Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **8(3),** 11-15, March **(2018)** *Res. J. Chem. Sci.*

Effect of pH on the extraction of Silver from X-ray films using Red mangrove Bark Ash Solution

Kaine Okorosaye-Orubite[1*] and Chioma Don Lawson[2]
[1]Department of Pure and Industrial Chemistry, University of Port Harcourt, Rivers State, Nigeria
[2]Department of Science Laboratory Technology, School of Science, Port Harcourt Polytechnic, Rivers State, Nigeria
kaineorubite@yahoo.com

Available online at: www.isca.in, www.isca.me
Received 2nd January 2018, revised 4th March 2018, accepted 15th March 2018

Abstract

This work investigated the effect of change in pH of Red Mangrove Ash Bark Solution (RMBAS) as stripping solution for the extraction of Silver from waste X ray films. using Four sets of Mangrove bark ash, 10, 20, 50, 70 and 100g were weighed and each dissolved in 500 ml of de-ionised water and left to homogenize for 48 hours before filtration, these solutions were alkaline tested to be alkaline. Another set of six solutions were prepared from the100g solution with pH values adjusted to acidic and neutral by 1 M HCl acid (pH 2.5,3.5,4.0, 5.0 6.0 7.5). Waste X ray films (cut into pieces) were kept in each solution in a water bath at 60^{O}C and stirred at intervals for 1 hour until the films appeared clean and free from the dark spots. The stripping solutions were analysed for Silver using Solar Thermo Atomic Adsorption Spectrometer (Flame AAS) model S4- 71096. Results obtained showed that pH of the stripping solutions affected the extraction of Silver from the waste X ray films. Silver was recovered more as Ag^+ than as $Ag(OH)_2{}^+$. Higher concentrations of Ag^+(28.50 -13.36mg/kg) was recorded for the acidic stripping solutions than the alkaline (3.94 mg/kg) or neutral solutions (8.72-5.30mg/kg). Amount of recovered Silver ion decreased as the pH of the solution increased. Therefore, more Silver was extracted as the ion; Ag^+ by the acidic RMBAS solution with pH 2.5 -5.0 .Higher concentrations of RMBAS had previously been confirmed to strip Silver from photographic wastes in the complex ion form, $Ag(OH)_2{}^+$. This work has therefore established that under same stripping conditions, higher concentrations of acidic RMBAS extract Silver as Ag^+ rather than, $Ag(OH)_2{}^+$ from waste X ray films.

Keywords: Silver, stripping solution, pH, complex ion, acidic RMBAS.

Introduction

Silver like most metals find wide use in our world today. From making jewelries, mirrors, alloys, photographic materials etc. Silver is obtained in nature from its ore, Argentite. However due to depleting natural source scientists continue to find alternative means like recycling to obtain Silver. About 25% of world's Silver needs are obtained through recycling[1]. Most of the silver produced is used in the production of photographic and imaging materials like X-ray films. Silver has the ability to react with light to produce images. X-ray films for general radiography consist of emulsion-gelatin containing radiation sensitive Silver halide crystals, such as silver bromide or silver chloride and a flexible, transparent, blue-tinted base. When X-ray light strikes the grains of the sensitive Silver halide in the emulsion, some of the halides (bromine) ions are liberated and captured by the Silver ions. The exposed grains become more sensitive to the reduction process when exposed to a chemical solution or a developer, unexposed Silver ions remain on the film as dark spots[2]. Silver recovery methods from X-rays or other photographic films are based on stripping these unexposed ions with stripping solutions[3]. From literature, stripping solutions may contain anions that are able to form soluble compounds with Silver on the film and are leached into the solution. Thereafter precipitation processes are used to recover metallic Nitric acid as stripping solution to leach processed radiographic films of silver solution has been reported[4]. So also was the use of NaOH as stripping solution for waste X-ray films[5]. Cassava solution found use as stripping solution to recover Silver from industrial wastes[6]. Plantain peels ash solution was reported as effective stripping solution by to recover Silver from waste photographic films[7]. The effectiveness of plantain peels was attributed to KOH in the ash solution; this was the basis for also using Mangrove ash solution as stripping solution[8]. The Potassium ion concentration in Red Mangrove Bark ash solutions had earlier been measured to be between 19.50 -31.91 gm/dm^3 [9]. Both plantain ash and mangrove ash solutions stripped Silver from the photographic wastes. However the authors observed that the stripping solutions were most effective at low concentrations. Higher concentrations of stripping solution recovered smaller amounts of Silver from the photographic films and solutions. This, the authors attributed to the complex forming ability of Silver. Higher concentrations meant more OH^- and Silver may have formed complex ion with –OH ions in solution and was not free for detection. Metallic extraction from solutions are affected by temperature, concentrations, pH of the solution, other metal ions at the same aqueous phase (co extraction), as well as all kinds of cationic species existing in the solution[10]. From reported work using NaOH solution, the appropriate stripping temperature range for gelatin – silver layer of used photographic film was observed between 70–80^{0}C[5]. Same was confirmed by previous works by this author[11].

The pH of a solution is a critical factor in metal extraction because metals dissolve in acids. Therefore the extractability of metal complexes is greatly influenced by the acidity of the aqueous phase. Under certain conditions, favourable extraction of a metal may occur at low pH values. For instance the extraction percentage of $Cu^{2+,}$ Co^{2+} and Ni^{2+} exceeded 80% at pH 3, almost 100% for Cu^{2+} and Ni^{2+} at pH 4 and a little less for the Co^{2+}, for Pb^{2+}, pH 6 gave 90% extraction[12]. Metal ion extraction from bauxite ore gave higher extraction at pH 2 compared to other pH values[13]. It was further observed that high leaching rates were achieved under oxidizing conditions and low pH values[13]. Copper extraction from sulphate solution using LIX 984N was maximum at optimum pH of 3.5 and adsorption of Fe(II) ions was pH dependent and optimal at lower pH values[14]. In their work, evaluating the effect of pH and temperature for achieving maximum uptake of metals using coat of fluted pumpkin, the unmodified fluted pumpkin seed coat was found more favourable for the extraction of $Cd^{2+,}$ Ni^{2+} and Pb^{2+} at low pH 2[15]. Sometimes the efficiency of the extraction process is achieved at high pH values. In such instances varying pH may introduce masking agents which affect extraction of the metal. The extraction of Cu^{2+} from aqueous solution of SO_4^{2-} into 0.05 M HTcP/$CHCl_3$ was more efficient at relatively high pH values irrespective of SO_4^{2-} in the buffered phase[16]. Also the biosorption of Pb^{2+} using Vernonia Amygdalina biomass, increased with increase in pH until a maximum was achieved at pH 6[17]. Waste photographic materials e.g. X- rays films contain unexposed Silver or soluble Silver salts which constitute various health hazards if not properly disposed off. Hospitals generate large tons of X-ray films which are discarded after medical interpretation. Several instances are reported where X-rays films are often not disposed according to standard methods[18,19]. The ecological impact of this defective disposal process may also be hazardous to the eco system. Recovery of Silver is therefore not only economical but also a way of ridding the environment of possible contamination by Silver compounds from these wastes. Sequel to previous observation that larger amount of mangrove ash extracted Silver more as complex ion, ($Ag(OH)_2^+$) than as free ion (Ag^+) from photographic wastes, this work investigates favourable stripping condition that will extract more Silver ion from X-ray films using RMBAS. The effect of varying the pH of the stripping solution (RMBAS) on the recovery of Silver ion from waste X-ray films was studied in this research.

Materials and methods

The red mangrove (Rhizophora mangle L) bark was obtained from Timber plank market, mile II Diobu, Port Harcourt, Rivers state, Nigeria. They were extensively washed with de-ionized water and air-dried in sun for 120 hours to remove water content in the sample. The dried sample was then converted to finely granulated ash by burning. Four sets (10, 20, 50, 70 and 100g) of the burnt ash were weighed and each dissolved in 500 ml of de-ionised water and left to homogenize for 48 hours, thereafter they were filtered using Whatman filter paper. Each of the filtrate was made up to 1000 ml mark with de-ionised water. These were labeled as the stripping solutions. The pH of these solutions were measured using a pH meter.

Effect of pH: Another set of 6 stripping solution was made from 100g of ash whose pH was adjusted using 1.0 M HCl to pH 2.5, 3.5, 4.0, 5.0, 6.0 and 7.5. X-ray films were collected from O.B Lulu Briggs Health Centre, University of Port Harcourt, and Rivers State, Nigeria after an approval from the Director of the Health Centre. They were cleaned with cotton wool dipped in ethanol to remove the dust and dirt and cut into small square pieces. About 30 pieces of cut films were soaked in each stripping solution. The beakers were put into a water bath mentained at 60^{0}C for 1 hour, stirring at intervals, until the films appeared clean and free from the dark spots. The supernatant solutions were removed from the water bath, allowed to cool while the stripped films were discarded. The stripping solutions (50 ml) of each were measured into a volumetric flask for AAS analysis by Solar Thermo Atomic Adsorption Spectrometer (Flame AAS) model S4- 71096. Values recorded are means of three replicate measurements. All reagents used are of analar grade and de-ionised water was used throughout the experiment.

Results and discussion

PH of RMBAE solution: The pH of RMBAE solutions was all alkaline as in Table-1. The pH range was between 9.33 – 9.89. Similar result was reported in previous works[8,9,12]. This is further confirmed by slippery nature of the solutions of the ash which turned red litmus red. Plant ash solutions are known to contain KOH a strong base[20].

Table-1: pH values of the RMBAE solution.

Amount of RMBAE (g)	pH Values
10	9.33
20	9.68
50	9.77
70	9.88
100	9.89

Recovery of Silver from X- ray films by RMBAS: Silver ion obtained from the unadjusted RMBAS is given in Table-2.

Table-2 further confirms earlier work[8] that RMBAS strips Silver as ion from used X-ray films and that lower concentration of stripping solution extracts the highest amount of Silver ion. The 10g solution extracted 4.86g of Ag^+ while the 100g solution extracted the least amount of 1.14g of Ag^+. This trend has been observed in all works done with either Plantain or Red Mangrove ash solution as stripping solution. The probable cause was attributed to the availability of more OH^- ion in solution at higher concentration and the possibility of complex formation with Ag^+ to give the two coordinate complex, Ag $(OH)_2^+$.

Table-2: Ag^+ recovered from unadjusted stripping solution.

Amount of RMBAE (g)	pH Values	Amount of Ag^+ recovered
10	9.33	4.86
20	9.68	3.62
50	9.77	3.49
70	9.78	3.90
100	9.89	1.14

Table-3: Ag^+ recovered from pH adjusted stripping solutions.

Sample pH of stripping solution	Ag^+ (mg/l)	OH^- (mg/l)
9.8	3.94	80.42
7.5	5.30	73.52
6.0	8.72	64.81
5.0	13.36	41.37
4.0	17.49	30.08
3.5	21.15	18.76
2.5	28.50	12.28

From Table-3, stripping solutions are grouped as i. alkaline pH, 9.78, ii. neutral, pH 6.0 -7.31 and iii. acidic pH, 2.5-5.0. It is evident from the figures that more Silver was extracted by the acidic stripping solutions followed by the neutral and basic stripping solutions. Consequently solution with the lowest pH (2.5) extracted the highest amount of Silver ion (28.50mg/l) while pH 9.78 had Silver extracted as 3.94mg/l. It follows therefore that amount of Silver extracted decreased as the pH values of stripping solution increased. The unadjusted stripping solutions which were alkaline extracted the smallest amount of Silver ion. Similar result was reported while investigating the effect of pH on metal extraction from Bauxite ore by *Thioba illus Ferrooxidans*[13]. Higher extraction was attained at pH 2 compared to other pH values. They opined that increase in pH led to increase in negative charges on the bacterial surface and subsequent attraction by positively charged metal ions. Hence metal ions were not released into the solution. Table-3 also shows that the amount of OH^- ions in solution is high at alkaline pH values. The pH of the RMBAS is alkaline in nature, more ash dissolved results in more OH^- ions but less Ag^+ ions in solution. The possible complex ion formation by OH^- with Ag^+ ions may be responsible for reducing the concentration of Ag^+ ions in the stripping solution as shown in equation (1). Complex formation reactions are most times equilibrium reaction. Formation of the complex ion can be illustrated by equation (1) below,

$$Ag^+ + 2OH^- \leftrightarrow Ag\,(OH)_2^+ \quad (1)$$

Hydrochloric acid (HCl) is a source of chloride ions. Therefore adjusting the pH of stripping solution with HCl solution introduced H^+ and Cl^- ions (equation-2).

$$Ag^+ + 2OH^-(+ H^+ + Cl^-) \leftrightarrow Ag\,(OH)_2^+ \quad (2)$$

$$2OH^- + H^+ \leftrightarrow H_2O \quad (3)$$

OH^- ions are removed from the solution as they combine with H^+ ions to give water equation (3). From Le Chaterlier's principle, it can be deduced that, the equilibrium favoured the backward reaction in order to replace OH^- ions. This favoured Ag^+ availability in solution. Likewise as the concentration of Cl^- increased the equilibrium further favoued the production of more Ag^+ ions rather than $Ag(OH)_2^+$. This may explain why the lowest pH (2.5) obviously containing the highest concentration of H^+ and Cl^- ions had the highest amount of Silver ions measured as shown in Table-1. However as the pH values increased (high pH values) the equilibrium favoured the forward reaction which means more of the complex ion, $Ag(OH)_2^+$, is produced with lesser amount of Ag^+ ions in solution. This condition is collaborated by the corresponding concentration of OH^- ions. Also the solubility of metal complexes in water depends upon the presence of hydrophilic groups such as COOH, SO_3H, NH_2 and OH. When both acidic and basic groups are present in solution, the complex will be soluble over a wide range of pH; otherwise although the metals remain in solution, they fail to give normal ionic reactions[21]. From Figure-1 it is evident that higher concentration of OH^- (associated with alkaline solutions) produce smaller amounts of Ag^+ ions or Ag $(OH)_2^+$, did not dissociate. Similar work reported that improved Silver recovery was observed when the pH was lowered from pH 7.5 to 3.0 at 30g/L nitric acid in the solution[4]. This is an indication that improved Silver recoveries could be achieved under acidic conditions.

In addition to solubility effect, the pH of the extraction solvent can affect an extractable or leacheable's profile if the specific extractable or leachable is affected by a process that is dependent on pH[22].

From the foregoing it can be established that the solubility of the Silver ion in RMBAS solution is pH dependent since the profile of Silver is obtained either as Ag^+ or the complex ion, Ag $(OH)_2^+$ at different pH values. The significance of obtaining Silver as Ag^+ lies in the possibility of its precipitation to obtain Silver metal. On the other hand extracting Silver from the waste X ray film as Ag $(OH)_2^+$, indicates that RMBAS can be used to clean up photographic effluents before they are discarded.

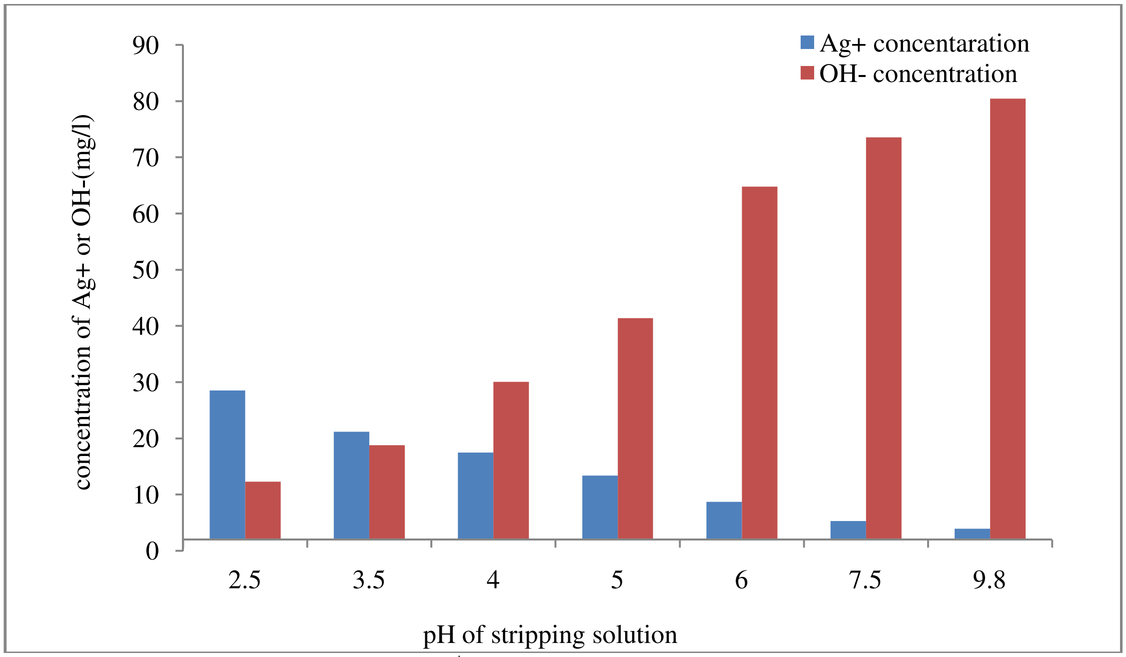

Figure-1: Concentration of Ag^+ and OH^- ions in stripping solution at different pH.

Conclusion

This work has further presented RMBAS as stripping solution for Silver in waste x ray films. Silver was extracted in the ionic form either as Ag^+ or $Ag(OH)_2^+$. At higher concentrations of RMBAS, Silver extracted was in the complex ion form $Ag(OH)_2^+$. However at low pH or acidic RMBAS, the complex ion dissociates to Ag^+ to give more Silver ions in solution. The effect of pH on the solubility of $Ag(OH)_2^+$ in order to obtain more Silver ions was established. Therefore higher concentrations of RMBAS with pH 2.5-5.0 (acidic solution) can extract Silver from waste X ray films as Ag^+. In other words Silver can be extracted more as the ion, Ag^+ by acidic RMBAS. The implication of this is that more Silver can be precipitated and subsequently purified using acidic RMBAS as extractant or stripping solution.

References

1. Dahne W. and Schriftenr (1990). Great Divide Mountain Bike Route. 63, 231-247.
2. Grant H. (1979). Modern Photographic processing. John Wiley and sons, New York, 1. ISBN -13: 978-0471042860
3. Masebinu S.O. and Muzenda E. (2014). Review of Silver Recovery Techniques from Radiographic effluent and X-ray film waste. *Proceedings of the world congress on engineering and computer science*, October San Francisco, USA, 2, 22-24.
4. Arslan V., Ucurum M., Vapur H. and Bayat O. (2010). Recovery of Silver from waste radiographic films by chemical leaching. *Asian Journal of Chemistry*, 23(1), 67-70.
5. Nakiboğlu N., Toscali D. and NİSLİ G. (2003). A novel silver recovery method from waste photographic films with NaOH stripping. *Turkish Journal of Chemistry*, 27(1), 127-133.
6. Ajiwe V.I.E. and Anyadiegwu I.E. (2000). Recovery of Silver from Industrial Waste, Cassava Solution Effect. *Sep. Purif. Technol.*, 18(2), 89-92.
7. Orubite-Okorosaye K. and Jack I.R. (2011). Recovery of silver from waste x-ray films using plantain peels ash solution. *International journal of physical science*, 3(1), 116-120.
8. Orubite K.O. and Chioma Donubari Don-Lawson (2016). Red Mangrove ash as extractant for Silver in photographic wastes. *Journal of Scientific Research and Studies*, 3(3), 61-67.
9. 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*) bark aqueous extract (rmbae) in buffer media. *Scholars research library. Arch. Appl. Sci. Res*, 6(6), 61-66.
10. Urszula Doma´nska and Anna Rekawek (2009), *Journal of Solution Chemistry*, 38, 739-775. DOI 10.1007/s10953-009-9402-7
11. Orubite K.O. and Jack I.R. (2012). Estimation of Silver content in some photographic wastes. *Am. J. Sci. Ind. Res.*, 3(6), 390-394.
12. Fetouhi B., Belarbi H., Benabdellah A., Kasmi-Mir S. and Kirsch G. (2016). Extraction of the heavy metals from the aqueous phase in ionic liquid 1-butyl-3-methylimidazolium

hexafluorophosphate by N-salicylideneaniline. *Journal of Material Environmental Science*, 7(3), 746-754.

13. Shalkh S.M., Khan Z.S. and Ade A.B. (2010). Effect of pH on metal extraction from Bauxite ore of Thiobacillus Ferrooxidans. *Journal of Scientific Research*, 2(2), 403-406.

14. Onojake M.C., Obi G. and Osakwe J.O. (2015). Banana peel as a low cost adsorbent for the removal of Ni^{2+}, Cu^{2+} and Fe^{2+} from industrial effluents. *Journal of Chemical Society of Nigeria*, 40(2), 59-62.

15. Okwunodulu F.U., Odoemelam N.O. and Eddy N.O. (2015). Temperature and pH influence in sequesting Cd (II), Ni (II) and Pb (II), ions from synthetic waste water using fluted pumpkin seed coat. Proceedings of the 38th annuaual International conference, workshop and exhibition of the Chemical Society of Nigeria, 6-11 Sept, 265-274.

16. Chuku U.J., Anyanwu C. and Orubite K.O. (2016). Effect of sulphate and nitrate ion on the extraction of copper (11) metal ions from aqueous media using 2, 2,- Trichloro-1- (5-Hydroxy-3-methyl-1-phenyl-1H-Pyrazol-4-yl) ethanone in chloroform. *Journal of Chemical Society of Nigeria*, 41(1), 43-48.

17. Obi (2015). Removal of lead from aqueous solution with Vernonia Amygdalina stem biomass. *Journal of Chemical Society of Nigeria*, 40(2), 41-44.

18. Sidi M., Nwobi C. and Dambatta A.H. (2017). An investigation into the radiological waste management of selected centers in Kano metropolis, Nigeria. *West African Journal of Radiology*, 24(1), 20-24.

19. Oyekale A.S. and Oyekale T.O. (2017). Healthcare waste management practices and safety indicators in Nigeria. *BMC public health*, 17(1), 740.

20. Ronald C.S. and Hansford T. (1988). Essentials and soil amendments for plants; sources and use for agriculture. *Technol. Eng*., (1017-1021), 9-12.

21. Husain Asif (2017). Theoretical Basis of Analysis: Complexometric Titrations, pharmacy e- book (pharmaceutical Analysis). Edition: First, Publisher: NISCAIR, New Delhi, 32.

22. Jenke D., Zietlow D. and Sadain S. (2004). Leaching of organic acids from irradiated EVA plastic as a function of solution pH and polarity. *PDA journal of pharmaceutical science and technology*, 58(1), 24-31.