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GOLD RECOVERY USING CITRUS SINENSIS PEELS AS BIO-ADSORBENT

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ABSTRACT

The recovery of gold from electronic waste using locally available and environmentally friendly materials were investigated. Bio-adsorbent for gold recovery was prepared from Citrus sinensis peels through mechanical processing and chemical modification. Some ceramic computer processor units were leached using aqua-regia as lixiviant. Gold was recovered from the solution using the prepared bio-adsorbent and Sodium Meta Bisulphite (SMB). The recovery efficiency of the bio-adsorbent was determined and results compared to that of SMB. The adsorption of gold at different contact times was determined and the concentration of gold in solution was found using Agilent 4100 Micro Plasma Atomic Emission Spectroscopy (MP-AES). The results obtained showed that the bio-adsorbent has an adsorption capacity of 98.4% for gold and an adsorption kinetics correlation coefficient of 0.99989. This is comparable with SMB which has 95.4%. adsorption capacity and an adsorption kinetics correlation coefficient of 0.98597. The higher adsorption capacity of the bio-adsorbent is attributed to the binding sites and the chemical modification which increases the reducing properties of the functional groups present in the Citrussinensis peels.

Keywords: *Bio-adsorbent, lixiviant, biosorption, recovery, adsorption capacity, gold selective, aqua regia*

1.0 Introduction

Gold is a special metal used in smartphones, computers, and other electronic devices. Gold is significant due to both its color and sales price profit potential. It has the characteristic of high conductivity and general resistance to oxidation in varying environments resulting in its use in circuit boards of cellular phones and numerous electronic connectors. The indispensable and non-substitutable nature of gold makes it a strategic resource. [1]. A printed circuit board used in cellular phones and personal computers contains about 280g of gold per ton of waste[2,3]. Available records show that there are deposits of E-waste in Nigeria[4]. The increasing demand for gold and its high value makes the recycling of it from secondary sources(E-waste) a necessity.

There are several methods currently used for the recovery of precious metals from E-waste. The methods could be Pyrometallurgical, hydrometallurgical, bio-hydrometallurgical, electro-hydrometallurgical [5]. Among these methods, hydrometallurgical is most efficient through the solvent extraction process[6,7]. Different leaching agents have been investigated. This includes thiosulphate leaching, [8], cyanide leaching [9], HCl leaching, aqua -regia leaching [10].

The recovery of gold in the leached solution is carried out through different techniques: adsorption [11], solvent extraction [12], ion exchange [13], precipitation [13], electrolytic process and pressure oxidation [13,14], vacuum pump oil [15], biosorption [16]. The use of bio-adsorbent is a key technology for the selective recovery of gold from the chemically leached solution [10]. This paper is centered on the development of an economical, environmentally friendly, and highly gold selective bio-adsorbent from locally sourced materials. This is in pursuance of Executive Order 5 in Nigeria which encourages the use of local content in all spheres of endeavors. Hence the use of CitrusSinensis peels as bio-adsorbent for recovery of gold from E-waste.

2.0 Materials and Methods

The following materials were used for the process: Printed circuit boards collected from discarded computers, powdered orange peels, freshly prepared aqua regia solution, dilute sulfuric acid and sodium hydroxide solution, sodium meta bisulphate ($Na_2S_2O_5$), potassium hydroxide (KOH). The following equipment were used during the research work: Fume hood, test tubes and stirrer, pH meters and laboratory thermometers, Agilent 4100 Micro-Plasma Atomic Emission Spectroscopy (MP-AES).

The bio-adsorbent used in the extraction process was made from CitrusSinensis peels. The peels were room dried, milled to powder using a grinder. The resulting powder was chemically treated with concentrated Sulphuric acid and sodium hydroxide and then sieved. The collected E-waste was weighed and dissolved in freshly prepared aqua regia solution. The amount of gold dissolved in the solution was determined using Micro Plasma Atomic Emission Spectroscopy (MP-AES) analysis. The concentration of gold in the solution was determined after a contact time of 30, 60,120, and 240 minutes.

Gold was recovered from the solution using the prepared bio-adsorbent by adsorption process. The gold (III) present in the solution was adsorbed through complexation with functional groups and reduction. The inherent affinity of the functional groups for gold ions was increased through chemical modification. The binding sites for gold increased hence increasing gold selectivity and adsorption capacity. The recovery capacity was compared to that of sodium Meta Bisulphite (SMB) which is an established standard.

The gold rich bio adsorbent was mixed with flux in a cupola and strongly heated to a temperature between 600 - 800^0C. The orange peels bio adsorbent decomposed at a temperature of 200 - 300^0C. Gold melts at a temperature of 1064^0C and so remain unmolten.

The percentage recovery was calculated using the formula:

$$\text{Recovery} = [(C_0 - C) / *C_0] * 100 \; [15] \qquad (1)$$

Where C_0 is the initial concentration of gold in solution

Cis the concentration of gold in the solution after a given contact time with adsorbent.

The selectivity of the adsorbent for gold was tested by EDXRF analysis of the recovered metal powder

3.0 Results and Discussion

3.1 Results

The gold concentration in the samples was determined using the Agilent 4100 MP-AES at a wavelength of 267.595 nm and the results are illustrated in Figure 1 shown below. The MP-AES results showed that the initial concentration of gold before recovery was approximately 23.65 ppm. The concentration of gold in the solution decreases as the contact time with the adsorbents increases.

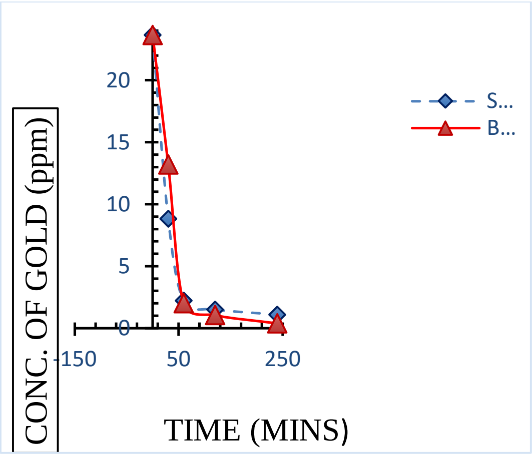

Figure 1: Graph of Gold Concentration with time in SMB and Bio-adsorbent.

The result showed that within the first 30 minutes, SMB recovered gold faster than the prepared bio-adsorbent. But after an hour of contact time, the bio-adsorbent exhibits a significant recovery higher than that of SMB.

The recovery efficiency was determined using equation (1) above and the result is illustrated in Figure 2.

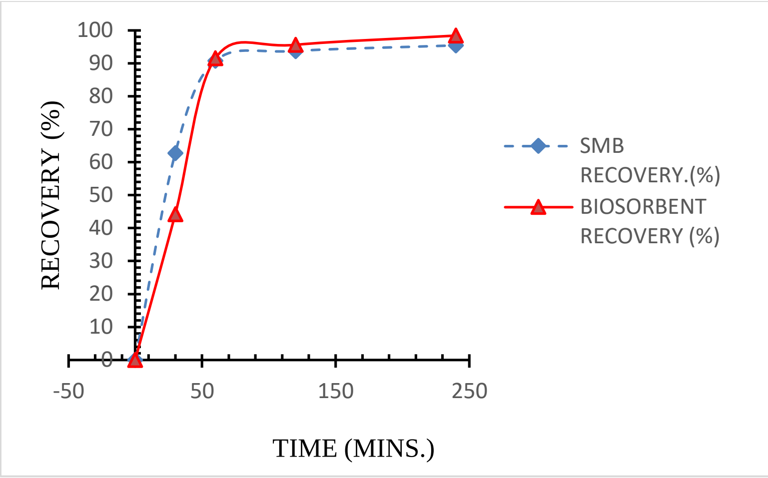

Figure 2: Graph Showing Gold Recovery of SMB and Bio-adsorbent with time.

The result showed that the recovery efficiency was initially higher for SMB within the first 1 hr. Thereafter, more gold was recovered from the bio-adsorbed. This could be attributed to the bio-adsorbed having a higher sensitivity for gold over time.

ED XRF Analysis of Metal Powder.

The recovered Metal powder was subjected to ED XRF analysis to determine the metals present. The result is shown in Figure 3.

The result showed that gold is the prominent metal in the powder.

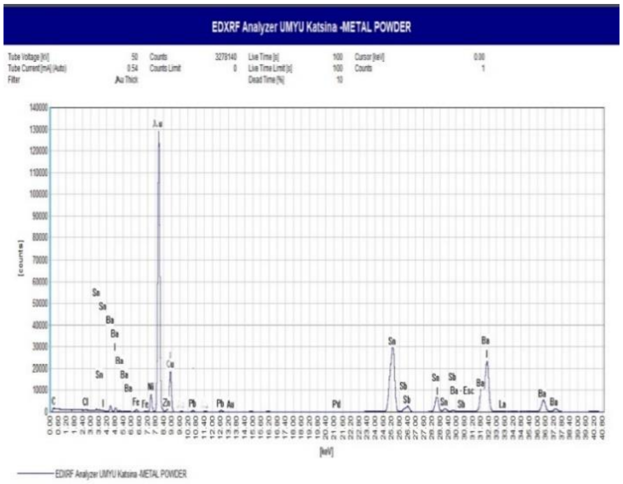

Figure.3. EDX - RF Result of Gold Powder.

The result in Figure 3 showed that the bio adsorbent could be highly gold selective since the prominent metal in the powder is gold.

3.2 Discussion of results.

Aqua regia is made up of two definite proportions and each of the components has a definite function which together helps in dissolving metals like gold. Aqua regia consists of nitric acid which acts as a strong oxidizing agent. This nitric acid converts the gold medal to their corresponding ions by oxidation. The formed metal ions (Au^{3+}) then form coordination complexes with the chloride ions released from the HCl. This results in the removal of gold from the E-waste and its dissolution as shown by equation 2

$Au_{(s)} + 3\ NO_3{}^{--}{}_{aq} + 6\ H^{+}\ aq \rightarrow Au^{3+}{}_{aq} + 3NO_2 + 3H_2O_{(l)}$ (2)

The coordination complex is then formed as shown below.

$Au^{3+}{}_{aq} + 4Cl^{-}{}_{aq} \rightleftarrows AuCl_4{}^{-}{}_{aq}$ (3)

This tetrachloroaurate present in aqua regia then quickly dissolves to form chloroauric acid ($HAuCl_4$).

The chloroauric acid was treated with sodium metabisulphite and the orange peel bio-adsorbent respectively.

The reduction of gold with sodium bisulphate is according to the equation (4) and (5)

$S_2O_5{}^{2-}{}_{(s)} + H_2O_{(aq)} \rightarrow 2HSO_3{}^{-}{}_{(aq)}$ (4).

$3\ HSO_3{}^{-}{}_{(aq)} + 2\ Au^{3+}{}_{(aq)} + 3H_2O_{(l)} \rightarrow 3HSO_4{}^{-}{}_{(aq)} + 6\ H^{+}{}_{(aq)} + 2\ Au^{0}{}_{(s)}$. (5)

The adsorption mechanism of the bio-adsorbent is attributed to the electrostatic attraction and reduction of gold (III) which is accompanied by the corresponding oxidation of the hydroxyl group to the carbonyl group. The results obtained with the bio-adsorbent are in line with the work of Maria et al in which gold is recovered from Simulated Hydrometallugical liquor by Adsorption on Pine Back Tanin Resin as reported in [17]. The result of the reduction is shown in the equation (6) below:

$AuCl_4{}^{-}{}_{(aq)} + 3\ R\text{-}OH_{\ (l)} \rightarrow Au^{0}{}_{(s)} + 3\ R{=}\ O_{(l)} + 3H^{+}{}_{(aq)} + 4Cl^{-}{}_{(aq)}$ (6)

The recovery capacity of the bio-adsorbent was compared with that of SMB which is an established gold absorbent. The result shows that the bio-adsorbent gave a significant adsorption capacity for gold. Chemical modification of such bio-adsorbents could increase their adsorption capacity due to adjustments in functional groups as reported by [18].

The chemical modification also increases the binding sites and hence increases adsorption capacity due to the adjustment in functional groups [19].The Gold (III) present in an aqueous solution is adsorbed on the surface of the bio-adsorbents and reduced into elemental gold as follows. The process involves the interaction of the positively charged gold (III) ion with oxygen atoms of hydroxyl groups and other oxygen atoms of polysaccharide molecules or tannin compounds contained in bio-adsorbents followed by adsorption forming stable five-membered chelate rings. This mechanism is reported widely by [20].

The adsorption kinetics was carried out and the results validated using Pseudo-second-order Integrated rate equation showed that the bio-adsorbent gave a better correlation with an R^2 value of 0.9999 while SMB gave an R^2 value of 0.9859. This further proves the higher adsorption capacity of the bio-adsorbent over the conventional adsorbent, SMB.

4.0 Conclusion.

Based on the result obtained, the following conclusions were drawn.

1. The study showed that there is a considerable number of precious metals in electronic waste and gold could be recovered from E-waste using bio-adsorbent prepared from Citrus Sinensis peels.
2. The higher adsorption efficiency value of 98.4% of the bio-adsorbent showed that it could replace SMB which has a value of 95.4% in the recovery of gold from the acidic medium.
3. The higher recovery capacity of the bio-sorbent could be attributed to the presence of binding sites and the high reducing properties of the chemically treated Citrus Sinensis peels.

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