Coordination of metal ion with cyclodextrin.

enzyme, α -CGTase (100 μ L) and a complexing agent, butan-1-ol or octan-1-ol (5% v/v) were added after 2 h duration of adding the former. The reaction was left to run at 50 °C with continuous stirring at 200 rpm. The reaction content was analyzed after 4 and 7 days. The enzyme was then deactivated by 1 M HCl and the pH of the mixture was adjusted to 7 using 1 M NaOH. The insoluble CD-butanol complex was obtained after centrifuge, and it was resuspended in water. The complex was broken down to free the CD by distilling off the butanol. The α -CD was crystallized at 5 °C and analyzed by UV-vis spectroscopy using PerkinElmer Lambda 365 UV/VIS Spectrophotometer.

2.2. General Procedure for the Extraction of Gold from Electronic Waste and Soil by α -CD

300 g of electronic scraps (CPU, RAM) were dissolved in a 500 mL sodium bromide/nitric acid mixture (NBN) or AR. The digest was characterized by atomic absorption spectroscopy (AAS) using AA500 from PG Instrument to determine the amount of gold present. The pH which was <2 forming HAuBr_4 was then adjusted to 4 - 6 by KOH (1 M) for optimum recovery by α -CD. The filtrate (50 mL) was mixed with crude α -CD (~0.1 M, 10 mL) forming a reddish-brown precipitate. The precipitate was dispersed in 50 mL of distilled water and then reduced by $\text{Na}_2\text{S}_2\text{O}_3$ (4 g) to elemental gold in a sludge form. For recovery of gold from the soil, 150 g was dissolved in 250 mL of NBN or AR. The recovered gold was analyzed by AAS. The reaction was repeated using pure commercially available α -CD (0.1 M) for comparison.

3. Results

Herein, we report the first study employing the metal coordination property of α -CD to capture gold from matrices containing other metal ions and organic residues.

3.1. Extraction and Characterization of Starch

The first step was to extract starch from cassava and yams using a method described by Adikwu *et al.* [16] but with some modification. Blue-black colouration using iodine was used as a positive indicator of starch. α -CD was synthesized by the action of the enzyme α -CGTase on the amylose component of the starch. The amylose/amylopectin content was determined where 34.38% and 41.25% amylose was present in cassava and yam starch, respectively.

3.2. Synthesis of α -CD

Gelatinized starch was refluxed with α -CGTase extracted from *E. coli* (≥ 90 U/mL activity). The reaction was monitored by UV-vis spectroscopy where both the pure reference standard and the synthesized α -CD (crude) had a λ_{max} of 220 nm (Figure 2). Yam starch yielded more α -CD than cassava starch as shown by the higher absorbance in the UV-vis spectrum (Figure 2) of the former which is

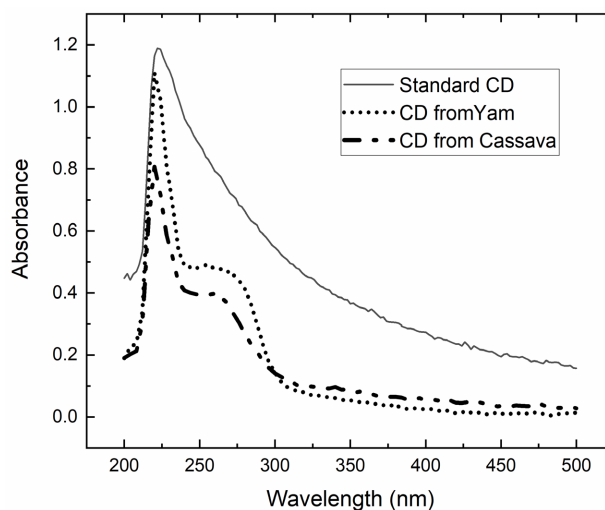


Figure 2. UV-vis spectrum of pure vs synthesized crude α -CD from yam and cassava starch.

in agreement with the higher amylose (41.25% vs 34.38%) content in yams compared to cassava.

The synthesized crude α -CD was further checked with Fourier transform infrared (FTIR) using Shimadzu IRTracer-100 spectrometer for the presence of the hydroxyl functional groups (O-H bond absorption at 3288 cm^{-1}) and key fingerprint sections making the skeleton of α -CD indicated by C-H, C-O and C-O-C with the very close IR absorption bands in both pure and crude α -CD extracted (**Figure 3**).

The reaction was optimized for temperature, reaction time, nature of the complexing agent to recover α -CD from the solution phase, and the pH and nature of the medium used (**Table 1**). Cyclodextrins are highly soluble in water posing difficulty in obtaining a sufficient quantity in solid form. The quantification reported in **Table 1** was for crude extract analyzed by UV-vis spectroscopy with reference to a calibration line of standard α -CD. Recovery of α -CD at pH 8.0 (35%) was high compared to pH 7.0 (29.2%) in sodium phosphate dibasic buffer with pH adjusted by aqueous sodium hydroxide (**Table 1**, entries 4 and 5). It is worth saying that distilled water (pH 6.8) was our solvent of choice with a yield of 84.9% of crude α -CD (**Table 1**, entry 1). It was observed the starch to α -CD conversion required long reaction times with a significant improvement from 31.1% to 35% after 4 and 7 days, respectively (**Table 1**, entries 1 and 2). Nevertheless, sufficient CD recovery is possible from starch sources with high amylose content as observed with yam starch (33.1%) after 4 days compared to the 31.1% synthesized α -CD from cassava starch in the same duration (**Table 1**, entries 2 and 3). Octanol was a better complexing agent recovering more α -CD than butanol (54.5% vs 35%) (**Table 1**, entries 1 and 6). This is in agreement with what has been reported in the literature [17]. A recovery of 63.2% crude α -CD was achieved using 20 g of starch (**Table 1**, entry 7) promising large-scale production.

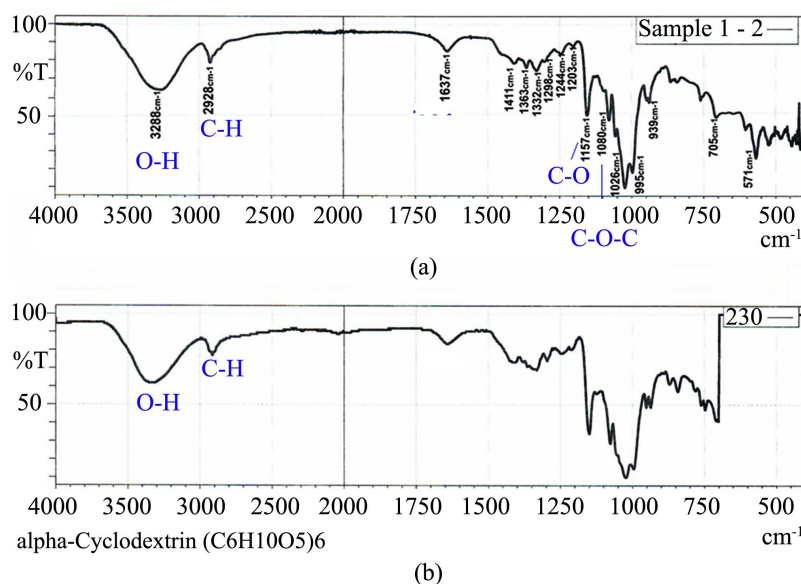


Figure 3. FTIR spectra of crude α -CD (a) versus pure commercial α -CD (b).

Table 1. Synthesis of α -CD by α -CGTase catalyzed breakdown and cyclisation of starch.

Entry	Starch source	Complexing agent	Reaction time (h)	pH	Recovery (%)
1	Cassava	Butanol	168	6.8	35
2	Cassava	Butanol	96	6.8	31.1
3	Yam	Butanol	96	6.8	33.1
4	Cassava	Butanol	168	7.0 ^a	29.2
5	Cassava	Butanol	168	8.0 ^a	35
6	Cassava	Octanol	168	6.8	54.5
7	Cassava	Octanol	168	6.8 ^b	63.2

¹Unless stated, all reactions were performed using α -CGTase (100 μ L, ≥ 90 U/mL activity), 0.5 g of starch in 10 mL distilled water at 50 °C with continuous shaking at 200 rpm for 96 - 168 h. ^aReactions were performed in sodium phosphate dibasic. ^b20 g of starch in 100 mL of distilled water using 900 μ L of the enzyme.

It is worthy to mention that performing the reaction at 60 °C gave no significant improvement in the yield of α -CD (Figure 3). A higher temperature could not be used to prevent denaturation of the enzyme and the formation of undesired by-products evident from the rough baseline. Further, yams were not used as the starting material for the synthesis of α -CD despite high amylose content and the shorter reaction time, because of the low starch (11%) obtained compared to 20% starch by mass using cassava. In addition, crude α -CD from yams was pale lilac which required further treatment before spectroscopic analysis.

3.3. Recovery of Gold by α -CD

With the sufficient recovery of α -CD (>60%), its ability to coordinate with gold

was investigated. All reactions were performed in the same pot without the need to first isolate α -CD. The pH of the mixture was adjusted to 4 - 6 by sodium hydroxide to obtain optimal conditions for gold-CD coordination. Crude α -CD was added to the dissolved metal ions and the Au ions were precipitated as a reddish-brown α -CD-Au complex. The precipitate was recovered by filtration and reduced by sodium thiosulphate to obtain the gold. The presence of gold was confirmed qualitatively by the dark colouration using stannous chloride and was quantified by AAS. NBN proved better than AR in digesting electronic waste. This was evident from the higher concentration of gold in NBN (**Figure 4**). On the contrary, the amount of Au in the NBN digest of the gold-containing soil sample was lower than in AR (13.33 ppm vs 18.33 ppm). This is probably due to fewer metals in the soil allowing mostly the presence of gold in the AR digested mixture. Also, the numerous contents in electronic waste both metallic and plastic could have led to side reactions that prevented free gold ions in digested mixture analyzed.

The optimal pH for efficient α -CD-Au coordination was also investigated (**Table 2**). The per cent recoveries of Au by crude α -CD were 22.9%, 19.1% and 19.7% at pH 4, 5 and 6, respectively (**Table 2**, entries 1 - 3). Although there is no clear correlation of recoveries with the rising pH using crude α -CD, however with a 2-fold higher concentration of pure α -CD which recovered 78.8%, 37.5% and 64.2% of Au at pH 4, 5 and 6, respectively (**Figure 5**) indicating the reaction is favoured by low pH. Nevertheless, 70.8% Au recovery was achieved by crude α -CD from the NBN-soil digest of the sample obtained from an artisanal gold mine (**Table 2**, entry 4). For gold recovery from the soil sample, crude α -CD almost matches purified α -CD (79.2%).

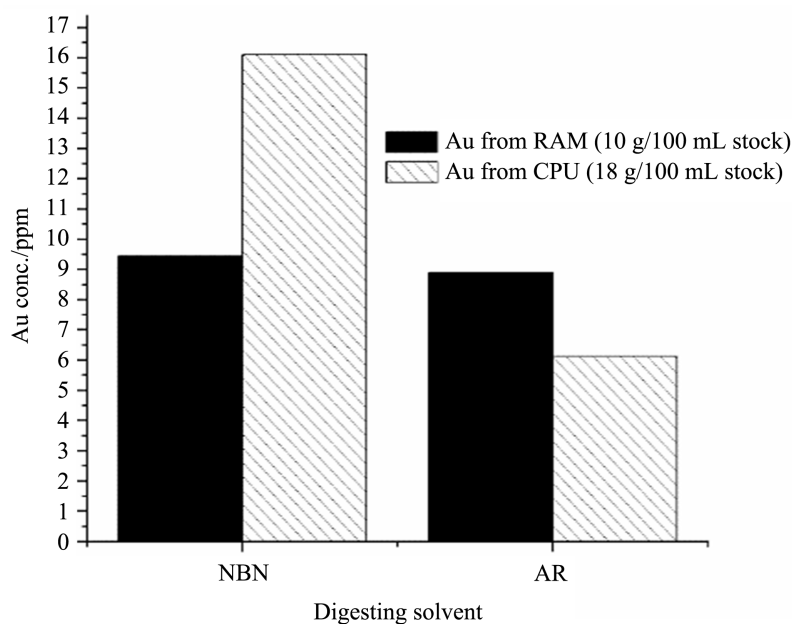


Figure 4. Comparison of gold content on CPU and RAM chips, and the Au-dissolution capacity of AR versus NBN solvent systems.

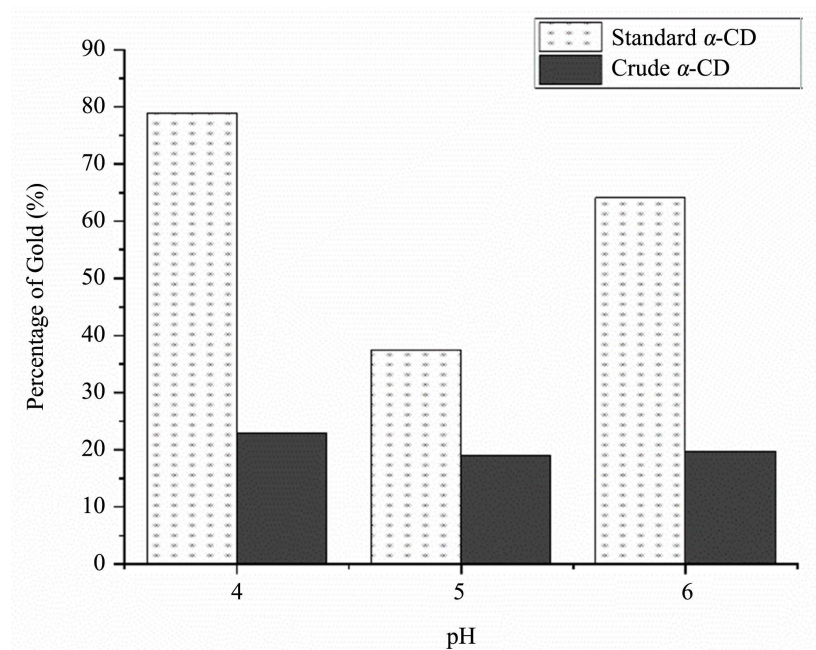


Figure 5. Recovery of Au using crude and pure α -CD at pH 4 - 6.

Table 2. The effect of pH on α -CD-Au coordination process.

Entry	pH	Concentration (ppm)	Recovery (%)
1	4	20.001	22.9
2	5	16.667	19.1
3	6	17.222	19.7
4	4	9.444	70.8 ^a

¹Unless stated all reactions were performed using crude α -CD (0.1 M), electronic-waste (CPU and RAM chips) stock solution containing 87.33 ppm of gold in NaBr/HNO₃ (pH 4 - 6). ^aSoil containing 13.333 ppm of Au.

4. Discussion

Gold recovery by α -CD was compared with cyanide extraction using potassium cyanide (KCN) and activated carbon (AC) and mercury amalgamation. The percentage recovery of gold from 150 g gold concentrate of electronic waste using KCN/AC and α -CD was observed and calculated. The concentration of recovered gold using α -CD (0.1 M) was highest at pH 4 giving 20 ppm with 22.9% recovery while recovery of 31 ppm (35.5% efficiency) was obtained using KCN (0.1 M)/AC. Similarly, using soil as a source of the gold concentrate α -CD made a better recovery (70%) as compared to the KCN/AC (35.6%). The extraction process using α -CD was also compared against mercury amalgamation. It has been reported that using mercury amalgamation recovers 35.5% to 44% of gold [18] [19]. This was by far a less substantial result relative to the biodegradable and environmentally benign α -CD derived from selected non-edible plants. The poor recovery of gold from electronic waste (22.9%) by α -CD is attributed to the

competition for the hydroxyl sites of α -CD by other metal ions like copper, tin and several others making up the which present in the digested AR and NBN digests of RAM and CPU chips used. Low metal ion concentrations and few metals in soil explain the relatively high recovery (70.8%) using the same crude α -CD.

5. Conclusion

The metal coordination potential of α -CD offers a solution to the recovery of precious metals and heavy-metal-pollutant mitigations by the waste in our surroundings. The observed ability of α -CD to capture gold in the presence of other metals both from electronic waste and soil offers a cheap and environmentally benign alternative to the current use of pollutive and toxic chemicals in artisanal mines and other gold recycling activities.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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