Extraction of Silver from Waste X-Ray Films using Coconut (*Cocos nucifera L.*) Shell Aqueous Extract

[1]Gbarakoro, S. L. & [2]Akinfolarin, O. M.
[1]Department of Science Laboratory Technology,
School of Applied Science,
Ken Saro – Wiwa Polytechnic,
Bori, Rivers State, Nigeria
[2]Department of Chemistry,
Faculty of Science, Rivers State University,
Nkpolu-Oroworukwu, Port Harcourt,
Rivers State, Nigeria
slgbarakoro45@gmail.com

Abstract
The aqueous extract of coconut (Cocos nucifera L.) shell has been used to extract silver from waste x-ray films and to determine the potassium ion concentration in it by titrimetric method. Coconut shell ash (20, 40, 60, 80, 100g) were dissolved in 500cm^3 of distilled water for 48 hours, stirred at intervals and titrated. The pH values of the alkaline solutions obtained were 10.9, 10.9, 10.9, 11.3, and 11.3 with respect to the 20, 40, 60, 80, and 100g dissolved. The alkaline solutions were standardized and the results obtained from the titration reaction reveals that there was generally low levels of potassium ion concentration. Also, there was an increase concentration in 20-60g and decrease of concentration in 80-100g ash solution. The coconut shell aqueous extract (CSAE) was used to extract the waste x-ray films at 100^{O}C for 55 minutes. 100ml of 1.5M solution of sodium sulphide was added to precipitate the extract in each beaker. The concentration of silver in the X-ray film was determined using different concentration as solution for extracting the films and as extractant. The extracts obtained were analysed using Atomic Absorption Spectrophotometer (AAS) model GBC Avanta version 2.02 and the concentrations of silver in extracts were 1.433, 2.104, 2.362, 2.390 and 3.065ppm. This work is a proof that another agricultural waste material can be used to extract silver from waste x-ray films.

Keywords: *Coconut shell aqueous extract; silver; extraction; x-ray films; titrimetric; potassium ion; AAS*

1. Introduction

The rapid increase in industrialization and urbanization worldwide had lead to serious pollution of our environment today. Humans produced waste waters that are frequently laden with poisonous heavy metals such as silver, copper, mercury, lead, iron, etc. (Ashish *et al*., 2012), that find their ways into the environment. Silver is a soft, white, lustrous transition metal found in nature. Silver is also a by-product of metallurgical and industrial processes and it is often found deposited as a mineral ore associated with other elements such as lead, copper and antimony (Radha and Arun, 2010; Subramanian *et al*., 2012).

Silver is a metal of commercial importance which is applicable in jewelry and corrosion resistant alloys. Due to its excellent properties of electrical and thermal conductivity and ductility, silver has find wide applications in the fields of aerospace and communications. It is also used in the chemical industry (as catalyst, conductor and chemical sensor), in electroplating, medical equipment, electronic equipment and photographic materials. The sensitivity of silver to light has resulted in its wide application in most photographic and x-ray materials (Mendoza and Kanata, 1996). Silver is unique in its property as it reacts to light and produce images in applications such as photography and radiography (x-rays). No other metallic element possesses these properties. During development, only 25% of the silver formed the developed image (Jacobson and Jacobson, 1976). The remaining unexposed and unreduced silver halide is removed during the fixing process (Grant, 1979; Orubite-Okorosaye and Jack, 2012). Therefore, during development and printing, silver is released from photographic films, papers and plates and can be successfully recovered from scrap films, scrap printing papers and waste streams for reuse. Silver is released from image processing operations as silver thiosulphate, which degrades in the presence of oxygen to primary silver sulphide, and to a much lesser extent, silver halide complexes. Due to the high photosensitivity of silver halide, about 8.3% of silver is used in photography (Samson and Edison, 2014). Abdel-Aal and Farghaly (2007) reported that 1 kg of develop x-ray films contains 14-17g of silver.

The x-ray film is a gelatin-covered polyester base. It is the medium that displays the radiographic image. It consists of single or double emulsion of silver halide particularly, silver bromide (AgBr) which when exposed to light, produces a silver ion (Ag^+) and an electron. The silver can be reclaimed from scrap x-ray film in a process called silver recovery. The waste x-ray films contain 1.5 to 2% (w/w) black metallic silver which is recovered and reused (Shankar *et al*., 2010).

Amidst the numerous agricultural waste materials, coconut (*Cocos nucifera L.*) can be used to recover silver from waste x-ray films. Coconut which is cultivated in almost the entire tropical belt of the world is native to coastal areas of Southern Asia. Philippians, Indonesia, Malaysia, Sri Lanka and India are the front ranking coconut growing countries and together they account for the coconut growing area of the world, representing an area of over seven million hectares (Manisha and Shyamapada, 2011). Coconut, a tall palm tree of 12-30m, belonging to the family *Arecaceae*, produces both matured and tender nuts at intervals. Every part of the coconut plant is useful; the leaf and trunk provide building material, and the root is used as medicine. The fruit is eaten all over the tropical and subtropical regions. The envelop (mesocarp) called the husk, is processed into rope, carpets and geotextiles. The hard brown shell (endocarp) can be processed into very high-quality activated charcoal. The inner part of the net (endosperm) is divided into two edible parts: a white kernel and a clear liquid (coconut water). Coconut shell is the strongest part and is located in between the coconut shell and husk. The shell is usually discarded as wastes after eaten the edible parts. Coconut shell is an agricultural waste and is available in large quantities through the tropical countries of the world. It can be used as a source of raw materials for the industry. Madakson *et al*., (2012) used spectroscopic and microscopic techniques to characterized coconut shell ash for potential utilization in media matrix composites for automotive applications. X-ray fluorescence (XRF), Fourier Transform Infrared Spectroscopy (FTIR) as well as density, particle size and refractoriness were used for the characterization of the coconut shell ash. The result confirms that SiO_2, Al_2O_3, MgO and Fe_2O_3 were found to be major constituents of the ash. Coconut is a potassium loving plant. In coconut, potassium acts as an activator of many enzymes, improves development of the kernel, help in the translocation of starch from the root to the nuts, regulate the plants metabolism and control the transport of metabolites for cell division (Manciot *et al.*, 1981).Thus, the yield of coconut is enhanced by the above mentioned functions (Manciot *et al.*, 1981).

Some researchers have recovered silver from x-ray and photographic films using agricultural wastes. Some of these researchers include Orubite-Okorosaye and Jack (2012), who estimated silver content in some photographic wastes, using different concentrations of plantain ash solution (PAS) for stripping the films and as extractant. Ajiwe and Anyadiegwu (2012) recovered silver from industrial wastes, cassava solution effects. Jayant *et al*., (2015) extracted silver from waste x-ray films using protease enzyme. Red mangrove bark ash has equally been used as extractant to recover silver from photographic waste (Okorosaye-Orubite and Don- Lawson, 2016). Okorosaye-Orubite and Gbarakoro (2018) also extracted silver from photographic waste using cocoa husk ash solution (CHAS). Recently, potassium ion concentration has been isolated and determined in plants (George *et al*., 2014). Plants are richer in potassium than sodium or calcium since they take up more potassium (Okorosaye-Orubite and Don- Lawson, 2016).

Since an insufficient amount of silver is produced worldwide compared with the high demand of silver which is increasing by 2 to 2.5% yearly (Samson and Edison, 2014), coupled with the fact that coconut shells are discarded as wastes in our environment, there is therefore a need for converting these wastes into useful ventures for economic and environmental benefits. This is the main reason of using coconut shell as an extractant for silver recovery from waste x-ray films, which has not been reported in this work. Therefore, the present paper describes the use of coconut shell, which is a cheap and available agricultural waste, in extraction of silver from waste x-ray films thereby making silver available for use and also to make this waste another source of raw material that is vital and valuable to the industry.

2. Materials and Methods

2.1 Materials / Sample Collection

The X-ray films were collected from the radiological unit of the General Hospital, Bori, eastern Niger Delta, Nigeria while the Coconut shell was also obtained in large quantity from Bori main town, Nigeria.
All chemicals and reagents used were of analytical grade. Model GBC Avanta version 2.02 Atomic Absorption Spectrophotometer was used.

2.2 Methods

2.2.1 Sample Preparation

Preparation of Coconut Shell Aqueous Extract (CSAE)

The coconut shell obtained was washed with deionized water, sun dried for 72 hours (3 days) at ambient temperature and further oven dried at 80^{0}C for 48 hours. The dried sample was burnt to obtain finely granulated ash. Ash of weight 20, 40, 60, 80 and 100 grams were weighed into five (5) separate 1000ml beakers. They were soaked in 500ml of distilled water and allowed to stand for 48 hours (2 days) with stirring at intervals. Thereafter, the solutions were filtered using a Whatman filter paper to obtain coconut shell aqueous extract (CSAE).

2.2.2 Preparation of X-Ray Film

The X-ray films collected were washed with distilled water and wiped with cotton wool impregnated with ethanol and oven dried at 100^{o}C for 15 minutes after which the films were cut into 4x4 cm sizes.

2.2.3 Extraction of Silver from X-ray Film

Equal quantity of x-ray films were weighed and distributed into five (5) separate 500ml beakers. Thereafter, 300ml of each of the aqueous extract was measured and added to the beakers labeled 20, 40, 60, 80 and 100g. The beakers were heated at 100^{o}C for 60 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. Precipitates formed were allowed to dry overnight at ambient temperature.

2.2.4 Standardization of Coconut Shell Aqueous Extract (CSAE)

The pH values of each CSAE were determined using a pH meter (pHeP Pocket sized) and the various portions of the coconut ash solutions were standardized by titrimetric method using 1M HCl as the titrant.

2.2.5 Test for Silver

The recovered product was tested for silver using streak test with nitric acid and potassium chloride.

2.2.6 AAS Analysis

The different grams of aqueous extracts of Coconut shell obtained were analyzed for silver ion concentration. The silver lamp (hallode cathode lamb) 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 was aspirated into the flame and atomized using GBC Avanta version 2.02 Atomic Absorption Spectrophotometer.

3. Results

Table 1: Physical parameters of the coconut shell aqueous extract (CSAE)

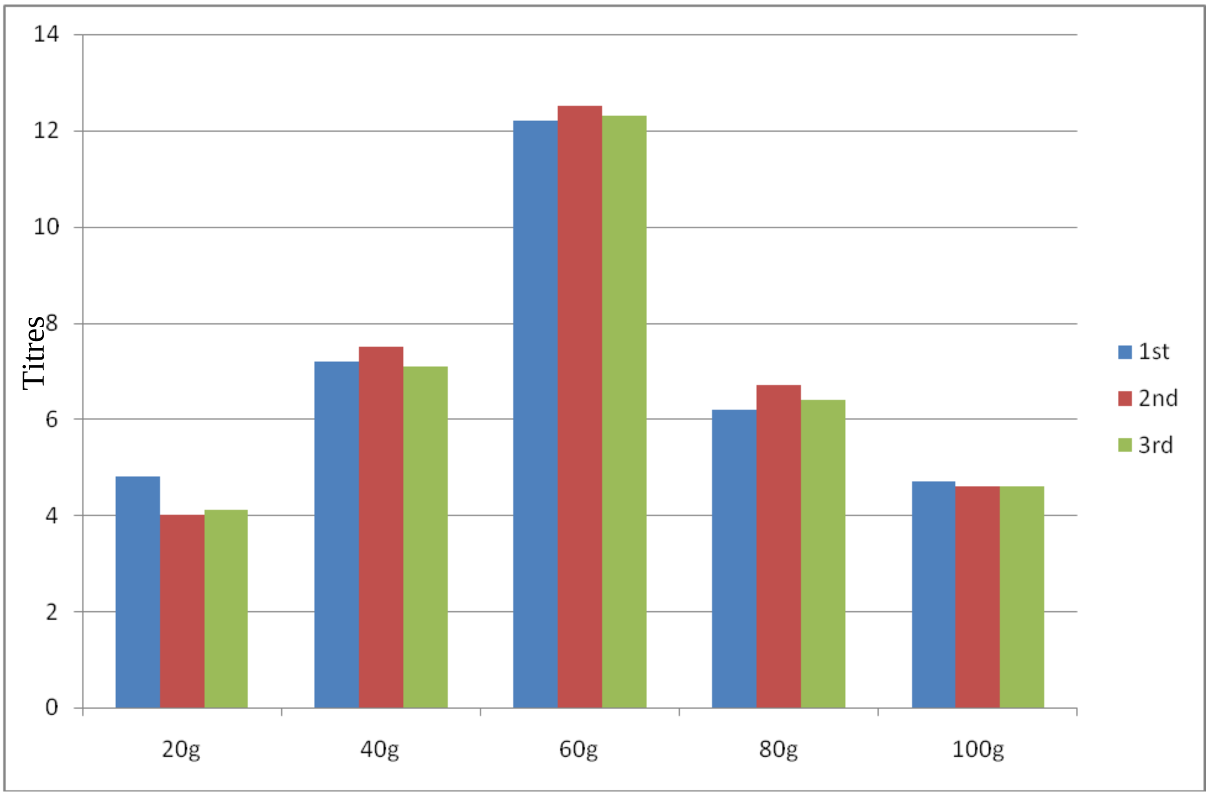
S/N	CSAE	Observation
1	Colour of solution	Umber
2	Touch of solution	Slippery

Table 2: Titre values, pH and concentration of CSAE

Weight of CSA dissolved (g) in 500ml solution	Conc. Of Acid used (M)	1st (cm^3)	2nd (cm^3)	3rd (cm^3)	Vol. of Acid used (cm^3)	Conc. Of CSAE (g/cm^3)	pH of CSAE
20	1.00	4.80	4.00	4.10	4.30	0.172	10.9
40	1.00	7.20	7.50	7.10	7.20	0.288	10.9
60	1.00	12.20	12.50	12.30	12.30	0.492	10.9
80	1.00	6.70	6.70	6.40	6.40	0.256	11.3
100	1.00	4.70	4.60	4.60	4.60	0.184	11.3

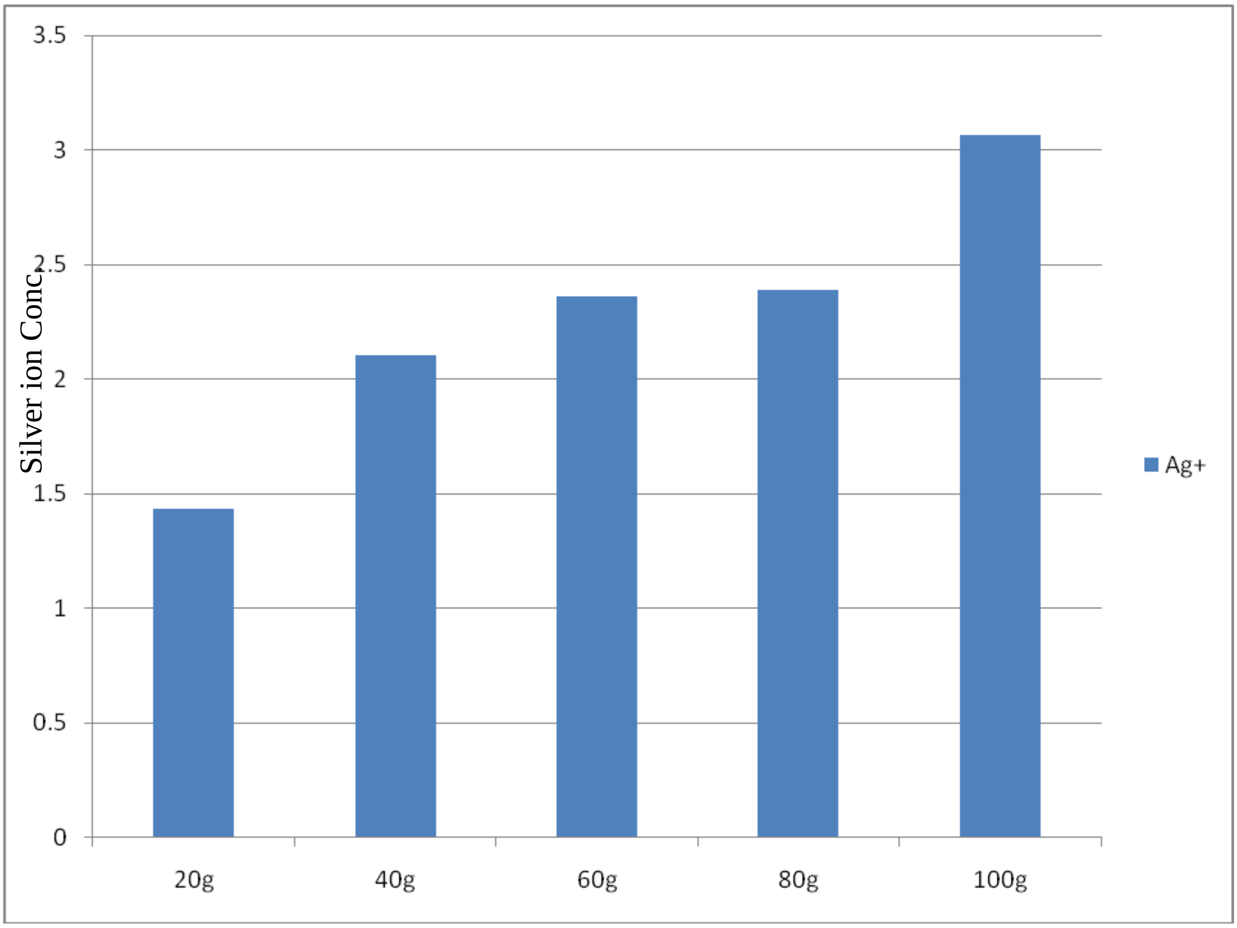
Table 3: Weights of extracts obtained from films and concentration of silver in extracts

Conc. of CSAE (mol/cm^3)	Vol. of CSAE (cm^3)	Amount of extract (x 10^{3}mg)	Conc. of silver ion (ppm)
0.172	300.00	2.20	1.433
0.288	300.00	3.40	2.104
0.492	300.00	4.00	2.362
0.256	300.00	4.60	2.390
0.184	300.00	5.80	3.065



Grams CSAE

Figure 1: Titre values of the different grams of CSAE



Grams CSAE

Figure 2: Concentration of silver (ppm) in different extracts

4. Discussion

The result in Table 1 shows that the coconut shell aqueous extract produced an alkaline solution in deionised water. This agrees with the physical properties of a base. The colour of the solution varied from colourless (20g of ash) and gradually changed to darker golden colour (100g of ash). This may be due to the higher concentration of alkaline ions in solution as the quantity of ash increased. They are in agreement with previous works on plant ash solution (Orubite-Okorosaye and Jack, 2012; George *et al.*, 2014; Okorosaye-Orubite and Gbarakoro, 2018). It has been reported that plant ash solutions contain more of potassium in the form of potassium hydroxide than sodium and calcium (Ronald and Hansford, 1988).
The value of the pH obtained for the different grams of coconut ash aqueous extract are shown in Table 2. The pH range from 10.90-11.30 is an obvious sign of alkalinity. They are in agreement with previous studies on agricultural waste ash solutions (Orubite-Okorosaye and Jack, 2012; Okorosaye-Orubite and Gbarakoro, 2018).

Table 2 also shows the result obtained from standardizing the ash solution. The concentration of potassium ion, K^+ was obtained by titration of the various portions of ash solution with standardized solution of 1M HCl. The result indicates that the CSAE neutralized 1M HCl, confirming that alkaline potassium ion; K^+ is present in the solution. The potassium ion, K^+ which replaces the silver ion, Ag^+ in solution acts as the extractant for silver in the coconut shell, and precipitates as silver hydroxide $Ag(OH)^+$. Concentrations of CSAE obtained were 0.172, 0.288, 0.492, 0.256, and 0.184 for dissolved ash of weights 20, 40, 60, 80, 100g respectively. This shows that there was an increase concentration in 20-60g and decrease

concentration in 80-100g ash solution. The increase in concentration in 20-60g as expected, agrees with the works of Orubite-Okorosaye and Jack, (2012); Okorosaye-Orubite and Gbarakoro (2018). This means that increase in the ash in solution leads to more constituent ions, hence the higher concentrations. The decrease in the concentration in 80-100g ash solution could be as a result of the extraction of more impurities in addition to silver by the higher concentrations of CSAE. This has earlier been observed by Okorosaye-Orubite and Don-Lawson (2016). Notice that when Ag^+ ion is present, the AAS instrument will measure the concentration of Ag^+ ion. When the concentration of ash is much, OH^- ion will be obtained. The OH^- ion will surround the Ag^+ ion to form the $Ag(OH)^+$ complex.
The weight of silver extracted from x-ray films is presented in Table 3. The grams of extracts increased progressively as quantity of ash increased; 2.20, 3.40, 4.00, 4.60, and 5.80g of extract were obtained for 20, 40, 60, 80 and 100 grams of ash respectively. Hence, quantity of ash dissolved, showed reliance on the amount of extract obtained.

Table 3 also shows the concentration of silver ion in the extracts. The result reveals that lower concentrations of silver ions were obtained in higher concentration of coconut shell aqueous extract (CSAE). The values obtained were 1.433, 2.104, 2.362, 2.390 and 3.065 ppm. The values prove that coconut shell aqueous extract (CSAE) truly extracts the film of silver. The amount of silver in the extracts increased as concentration of CSAE increased.

5. Conclusion

This work reveals that the efficacy of coconut shell aqueous extract (CSAE) in the extraction of waste x-ray film is more at lower concentrations than at higher concentrations. Low concentration of CSAE extracts more silver than higher concentration of same solution. However the fact remains that the silver ions have been extracted from x-ray film. The free silver ions are poisonous to the environment and so any means of reducing the silver content will be an advantage to the environment. The titrimetric analysis showed that CSAE contained potassium ion, $K^{+.}$ Coconut shell waste discarded is hereby recognized as a practical material in the extraction of silver from x-ray films which are enriched with silver. It is therefore recommended that agricultural wastes such as coconut shell which is less expensive and readily available should be used as extractant in the recovery of silver from x-ray films before they are discarded into the environment.

References

Abdel-Aal, E.A. and Farghaly, F.E. (2007). Preparation of silver powders in micron size from used photographic films via leaching cementation technique. *Powder technique.* 178: 51-55.

Ajiwe, V. I. E. and Anyadiegwu, I. E. (2000). Recovery of silver from industrial waste, cassava solution effects. *Separation and purification technology*, 18:89-92.

Ashish, M., Kishan, S. Jaimin, P. and Kalpesh, P. (2012). Extraction of silver from photographic waste. *International Journal of Emerging Technology and Advanced Engineering.* 2(2):599-606.

George, D.M.C., Waribo, H.A. Orubite-Okorosaye, K. and Bills, U. S. (2014). Determination of potassium ion concentration in red mangrove (*Rhizophora Mangle L.*) bark aqueous extract (RMBAE) in buffer media. *Archives of Applied Science Research. 6(6):61-66.*

Grant, H. (1979).Modern photographic processing, vol. 1, John Wiley and sons, New York.

Jacobson, C.I. and Jacobson, R.E. (1976). Developing: The negative techniques, 8th edition, London, Focal Pr.

Jayant, P. P., Pallavi, S. P., Patil, I. D., and Umesh, B.D. (2015). Extraction of silver from X ray films using Protease Enzyme. *International Journal of advanced Biotechnology and Research*, 6(2):220-226.

Madakson, P. B., Yawas, D. S. and Apasi, A. (2012). Characterization of coconut shell ash for potential utilization in metal matrix composition for automobile applications, 4(3):1190-1198.

Maniciot, R., Ollagnier, M. and Ochs, R. (1981). Potassium nutrition and fertilization of the coconut around the world. *Potash Revie,*. 12:1-12.

Manisha, D. and Shyamapadal, M. (2011). Coconut (Cocos nucifera L., Arecaceae): In health promotion and disease prevention. *Asian pacit journal of tropic medicine*, 214-247.

Mendoza, C. S. and Kanata, S. (1996). Silver extraction for pollution control of photographic fixing solution with tetramethytturam disulphide. *Bull. Chem.. Soc. Jpn*., 69: 3499-3504.

Okorosaye-Orubite, K. and Don-Lawson, C. D. (2016). Red mangrove bark ash as extractant for silver in photographic waste. *Journal of Scientific Research and Studie*, 3(3):61-67.

Okorosaye-Orubite, K. and Gbarakoro, S. L. (2018). Extraction of silver from photographic waste using cocoa husk ash solution. *International Journal of Engineering Science and Research*, (3)40-43.

Orubite-Okorosaye, K. and Jack, I. R. (2012). Estimation of silver content in some photographic waste. *American Journal of Scientific and Industrial Research,* 3(6):390-394.

Radha, K. V. and Arun, C. (2010). Recycling of exposed photographic x-ray films and recovery of silver using bromelain. *Transactions on Ecology and the Environmen,*. 142: 421-429.

Ronald, C. S. and Hansford, T. (1988). Essentials and soil amendments for plants, sources and use for agriculture. *Technol., Eng.*, (017-1021), 9-12.

Samson, O. M. and Edison, M. (2014). Review of silver recovery techniques from radiographic effluent and x-ray film waste. *Proceedings of the world Congress on Engineering and Computer Science*, (2): 22-24.

Shankar, S., More, S. V. and Seeta L. R. (2010). Recovery of silver from waste x-ray film by alkaline protease from *Conidiobolus coronatus*. *Kathmandu university journal of science, engineering and technology*, 6 (1): 60-69.

Subramanian, P.A., Kebede, N. M. and Abraha, G. A. (2012). Extraction of silver from spent x-ray and photographic fixer solution in Tigray region, Ethiopia. *An Indian Journ,*. 7(6):233-238.