Extraction of Silver from Photographic Waste Using Cocoa Husk Ash Solution

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Abstract: ***Silver recovery from photographic wastes (X-ray films) using cocoa husk ash solution (CHAS) as extractant has been determined in this study. Cocoa husk ash (20, 40, 60, 80 and 100g) was dissolved separately in 500ml of distilled water for 48 hours with stirring at intervals, followed by filtration. The alkaline solutions obtained were standardized by titrimetric method and used to leach the X-ray films. 100ml of 1.5M solution of sodium sulphide was added as precipitant to each beaker containing the extracts. Silver was identified using simple laboratory tests. Precipitates weighed 1.90, 2.70, 3.60, 4.10 and 6.20g with respect to quantity of ash dissolved. Analysed by Atomic Absorption Spectrophotometer model GBC 6600, silver in extracts were 56.586, 51.932, 64.185, 62.136 and 63.583mg/kg. Evidence is hereby given of another waste material that can be utilized in the extraction of silver from photographic wastes.***

Keywords: Cocoa husk ash solution; photographic wastes; precipitants; silver, AAS, titrimetric

1. Introduction

Toxic heavy metals such as silver, copper, mercury, cadmium, etc., are introduced into the environment due to increase in industrialization and urbanization. The soluble form of these heavy metals poses threat to both plants and animals because it is easily transported. In humans, these heavy metals when absorbed can result to severe dysfunction of kidney, liver, brain, reproductive system and central nervous systems [1]. The soluble salts of silver constitute various health hazards in humans, although, in its pure form, low impact is observed [2 [3]. Furthermore, due to increase in the demand for silver (which has affected its price in the international market) and depleting natural sources, the cost of silver has risen tremendously in recent years [4.] Therefore the recovery of silver from their wastes has both environmental and economic benefits.

Silver find wide applications in our world. It is used in making jewelries, ornaments, currency coins, as well as mirrors, batteries and as catalyst in chemical reactions. Silver compounds are main constituents of photographic films. Fortunately, much of silver used by the photographic industries and hospitals for X-ray, photographic films and other solutions can be recovered [5]. Scraps such as photographic films, X-ray films and jewelry are major sources of silver recovery [6]. The average amount of silver in the X-ray film is reported as 1.5-2.0% (w/w) black metallic silver [7], [8]). Recycling provides 25% of the world's silver needs while 75% is obtained from photographic wastes [7], [3]).

X-ray or photographic films are coated with thin layers of gelatin, impregnated with silver halides (AgCl and AgBr). When exposed to light, silver reacts to produce images. The unexposed silver ions are left behind on the film which appears as dark spots.

Various agricultural waste materials have been used for silver recovery from photographic wastes. Some reported include cassava solution [6], [9] plantain peels ash solution [10]; oxalic acid as leaching agent [11] red mangrove bark solution [3]. Cocoa (*Theobroma cacao*) tree is a small (4-8m) tall evergreen tree in the family *Malvaceae,* widely grown in the tropics. Its seeds, cocoa beans are eaten all over Africa and in Central and South America, with the husks being discarded as wastes. Cocoa husk is the encasement for the cocoa fruit; it has a rough, leathery peel about 2-3cm thick. Cocoa husks have been used for a variety of domestic and industrial purposes. Cocoa pod husk has been reported a renewable source of energy in Indonesia [12]. According to Australian plantation- to -bar manufacturer, Daintree Estates [13] waste cocoa shells (husks) are rich in fibre and anti oxidants and carry great potentials as food ingredients. Cocoa pod husk meal has been utilized as feed to pigs, poultry, fish and ruminants also as organic fertilizer and even soap making in Nigeria. Though Nigeria is one of the five most important cocoa producing countries still, 1.5 million MT of cocoa pod husks are wasted annually in the country [14]. There is therefore a need to explore more avenues where these wastes can be relevant. This is the basis of using cocoa husk ash to extract silver from photographic wastes which has not been reported, in this work. The ash solution of discarded cocoa husks was used to strip or leach photographic wastes (X-ray films) of silver using different concentrations of CHAS. Silver will be precipitated from leachates with sodium sulphite (NaS). The quantity of silver in the photographic waste will be related to the concentrations of CHAS. The outcome of this work will not only highlight the economic value for both wastes (X-ray films and cocoa husks), but also contribute to the proper disposal of both wastes. Specifically cocoa husk ash will add to the list of extractants for silver in photographic wastes.

2. Materials and Methods

Materials

The X-ray films were collected from the radiological unit of the General Hospital, Bori in Rivers State, Nigeria while the cocoa husk was obtained in large quantity from Luubara town in Ogoni, Rivers State, Nigeria. All chemicals and reagents used were of analytical grade. Model GBC 6600 Atomic Absorption Spectrophotometer was used.

Sample Preparation
Preparation of cocoa husk ash solution

The cocoa husk obtained were cut into pieces, sun dried for 72 hours (3 days) at ambient temperature and further oven dried. They were ashed at temperature of 180°C for 4 hours using a muffle furnace. Ash of weight 20, 40, 60, 80 and 100 grams were weighed into five separate beakers. They were soaked in 500ml of distilled water and allowed to stand for 48 hours (2 days) with stirring at intervals. The resultant mixtures were filtered using Whatman filter paper to obtain Cocoa Husk Ash Solution (CHAS).

Standardization of cocoa husk ash solution (CHAS)

The pH values of each CHAS were determined using a pH meter and they were standardized by titrimetric method using 1M HCl is the titrant.

Preparation of X-ray Films

The X-ray films collected were washed with distilled water and wiped with cotton wool impregnated with ethanol and oven dried at 100°C for 15 minutes after which the films were cut into 4×4cm sizes.

Extraction of Silver from X-ray Films

X-ray films (equal quantity) were weighed and distributed into five (5) separate 500ml beakers. Thereafter 300ml of each extract was measured and added to the beakers labeled 20, 40, 60, 80 and 100g of CHAS. The beakers were heated at 100°C for 55 minutes using a water bath with occasional stirring after which the extracts solutions were allowed to cool for 15 minutes. Then 100ml of 1.5M solution of sodium sulphide was added as precipitant to each beaker containing the extracts. The solutions were swirled and allowed to settle for 15 minutes precipitate formed were allowed to dry overnight at ambient temperature.

Test for Ag^+

The extracts were tested for silver using streak test with HNO_3 and KCl.

AAS Analysis

Sample Digestion

The extracts obtained were digested using nitric acid and perchloric acid mixed in the ratio 4:1. Then 20ml of the acid was measured and added to each extract then heated at 80°C for 20 minutes and filtered into a 50ml volumetric flask. This was used as the stock solution for the AAS analysis.

The silver lamp (hallode cathode lamp) sensitive to only silver was used. Each sample was placed in a test tube and the capillary tube of the AAS machine was put into one. The flame was put on, the sample aspirated into the flame and atomized. Hence, excited atoms which are silver in the sample absorbed the emitted light from the lamp and on return to grand state emitted light which was transduced and quantified as a concentration of silver present. The procedure was repeated for all the samples.

3. Results and Discussion

Results

Table 1: Titre values, $_pH$, and concentration of CHAS

Weight of CHA dissolved(g) in 500ml	Conc. Of Acid used (M)	Titres (cm^3)			Vol. of Acid used (cm^3)	Conc. Of CHAS (g/cm^3)	$_pH$ of CHAS
		1^{ST}	2^{ND}	3^{RD}			
20.00	1.00	12.10	11.90	12.00	12.00	0.48	10.50
40.00	1.00	18.40	18.30	18.10	18.20	0.72	10.80
60.00	1.00	23.20	23.40	23.50	23.37	0.94	11.10
80.00	1.00	27.60	27.80	27.80	27.73	1.11	11.10
100.00	1.00	35.20	35.40	35.20	35.27	1.41	11.30

Table 2: Weights of extracts obtained from films and concentration of silver in extracts

Conc. Of CHAS (mol/ cm^3)	Vol. of CHAS (cm^3)	Amount of Extract ($x10^3mg$)	Conc.of silver (mg/Kg)
0.48	300.00	1.90	56.586
0.72	300.00	2.70	51.932
0.94	300.00	3.60	64.185
1.11	300.00	4.10	62.136
1.41	300.00	6.20	63.583

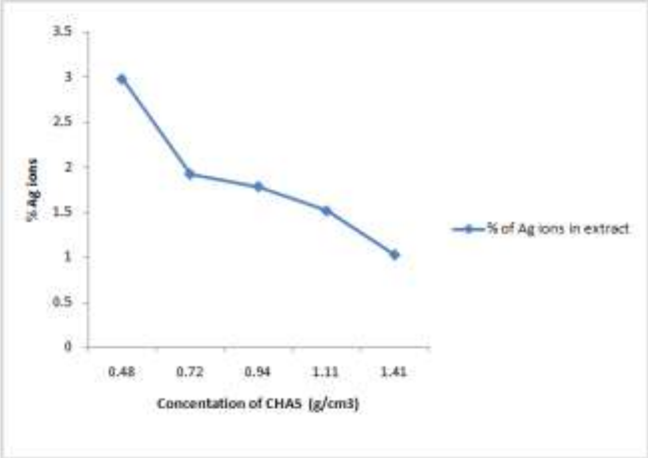

Figure 1: Percentage of Ag ions in extract

4. Discussion

Concentrations and pH of CHAS

The pH values obtained for the different grams of cocoa husk ash dissolved are shown in Table 1. The pH ranged from 10.50 – 11.30 an obvious indication of alkalinity. They are in agreement with previous studies on plant ash solutions [3] and Orubite and Jack [10].

Plant ash contains potassium and sodium and calcium which dissolve in water to give alkaline solutions [15].

Table 2 is result obtained from standardizing the ash solutions.

Concentrations of CHAS obtained were 0.48, 0.72, 0.94, 1.11 and 1.4g/cm^3 for dissolved ash, 20, 40, 60, 80, and 100g respectively. This clearly shows that increase in quantity of ash got more concentrated solution as expected. More ash in solution means more constituent ions hence the higher concentration.

Test for Ag^+

The appearance of a milky precipitate was observed as a proof for the presence of silver in the products obtained.

X-ray Films Extracts

The weight of precipitates obtained from precipitation with NaS is shown in table 2. The grams of extracts increased progressively as quantity of ash increased. i.e. 1.90, 2.70, 3.60, 4.10 and 6.20g of extracts were obtained for 20,40,60,80, and 100 grams of ash respectively. As more ash was added, concentration of CHAS increased and there were more Ag^+ ions to react with the precipitant. Hence quantity of ash dissolved, showed dependence on the amount of extract obtained.

AAS analysis

The concentration of silver ions in the extracts as measured by the AAS instrument is presented in table 2. The values confirm that CHAS actually stripped the film of silver. Of course the AAS instrument measured the exact amount of silver in the extracts because silver lamp, sensitive to only silver was used. The concentration of silver present also raises environmental concern as they were far above the specified amount of 1-5 µg/litre [16]. In aquatic plants, 130µg Ag/litre is capable of causing a retardation of growth [17].

Amount of silver in the extracts increased as concentration of CHAS increased. The percentage of silver in the extracts was calculated as shown in fig. 1. It can be deduced form the plot that percentage of silver obtained from the different extracts decreased as the concentration of CHAS increased. Therefore the observation that more extracts were obtained in higher concentration of CHAS does not portray that more silver ions were extracted. The ratio of Ag ions to grams of extracts obviously decreased as CHAS concentration increased. Fig. 1 also reveals that impurities form higher percentage of the extracts and that percent impurity increased as concentration of CHAS increased. This trend was reported in previous works [13] and [10]. The chelating properties of Ag and subsequent formation of the Ag $(OH)_2{}^{2+}$complex ion once more is credited for the reduction of free Ag^+ ions for detection by the AAS instrument.

5. Conclusion

Cocoa husk ash has been used as extractant for the recovery of silver from X-ray films. An increase in the amount of CHA causes a corresponding increase in both concentration of CHAS and pH. Higher concentrations of CHAS are efficient in the stripping process than lower concentrations. However the percent purity of the extracts decreased as CHAS concentration increased. Therefore, the use of higher concentration of CHAS is recommended for stripping X-ray films of silver before they are discarded. While relatively pure silver can be obtained using lower concentrations of CHAS.

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