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Burtt, C.M. and Senanayake, G. (2016) Effect of reductants and stabilizers on ageing of gold nanoparticles at pH2–12 and application of nano-gold to study non-cyanide leaching in sodium hypochlorite/chloride solutions using UV–Visible spectroscopy. *Hydrometallurgy*, 164 . pp. 166-176.

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Effect of reductants and stabilizers on ageing of gold nanoparticles at pH 2-12 and their application to study gold leaching in sodium hypochlorite/chloride solutions using UV-Visible spectroscopy

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Abstract

Despite the growing interest in non-cyanide lixiviants for leaching gold from ores/concentrates and recyclable waste material one of the main challenges in testing novel lixiviants is the slow reaction of gold dissolution which generally takes long hours of experimentation and high cost. The increased interest in naturally occurring nanoparticulate gold component in ore deposits and exploration samples also encourages research in this area. Gold nanoparticles in aqueous medium exhibit strong characteristic absorption peaks in the visible region of the electromagnetic spectrum due to the Surface Plasmon Resonance (SPR). The very large surface area to volume ratio of nanoparticles leads to fast dissolution kinetics. These two properties allow chloride leaching of gold to be conveniently studied by the use of UV-Visible spectroscopy of gold nanoparticles produced in the laboratory in sodium hypochlorite/chloride solutions. However, the method of production also controls the properties of gold nanoparticles. In this study, nine methods were used for the synthesis of gold nanoparticles using different reagents as reductants and stabilizers: D-glucose, trisodium citrate, sodium borohydride, ascorbic acid, heparin, hydrazine sulfate, monosodium glutamate, gelatine, starch (both with and without ethylene glycol), polyvinyl alcohol (PVA), cetyltrimethylammonium bromide (CTAB) and tannic acid. The UV-Visible spectra and the dissolution rates per unit surface area of nanoparticles in NaOCl/NaCl solutions are compared to show similar leaching behaviour between nanoparticles and bulk gold which encourages further studies with other non-cyanide gold lixiviants.

Key words:

Gold, nanoparticles, reductants/stabilisers, leaching, chloride/hypochlorite, UV-visible spectra

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1. Introduction

One of the most rapidly growing areas of research in science and engineering in the twenty first century is the science of nanotechnology. Gold nanoparticles are one of the most intensely studied nanomaterials due to their exceptional physical and optical properties. To date most of the literature dealing with the properties of gold nanoparticles is directed towards their potential applications in biology (Wyckoff, 1963), medicine (Polte et al., 2010) and the production of novel materials (Turner et al., 2008). The nanoparticulate gold component in ore deposits and exploration samples (Hough et al., 2011) encourages further research into the leaching of gold nanoparticles produced in the laboratory for comparison. Gold nanoparticles exhibit strong characteristic absorption peaks in the visible region of the electromagnetic spectrum due to the Surface Plasmon Resonance (SPR). The very large surface area to volume ratio of nanoparticles leads to fast dissolution kinetics. These two properties allow the leaching of gold nanoparticles to be conveniently studied by the use of UV–Visible spectroscopy over smaller timescales in order to compare with the leaching behaviour of massive gold.

The leaching of gold in oxygenated/aerated alkaline cyanide solutions to produce $\text{Au}(\text{CN})_2^-$ followed by (i) carbon adsorption, (ii) elution and (iii) electrowinning or cementation of gold by zinc dust is the most widely accepted set of unit operations for the extraction of gold from ores (Marsden and House, 2006). However, non-cyanide processes and resin-in-pulp technology for leaching, separation and recovery of gold has attracted the attention of researchers and industry due to the non-applicability of cyanide for some gold ores and concentrates. Amongst the non-cyanide leaching systems thiosulfate and chloride systems have proven to be advantageous due to faster leaching kinetics (Ritchie et al., 2003;

Ferron et al, 2003; Senanayake, 2004, 2005, 2012; Choi et al., 2012; Zhang and Senanayake, 2016). Despite the growing interest in non-cyanide lixiviants for leaching gold from ores/concentrates and recyclable waste material one of the main challenges in testing novel lixiviants is the slow reaction of gold dissolution which takes long hours of experimentation and high cost. Although the use of gold nanoparticles can speed up the leaching reaction due to large surface area per unit mass and thus facilitate further research into non-cyanide lixiviants, the stability of gold nanoparticles and their properties also depend on the method of preparation using different reagents as stabilisers and reductants.

Previous work has focused on the use of gold nanoparticles for leaching studies in cyanide and thiosulfate systems (McCarthy, 1998; Zhang et al., 2004, 2008; Senanayake and Zhang, 2012). The main objectives of the present study are to conduct a preliminary investigation of the use of unstabilized nanoparticles to study the chloride leaching of gold and determine the dependence of variables such as reagent concentrations and pH on leaching rates. Most suitable leaching parameters from the preliminary investigation will be used to compare the leaching of stabilized gold nanoparticles produced by various methods. A comparison between the leaching rates of the stabilized gold nanoparticles will be used to determine if the coatings on the nanoparticles will significantly interfere in the leaching process. These results, along with the stability of gold nanoparticles under storage conditions will be used to determine the best stabilized gold nanoparticles for further leaching studies with chloride solutions and other lixiviants in future studies.

Gold forms chloro-complexes of the two oxidation states (I) and (III): Au(I)Cl_2^- and Au(III)Cl_4^- with the standard reduction potentials shown in equations 1 and 2. The dissolved chlorine in water undergoes a disproportionation reaction to produce Cl^- and HClO (or ClO^-) depending upon the pH according to equations 3 and 4. Both HOCl and OCl^- can act as oxidants for gold according to equations 6-9. The general consensus of the stages of the

proposed reaction mechanism for gold dissolution can be summarised using several equations: (i) the formation of an intermediate Au(I)Cl on the gold surface (equation 10), (ii) the formation of a secondary intermediate Au(I)Cl_2^- which is diffused away to the solution or oxidized further to Au(III)Cl_4^- (equation 11). Whilst the chemical reaction of gold is fast the dissolution rate is proportional to the chloride ion concentration indicating that the mass transport of chloride ions to the gold surface is rate controlling (Putnam 1944; Nicol, 1980; Marsden and House, 2006).

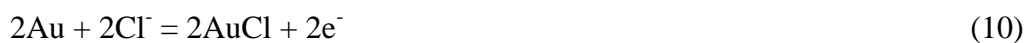
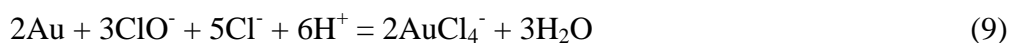
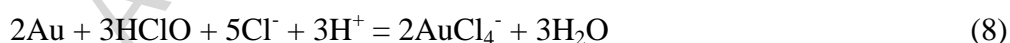
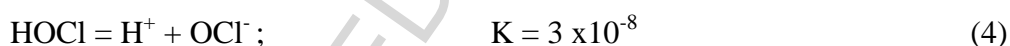
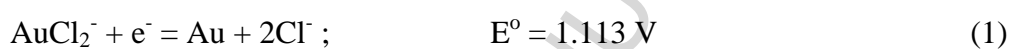


Figure 1 shows the Eh-pH diagram (Brandon et al, 2003) and summarise some of the predictions related to gold leaching: (i) the redox couple for leaching gold can be $\text{O}_2/\text{H}_2\text{O}$ at pH 1, Cl_2/Cl^- , HOCl/Cl^- or OCl^-/Cl^- , (ii) gold leaching can take place via AuCl_2^- at $\text{Eh} > 0.8$

V, (iii) in alkaline solutions gold leaching is retarded by the precipitation of $\text{Au}(\text{OH})_3$ in the pH range 8.5-13, (iv) leaching is facilitated in strongly alkaline solutions due to the formation of $\text{Au}(\text{OH})_4^-$ or HAuO_3^- . The dependence of chemical speciation in $\text{Cl}_2/\text{HOCl}/\text{OCl}^-/\text{Cl}^-$ system and $\text{Au}/\text{AuOH}/\text{AuCl}_2^-/\text{AuCl}_4^-/\text{Au}(\text{OH})_3$ on the pH and chloride ion concentration is also evident from Figure 1, which in turn controls the leachability of gold.

There are many methods that can be used for the synthesis of gold nanoparticles, one of the most commonly used procedures, involves the chemical reduction of gold(III) salts with citrate (Turkevich et al., 1951). Gold nanoparticles produced by this method must be kept in solutions of acidity around pH 6 and above during storage due to their instability in acidic solutions of $\text{pH} < 6$. In the presence of sodium chloride concentrations in excess of 0.03 M the nanoparticles will irreversibly aggregate and precipitate out of solution (Jans et al., 2010). Gelatine has been used as a stabilizer for gold nanoparticles during the study of gold leaching in cyanide (McCarthy, 1998) and thiosulfate (Zhang et al., 2004, 2008; Senanayake and Zhang, 2012) solutions to investigate the effect of concentration of the main reagents and background salts. However, the use of gelatine stabilised gold nanoparticles for leaching with chloride solutions is problematic due to the gelatine coating being unstable and salting out in acidic solutions containing high concentrations of salts (McBain and Kellogg, 1928).

For the gold nanoparticles to be viable for the study of leaching reactions in chloride solutions the nanoparticles should satisfy two requirements: (i) stable for long periods of storage after synthesis, but should react with NaOCl/NaCl , (ii) stable to any changes in pH so that the UV-Visible absorption peak of solutions of low pH does not disappear or change appreciably in shape, absorbance or wavelength. Although the spectra of the nanoparticles prepared using different reagents differ in properties, the initial concentration and absorbance can be used to calculate the diameter (Haiss et al., 2007) and hence the rate per unit surface

area. The instability of citrate as a stabilizing agent and the sensitivity of gelatine coatings to the presence of chloride/hypochlorite solutions have prompted the present study to search for methods of producing stabilized gold nanoparticles suitable for the study of gold leaching reactions in these solutions at pH 2-12. The results of this study should offer a range of reagents to produce gold nanoparticles suitable for testing the leaching behaviour in a range of non-cyanide lixiviants.

2. Experimental

2.1. Chemicals and Materials

All reagents used in this study were of analytical grade (Sigma Aldridge) and were used as received, unless otherwise stated. All preparations involving gold nanoparticles used Millipore water. All glassware and equipment used for the syntheses were rinsed three times with aqua regia solution then three times with distilled water and finally three times with Millipore water to remove any contaminants that can cause oxidation of gold that could degrade the nanoparticles.

2.2. Synthesis and stabilization of gold nanoparticles

A total of nine different methods of producing gold nanoparticles were considered using a variety of different reductants and stabilizers reported in the literature with some modifications to suit the parameters of this study. The chemical structures of the reagents used as reductants and stabilizers are shown in Figure 2. The unstabilized and gelatine stabilized gold nanoparticles were produced by the standard procedure (Turkevich et al., 1951, Zhang, 2008). The starch stabilized gold nanoparticles were produced using the method proposed by Kemp et al. (2009) and modified with the addition of starch

(Raveendran et al., 2003). Another method, which employs ethylene glycol (EG) to improve the life of the gold nanoparticles that were already coated with starch molecules was also used (Hussain et al., 2009). Polyvinyl alcohol (PVA) was used as a stabilizer for gold nanoparticles (Pimpang and Choopun, 2011) while heparin was used as both a reductant and a stabilizer, to produce stabilized gold nanoparticles (Guo and Yan, 2008). Nanoparticles of relatively large size were synthesized by employing tannic acid (Nutt et al., 2006). For comparison with the procedure used by Turkervich (1951), monosodium glutamate (MSG) was used to produce unstabilized gold nanoparticles (Johan et al., 2012). One method that was used to control the size of the nanoparticles during the synthesis, was to prepare small nanoparticles by rapid reduction with sodium borohydride and then growing them in a solution of gold(III) chloride using ascorbic acid (a weaker reductant) and stabilizing them with cetyltrimethylammonium bromide (CTAB) (Jana et al., 2001).

2.3. UV-Visible spectroscopy

UV-Visible spectroscopy was used to characterize the gold nanoparticles, to determine their ageing characteristics and leachability and monitor the leaching reactions under different conditions. UV-Visible spectra were recorded for the nanoparticle characterization using an *Ocean Optics USB4000 Fibre Optic Spectrometer* fitted with a *USB-ISS-UV-VIS Integrated Sampling System for Cuvettes* with a spectral range of 200 nm to 1100 nm, operated by *SpectraSuite*[®] software. Some of the spectra were recorded on a *Hewlett Packard 8453 Diode Array Spectrophotometer*, controlled by Agilent's Chemstation software. All spectra were measured in a 1 cm path length quartz cuvette. A *Shimadzu UVmini-1240* UV-Visible spectrophotometer with a spectral range of 190 nm to 1100 nm was used for the preliminary leaching tests which used 1 cm path length disposable plastic

cuvettes. The absorbance measurements were entered manually into an Excel spreadsheet for data analysis.

2.4. Ageing and leaching

The stability of gold nanoparticles synthesized for this study was determined by ageing the nanoparticles over 14-176 days and measuring the spectra at various time intervals throughout their respective aging periods. In order to determine the stability of nanoparticles in acidic and basic solutions during storage (ageing), the pH was adjusted to values between 2 and 12 in the absence of NaOCl/NaCl and then spectra were recorded at different time intervals at these pH values.

The preliminary leaching tests were conducted on unstabilized gold nanoparticles synthesized by reduction with citrate. For most tests absorbance measurements of the reaction mixture were taken every 10 seconds for the first 10 minutes, after which another leach test was initiated, and then at convenient random intervals until the leaching reaction slowed to such an extent that the absorbance readings remained constant over a longer period of time. The effect of NaCl concentration was determined at pH 6 by holding the concentration of NaOCl constant and varying the concentration of NaCl. Once the most suitable NaCl concentration was determined the NaOCl concentration was varied. The pH of the leach solution was then varied to determine the most suitable pH.

The pH was selected on the basis of the results of earlier leaching experiments with unstabilized gold nanoparticles. For comparison, unstabilized gold nanoparticles leached with molar ratios of $[\text{NaOCl}]/[\text{Au}] = 9.4$ and $[\text{NaCl}]/[\text{Au}] = 45$ times the stoichiometric gold concentration were also tested. They were known to have a comparable particle size and high leaching rate, as determined from the initial leaching tests. Subsequent leach tests with a greatly increased chloride concentration showed significant improvement in leaching

efficiency (%). Some leaching experiments were conducted at pH 4 with the same stoichiometric amounts of NaOCl and NaCl at the molar ratios: $[\text{NaOCl}]/[\text{Au}] = 16.7$ and $[\text{NaCl}]/[\text{Au}] = 240$, respectively.

3. Results and discussion

3.1. General properties of gold nanoparticle

3.1.1 Calculation of initial particle size

The diameter of the gold nanoparticles prepared for this study listed in Table 1 were calculated from the initial gold concentrations and the initial absorbance using equation 12 (Haiss et al., 2007), where A_{spr} = Absorbance of the surface plasmon resonance peak, C_{Au} = Initial concentration (mM) of gold nanoparticles, and d = diameter (nm) of gold nanoparticles. This calculation can only be used accurately to determine the size of gold nanoparticles in the diameter range of 5 – 50 nm. Due to their relatively large size, the particle size of the tannic acid stabilized gold nanoparticles was estimated from tabulated data (Haiss et al., 2007).

$$d = \left(\frac{A_{spr}(5.89 \times 10^{-6})}{C_{Au} \exp(-4.70)} \right)^{1/0.314} \quad (12)$$

The diameter of gold nanoparticles stabilized with gelatine, starch, MSG and heparin was calculated using the ratio of absorbance and equation 13 (Haiss et al., 2007), where, A_{450} = Absorbance at 450 nm. It was assumed that not all of the gold in these solutions was reduced to metallic gold, causing an underestimation of the diameter based on equation 13 due to the following reasons: (i) small gold nanoparticles can produce dampening and

broadening of the SPR peak caused by quantum size effects and inelastic scattering of the d-band electron holes (Palpant et al., 1998; Haiss et al., 2007), (ii) unreacted AuCl_4^- in solution can introduce two additional absorption peaks at 225 nm and 315 nm. However, due to the low concentration of gold (<0.5 mM in most cases) these peaks would have been obscured by the absorption edge for gold nanoparticles that appears in their spectra below 500 nm. This absorption edge is produced by d-band electronic transitions (Berciaud et al., 2005). The lack of significant broadening of the SPR peak, which accompanies dampening, validates the assumption of incomplete reduction of gold ions to elemental stage leading to the use of equation 13 for calculating the diameter of the gold nanoparticles.

$$d = \exp\left(\frac{3A_{spr}}{A_{450}} - 2.2\right) \quad (13)$$

3.1.2 Concentration, pH and spectra

The pH values and other properties of the solutions of gold nanoparticles synthesized using different reductants and stabilizers in this study are presented in Table 1, along with the spectra shown in Figure 3. Due to their relatively large size of 61.8 nm (Table 1) the tannic acid stabilized gold nanoparticles show a larger peak (curve 1). The high absorbance of the CTAB stabilized gold nanoparticles (curve 2) is due to the high concentration of 0.78 mM gold. Slight differences in the wavelengths of maximum absorbance for each of the nanoparticles, which depends on factors such as: particle size, coating thickness and the refractive index of the solution and coating (Haiss et al., 2007), are demonstrated by the listed values in Table 1.

3.2 Effect of ageing on stability

The purpose of these experiments was to test the reliability of stability of gold nanoparticles during storage and after pH adjustments, rather than during leaching. The stability of synthesized gold nanoparticles during storage over a reasonably long period of time avoids the repeated preparation of fresh nanoparticles required for the experimental program.

3.2.1 Ageing in solutions of natural pH

The relative stabilities represented by the % decrease in absorbance and positive or negative shift in SPR peak wavelength of the gold nanoparticles produced in this study over different storage times are listed in Table 2. The gold nanoparticles stabilized by tannic acid were not tested for stability for reasons that will be explained later. Some important points to note from Table 2 are:

- (i) Only the gelatine, PVA and starch/EG stabilized gold nanoparticles were stable over the respective periods of ageing (Table 2) at their natural pH.
- (ii) Gold nanoparticles stabilized by starch, CTAB and heparin and the gold nanoparticles produced by reduction with MSG were relatively unstable compared to the gold nanoparticles described in (i).
- (iii) The wavelength as well as the absorbance of the SPR peaks for nanoparticles produced by reduction with citrate change with time. However, after several months the rate of change decreased considerably and the nanoparticles became more stable. The absorbance decreased by a total of 19% over first 363 days but only 4.1% over the last 37 days. These nanoparticles maintained a sharp and intense peak for at least a year.
- (iv) For most of the nanoparticles the SPR wavelength remained stable but the absorbance did not.

3.2.2 Ageing of nanoparticles prepared using starch, MSG and PVA in solutions of adjusted pH

(a) Starch

The starch stabilized gold nanoparticles show the following trends:

- (i) Immediately after pH adjustment the nanoparticles were stable only in solutions maintained at a pH range of 6-10.
- (ii) The absorbance decreased in solutions maintained at pH 4 and pH 12.
- (iii) There was only a very small flat peak in the solution maintained at pH 2.
- (iv) The results shown in Figure 4b indicate that: after only three days even the peaks in solutions maintained at pH 6-10 had a lower absorbance; at pH 4 and pH 12 the peaks were very small; the peak at pH 2 had completely disappeared.

(b) MSG

The spectra of unstabilized gold nanoparticles produced by the reduction with MSG aged in solutions of natural and adjusted pH (Figure 4c) show the following trends:

- (i) After pH adjustment the peaks broadened until they were no longer present in solution of pH 6 and below.
- (ii) Figure 4d shows that only the nanoparticles at pH below 10 were stable after 11 days with only a small peak in solutions of pH 8.
- (iii) At pH 6 and below there were no peaks at all. These nanoparticles were even less stable than those produced by citrate reduction.

(c) PVA

The PVA stabilized gold particles showed the following trends:

- (i) According to Figure 4e gold nanoparticles were exceptionally stable in solutions above pH 4 with very little variation in peak shape, absorbance and wavelength.
- (ii) Even at pH 2 there was still a distinct peak. Figure 4f shows that in solutions of pH above 2, PVA stabilized gold nanoparticles are quite resistant towards pH changes for long periods of time.
- (iii) After ageing for 46 days in solutions of adjusted pH the peak at pH 2 still remained, but with a reduced absorbance whilst between pH 4 and pH 12 only slight differences in absorbance were evident.

3.3. Effect of stabilizers on gold leachability

3.3.1 Non-suitability of gelatine stabilised nanoparticles for leaching studies

During tests performed with gelatine stabilized gold nanoparticles the reaction with NaOCl/NaCl was either so rapid that it was not observable by the UV-Visible spectrophotometer or there was no measurable reaction. Once lixivants were prepared where the dissolution reaction could be measured a series of tests were conducted with varying ligand and oxidant concentrations. For many of the tests with gelatine stabilized nanoparticles there was an initial decrease in absorbance of the solutions corresponding to dissolution of the gold nanoparticles followed by an increase in absorbance and the appearance of a white cloudy suspension which obscured the leaching reaction. These leaching tests confirm that gelatine stabilized gold nanoparticles are not suitable for the study of gold leaching reactions in acidic chloride solutions, despite their success in cyanide and thiosulfate solutions described previously (McCarthy, 1998; Zhang et al., 2004, 2008; Senanayake and Zhang, 2012).

3.3.2 Other systems suitable for leaching studies

The absorption spectra of the gold nanoparticles consist of contributions of both absorbed and scattered light. Whilst the absorption cross section of a gold nanoparticle of radius R (smaller than the wavelength of incident light) decreases with R^3 the scattering cross section decreases with R^6 thus the total absorbance of the solution is related to the size of the gold nanoparticles (Van Dijk et al. 2006). Table 3 lists the leaching efficiency (%) in chloride media after 30 min based on Eq. 14, where $A_{t=0}$ is the initial absorbance and A_t is the absorbance after time t , based on the assumption that all solutions obey the Beer-Lambert law (Zhang et al., 2004).

$$\% \text{ Dissolution} = \text{Leaching efficiency (\%)} = \frac{100(A_{t=0} - A_t)}{A_{t=0}} \quad (14)$$

The results show that a large fraction of unstabilized gold nanoparticles (94%) was readily leached with NaOCl/NaCl. The extent of leaching of the PVA stabilized gold nanoparticles was moderately high (59%) and was only exceeded by that of the unstabilized (citrate, 94%) and starch stabilized gold nanoparticles in the absence of ethylene glycol (73%). This indicates that the PVA coating on the nanoparticle surface did not significantly interfere with the leaching reaction in the NaCl/NaOCl system.

However, when ethylene glycol was added to improve the lifetime of the nanoparticles the amount of gold leached decreased significantly to 13%. A possible reason for this is that as the ethylene glycol increases the lifetime of the nanoparticles by making them more resistant to aggregation and that the resistance allows them to tolerate higher concentrations of dissolved salts as well as the oxidant, causing the lower leaching efficiency.

The CTAB stabilized gold nanoparticles prepared by the seeded growth method did not leach to an appreciable leaching efficiency (23%). This may be due to CTAB, being a surfactant (Jana et al., 2001), which may be blocking the access of the chloride ligand and

hypochlorite oxidant to the nanoparticle surface. There was only a very moderate amount of leaching (33%) of the unstabilized gold nanoparticles produced by reduction with MSG which may be due to the instability of these nanoparticles. The moderate leaching efficiency of the heparin stabilized gold nanoparticles (40%) could be due to the surface coating of the heparin molecules preventing access to the surface of the gold nanoparticles to reagents. This appears to be the most likely cause of the very poor leaching behaviour (0%) of the tannic acid stabilized gold nanoparticles. This behaviour indicates that tannic acid probably formed an impenetrable coating on the gold that completely blocked access of the reagents to the gold surface, as expected from the structure shown in Figure 2. This makes tannic acid stabilized gold nanoparticles extremely stable in chloride solutions but also makes them unsuitable for the study of leaching reactions in the NaCl/NaOCl system. Therefore, they were not subjected to ageing experiments previously described in section 3.2. To accurately compare the initial leaching rates of gold nanoparticles their size had to be taken into account as the leaching rates increase due to the higher surface area of smaller sized particles, as described in Section 3.5.

3.4. Effect of main reactants and pH on gold leachability

As can be seen in Figure 5a, the leaching efficiency of gold at the two lowest concentrations gave almost identical variations as a function of time. Although the results show that the leaching efficiency increased with the increase in chloride ion concentration at pH 6 in the presence of 1.88 mM NaOCl the final leaching efficiency was less than 50%. Therefore, for all subsequent tests the concentration of NaCl was maintained at 18.0 mM and the concentration NaOCl was varied to determine its effect on nanoparticle leaching.

The results listed in Table 4 show a general increase in leaching efficiency with the increase in the concentration of hypochlorite. Figure 5b shows little difference between the

leaching curves for concentrations higher than 2.25 mM. Thus, the next series of tests at different pH values were conducted at this concentration of hypochlorite. The results presented in Table 4 and Figure 5c illustrate the dramatic effect of pH in NaOCl/NaCl system has on the leaching efficiency. Figure 5c shows three different types of behaviour of gold dissolution depending upon pH: (i) high dissolution at $\text{pH} \leq 4$, (ii) medium dissolution at $\text{pH} 5.03\text{-}7.28$, and (iii) low dissolution at $\text{pH} 10.4$. The gold dissolution at pH values equal to or lower than 4.06 remained well above 90% after 98 s. The leaching reaction was very rapid, taking only just over 9 minutes to leach 99.4% of the gold nanoparticles. At pH 6.63 the extent of gold dissolution was 73.4% which then decreased to 14.7% as the pH increased to pH 10.7, indicating that a small fraction of the nanoparticles were leached even after 59.1 minutes.

3.5. Initial leaching rates per unit surface area

The total available surface area of the gold nanoparticles for the leaching reactions was determined using equation 15, assuming a spherical shape for the gold nanoparticles and based on the face centred cubic (FCC) structure of metallic gold ($L = 0.407825$ nm; 4 atoms/unit cell (Wyckoff, 1963):

$$SA_{\text{total}} = \frac{1.5C_{\text{Au}}N_{\text{A}}V_{\text{Au}}}{d} \quad (15)$$

where, C_{Au} = the initial gold concentration in mol m^{-3} , SA_{total} = the total available surface area (m^2) of the gold nanoparticles per litre of solution at C_{Au} , V_{Au} = volume (m^3) of unit cell for the metallic gold crystal structure, N_{A} = Avogadro's number = 6.0221×10^{23} atom/mol, d = calculated diameter (m) of the gold nanoparticles from Section 3.1.1. The number 1.5 represents the surface area to volume ratio of the FCC unit cell $\left(\frac{6}{d}\right)$ divided by the number of

gold atoms in a unit cell. Thus, the rates calculated using equation 15 take into account the initial gold concentration, volume of solution and the diameter of the nanoparticles.

The leaching curves were determined by calculating the fraction of gold leached (X) from the fractional decrease in absorbance: $X = (A_{t=0} - A_t)/A_{t=0}$. From the fraction of gold leached the number of moles of gold dissolved was determined. The result was divided by the initially available surface area of all the gold nanoparticles in solution to determine gold leach rate per unit surface area ($\mu\text{mol m}^{-2} \text{s}^{-1}$). The initial conditions and the calculated initial rates are presented in Tables 4 and 5.

Figure 6a shows the variation of initial rates of gold leaching per unit area as a function of the concentration of NaCl and NaOCl at pH 6 as well as a function of pH in the pH range 2.16-10.7 at the fixed concentrations of 1.88 mM NaOCl and 18 mM NaCl. The decreased dissolution rates at higher pH range can be accounted for by examination of Figure 1 which shows that AuCl_4^- is not the dominant species in solution in this pH range. A close inspection of the Eh-pH diagram in Figure 1 shows that the AuCl_4^- species is most stable below pH 7 which corresponds to the stability region for hypochlorous acid. The Eh-Log[Cl⁻] diagram of gold-chloride system shows that increasing the chloride concentration is beneficial for leaching gold as the stability region for AuCl_4^- species at pH 1 lies far to the right of the diagram in the region where the chloride concentration is high (Senanayake, 2004). The initial rates per unit area increased from $0.03 \mu\text{mol m}^{-2} \text{s}^{-1}$ to $0.64 \mu\text{mol m}^{-2} \text{s}^{-1}$ when the concentration of NaCl was increased from 1.13 mM to 18.0 mM. The latter is of the same order as the reported value of $0.22 \mu\text{mol m}^{-2} \text{s}^{-1}$ for thiosulfate leaching of gold nanoparticles of similar size (32 nm) reported by Zhang et al. (2008). The leaching results for 0.16 mM of gold nanoparticles at 18 mM NaCl listed in Table 4 shows that the rate increased with increasing hypochlorite concentration, from $0.36 \mu\text{mol m}^{-2} \text{s}^{-1}$ at 0.75 mM up to a higher value of $1.25 \mu\text{mol m}^{-2} \text{s}^{-1}$ at 3.0 mM NaOCl. This can be rationalized by considering Figure 1

and taking into account equations 3-4 for the formation of HOCl which is a stronger oxidant than NaOCl (Baghalha, 2007). Figure 6b shows a logarithmic plot of rate as a function of NaCl concentration. The linear relationship of slope 1 indicate that the kinetics of nanoparticle leaching follows the same trend as the bulk gold reported in previous reviews (Senanayake, 2004) with a first order dependence with respect to chloride ion concentration. Although the initial rates of gold dissolution for gold nanoparticles is similar to the rates for massive gold the much larger surface area to volume ratio for gold nanoparticles leads to faster overall leaching efficiencies.

Nam et al. (2008) reported that AuCl_4^- will not be the stable species in solution if the Eh is below 0.8 V and pH below 6 as a result of the decrease in Eh due to the consumption of NaOCl during the leaching reaction. The moderately low leaching efficiencies for low concentrations of NaCl and NaOCl at pH 6 shown in Table 4 may be due to these factors. Gold can also precipitate if the chloride concentration is not in excess (molar ratio: $[\text{Cl}^-]/[\text{Au}] \gg 4$, Nam et al., 2008). However, this ratio lies between 7.1 and 112.5 during the tests conducted in preliminary investigations. Thus, leaching rather than precipitation is likely responsible for the decrease in solution absorbance during leaching. To confirm the fact that the reduction of absorbance of the solutions of gold nanoparticle was actually the result of leaching and not destabilisation, gold and platinum electrode potentials (versus the standard hydrogen electrode) were recorded during leaching. Moreover, the measured potentials during the dissolution of gold nanoparticles (Figure 7) show that E_{Au} remain lower than E_{Pt} but lies within the stability range of AuCl_4^- shown in Figure 1. No visible precipitate was observed for any of the solutions after leaching was completed which, coupled with the potential measurements, confirms that the decrease in absorbance of the gold nanoparticle solutions was due to leaching.

The initial rates of the leaching reactions presented in Figure 8 are based on the results reported in Table 5, under a random set of conditions which involved much higher concentrations of reagents than the listed values in Table 4. Figure 8 shows that the unstabilized gold nanoparticles synthesized by citrate reduction are rapidly leached. Other systems follow the descending order of rates: citrate > starch > PVA > Heparin > starch+EG > MSG > CTAB > tannic acid. Table 6 compares the initial leaching rates of the citrate and PVA stabilized gold nanoparticles synthesized in this study to those produced in previous studies by Zhang et al. (2004, 2008). The initial leaching rates of the gold nanoparticles stabilized by citrate ($1.54 \mu\text{mol m}^{-2} \text{s}^{-1}$) and PVA ($0.95 \mu\text{mol m}^{-2} \text{s}^{-1}$) in NaOCl/NaCl at pH 4 were 3 and 2 times higher, respectively, than the initial leaching rates of the citrate stabilized gold nanoparticles in ammoniacal copper(II)/thiosulfate at pH 9.5 ($0.47 \mu\text{mol m}^{-2} \text{s}^{-1}$). This result highlights the very fast kinetics of leaching in chloride solutions. The initial rate of $1.54 \mu\text{mol m}^{-2} \text{s}^{-1}$ for the dissolution of the unstabilized gold nanoparticles in a solution of 2.25 mM NaOCl and 18.0 mM NaCl at pH 4 and 25 °C measured in this study (Table 4) increased to $3.22 \mu\text{mol m}^{-2} \text{s}^{-1}$ when the particle size decreased from 22.28 nm to 3.54 nm. This rate is slower than the rate of $7 \mu\text{mol m}^{-2} \text{s}^{-1}$ for the dissolution of massive gold in 27 mM NaOCl and 85 mM NaCl at pH 7 and 20°C reported by Tran et al. (2011). This indicates the influence of the concentration of oxidant and ligand, pH, particle size and temperature on the rate of gold dissolution and further studies on the effect of such factors and the effect of other non-cyanide gold lixivants will be conducted with gold nanoparticles reduced/stabilised by citrate and PVA.

4 Summary and Conclusions

Various methods for synthesizing stabilized gold nanoparticles were investigated. Based on the stability over long periods of storage in solutions of different pH in the range 2-12 and leachability, the nanoparticles produced using citrate, PVA and heparin as

reductants/stabilizers appear to be the most suitable for further studies. Of the stabilized gold nanoparticles synthesized for this study only those stabilized by PVA were able to meet all criteria. These nanoparticles were exceptionally stable over long ageing times in solutions at pH 4 and above. Even at pH 2 these nanoparticles still maintained a moderately suitable peak which can be used to monitor the extent of leaching. The initial leaching rates for these nanoparticles were comparable to those for unstabilized gold nanoparticles synthesized by citrate reduction and it was clear that the coating of PVA did not significantly prevent access of the chloride ligands to the gold surface, allowing them to be readily leached. The initial leaching rates of gold nanoparticles are faster in chloride solutions than they are in thiosulfate solutions as expected and therefore warrants further studies with other non-cyanide lixiviants.

Acknowledgments

Authors would like to express sincere thanks to the School of Engineering and Information Technology of Murdoch University and Stuart Kelly, Ken Seymour and Andrew Foreman for lending their technical expertise.

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Figure 1

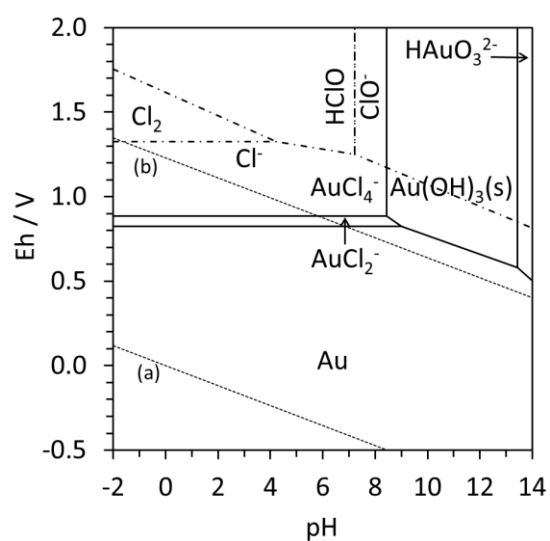


Figure 1 - Potential-pH diagram for gold chloridation (Au-H₂O-Cl⁻) at 25⁰C with all soluble gold chloride species at 10⁻³ M and 5 M Cl⁻ (reproduced from Brandon, et.al., 2003; (a) and (b) represents H⁺/H₂ and O₂/H₂O lines)

Figure 2

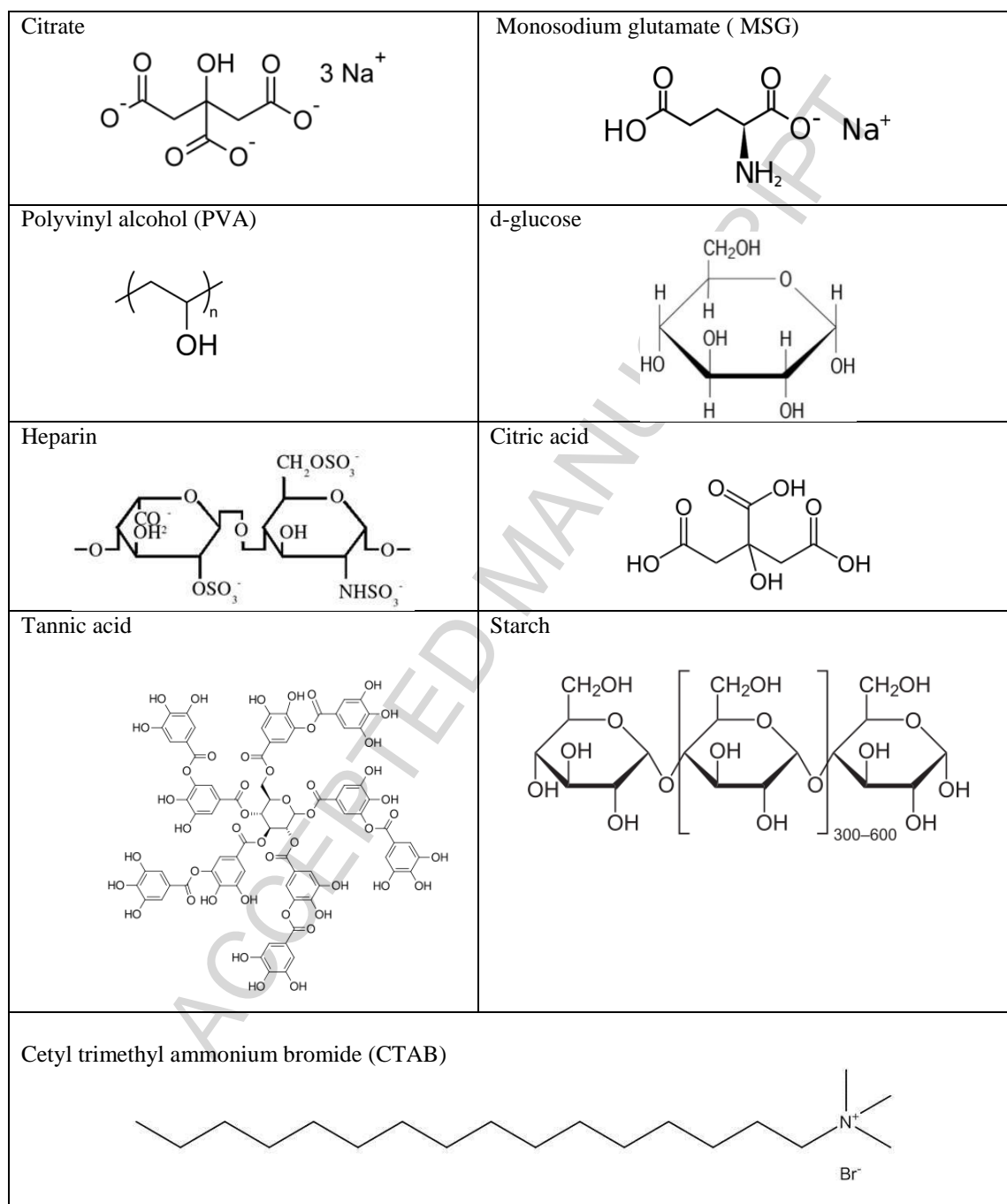
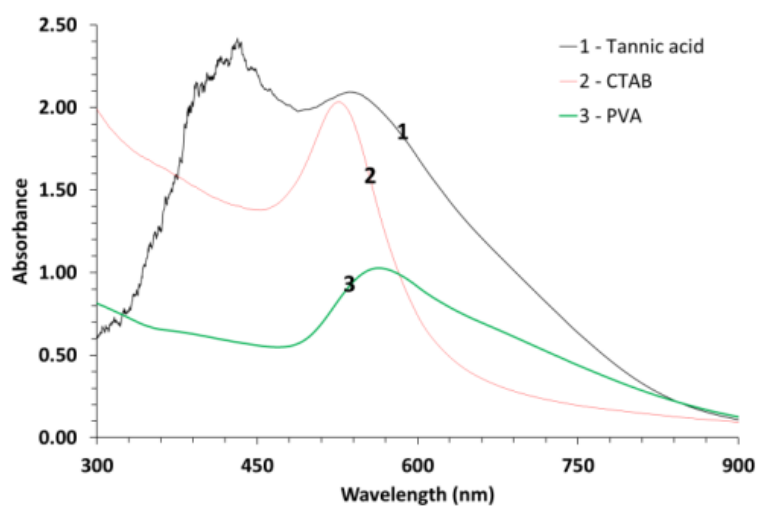


Figure 2 - Structures of reductants and stabilizers for synthesising gold nanoparticles

Figure 3

(a)



(b)

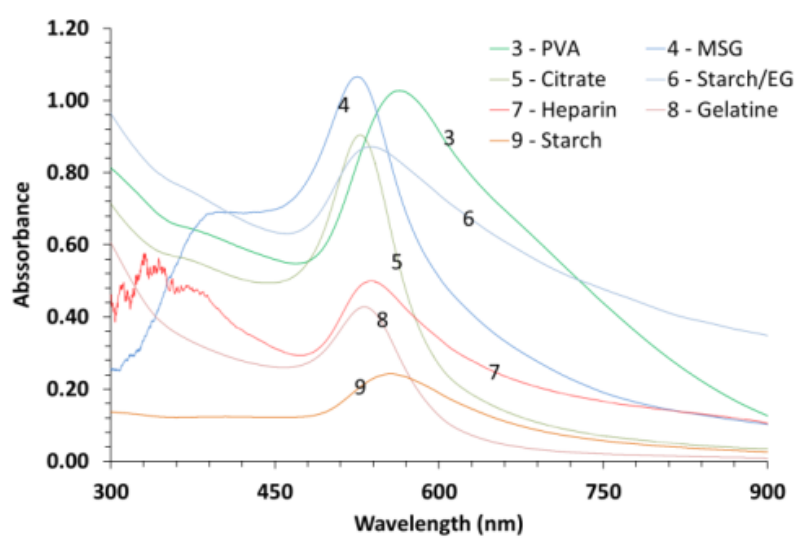


Figure 3 - Spectra of the gold nanoparticles produced by the various stabilizers from Table 1; a) tannic acid (1), CTAB (2), PVA (3); b) PVA (3, shown for comparison), MSG (4), citrate (5), starch with EG (6), heparin (7). Gelatine (8) and starch (9).

Figure 4

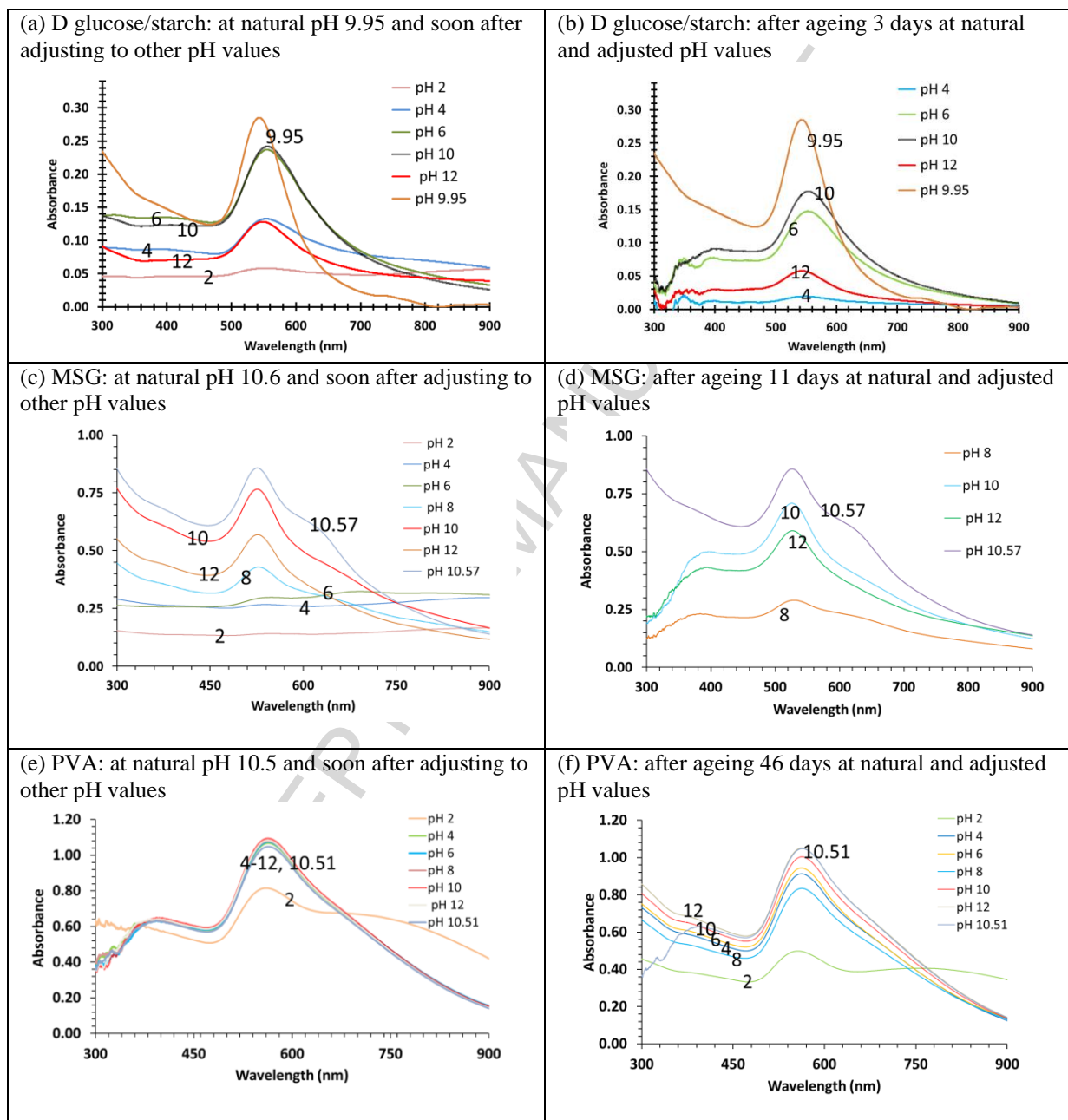


Fig. 4 –Spectra of gold nanoparticles synthesised using different reagents/stabilizers at natural and adjusted pH before and after ageing (see Table 1)

Figure 5

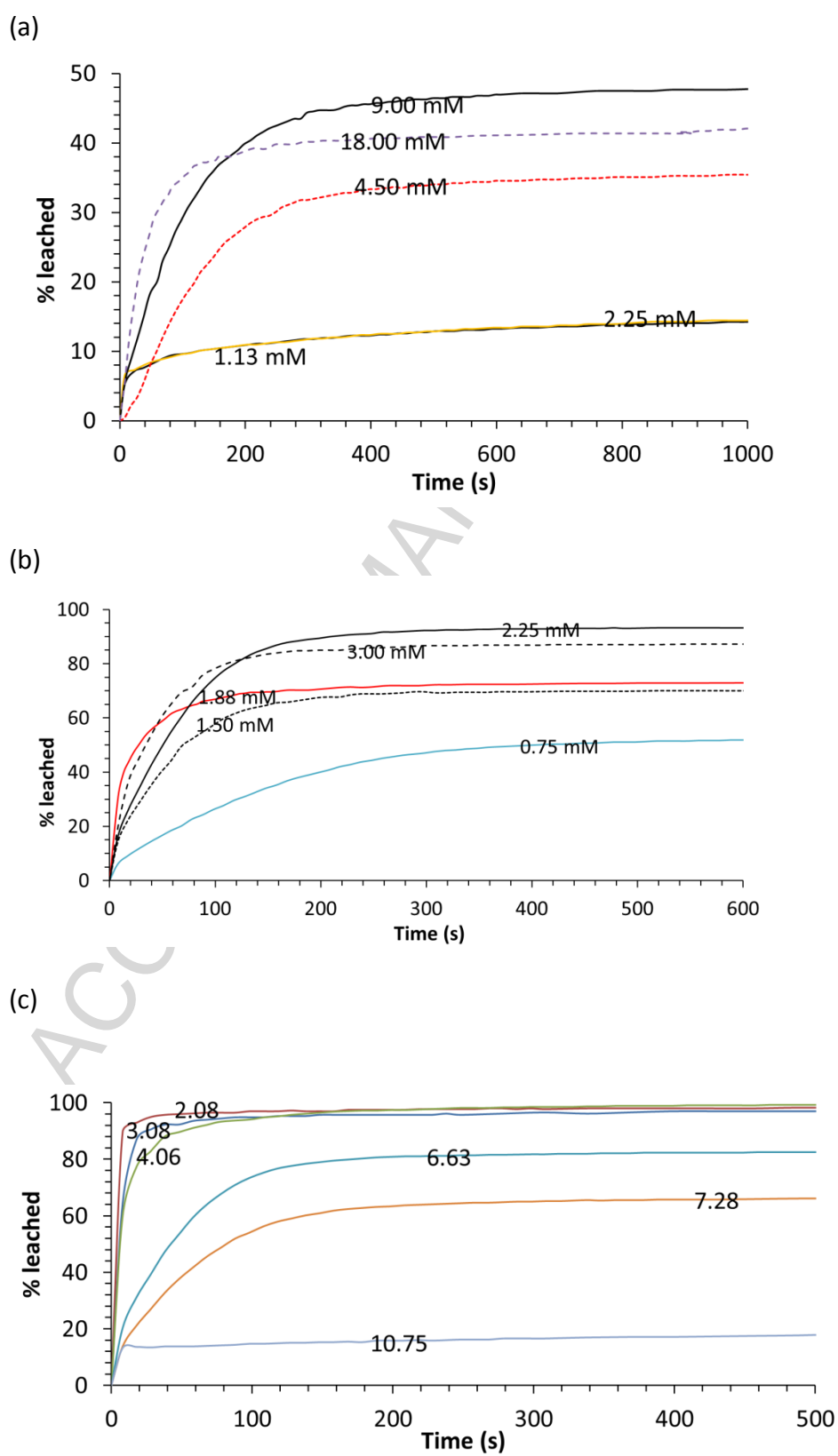
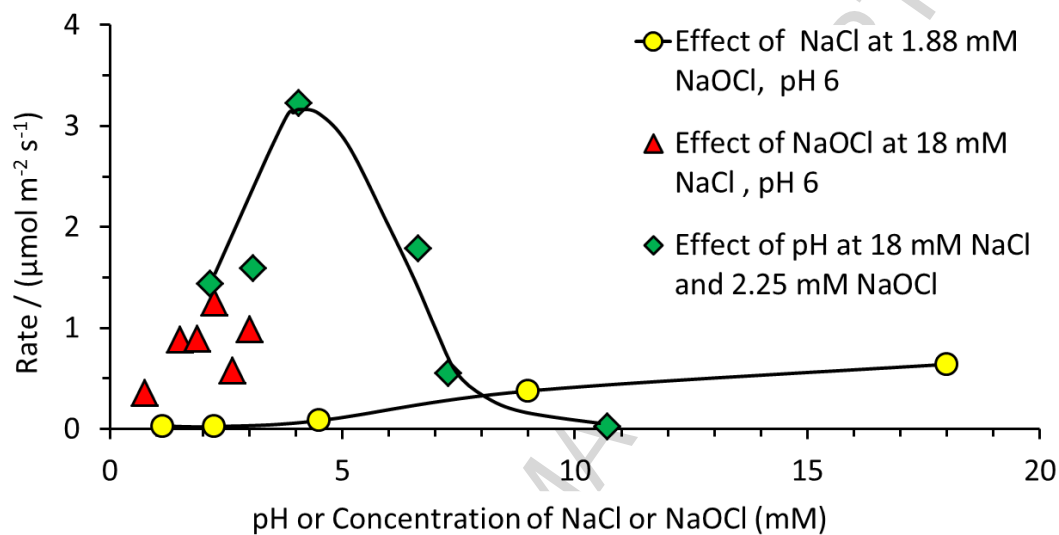


Fig. 5—Leaching curves gold nanoparticles at 0.16 mM: (a) effect of NaCl (at 8.59 nm, pH 6 and 1.88 mM NaOCl), (b) effect of NaOCl (at pH 6, 8.59 nm and 18.0 mM NaCl), (c) effect of pH (at particle size 3.54 nm, 2.25 mM NaOCl and 18.0 mM NaCl).

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Figure 6

(a)



(b)

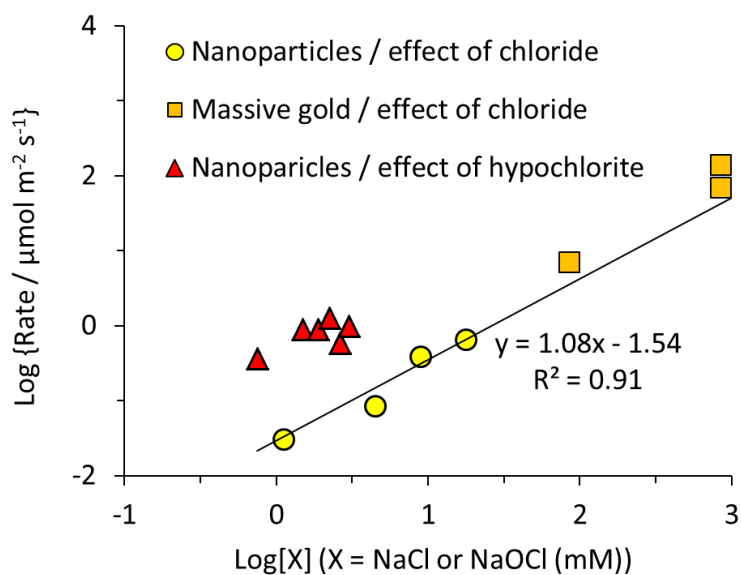


Fig. 6- Effect of pH and reagent concentration on initial rates of gold leaching (data for nanoparticles from Table and massive gold from Senanayake (2004)).

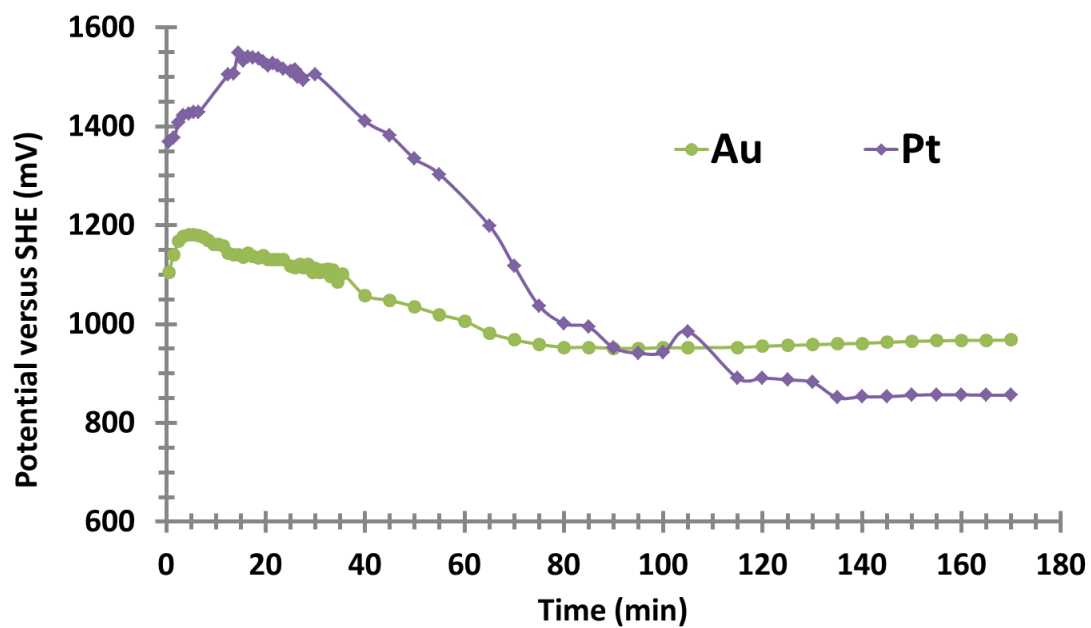


Fig. 7- Electrode potentials during leaching of gold nanoparticles in chloride solutions (0.16 mM Au, 18 mM NaCl, 2.25 mM NaOCl, pH 4, 25 °C).

Figure 8

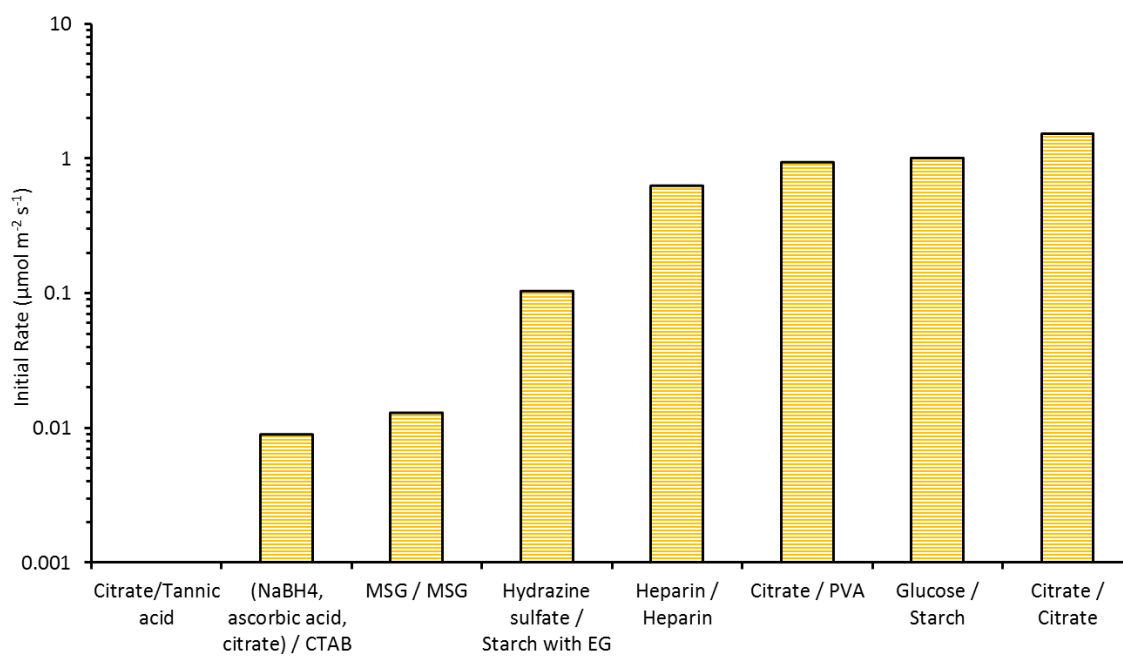


Figure 8 - Initial leaching rates of gold for nanoparticles with different stabilizers.

Table 1 - Properties of gold nanoparticle solutions.

Reagents for synthesis		[Au] mM	Natural pH	SPR wavelength (nm)	Initial absorbance	d (nm)
Reductant	Stabiliser					
Citrate	Citrate ^a	0.161	10.9	518.5	0.793	22.3
Ascorbic acid	Gelatine	0.199	6.65	545.0	0.304	5.18 ^b
D-glucose	Starch	0.383	9.95	533.8	0.968	18.6 ^b
NaBH ₄ , ascorbic acid, Citrate	CTAB	0.785	10.9	525.0	1.515	8.41
Citrate	PVA	0.251	10.5	564.1	1.028	28.4
Heparin	Heparin	0.362	9.77	535.1	0.500	15.2 ^b
hydrazine sulfate	Starch with EG	0.444	6.97	534.0	1.264	16.7
MSG	MSG	0.475	10.6	525.4	0.972	10.9 ^b
Citrate	Tannic acid	0.296	9.24	536.3	2.093	61.8

a. Unstabilised

b. Calculated from ratio of absorbance (A_{spr}/A_{450}) in equation 13.

Table 2 - Stability of SPR peak of gold nanoparticles

Reagents for synthesis		Natural pH	Storage time (days)	Decrease in Absorbance % (dA)		Change in wavelength (%)	
Reductant	Stabiliser			Total during stage	Per day	Total during stage	Per day
Citrate	Citrate*	10.9	37	4.12	0.11	-0.23	-0.006
Ascorbic acid	Gelatine	6.65	176	3.26	0.02	-0.54	-0.003
D-glucose	Starch	9.95	23	51.9	2.26	1.35	0.059
NaBH ₄ , ascorbic acid, Citrate	CTAB	10.9	21	31.1	1.48	0.30	0.015
Citrate	PVA	10.5	74	8.95	0.12	0.26	0.004
Heparin	Heparin	9.77	21	32.2	1.53	0.42	0.020
hydrazine sulfate	Starch with EG	6.97	14	6.63	0.47	0.00	0.000
MSG	MSG	10.6	14	27.8	1.98	-0.24	-0.017

*Refers to unstabilised gold nanoparticles in text

Table 3 - Extent of leaching of gold nanoparticles

Reagents for synthesis		[Au] mM	Leaching efficiency (%) after 30 minutes
Reductant	Stabiliser		
D-glucose	Starch	0.2873	72.9
NaBH ₄ , ascorbic acid, Citrate	CTAB	0.4099	23.1
Citrate	PVA	0.1882	58.9
Heparin	Heparin	0.2036	40.4
hydrazine sulfate	Starch with EG	0.2498	12.6
MSG	MSG	0.2671	33.1
Ascorbic acid	Gelatine	0.1493	Undetermined
Citrate	Citrate*	0.1600	94.0*
Citrate	Tannic acid	0.2957	0.00

[NaCl] = 600[Au], [NaOCl] = 25[Au], pH = 4, Temp = 25⁰C

*Unstabilized, [NaCl] = 45 [Au], [NaOCl] = 9[Au], pH = 4, Temp = 25⁰C

Table 4 - Effect of pH, chloride and hypochlorite concentration on leaching unstabilized gold nanoparticle

[NaOCl] (mM)	[Cl ⁻] (mM)	pH	Initial rate ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	% Au Leached after 98 s	Time (min)	Final % Au leached
1.88	1.13	6	0.030	9.60	60.1	17.4
	2.25		0.025	9.60	94.1	17.9
	4.50		0.084	17.2	150	41.2
	9.00		0.377	28.9	31.1	48.5
	18.0		0.641	34.7	21.6	43.1
0.75	18.0	6	0.359	20.5	49.1	48.7
1.50			0.890	43.6	26.1	57.1
1.88			0.898	28.8	21.9	43.1
2.25			1.250	62.8	29.1	82.7
2.63			0.579	64.3	62.1	73.1
3.00			0.989	53.0	41.1	62.9
2.25	18	2.16*	1.437	97.0	34.1	98.5
		3.08*	1.593	94.8	26.1	97.8
		4.06*	3.225	94.0	9.1	99.4
		6.63*	1.788	73.4	14.6	83.2
		7.28*	0.557	54.0	43.1	67.8
		10.7*	0.023	14.7	59.1	24.0

Fixed values 0.16 mM Au, 8.59 nm particle size, Temp = 25°C
 *3.54nm particle size

Table 5 - Summary of leaching results.

Reagents for synthesis		[Au] (mM)	[NaOCl] (mM)	[NaCl] (mM)	SA _{total} (mm ²)	Initial rate ($\mu\text{mol m}^{-2} \text{s}^{-1}$)
Reductant	Stabiliser					
D-glucose	Starch	0.3830	9.57	229.6	1.264	1.024
NaBH ₄ , ascorbic acid, citrate	CTAB	0.4099	10.2	245.9	2.986	0.009
Citrate	PVA	0.1881	4.70	112.9	0.407	0.949
Heparin	Heparin	0.2714	6.78	162.8	1.098	0.631
Hydrazine sulfate	Starch with EG	0.3330	8.32	199.8	1.219	0.105
MSG	MSG	0.3561	8.90	213.7	2.007	0.013
Citrate	Citrate	0.1605	2.25	18.0	0.441	1.54
Citrate	Tannic acid	0.2957	7.39	177.4	0.295	0.0

Fixed values pH 4, Temp = 25°C

Table 6 – Comparison of initial leaching rates of gold nanoparticles to selected literature values.

Reductant	Stabiliser	d (nm)	Initial rate ($\mu\text{mol m}^{-2} \text{s}^{-1}$)	
			This work (chloride)	Zhang et al. (2008) ^(a) (thiosulfate)
Citrate	Citrate	22	1.54 ^(b)	
Citrate	Citrate	3.5	3.22 ^(b)	
Citrate	PVA	28	0.95 ^(c)	
Citrate	Citrate	10		0.47
Citrate	Citrate	32		0.22
Ascorbic acid	Gelatine	16		0.10
		20		0.11
		25		0.09
		30		0.10

a) Initial conditions - 25°C, pH 9.5, 0.10 mM Au, 1.5 mM Cu(II), 20 mM Na₂S₂O₃, 120 mM (NH₃ + NH₄⁺)

b) Initial conditions - 25°C, pH 4, 0.16 mM Au, 2.25 mM NaOCl, 18 mM NaCl

c) Initial conditions - 25°C, pH 4, 0.25 mM Au, 4.70 mM NaOCl, 113 mM NaCl

Highlights

- Synthesis of gold nanoparticles using nine different methods
- UV–Visible spectroscopy to calculate the initial diameter
- Stability, ageing and leachability monitored using UV-Visible spectra.
- Leaching rates per unit area determined in chloride/hypochlorite solutions
- Leaching rates per unit area of nano-gold and massive gold are comparable
- Nano-gold can be used to test other non-cyanide lixivants

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