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# Investigating the feasibility of using agricultural waste as an adsorbent of gold ions in small scale gold processing plants

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### Abstract

The recovery of precious metals like gold is increasing each day due to its high market prices along with diverse applications. Bio-sorption represents a biotechnological innovation as well as a cost effective and excellent tool for recovery of precious metals from aqueous solutions. This study offers an overview of a recent scenario of bio-sorption studies carried out on the use of some promising bio-sorbents which could serve as an economical means for recovering gold for small scale gold processing plants. Results show that activated carbon (control) has the highest adsorption efficiency since it contains more active site on the carbon molecules. The activated maize corn cob had the highest adsorption efficiency (77.09%) compared to all other agricultural adsorbents. Banana peels showed a significant adsorption efficiency of 56.87%.

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Keywords: Bio-sorption, Cupellation, Agricultural waste, Isotherm

## 1. Introduction

The demand for gold has been increasing since it is used as a monetary standard and its wide utilization in different applications. Gold is commonly used in electronics, jewelry, and anti-arthritis drugs [1]. The increased demand for gold has pushed for a growing interest in the recovery of gold from pregnant solution and waste solutions such as those from refining or mine effluents with high concentrations of gold. To that end, some have investigated the recovery of gold using bio-sorbents such as algae, fungi and yeasts [2]. Activated carbon has traditionally been used to adsorb gold from aqueous solutions but however, its manufacture and regeneration poses several constraints and represents a major portion of the operating cost in a mining operation [3]. A number researchers have used different waste material in the recovery of gold [4-7]. Recently, selective adsorption of gold by discarded agro waste materials such as rice husk carbon and barley straw carbon has been reported and shows great potential.

Agricultural waste has shown a significant ability for adsorbing heavy metals and precious minerals and it can be a good adsorbent if activated. The gold may be adsorbed from pregnant solution using cheap agricultural waste and the loaded adsorbent is then collected and smelted with flux to recover the solid precious metal. Low cost bio-sorbents derived from agricultural waste also have the advantage of good adsorption characteristics. The wastes constitute a significant proportion of worldwide agricultural productivity. It has been estimated by various sources that this wastes can account for over 30% of worldwide agricultural productivity. When discharged to the environment, agricultural waste can be both beneficial and detrimental to living matter. The waste could be used as resource materials in many engineering applications such as in energy generation, chemical extraction and adsorption purposes [8].

Bio-sorption is a metabolism independent process that occurs in the cell wall [9], and the mechanism responsible for the metal uptake may differ according to the biomass type. Cost effectiveness is the main attraction of metal bio-sorption. Since bio-sorption often employs dead biomass, this eliminates the need of nutrient requirement and can be exposed to environments of high toxicity [10]. A major advantage of bio-sorption is that it can be used in situ, and with proper design may not need any industrial process operations with the ability of integration with many systems in the eco-friendliest manner. The objective of this paper is to investigate the recovery of gold using different bio-sorbents. This will in turn reduce use of toxic mercury and gold in gold recovery by small scale miners.

#### 3. Materials and Methods

#### 2.1 Agricultural waste activation

All the adsorbents (banana peels, orange peels, activated carbon, rice husks, maize corn cobs, groundnut shells) were washed with water and then dried in oven at 60°C for 12 hours. They were then crushed and sieved to obtain a particle size fraction of 2.0 to 3 mm and stored in an air tight container awaiting further use.

Specified masses of the dried adsorbent particles were soaked in 100 ml phosphoric acid solution to get the required impregnation ratios of carbon. The mixture was continuously stirred at ambient temperature for 2 hours and left to soak for 12 hours to allow penetration of the acid into the adsorbent. After the stipulated soaking time, the adsorbents were oven dried at 110 °C for 24 hours, so as to achieve adsorption of the acid on to the carbon. The samples were cooled in a nitrogen atmosphere for 12 hours. The product was washed with cold deionized water until phosphate ions were no longer detected on application of the lead nitrate test [11]. The product was finally air dried at 105 °C for 3 hours. Figure 1 shows the final result after the activation of banana peels.



Figure 1: Snapshot of a sample of banana peels after activation

#### 2.2 Adsorption process

A solution containing gold of known concentration was poured into 2 distinctively marked 200 ml beakers. Two separate samples of the same adsorbent each weighing 3 grams were weighed and placed in the 2 beakers. The beakers were placed on the magnetic stirrers and allowed to rotate. Samples from each beaker were collected in 20 minute intervals and poured into empty separate containers. The beakers were again placed on the magnetic stirrers and allowed to stir, and this was repeated for 120 minutes. The collected samples were taken to the assay laboratory for analysis using an Atomic Absorption Spectrometer (AAS).

# 2.2 Calcination method to recover the gold from the adsorbents

A well homogenised sample of the loaded adsorbent was weighed on an analytical balance (1 gram samples). The samples were individually thoroughly mixed with the suitable weighed flux; the charge was then put into a crucible. Inquartation silver was added to each sample to provide the high silver to gold ratio necessary in the parting process and to aid in the handling of the bead. The sample-flux mixtures in the crucibles were fed into a fusion furnace operated at a temperature of 1070°C for 30-45 minutes. The crucible was then removed from the fusion furnace and the molten charge poured into cast iron moulds. On solidification, the lead button was separated from the slag by means of a hammer on an anvil.

The lead button was hammered to remove slag adhering to it and flattened. The hammered lead button was then placed in a preheated cupel and placed in a muffle furnace kept at about 980 °C. Cupellation was continued until all the lead had been oxidised and removed (at this point the gold-silver prill looks dull). The cupels were removed from the muffle and allowed to cool. The gold and silver bead was flattened using a hummer, allowing for rapid parting. The bead was placed in a parting cup and filled to 2/3 full of HNO<sub>3</sub>. The parting cups were heated on a hot plate until the evolution of gas bubbles ceased and gold appeared as a black spongy mass. Silver nitrate from the gold bead was then removed completely from the parting cup by washing. Incomplete washing was indicated by stains on the parting cup after annealing. The silver nitrate was kept for reuse. The gold prill was washed two times with ammonia to completely remove chlorides/ silver nitrate and then placed on a warm hot plate to remove all the moisture. The gold prill was annealed, allowing the gold to regain its normal metallic lustre. After the annealing process the prills were taken for final weighing using a Sartorius micro balance to weigh the gold prills.

#### 4. Results and Discussion

#### 3.1 Agricultural waste adsorption results

Table 1 shows the adsorption efficiencies of the various adsorbents after 120 minutes of exposure to a gold loaded aqueous solution.

Adsorbent	Adsorption Efficiency	
	%	
Orange peel	6.22	
Maize corn cob	77.09	
Rice husks	46.24	
Ground nut shells	53.88	
Banana peel	56.87	
Activated Carbon	95.91	

Table 1: Optimal adsorption efficiencies after 120 minutes

Results show that activated carbon (control) has the highest adsorption efficiency since it contains more active site on the carbon molecules. The activated carbon which is derived from coconut shell adsorbed more gold ions compared to all the agricultural waste since the activation of the carbon is more accurate compared to the acid activation that was used for the activation of the agricultural wastes [12]. The activated maize corn cob had the highest adsorption efficiency (77.09%) compared to all other agricultural adsorbents. Banana peels showed a significant adsorption efficiency of 56.87%. For the next activity activated carbon, maize corncob and banana peels were used since there showed a high adsorption efficiency.

3.2 Incineration of the adsorbent in Aqua regia and flux to recover gold solid

Table 2 shows the amount of gold (per tonne of adsorbent) recovered after smelting the adsorbents in aqua regia (g/t).

Type of adsorbent	Amount of gold recovered from smelting one gram / (g)				
	Sample 1	Sample 2	Sample 3	Sample 4	
Activated carbon (control)	3.70*10-4	3.56*10-4	4.02*10-4	3.76*10-4	
Banana peels	0.50*10-4	0.88*10-4	0.36*10-4	0.58*10-4	
Maize corn cobs	2.00*10-4	2.01*10-4	2.20*10-4	2.07*10-4	

Table 2: Amount of gold recovered per tonne of each adsorbent

Results show that for every tonne of carbon used for adsorption in a time interval of 2hrs, 376 grams would be recovered by the destructive stripping process of incinerating the pregnant carbon with flux. And for a tonne of banana peels 58grams of gold would be recovered, and from maize corncob 207grams of gold would be recovered. This shows that the maize corn cob is the best adsorbent that can be used for the gold adsorption.

There are several models for predicting the equilibrium distribution. However, the following the Langmuir and Freundlich models are most commonly observed. The Langmuir Isotherm is an equilibrium model assuming that all adsorption sites are equally probable, monolayer coverage and a second order reaction.

$$S_v + A = S.A$$

 $q_A = [S.A].A_{ad}.MW_A$ 

where  $S_v$  – Vacant adsorption site on adsorbent in mol/L adsorbent, A – adsorbate in solution in mol/L solution, S.A – adsorbate bound to adsorbent site in mol/m<sup>2</sup>,  $A_{ad}$  – surface area per gram adsorbent in m<sup>2</sup>/g

After derivation the following expression is obtained:

 $Qe = \frac{bCeQo}{1+bCe}$ 

The Freundlich Isotherm is empirical and very widely used. It can be represented by;

 $Qe = K_f Ce^{1/n}$ 

where  $K_f$  is an indicator of adsorption capacity. The higher the maximum capacity, the higher the  $K_f$ . 1/n is a measure of intensity of adsorption. The higher the 1/n value, more favorable is the adsorption. Generally n < 1, 1/n > 1. n and  $K_f$  are system specific constants. To determine which model to use to describe the adsorption for a particular adsorbent/ adsorbate isotherms experiments are usually done. Data from these isotherm experiments are then analysed using the following methods that are based on linearization of the models. For the Langmuir model linearization gives:

 $\frac{Ce}{Qe} = \frac{1}{KQo} + \frac{Ce}{Qo}$ 

A plot of Ce /Qe versus Ce should give a straight line with intercept: 1/Qo and slope :  $\frac{1}{KOO}$  where Qe =  $(\frac{CO-C}{m})V$  and

 $C_e = C_o - C_x$ 

For the Freundlich isotherm the log-log version used,

 $\log Q_e = \log K_f + 1/n \log C_e$ 

A log-log plot should yield an intercept of log  $K_f$  and a slope of 1/n.

Table 3 gives the values used for determining the effectiveness of the Langmuir model in predicting the equilibrium distribution, and Figure 2 gives a corresponding plot of Ce/Qe versus Ce. Table 3also depicts the values used for determining the effectiveness of the Freundlich model in predicting the equilibrium distribution, and Figure 3 gives a corresponding plot of log Qe versus log Ce.

Langmuir isotherm values		Freundlich isotherm values		
Ce/Qe	Ce	Log Qe	Log Ce	
0.05	1.69	1.529	0.2279	
0.10	1.86	1.2695	0.2695	
0.15	2.08	1.1430	0.3180	
0.70	2.22	1.0453	0.3464	

Table 3: Langmuir and Freundlich isotherm values



Figure 2 (a) plot of Ce/Qe versus Ce for the Langmuir model (b) plot of log Qe versus log Ce for the Freundlich model

From the effect of varying mass of the adsorbent the adsorption favours the Freundlich Isotherm more than the Langmuir. Also running the adsorption at different pH values will determine whether the adsorption will support the Freundlich isotherm or not. If the produced graphs of "amount of gold adsorbed vs amount of gold in solution" are parallel it proves that the adsorption of gold ions into maize corncob supports the Freundlich isotherm. The values of the amounts of gold adsorbed and the amount of gold in solution at different pH values and at different time intervals were also obtained. Figure 3 provides a plot of the corresponding amounts of gold adsorbed versus the amount of gold in solution at different pH values.



Figure 3: Amounts of gold adsorbed versus the amount of gold in solution at different pH values

The pH variation supports that the adsorption of gold ions into maize corn cob favors the Fredliunch isotherm.

#### Conclusions

This study confirmed that agricultural waste can be used to adsorb the gold ions. Acid activated corn cob is a very good adsorbent of gold ions (especially the  $Au(CN)_2$  ion) compared to the other adsorbents used in the study. More studies are needed in activating the agricultural waste so as to increase the loading capacity of the waste. More studies should be carried out to optimise the smelting process and increase recovery from 50% to 90%, because most of the gold is lost during this method of smelting the loaded adsorbent. An agglomeration technique like sintering should be applied so as to increase the tensile strength of the activated maize corn cob to avoid the disintegration of the adsorbent during the adsorption process.

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