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Chapter 4

Adsorption of Gold on Granular Activated Carbons and New Sources of Renewable and Eco-Friendly Activated Carbons

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4.1 Gold, a Historical Perspective

Gold is a metal that has fired the imagination of humanity for thousands of years and even today its allure continues to captivate the human mind. With a crustal abundance of only around 3–5 ppb, gold's scarcity has given the precious metal a unique status among many past and present civilizations. Its opaque, bright yellow color, and metallic lustre defines its physical beauty. The social structure and cultural atmosphere of many early civilizations valued gold so highly that they incorporated the ductile and malleable metal into lavish jewelry and elaborated ornaments for both decoration and religious purposes. Importantly, gold is chemically stable and not subject to atmospheric oxidation, and many of the artefacts that have survived from ancient civilizations still retain their physical beauty and lustre. Many civilizations, past and present, have used gold for the long-term building of wealth. Thus, ensuring the demand for this scarce metal is always high. Over the centuries, acquiring and building a gold

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reserve was a secure method for a country to develop stable, accessible, and reliable store of national wealth that could be used to offset the effects of inflation, economic crises, and geopolitical instability. Today, gold reserves held by many governments, central banks, and investment funds are used as a monetary base for supporting their international commerce and transactions. Furthermore, a country's solvency in many cases is equated to its gold reserves.

4.2 Properties of Gold

The chemical symbol for gold is Au and is derived from *aurum*, the Latin word for gold. The pronounced yellow color and metallic lustre of gold clearly distinguishes it from other pure metals that usually range in color from silvery white to various shades of grey. The unique and characteristic yellow color is due to the electronic structure of the gold atom that readily absorbs electromagnetic radiation wavelengths less than 560 nm but reflects wavelengths greater than 560 nm. Gold has a face-centered cubic crystalline structure and at the atomic level has an electron configuration [Xe] $4f^{14}5d^{10}6s^1$. The metal's color results from the oscillations of the loosely bound valence electrons orbiting the gold atom [1,2]. Gold with an atomic number of 79 and an atomic weight of 197.0 has a relatively high density of 19.3 g cm^{-3} which makes it one of the few higher atomic number elements occurring naturally in its elemental form [3]. In its natural form, gold usually contains small amount of silver as well as those gold–silver alloys with a silver content greater than 20% are called electrum. Gold can also form other materials with minerals such as sulfides and tellurides. Gold's high density compared to solid rock allowed it to be recovered from alluvial placers using techniques such as panning and sluicing. Furthermore, gold's chemical stability and resistance to atmospheric oxidation allowed the metal to be considered as noble. Combined with various advantageous properties such as high ductility, high malleability, and a melting temperature of 1064°C, gold has been used in the manufacture of coinage, jewelry, and ornaments for thousands of years. However, the disadvantage of pure gold [24 carat] is its softness that makes it unsuitable for some forms of jewelry and ornamentation. Alloying gold with other metals can significantly change properties such as color, melting point, hardness, strength, and malleability. For example, when high percentage of copper is added to gold, its color becomes redder. The addition of small quantities of iron to gold changes its color to blue and the addition of aluminium transforms the characteristic yellow color to a purplish appearance. These alloys are rarely used since their properties make them difficult to shape and manufacture into products. This is of particular importance since around 50% of the world's consumption of new gold is used in the creation of jewelry, while investment in gold bullion by governments, central banks, and investment funds consumes 40%, and the remaining 10% is used in various industrial applications [4]. The industrial application predominantly involves depositing a thin layer of gold onto components to ensure good electrical conductivity and corrosion free electrical connectors in computers, electronic and electrical devices. Importantly, the electrical resistivity values for both silver (16 nΩ.m) and copper (17 nΩ.m) are superior to gold (22.1 nΩ.m) for electronic connectors, but unlike gold, both silver and copper are subject to atmospheric corrosion [5]. Gold has also been used as a catalyst since its light-off temperatures (temperature when the catalyst becomes functional) are between 200 K and 350 K. This temperature range is significantly lower than the 400–800 K range for the optimal performance for a platinum catalyst [6]. The medicinal use of gold compounds has been known for centuries and was believed to be beneficial for promoting good health. Today, there is even a branch of medicine known as chrysotherapy that uses primarily gold in medicinal compounds in a number of medical protocols. Gold(I) thiol compounds have been used in the treatment of certain diseases such as rheumatoid arthritis and autoimmune diseases [1]. And recently, gold nanoparticles have been used as carriers to deliver double-stranded DNA in gene-gun technology [7]. While other studies have shown that gold nanoparticles can passively cross the cancer cell barrier and accumulate in tumors, their good optical and chemical properties can be used advantageously in thermal treatment therapies to kill those tumors [8, 9].

4.3 Sources of Gold Ores

The gold present in the Earth today is believed to have come from two sources. The first is *via* a supernova event that occurred when two neutron stars had collided in space. The resulting explosion created various nuclear synthesis processes that formed a wide range of heavy elements. These expelled heavy elements condensed and then formed the solar system. During this period, the heavy elements falling onto the molten Earth ended up sinking to the core [10]. The second source comes from the bombardment of gold-loaded asteroid impacts around 4 billion years ago that enriched the Earth's crust and upper mantle [11]. The asteroid bombardment model explains why gold is widely distributed throughout the Earth's crust.

Gold ores can be formed within the Earth (Endogenetic) *via* hydrothermal processes. The process is initiated by igneous intrusions heating highly mineralized ground water. The heat enables the water to dissolve and absorb metals from the surrounding rock formations [12]. The heated, pressurized, and ore-rich waters flow via fractures in the overlying rock formations. The heat loss is experienced by the water flows as they travel through the surface formations resulting in precipitation and the formation of solid ore in fractures. These ore filled fractures or hydrothermal deposits can produce vein, and lode deposits consists of microscopic particles of elemental gold embedded within quartz, calcite, and other minerals [13]. Gold ores can also be formed at the Earth's surface (Exogenetic) due to the effects of weathering from either or both wind and water erosion of ore-rich hard rock deposits [14]. The eroded ores eventually end up in alluvial deposits called placer deposits located in river systems and coastal regions. Placer deposits can consist of free flakes, grains and due to the action of water, flakes and grains can be welded to form larger nuggets [15]. A stream placer is formed when a water flow (stream or river) carrying minerals starts to slow down. As water velocity decreases, heavy minerals drop out first and the lighter minerals continue to fall out as the velocity decreases. Because of gold's much higher density (19.32 g cm^{-3}) compared to most rock materials ($\sim$2.7 g cm^{-3}), concentrating and extracting can be achieved using straightforward techniques such as panning and sluicing [16]. Stream placer deposits were the first to be mined in ancient times, where the river sands could be gently washed away with water leaving behind the heavier gold particles. The particles were then refined by smelting before being used in the manufacture of jewelry and ornaments.

4.4 Gold Extraction and Recovery Processes

4.4.1 *An overview of gold extraction processes*

The average concentration of naturally occurring gold in the Earth's crust is around 5 ppb with many low grade ore deposits as low as 3–10 ppm. The naturally low concentrations of gold mean that some enhancement of concentration is needed to achieve an economically viable mine development. Therefore, the nature of the ore deposit ultimately determines the type of mining operation and mineral processing techniques needed to separate the gold from the bulk ore. This can be done using natural gravity concentration methods or by leaching processes. Historically, the early miners found gold ore in stream placer deposits located around streams and rivers. In this case, gold was concentrated using gravity-based techniques such as panning. Panning involve placing an amount of ore into the pan and then adding an appropriate amount of water. The pan would then be moved around in a horizontally circular motion. During this motion, the denser gold particles would eventually sink to the bottom of the pan, while the waste, less dense sediment is washed out of the pan. Other gravity techniques using the same principle would be sluiced ore-rich sediments through jigs or over grooved surfaces that capture the denser gold while the remaining sediment flowed over.

Liberating gold from lode or vein deposits, which contained microscopic elemental gold particles embedded within a mineral matrix proved more difficult as seen in Fig. 1. Extensive crushing prior to gold extraction was required with much of the fine gold particles lost during crushing. However, around the 10th century, mixing mercury with the crushed ore to alloy with the gold particles (amalgamation) significantly improved gold recovery. For centuries, the amalgamation technique was used in refining gold, but the process is no longer used by the majority of mining companies due to mercury's highly toxic nature and the advent of more efficient alternatives. Amalgamation is still used in third-world countries due to the straightforwardness of the technique, but it is nonetheless toxic and has the constant potential to create environmental problems.

Flotation has also been successfully used in processing gold ores. In this technique, the ore is mixed with water and chemical conditioning or frothing agents to form slurry. The slurry is then subjected to intense agitation via

Fig. 1 Elemental gold embedded within a quartz matrix from a West Australian mine

the introduction of pressurized air, during which differences in the surface properties of the constituents takes place. Gold particles in the ore tend to be surrounded by air bubbles, the remainder of the ore attracts water and then sinks. The mixture of gold particles and air bubbles forms a froth that is recovered by skimming off the froth and breaking it down outside the tank, thus liberating the gold.

Prior to the 20th century, the main gold extraction route used was chlorination and several processes were in use [17]. Some examples of chlorination processes at that time were the Deetken or Mears process that used chlorine gas [18], the Munktell process that used bleaching powder and sulphuric acid, and the Black–Etard process that used a mixture of potassium permanganate, salt, and sulphuric acid. Currently, chlorine and hydrochloric acid mixtures are still utilized in some refineries to process gold and platinum group metals. The cyanide process was developed by J.S MacArthur and the Forrest brothers in 1887 to deal initially with lower grade ores in South Africa and this has become the most common process for gold extraction today [19]. The process involves the dissolution of gold (and silver if present in soluble form) from the gold bearing ore via a dilute cyanide solution. The aurocyanide-complex ions in the slurry are then exposed to granular activated carbon absorbers. The porous structure and high surface area of the activated carbon absorbs and concentrates the gold complex. Once the carbon absorber is loaded with gold ions, it is then removed from the slurry and stripped of the gold. Because of the pre-eminence of the cyanide process, it will be discussed at length in Section 4.2.

Gold ores that cannot be recovered using gravity concentration methods or cyanide leaching are usually termed as refractory ores. Therefore, a pretreatment is needed to remove much of the surrounding rock matrix and expose as many of the embedded gold particles as much as possible. In this way, the gold particles can then be leached from the ore using a conventional cyanide leaching solution. Typical pretreatments that have been used are roasting, chemical oxidation, bio-oxidation, and pressure oxidation. Roasting involves heating atmospheric air between 450°C and 750°C to burn sulphurous minerals present in the ore, thus exposing embedded gold particles. Chemical oxidation methods using nitric acid at atmospheric conditions have been used with mixed results. Bio-oxidation using sulphur consuming bacteria in water solutions have been used, but the relatively extended retention times are generally too long due to slow bacterial oxidation rates. Other techniques, using oxygen and heat in high pressure autoclaves, have been used to oxidize sulphurous mineral-based gold ores. Autoclave operations can be controlled via oxygen pressure and temperature of the chemical reactions taking place. In the case of refractory ores, the nature of the ore determines the pretreatment requirements prior to mineral processing. If extensive pretreatment of the ore is needed prior to processing, it may not be economically feasible to refine the ore, despite there being gold present in the ore.

4.4.2 *Gold recovery from cyanide solutions*

4.4.2.1 *Introduction*

Today's gold producing operations have evolved to be highly sophisticated and technically efficient processes. Even before a mining operation begins, extensive exploration, prospecting, drilling operation and assaying are carried out to determine the feasibility and economic viability of operating the gold mine over its expected life. When the mine is operational, gold bearing ore is excavated from either open cut pits or from underground shaft operations. Prior to hydrometallurgical processing, the ore undergoes mechanical crushing. The smaller particles are then mixed with water and lime before more grinding. The finer particles are milled again in a ball mill until the bulk of the product (80%) is typically less than 70 microns. Hydrometallurgical processing of the ore consists of three major steps: (1) ore leaching, (2) solid liquid separation, and (3) purification and concentration [20]. Furthermore, each of the steps used in ore processing is usually optimized for a particular gold ore type. After processing, the gold undergoes refining and then smelting into bullions.

4.4.2.2 *Cyanidation of gold ores*

Oxidation states of gold include gold(I), gold(II), gold(III), and gold(V). But, it is gold(I) (aurous compounds) and gold(III) (auric compounds) that form useful stable complex compounds [1]. Gold dissolution can be achieved with the assistance of oxidizing agents and complexes. This is why all hydrometallurgical processes include a leaching stage to transfer gold from the ore into solution as an intermediate product. Today, the cyanidation method is the most commonly used process for leaching gold from ores globally, while both thiourea and chlorine-based processes are still used in gold operations. For more than a century, the cyanidation process has been successfully used worldwide to extract gold from both high-grade and low-grade ores. High-grade ores are processed using vat-based leaching, while low-grade ores undergo heap leaching. In the vat leaching process, a mixture of sodium cyanide and ore slurry is held in large tanks for several hours while agitators mix and circulate the slurry. Heap leaching involves piling crushed ore onto an impervious ground surface covering. Then, a dilute cyanide solution is sprayed across the top of the heaped pile. With time, the solution percolates down through the heap and leaches the gold from the ore under the action of gravity. At the base of the heap, the gold laden solution is collected for gold extraction. Once the gold is removed from the solution, it is then recycled to the heap.

The cyanidation process involves the dissolution of gold (and soluble silver if present) from the ore. During this process, metallic gold (Au^0) is oxidized and dissolved in a dilute alkaline cyanide solution. Lime is added to neutralize any acidic constituents present in the ore and the oxidant used is atmospheric oxygen. During leaching, Au^0 is oxidized at the anodic spot to form Au^1, while the oxygen is being cathodically reduced at another spot on the gold surface. In solution, the Au^1 ions form complexes with cyanide ions and are stabilized [21]. The dissolution reactions for gold was originally described by Elsner in 1849, but it was not until 1954 that Kudryk and Kellogg elucidated the electrochemical fundamental properties of this reaction [22]. Since then, numerous studies have investigated the dissolution mechanisms and passivation processes involved in aerated cyanide solutions [23,24]. There has been considerable debate over the exact mechanisms at play, however, the currently accepted mechanism for the dissolution of gold from its ores using a dilute cyanide solution (usually NaCN or KCN) is described by the reactions presented in Eqs. (1)–(3) [21]. The overall dissolution reaction is described by the Elsner equation (3).

$$2Au + 4CN^- + O_2 + 2H_2O \rightleftarrows 2Au(CN)_2^- + 4OH^-, \qquad (1)$$

$$2Au + 4CN^- + O_2 + 2H_2O \rightleftarrows 2Au(CN)_2^- + H_2O_2 + 2OH^-, \qquad (2)$$

$$4Au + 8CN^- + O_2 + 2H_2O \rightleftarrows 4Au(CN)_2^- + 4OH^-. \qquad (3)$$

In this oxidation mechanism, the processes proceed in three stages as presented in Fig. 2. During the first stage, an absorbed intermediate species

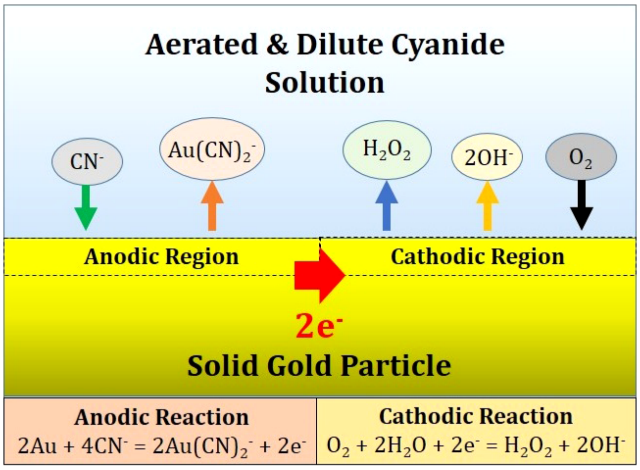

Fig. 2 Schematic representation of the electrochemical dissolution of gold into aurocyanide ions in an aerated dilute cyanide solution

($AuCN^{-}{}_{ads}$) is formed as shown in Eq. (4). In stage two, a complex occurs between the absorbed intermediate species ($AuCN^{-}{}_{ads}$) and the free cyanide (CN^{-}) as seen in Eq. (5). In the third stage, a passivation layer composed of Au (III) oxide (Au_2O_3) forms over the gold surface. However, this passivation requires highly anodic potential for passivation to occur [21].

$$Au + CN^{-} \rightleftarrows AuCN^{-}{}_{ads}, \tag{4}$$

$$AuCN^{-}{}_{ads} \rightarrow AuCN_{ads} + e-, \tag{5}$$

$$AuCN_{ads} + CN^{-} \rightleftarrows Au(CN)_2^{-}. \tag{6}$$

In aerated alkaline cyanide solutions, the anodic dissolution reaction presented in Eq. (4) is accompanied simultaneously by oxygen being reduced at cathode. This reduction reaction first described by Kudryk and Kellogg is presented in Eq. (7) [22].

$$O_2 + 2H_2O + 4e^{-} \rightleftarrows 4OH^{-}. \tag{7}$$

4.4.2.3 *Recovering gold from cyanide slurries*

4.4.2.3.1 Carbon adsorption processes

The carbon-in-pulp (CIP) is a well-known established and commonly applied process for the extraction of gold from cyanide leach slurries. Other variations of this process are carbon-in-leach (CIL) and carbon-in-column (CIC) and all processes that rely on gold being recovered from the enriched gold leached pulp by a suitable activated carbon/resin absorber. Activated carbon can be manufactured from a variety of raw organic products, but coconut shell carbon is preferred by the industry due to its strength, durability and its high adsorption capacity towards gold. During the process, leached pulp is pumped through a series of gently agitated tanks, at the same time, there is a counter flow of activated carbon. The flow rate is controlled so that there is significant retention time to allow appropriate interaction between the leached pulp and activated carbon. As the activated carbon material moves upstream the series of agitated tanks, it adsorbs and accumulates higher concentrations of gold as it comes into contact with higher grade leached pulp. Therefore, the leached pulp with the lowest gold concentration in the tanks comes into contact with the fresh or regenerated activated carbon first as seen in the schematic presented in Fig. 3 for a typical

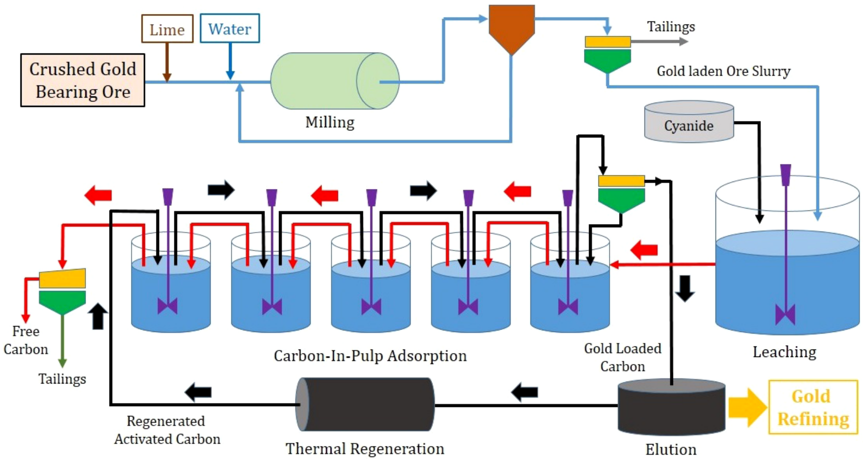

Fig. 3 Schematic of a representative CIP circuit for gold leaching and recovery

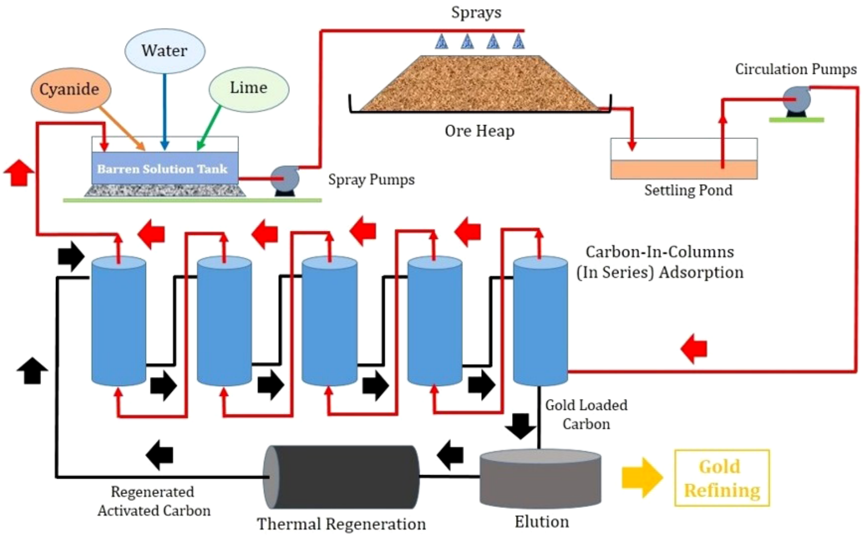

Fig. 4 Schematic of a representative Heap leaching circuit for gold recovery

CIP leaching and extraction circuit. While Fig. 4 presents a schematic diagram of a representative Heap leaching and gold extraction circuit. In Figs. 3 and 4, the black arrows indicate activated carbon flow through the circuit and the red arrows indicate the flow of leached product. Both procedures ensure efficient gold cyanide adsorption and minimize gold losses during adsorption [25]. The gold-loaded activated carbon is then separated from the leach pulp via vibrating screens that hold on to the coarse granular activated carbon. At the same time, the screens are fine enough to permit the pulp to flow through. The activated carbon is then transferred from the screens to stripping columns for desorption (elution) of gold cyanide and finally, the carbon undergoes regeneration and is recycled back into the circuit.

4.4.2.3.2 Electrowinning and refining of gold

The elution process produces a rich eluate solution that is transferred to electrowinning cells where gold and other metals are electrically deposited onto the cathodes. After deposition, the metallic material is treated with dilute sulphuric acid to dissolve metals such as zinc and copper if they are present. The remaining metallic material, usually consisting of gold and silver, is heated up to melting point to form an alloy called Dore. The Dore is then cast into moulds for assay and refining. Refining is achieved via electrolysis where silver and any platinum group materials are separated leaving pure gold. The gold can then be processed into bullion.

4.4.2.3.3 Merrill–Crowe process

The main advantage of the Merrill–Crowe process over CIP arises when there is a high silver to gold ratios. A general rule of thumb suggests that ratios greater than 4:1 favor Merrill–Crowe processing. This advantage results from the large carbon stripping and electrowinning processing required to handle large quantities of silver if present in the CIP process. The gold cyanide solution is separated from the slurry via diatomaceous earth-based filtration systems that produce a clarified solution. The gold cyanide solution then undergoes vacuum degassing to remove all oxygen contained in the solution. After oxygen removal, zinc dust is introduced to the clarified oxygen free solution. Because of cyanide's greater affinity for zinc compared to gold, the gold is precipitated along with silver in accordance with Eq. (8).

$$2\mathrm{KAu(CN)_2} + \mathrm{Zn} = \mathrm{K_2Zn(CN)_4} + 2\mathrm{Au}. \tag{8}$$

The precipitate containing gold and silver is filtered from the solution. The resulting precipitate is then mixed and blended with fluxes for smelting to produce impure metallic bars. The bars are then sent for refining, however, the refining process used will be dependent on the other metals present such as copper, silver or platinum group materials.

4.4.2.3.4 Resins and ion-exchange methods

The recovery of gold from aurocyanide solutions using ion-exchange resins is not widely used as activated carbon adsorbents due to the resin cost and the cost of specialized equipment needed for resin processing [24]. Currently, the Commonwealth of Independent States (CIS-Russia) extensively uses resins for the recovery of gold from aurocyanide solutions [26]. Like the CIP/CIL processes that are based on activated carbons, there are equivalent resin processes such as resin-in-pulp (RIP) and resin-in-leach (RIL). Both activated carbon and resin-based processes are similar in principle, the major difference occurring during the elution stage. Activated carbons must first be stripped of gold and then followed by a thermal regeneration stage before the carbons can be re-introduced into the processing circuit as seen in Figs. 3 and 4. However, in contrast to activated carbons, both gold stripping and regeneration can occur simultaneously if the appropriate elution agent is used [27–29]. Crucially, the fundamental difference between activated carbons and ion-exchange resin occurs in their respective adsorption mechanism. In activated carbons, the aurocyanide complex is adsorbed between the stacked uncharged graphitic layers that form their matrix [30], while the structure of ion-exchange resins contains large numbers of desirable functional groups with similar charge that are used to attract electrostatically and concentrate oppositely charged gold ions. This feature means that resins can be specifically tailored to promote high selectivity towards the aurocyanide complex found in conventional cyanide liquors [27]. However, the competitive adsorption of unwanted anions and subsequent gold stripping from the resin has made it less competitive to current activated carbon-based extraction processes.

4.5 Activated Carbon Absorbers

4.5.1 *Activated carbon*

Carbon is one of the most abundant materials present on Earth and the arrangement of its outer electrons allows it to make four covalent bonds with other carbon atoms and other elements. This catenation property explains why there are so many different forms and structures made of carbon atoms such as chains, rings, and polygonal shapes. It is the variation of these molecular geometries that give each carbon compound its distinctive properties [31, 32]. Activated carbon is an overall generic term for a range of highly porous carbonaceous materials that cannot be exactly defined or characterized by a single physical structure or chemical analysis [33]. The lack of this common single defining physical/chemical structure or analysis stems from the wide range of organic sources such as nuts shells, coal, peat, and wood that can be processed into activated carbon. The features of activated carbons that make it a highly desirable absorber for a number of engineering applications include a highly developed and reproducible microporous structure that promotes a very large internal surface area [34]. In addition, the large internal surface area also offers a high degree of surface reactivity that promotes a considerable adsorption capacity. The versatility of activated carbons towards a number of applications such as filtration, separation, and concentration of recoverable materials results from the ability to engineer the material's microporous structure and manipulate the functional groups present on their surfaces [35, 36]. Because of these advantageous properties, activated carbons have been extensively used in food and food beverage processing, chemical and pharmaceutical processing, gas separation and purification, and also water treatment operations [37–39]. The popularity of activated carbons in these particular applications is also reflected in the actual volumes being used. For example, world consumption in 2002 was around 750,000 tonnes [40–42] and during the following decade, consumption steadily increased to around 1.2 million tonnes by 2012 with an estimated value of USD 1,913 million. Forecasting for the 2013–2019 period by industry analysts indicates that the tonnage is expected to increase annually by 10.2%, while the expected value is predicted to increase by 11.9% annually and by 2019, the estimated value will be around USD 4,180 million [43].

4.5.2 *Source materials for activated carbons*

Activated carbons can be produced from a wide range of raw organic materials derived mainly from plants. Sources also include coal, peat, lignin, wood, and vegetable wastes from food processing. In terms of a mechanically strong and durable activated carbon, the hard shell of the coconut has been extensively used by the gold industry because of its superior adsorption properties coupled with its inherent strength [43]. Other nut-shell sources include almond, hazelnut, macadamia, pecan, and walnut while fruit stones such as apricot, cherry, peach, and plum have all been studied as precursor for activated carbons [44–51]. The importance of the inherent properties of the raw material cannot be underestimated since these properties have a significant influence on the final chemical and physical properties of the resulting activated carbon [52]. Highly desirable inherent properties include (1) high microporosity, (2) intrinsic hardness, (3) high density, (4) low attrition loss, (5) long service life, and (6) low ash content. For example, woody-based activated carbons with 1 g having more than 500 m^2 of surface area make good decolorizing agents for dye-contaminated water [53]. Alternative sources of raw materials that have been used to make activated carbons include bone, sugar, and tyres, agricultural waste and waste materials from municipal or industrial waste water treatment facilities [54–60].

There are two main forms of activated carbon. Powder is the first form and it has a large external surface area with a relatively small diffusion distance inside its pores. Thus, making the rate of adsorption very high and making this product ideal for solution-based adsorption applications. The raw material for these powders is usually sawdust, which after carbonization is chemically activated. But, unlike many granular forms, powdered activated carbons are not reusable [46]. Granular activated carbons are the second form of the material. These activated carbons are known for their highly porous structure giving them very high surface areas. The porous structure is composed of micropores (pore dia. <2 nm) and mesopores (pore dia. 2–50 nm) that promote the transport of molecules or particles within the porous matrix. This extensive array of interconnecting pore channels dramatically increases the surface area and greatly improves the adsorption capability of the activated carbon [61]. Furthermore, studies have shown the presence of chemically bonded heteroatoms located at the edges of carbon layers. The presence of heteroatoms such as oxygen, nitrogen, and hydrogen can influence the types of surface functional groups that can interact with the activated carbon [62]. Studies have shown that modifying the surface functional groups containing oxygen and nitrogen via thermal and chemical methods to promote coordination chemistry that can attract a variety of heavy metals [63–65]. Hence, granulated activated carbons have been extensively used in water purification as well as for the removal of toxic effluents from contaminated waters [66, 67].

In terms of gold recovery, Johnson patented a process that used a cyanide leach solution and activated carbon derived from wood charcoal [68]. However, a practical process for using cyanidation and granulated activated carbon to recover gold from solutions was only developed in the 1950s by Zadra *et al.* while working for the US Bureau of Mines [69]. Since then, there has been considerable interest from both the scientific community and industrial fields in investigating, understanding, and optimizing the adsorption and subsequent desorption of gold from activated carbons. Over the years, the gold mining industry has predominantly focused on two activated carbon-based technologies, namely CIP and CIL. Both technologies have enabled the industry to maximize extraction rates from ores, and in turn reduce processing and operating costs. Each process uses activated carbons derived from either peat or coconut shells, both of which have effective surface areas around 1000 m^2/g. In particular, activated carbons derived from coconut shells are strong, durable, and have a long service life, which mean that they can be regenerated many times.

4.5.3 *Carbonization and activation of raw materials*

4.5.3.1 *Introduction*

In general, the procedure for producing activated carbon is a two-step process. The first step is carbonization and its objective is to create a carbon structure with a high carbon content (ideally 80% and above). To achieve this goal, a pre-sized organic raw material is heated in an inert atmosphere. During this step, dehydration and the removal of volatiles take place in controlled temperature dependent procedure. Activation is the second step and involves developing a porous structure of molecular dimensions that dramatically increases the surface area of carbon. The final pore interconnectivity, pore volume, mean pore diameter, and surface area of the final activated carbon are all dependent on the nature of the raw material, temperature, and activation time and the type of oxidizing agent used [70, 71].

4.5.3.2 *Carbonization of raw materials*

Carbonization is performed at temperatures between 400°C and 800°C in the presence of an inert gas atmosphere on the organic raw materials. For example, commercial coconut-based carbons are usually carbonized at 500°C. The thermal treatments are designed to dehydrate, remove non-carbon species (carbon dioxide, carbon monoxide, oxygen, nitrogen, and hydrogen) and thermally decompose any volatile components [72]. Thermal treatment produces a carbonized mass with a poorly developed porous structure within the carbonized mass matrix [48, 72]. Manufacturers of activated carbon generally use a pretreatment procedure using dehydrating agents such as phosphoric acid, zinc chloride, or sulphuric acid to encourage porosity during carbonization [73,74]. During thermal treatment, the agents influence the pyrolytic decomposition, restrain tar formation, reduce the formation of acetic acid and methanol, and significantly improve the carbon yield. Lower treatment temperatures generally improve the size, interconnectivity and distribution of the pore structure within the final carbonized mass. Thus, the amount and type of agent combined with the appropriate treatment temperature are important factors in determining the quality and quantity of the carbon produced. Crucially, higher amounts of pretreatment agents result in larger pore structures being formed in the carbonized mass [44,71,75]. After carbonization, the carbon atoms present in the mass are grouped into stacks of flat cross-linked aromatic sheets. The spaces between the sheets that form the pores in some cases can be filled with products of decomposition or disordered carbon if the pretreatment agents fail to impregnate the mass [71]. Because of the poorly developed porous structure and low surface areas produced during carbonization, the adsorption capacity of the resulting carbonized mass is relatively low [57]. Therefore, a second procedure (activation) is used to further develop the porous structure and amplify the adsorption properties of the carbonized mass.

4.5.3.3 *Activation and carbon structure*

Activation leads to further development of the primary porous structure including further pore creation and dramatically increases the surface area of the various internal pores structures. Activation is typically carried out between 800°C and 1100°C in an oxidizing atmosphere. Typical atmospheres can consist of flue gas (source of carbon dioxide (CO_2)), steam or atmospheric air or various combinations of these gases [40,50,76]. During activation, disordered carbon located in spaces between the aromatic sheets and more reactive regions of the carbonized structure are exposed to oxygen and undergo endothermic reactions as described by Eqs. (9) and (10). Furthermore, steam (H_2O) reacting with the carbon structure produces carbon monoxide (CO), which is then accompanied by water to gas formation as described by Eq. (11) [71,76].

$$C + H_2O = CO + H_2 \qquad \Delta H^{o}_{1073\,K} = 136\,kJ, \tag{9}$$

$$C + CO_2 = 2CO \qquad \Delta H^{o}_{1073\,K} = 170\,kJ, \tag{10}$$

$$CO + H_2O = CO_2 + H_2 \qquad \Delta H^{o}_{1073\,K} = -34\,kJ. \tag{11}$$

The extent of activation will depend on the original organic material, type of gas or gas mixture used, the treatment temperature and overall treatment times [48]. The burnout of carbonaceous compounds and disorganized carbons between the aromatic sheets produce the final pore structure. During this time, significant pore widening occurs and produces pores with very large internal surface areas [45]. However, the burnout is not a uniform process due to difference in the crystalline properties produced during the initial carbonization process and results in variations in the size, texture, and distribution of pores. For example, when burnout is less than 50%, a micropore structure is formed. However, when burnout is between 50% and 75%, a widely varying pore structure is produced. Thus, by controlling the activation parameters, it is possible to engineer activated carbons with specific properties for particular applications [21,33,77,78].

4.5.4 *Physical and chemical properties of activated carbons*

The matrix of graphite is similar to activated carbons, but with a superior degree of order. X-ray diffraction studies have identified the presence of two types of structures occurring in activated carbons [18]. The first type is composed of regions of elementary crystallites comprising hexagonally ordered carbon atoms. In contrast, the second type is formed of disordered and cross-linked lattices of hexagonally ordered carbon atoms [79]. The

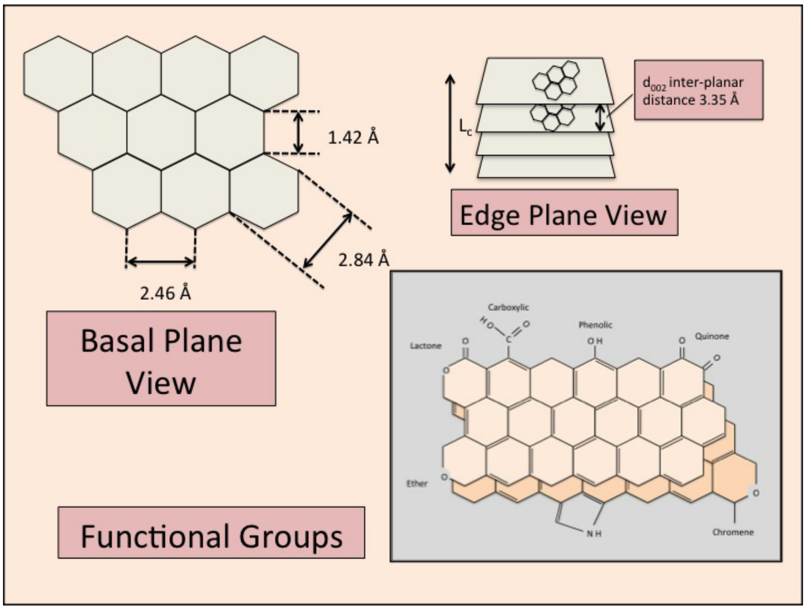

Fig. 5 Hexagonal arrangement of carbon atoms and some functional groups present in graphite and activated carbons

sizes of these elementary carbons are the direct result of the temperature used during activation. Typically, their width ranges from 2.0 to 2.3 nm while their heights vary 0.9–1.2 nm in height (see Fig. 5). Correspondingly, the nanometer scale crystallites present are usually around the diameter of a hexagonal arrangement of carbon atoms and a height of three layers [80].

Activated carbons are distinguished from other materials by their formidable adsorption capacity, high degree of porosity, and pore size distribution. In the case of activated carbons, Dubinin classified the size distribution of the pores into three groups [81]:

Type of Pore	**Pore width (w) range**
Micropores	$w < 2\,\text{nm}$
Transition pores/Mesopores	$2\,\text{nm} < w < 50\,\text{nm}$
Macropores	$w > 50\,\text{nm}$

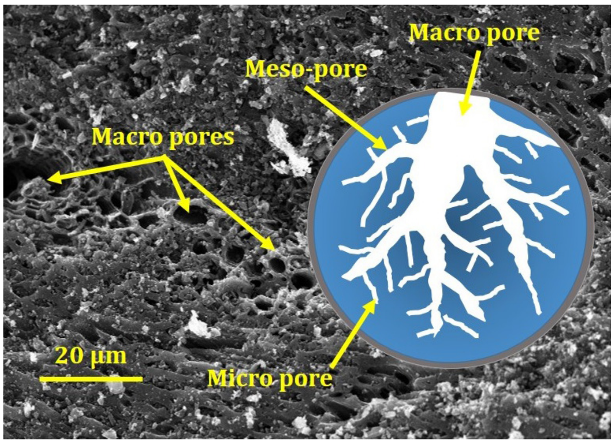

Fig. 6 SEM image of the coconut activated carbon showing surface pores and insert showing a representative pore structure

The classification of the different types of pores and their respective diameters is based on their width *w* [82]. The macropores contribute very little to the total surface area and do not play any significant role in promoting adsorption, but provide passage to the mesopores and the micropores as seen in Fig. 6. Both the mesopores and the micropores provide access to the interior of the carbon matrix. Importantly, the micropores formed and developed during activation are responsible for the very large surface area normally associated with activated carbons. Surface area measurements of solids are generally made using the Brunauer, Emmett, and Teller (BET) method. In this technique, the BET surface area value expresses the surface area in square meters per gram of adsorbent, covered by a monomolecular layer of nitrogen gas [83]. Generally, activated carbons have BET surface areas ranging from 500 m^2/g to 1400 m^2/g and for gold adsorption applications, it is typically around 1000 m^2/g. The mesopores make up less than 5% of the total internal surface area, while the micropores account for 95% of the total internal surface area and are the most important feature associated with the adsorptive action of the carbon [56].

The adsorption capacity of any activated carbon is not only determined by its physical porous structure, but also on its surface chemistry. The effect of surface chemistry and its influence in adsorption processes is not fully understood, but the surface chemistry of activated carbons can be associated with three main causes [18]: (1) Disruptions in the normal microcrystalline structure caused by edge and dislocation effects form residual carbon valances that can influence the adsorption of polar and polarisable species; (2) The presence of chemically bonded elements such as oxygen, nitrogen, and hydrogen in the original source material or chemical bonding between the carbonized mass and chemical species existing in the activating agents, and (3) The presence of inorganic matter such as ash components or residual activating agents that either enhance or adversely influence adsorption.

In terms of surface oxides, despite being a relatively minor component, they can have a drastic or significant influence on the overall chemical behavior of the carbon. The presence of these surface oxides can produce acid–base, redox, and catalytic properties as well as imparting a hydrophilic character to naturally hydrophobic carbon. For example, oxygen chemisorbed onto carbon can readily form C–O functional groups that can subsequently influence surface reactions, wettability, and electrical property of the activated carbon [18, 84]. Because of the effect of surface oxidation on surface chemistry, activated carbons are generally classified into two categories based on their acid–base character. The two categories are H-carbons and L-carbons, and are distinguished from each other by their respective pH values. H-carbons are characterized by their ability to adsorb H^+ ions when immersed in aqueous solutions with the result being an increase in the pH of the resulting solution, whereas L-type carbons preferentially adsorb OH^- ions present and generate higher pH values in the resulting solution [85]. H-carbons (protonated surfaces, $C–OH_2{}^+$) are activated at temperatures above 700°C with 1000°C being a typical thermal value. L-carbons (ionized surfaces, CO^-) are typically activated below 700°C, usually between 300°C and 400°C. Steam activated carbons are generally used for gold recovery and are typically activated at temperatures between 600°C and 700°C. And as a result, they can display both acidic and basic properties, but generally with more H-carbon type characteristics [18].

4.5.5 *Properties of activated carbons in the hydrometallurgy industry*

4.5.5.1 *Introduction*

Historically, charcoal material was first used to recover gold from ores, but the subsequent burning of the charcoal and smelting the ash to recover the gold proved to be uneconomical. However, the introduction of activated carbons into large-scale cyanide-based leaching processes by the gold industry in the 1970s made it possible to extract gold from low-grade ores and tailings economically. For optimum performance in a gold recovery operation, the selected activated carbon must have important properties such as high rates of adsorption, high gold-loading capacity together with high resistance to abrasion in the circuit [86]. These properties have made the use of activated carbon technically and economically more attractive compared to earlier gold recovering processes using cyanide leach solutions [87]. Two commercial types of activated carbons currently being used by industry are derived from peat and coconut shells. Figures 7 and 8 present scanning electron microscopy (SEM) surface images of commercial peat and coconut shell derived activated carbons. Both sets of figures clearly show the respective porous surface features of both activated carbons. In particular, factors such as high selectivity towards gold and the ability to reuse the absorbent in the extraction process has made the use of activated carbons an attractive option since the technology was introduced, thus making activated carbon-based CIP and CIL technologies

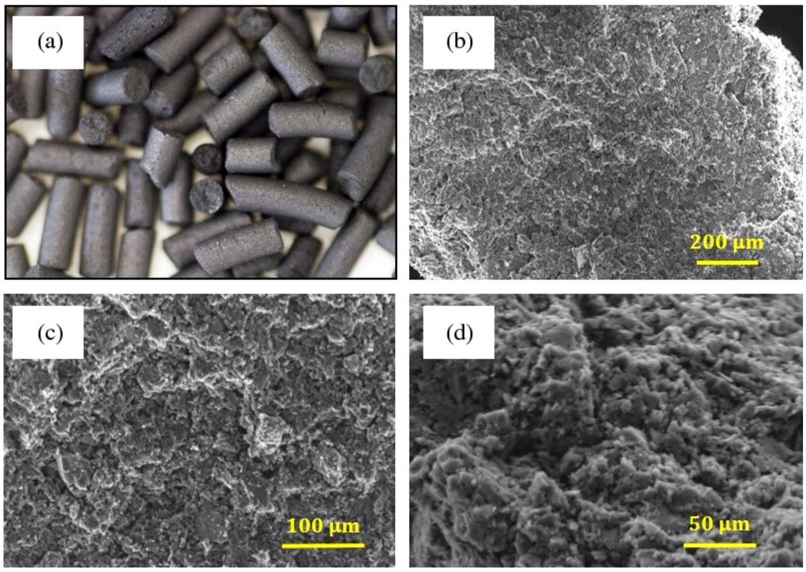

Fig. 7 Optical and SEM images showing the porous surface features of Norit peat derived active carbon

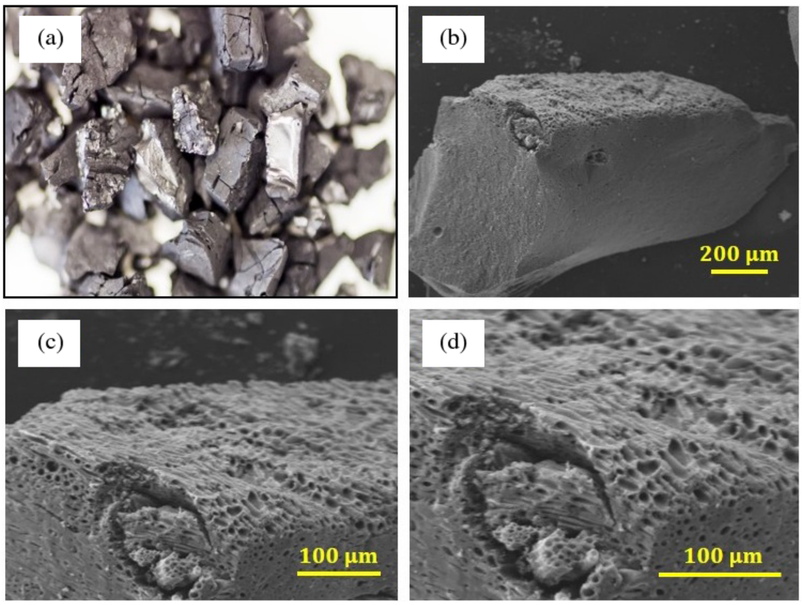

Fig. 8 Optical and SEM images showing the highly porous surface of coconut shell derived (Haycarb) activated carbon

the standard for the majority of gold mining operations throughout the world [88, 89].

4.5.5.2 *Gold adsorption mechanisms and loading on activated carbons*

Gold adsorption on activated carbons is dependent on a number of chemical and physical factors that influence both adsorption kinetics and gold-loading capacity. Initially, the adsorption rate of gold cyanide is fairly rapid and adsorption takes place on all accessible sites. Most of these adsorption sites are located in and around the macropores and possibly some of the mesopores. As the mass transport of gold cyanide species continues, adsorption kinetics steadily decreases until a pseudo-equilibrium is reached. From this point onwards, a much slower adsorption process takes place within the micropores [18]. Adsorption at this stage is much slower due to the effects of diffusion taking place along the tortuously long lengths of the micropores. Several studies have been undertaken to explain and model the complex nature of the diffusion mechanisms involved during the adsorption of gold cyanide on porous active carbons. These studies have proposed three rates of dependent diffusion mechanisms based on contact time and gold-loading capacity to explain the adsorption of gold cyanide. The three mechanisms are (1) film diffusion (mass transport), (2) pore diffusion, and (3) surface diffusion [87, 90–97]. And as discussed above, initial gold cyanide adsorption is rapid with adsorption taking place on all easily accessible sites and is explained by film diffusion (mass transport). Pseudo-equilibrium is reached when maximum adsorption capacity is achieved in the macropores and mesopores. Beyond pseudo-equilibrium, further adsorption takes place in the micropores. Film diffusion in the micropores is much slower and is more difficult due to the length and tortuosities of the micropore structures present in the activated carbon. Recent microtomography studies by Dai and Pleysier in Western Australia have confirmed the poor diffusion of gold cyanide within micropore structures. And as a result, the studies rule out the influence of pore diffusion and suggest surface diffusion is more dominant at higher gold loadings [92,97].

To clarify the position/location of gold cyanide complex (aurocyanide) adsorption sites on activated carbon surfaces, several studies have been undertaken. However, these studies have produced conflicting results and have consequently made it difficult to determine the exact adsorption mechanism. Surveying the literature reveals two possible mechanisms that can explain the adsorption of aurocyanide on the surfaces of micropores: (1) aurocyanide is adsorbed as an ion-pair of the form $M^{n+}Au(CN)_2^-$, and (2) aurocyanide is adsorbed via the decomposition of $Au(CN)_2^-$ to form AuCN [98–101]. Reviewing the literature reveals that the ion-pair model is the most widely accepted mechanism and studies have confirmed that aurocyanide adsorbs onto the walls of micropore as an ion-pair $M^{n+}Au(CN)_2^-$ [102–105]. In the ion-pair mechanism, M^{n+} is a cation that is most likely potassium, sodium, or calcium [98, 102–104]. Furthermore, functional groups produced during activation were also found to be responsible for the adsorption of aurocyanide [105–107]. The ion-pair mechanism is explained by Eq. (12), where $M^{n+}[Au(CN)_2^-]_n$ term is the adsorbed gold species attaching to the walls of the micropores.

$$M^{n+} + nAu(CN)_2^- = M^{n+}[Au(CN)_2^-]_n. \tag{12}$$

Spectroscopy studies have been used to investigate the nature of aurocyanide adsorption on activated carbon surfaces. Mössbauer spectroscopy studies have shown that aurocyanide anions adsorb to activated carbons surfaces through one of the cyanide ligands [108, 109]. While both X-ray photoelectron spectroscopic (XPS) and infrared (IR) studies have shown that aurocyanide ions tend to adsorb onto the small graphitic plates found in the activated carbon structure through an intact complex ion with a partial transfer of electrons to the gold (I) ion [110, 111]. Further adsorption studies have examined the influence of graphitic components found in activated carbons. The studies used ^{14}C labeled aurocyanide and revealed that adsorption predominantly occurred on the edge planes that occur in highly orientated pyrolytic graphite (HOPG) [112]. Similar aurocyanide adsorption studies using HOPG in the presence of Ca^{2+} via *in situ* scanning tunnelling microscopy was able to locate atomic scale clusters of gold. The gold was predominantly found along graphite basal and edge planes [113]. Similar *in situ* STM studies by Poinen *et al.* in aurocyanide solutions with calcium ions have shown atomically-sized filamentous gold structures present along and on the planes of HOPG (see Fig. 9) [114].

From an operational point of view for the gold industry, carbon activity is an important factor in determining aurocyanide adsorption within the process circuit. Importantly, carbon activity governs the amount of activated carbon necessary in each tank to carry out maximum adsorption. It also determines the required contact time needed, thus determining the size of the tank and the flow rate through the tank. And overall, carbon activity is used to determine gold within the process circuit and operational plant efficiency [115]. Mathematically, carbon activity and the subsequent gold loading within a gold processing circuit can be modeled using Eqs. (13)–(17). Equations (13) and (14) are used to determine the rate constant (k) and equilibrium constant (K).

$$\ln\left[\frac{[\mathrm{Au}]_{s,0}-\mathrm{B}}{[\mathrm{Au}]_s-\mathrm{B}}\right]=\mathrm{k}\left[\frac{KM_c}{M_s}+1\right]t, \tag{13}$$

$$\mathrm{B}=\frac{M_s[\mathrm{Au}]_{s,0}+M_c[\mathrm{Au}]_{c,0}}{KM_c+M_s}. \tag{14}$$

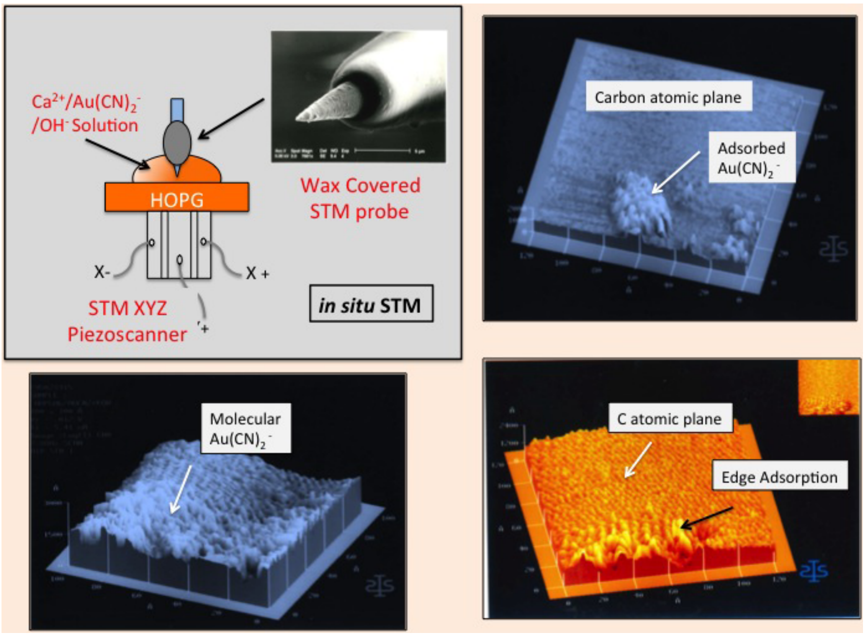

Fig. 9 *In situ* scanning tunnelling microscopy of HOPG under an alkaline aurocyanide (with added Ca $^{2+}$ ions) solution with micrographs depicting the carbon atomic plane and molecular adsorption of the aurocyanide complex (in plane and at the edge) [113, 114]

Given

$[\mathrm{Au}]_s$ or $[\mathrm{Au}]_s^t$ = concentration of gold in solution at time t,
$[\mathrm{Au}]_c$ = concentration of gold on the carbon at time t,
$[\mathrm{Au}]_{s,0}$ = concentration of gold at $t = 0$,
$[\mathrm{Au}]_{c,0}$ = concentration of gold in the carbon at $t = 0$,
$\Delta[\mathrm{Au}]_s^t$ = change in gold loading onto carbon from time zero to t,
M_c = mass of the carbon,
M_s = mass of the solution,
k, k' = rate constant,
K = equilibrium constant.

Both these constants are determined from a series of batch experiments where the gold concentration is continuously changing. Both constants are then used in Eq. (15) along with a constant gold concentration to determine the rate of gold holding in each stage of the processing circuit [90, 91, 116, 117].

$$\frac{\mathrm{d}[\mathrm{Au}]_c}{dt} = k(K[\mathrm{Au}]_s - [\mathrm{Au}]_c). \tag{15}$$

Furthermore, carbon activity can also be expressed by an empirical rate constant (k') that is determined experimentally by batch testing and is presented mathematically in Eqs. (16) and (17), where n = empirical constant. This alternative approach is frequently used for comparing different types of activated carbon, fouling of activated carbon, and the influence of dewatering reagents [118–120]. Moreover, comparative studies of various kinetic models have shown that Eq. (16) is suitable for modeling experimental data over an 8 h period [121].

$$\Delta[\mathrm{Au}]_c^t = k'[\mathrm{Au}]_s^t t^n, \tag{16}$$

$$\log \frac{\Delta[\mathrm{Au}]_c^t}{[\mathrm{Au}]_s^t} = n \log t + \log k'. \tag{17}$$

4.5.5.3 *Abrasion resistance and mechanical properties of activated carbons*

To be of practical benefit in the gold extraction processes, activated carbons need to have good mechanical properties that enable them to withstand the severe abrasion conditions encountered in typical aurocyanide adsorption circuits [46]. The breakdown of activated carbons in the gold extraction process not only represents the loss of carbon itself but also translates into a significant loss in gold. The major breakdown of activated carbons occurs as a result of wet attrition that occurs in the abrasive agitated pulp environment of the adsorption circuit. Other forms of attrition occur from dry abrasion, screening operations via transport within the circuit and during regeneration [87]. A technique that has been used to give indication of the performance of an activated carbon's resistance to particle size degradation under service conditions is the ball-pan method [122]. However, this method does not measure in-service resistance to degradation, but it does establish a measurable characteristic that can be used to grade and compare various activated carbons by the industry. The method involves placing a screened and weighed sample of activated carbon into a pan (of known hardness) with a number of stainless steel balls. The pan is then subjected to a combined rotating motion and tapping action for 30 min. At the end of this period, degradation is determined by weighing the quantity of carbon retained in the sieve. Based on this type of attrition testing, activated carbons are usually conditioned to remove imperfections and weak features in the granules before being introduced into the gold processing circuit. Prior conditioning minimizes the possibility of losing gold on undersize or structurally inferior carbon particles within the circuit. Importantly, conditioning can often indicate how effective the manufacturers have been careful in preparing the activated carbon [123]. Variations in the hardness of activated carbons can result from differences in the pore structure since softer carbon results from more of the carbon matrix around the pore structure being burned away during activation. Thus, making them less dense compared to activated carbons that have not experienced excessive burnout.

4.6 Renewable and Eco-Friendly Sources of Activated Carbons

4.6.1 *Agricultural Waste as Precursors for Activated Carbon Production*

Activated carbon can be generated from a wide range of natural and synthetic solid carbonaceous precursor materials. The two major sources of precursor materials include coal and agricultural crops and by-products [124–127]. Historically, many commercial activated carbons have been made from raw materials derived from coal, petroleum by-products, lignite, and peat [128–130]. Currently, the precursor sources for commercial activated carbons are derived from two main sources: (1) coal/lignite (42%) and (2) coconut/wood (45%) [131]. However, many of these activated carbons are expensive and non-renewable, which make them economically undesirable and ecologically unsustainable. Essentially, any material or compound with a high level of carbon and a low inorganic content can be used as a raw material for the production of activated carbons [126]. However, other factors such as the cost of the raw material as feedstock, composition of the raw material, the type and extent of activation needed and supply security must also be considered [132]. In particular, the most important factor that needs to be considered prior to converting a material into activated carbon is its physical and chemical properties [133]. For example, the raw material should have a high carbon content and have in-built porosity since these properties will significantly influence the character and nature of resulting activated carbon [134]. Furthermore, the influence of processing parameters such as carbonization temperatures, pretreatment additives, treatment periods, activation agents and temperatures all have an effect on the resulting activated carbons generated [135].

In recent years, the prospect of converting agricultural by-products into activated carbons has attracted considerable interest since it offers a renewable and relatively inexpensive source of raw materials [136,137]. The carbon content of many of these by-products is lower compared to more traditional precursor materials such as coal and peat, but their volume and lower costs have attracted the attention of both scientists and the agricultural sector [138]. To the agricultural sector, it offers an opportunity to produce an economically viable and renewable product from waste by-products and offset the costs currently incurred in processing, transporting, and disposing of waste by-products. Moreover, producing activated carbon from agricultural by-products can significantly reduce the environmental impact of waste pollution. For example, a wide range of agricultural waste by-products such as bamboo [139], husks [140], stalks [141], wood [142–144], nutshells, and stones [145, 146] are potentially eco-friendly and renewable precursors for activated carbon manufacture.

4.6.2 *Nutshells and fruit stones*

Millions of tonnes of waste nut shells and stones from a variety of fruits and nuts are produced by the global agricultural/food processing industry every year. Currently, the individual processors carry the cost of disposing very large quantities of waste nutshells and stones. Unfortunately, the volume of waste produced by annual crop production generally maintains this disposal cost. In particular, the cost will continue to increase with increasing crop production and the increasing costs associated with waste disposal. Any agricultural waste material, in particular, nutshells and stones from fruits are high in carbon which makes them an ideal precursor for the production of activated carbons. Using the agricultural waste from nuts and food-processed stone fruits as activated carbon precursors offers a renewable and eco-friendly resource that could effectively convert the waste into economically viable products [132]. For the last decade, studies have shown the potential of using nutshell and fruit stones as activated carbon precursors [147–149]. Recent studies have shown nutshells derived almond [150], hazelnut [151], macadamia [50, 61, 152], pistachio [153], pecan [154], and walnut shells [155, 156] from food processing industries are ideal precursors for activated carbons, while fruit stones from apricot [157–159], cherry [160], olives [161, 162], and peaches [163, 164] have all been used as precursors for the preparation of activated carbons. For example, Yalcin and Arol have investigated the adsorption of aurocyanide on activated carbons derived from hazel nutshells, peach, and apricot stones to ascertain their suitability as an alternative to activated carbon produced from coconut shells [48]. These adsorption studies found that activated carbon produced from both apricot and peach stones were comparable to those of currently used commercial products including coconut-based activated carbon. Similar studies have shown that relatively inexpensive waste products from the nut and fruit processing industries are capable of producing activated carbons high microporosity and high surface areas. However, more detailed studies are needed to examine the production, optimization, and application of activated carbon derived from precursor nutshell and fruit stone waste before this source of inexpensive agricultural waste can be commercially competitive with currently available activated carbon products in the market.

4.6.3 *Case study: Macadamia nut shells*

4.6.3.1 *Introduction*

Surveying the literature reveals that in recent years, there has been significant interest in using naturally available agricultural wastes for the production of activated carbons [136, 137]. Today, Australia uses approximately 18,000 hectares consisting of around 5.5 million trees for the cultivation of macadamia nuts along the coastal regions of northern New South Wales and Queensland. Macadamia nuts produced in these regions accounts for 40% of the global market and is valued at around AUS $150 million. Unfortunately, a consequence of producing large quantities of macadamia nuts is the serious problem of producing large quantities of waste nut shells and how to effectively dispose them [165]. In recent years, around 5 Mt of waste shells have been used as fuel to produce electricity for macadamia plant operations in the Gympie region of Queensland, thus only partially alleviating the waste problem [166]. However, falling coal prices are making nutshell-based fuel less competitive. Further complications arise because less than half of the waste can be used as fuel and increasing production levels are expected to increase annual waste material at rate of 10% [167].

Currently, the Australian gold industry imports peat and coconut shell derived activated carbons from overseas at a significant annual cost [168]. Therefore, an opportunity exists for converting waste macadamia nut shells into activated carbon and potentially reducing the operating costs of the Australian gold industry and also reduces their reliance on imported activated carbons. Importantly, macadamia nuts have a large cracking pressure (2.07 MPa or 300 psi) which indicates the inherent strength of the shell and should lead to a more abrasion resistant activated carbon suitable for CIP/CIL applications. Furthermore, adsorption studies using activated carbon derived from macadamia shells could be successfully used to remove organic contaminants from aqueous solutions and also could be used as precursor filters for molecular sieves [137,169,170]. Similar studies have shown that macadamia shell based activated carbons can adsorb a wide range of organic molecules and a range of metallic ions such as copper and gold [49,50].

4.6.3.2 *Conversion of waste macadamia nut shells to activated carbon granules*

The conversion procedure for producing activated carbon from a suitable raw material is two-step procedure. In the present case, a similar two-step procedure was followed and in the first step, waste macadamia shells were carbonized at 500°C for 45 min in a nitrogen atmosphere to prevent oxygenation of the carbon product. Carbonization also removed both water and volatiles retained by the shells. The following activation step was designed to promote the development of an extensive porous structure of molecular dimensions that dramatically increased the effective surface area of the carbon matrix. The activation agent used was carbon dioxide (CO_2)

and produced a significant increase in the BET surface area with increasing activation temperatures up to 900°C (1104.15 m^2/g) for treatment periods of 30 min. Similar studies carried out on coconut shells using the same two-step processing procedure produced a surface area of 1210.66 m^2/g at 900°C. Indicating that the macadamia shell derived activated carbon had a comparable surface area to activated carbons derived from coconut shells. Beyond this temperature, the surface area of macadamia derived activated carbon steadily declined and resulted from the degradation of the porous structure. The study revealed that the development of the porous structure and ultimately the surface area were dependent on the properties of the initial macadamia shell, activation temperature, and activation time [50]. Figure 10(a) presents an image of waste macadamia nutshells prior to the two-step conversion process and Fig. 10(b) presents the final activated carbon product after processing.

4.6.3.3 *SEM study of activated carbon granules*

SEM studies were undertaken to investigate the formation of porosity during activation. A representative image of an unprocessed shell is presented in Fig. 9(a) and reveals a non-porous and rough surface texture. Measurements indicate shell granules in the unprocessed state generally have surface areas ranging from 0.1 m^2/g up to around 0.15 m^2/g. The subsequent carbonization procedure resulted in both water and non-carbon materials such as waxes and oils being eliminated. Also occurring was the thermal decomposition of the shell to produce a solid carbon structure with a

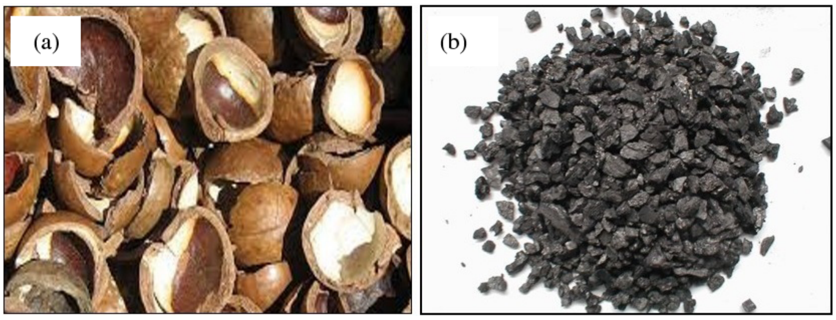

Fig. 10 (a) Waste macadamia nutshells prior to treatment and (b) resulting activated carbon produced at the end of the activation process

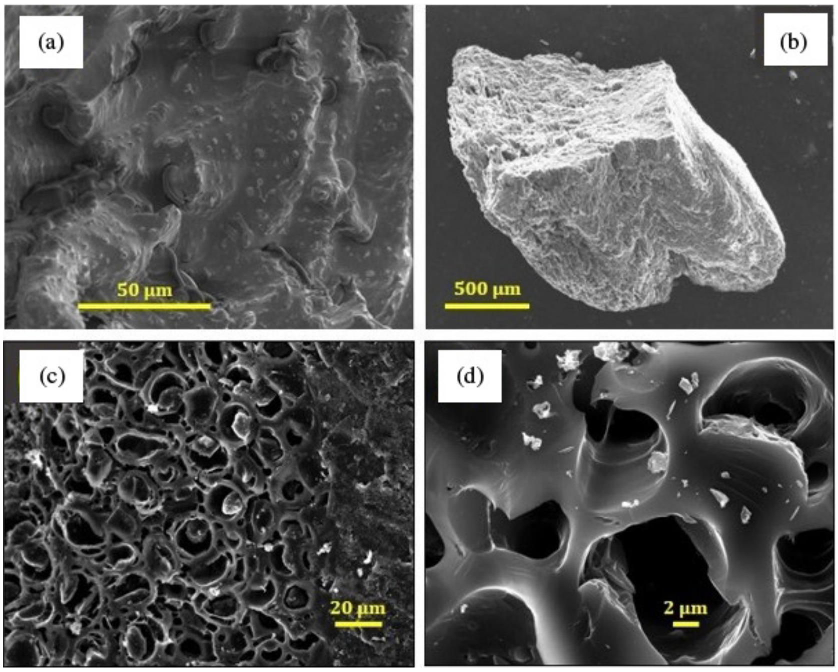

Fig. 11 Pore structuring and surface remodeling produced by the carbonization and activation steps; (a) surface of shell prior to processing; (b) representative activated carbon granule produced from a macadamia shell; (c) enlarged image of granule showing surface pore structure; (d) expanded image showing pores

rudimentary pore structure. During the following activation step, there was a significant improvement in pore development that produced highly porous activated carbon granules. Figure 11(b) presents a representative activated carbon granule produced from waste macadamia shells. The overall size of the granule is around 2 mm and surface features can be seen. The enlarged surface image presented in Fig. 11(c) reveals extensive pore development that is indicative of a highly porous material. Compared to the unprocessed shell granule presented in Fig. 11(a), we can see that carbonization and activation has created a highly porous structure with numerous surface pores providing access to inner regions of the granule as previous discussed and graphically presented in Fig. 6.

The growth in porosity corresponds to a dramatic increase in surface area and both are dependent on the activation temperature. This also

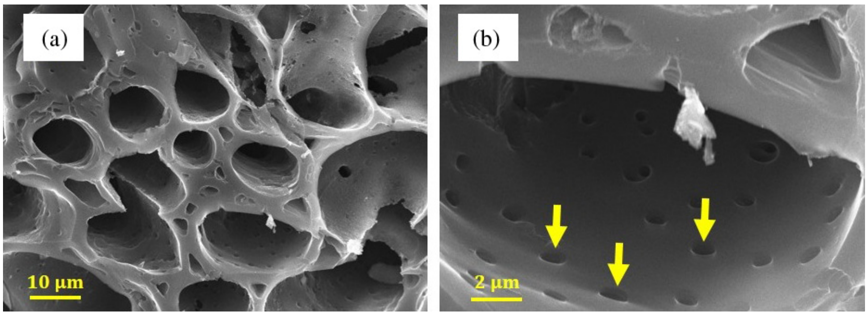

Fig. 12 (a) Cross-section view showing the extensive pore structure with macropores clearly evident and (b) enlarged view of a single pore showing an internal array of other minorpores.

translates to the adsorption capacity of the resulting activated carbon. Principally, adsorption occurs in the micropores, which generally accounts for about 95% of the total surface area of the activated carbon. Typically, the diameters of the micropores are less than 2 nm and the macadamia's activated carbon porous structure can be clearly seen in Fig. 12.

Figure 12(a) presents a cross-section view of the pore structure containing an array of pores. Figure 12(b) presents an enlarged image of a typical pore around 2 μm in diameter. Inspection of the image also reveals an array of finer pores scattered over its inner surface. Studies by Poinern *et al.* have shown the importance of enhanced micropore development and the resultant improvement in gold adsorbing ability of an activated carbon [50]. Their investigation also found that higher activation temperatures (∼900–1000°C) coupled with the resulting large surface areas had a significant impact on gold adsorption. For example, an activation temperature of 1000°C tended to produce an activated carbon capable of adsorbing 90% of the gold present in an aurocyanide solution within 8 h time period. Subsequent Energy Dispersive Spectroscopy and elemental mapping studies revealed the widespread presence of attached gold in the macadamia shell derived activated carbon. Their study also found that the macadamia shell derived activated carbon activated at 900°C and 1000°C was superior to commercially available coconut shell activated carbon [50]. However, their study also indicated that further research was needed to optimize the activation process to enhance the mechanical properties of the macadamia shell based activated carbon.

4.7 Concluding Remarks

Gold's allure has fired the imagination of humanity for thousands of years and continues to be a much sought-after metal. Today, the majority of the gold industry use a cyanide-based method for the extraction of gold from ores. Crucial to this globally used process is activated carbon with specific physical and chemical properties that have been engineered to enhance the adsorption of gold. However, today there is a need to find new sources of renewable and eco-friendly activated carbons. Relatively inexpensive, renewable and locally available agricultural waste materials have the potential to replace commercially imported activated carbons. Recent studies have shown promising results in producing activated carbons with large surface areas and high microporosities. The studies have shown that varying parameters such as activating agents, temperature and time can have a significant influence on properties such as pore size, porosity volume and surface area of the activated carbon. In particular, nutshells and stones from fruits produced by the food industry have a high carbon content and inherent strength that makes them an ideal precursor material for the production of activated carbons. Moreover, the constant and ever increasing supply of nutshells and stones offers an eco-friendly resource that can be converted into an economically viable product. However, before agricultural waste products such as nutshells and fruit stones can be totally converted into activated carbon products, there needs to be further detailed studies into optimizing material properties and developing cost-effective production techniques.

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