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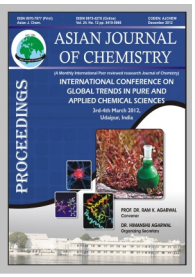

Determination of the Optimum Conditions for the Recovery of Silver from Photographic Fixer Solutions Used in Hospitals and Clinics at Anbar, Iraq†

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A low cost metal replacement method has been used to determine the optimum conditions for a typical recovery of silver from photographic fixer solutions used in different clinics. The chosen experimental perimeters were (i) pH range 4-5, (ii) suitable acid at concentration range 5-10 % (by weight), (iii) room temperature process condition, (iv) different waste metals and metal alloys, (v) reaction time 3-12 days, (vi) silver concentration in the manageable fixer solutions (< 5 mg/L). This method of using the above optimum conditions was found particularly suitable for the local treatment of fixer solutions in a manner which enables silver recovery at a considerably minimized cost and reduced environmental pollution.

Key Words: Silver recovery, Fixer solution, Yield and cost, Environmental pollution, Flame atomic absorption spectrophotometer, X-ray fluorescence.

INTRODUCTION

Silver halides are used as essential compounds in photographic film manufacturing due to their high sensitivity to light. This sensitivity feature has also been utilized in radiographic industry, whereby the silver halide gets converted into a soluble silver complex of the formula $Ag(S_2O_3)_2^{3-}$ upon treatment with fixer solutions containing sodium thiosulphate or ammonium compounds. The used fixer solutions, which are utilized in photography and radiography, are considered a significant source of the relatively valuable element of silver. The recovery of silver metal is an economically valuable process, as silver ranges between 2-7 g/L^{-1}.

On the other hand, the recovery of silver contributes to the environmental protection through controlling the concentration of silver ion and its toxic effect on microorganisms[2-4]. The environmentally safe concentration of silver ions should not exceed 5 ppm (5 mg/L) in fixer solutions before disposal[5]. Recovery methods of silver at high concentration can be summarized as:

Electrical method: This method is widely used for recovering silver at higher purity and it allows reusing the fixer solutions. However, the disadvantages of this method are the high cost of the process and the relatively low percentage yield of the recovered silver (90 %), necessitating a second treatment of the fixer solution to conform to the environmentally permissible concentrations[6-9].

Precipitation method: In this method, silver ions are precipitated as silver sulphide (Ag_2S) at a higher yield of silver (99 %). The major drawback of this method is the difficulty of filtering the sulphide product due to the small particle size, besides the difficulty of obtaining pure silver from the sulphide. These difficulties make this method uneconomical and environmentally inappropriate for the toxicity of the produced hydrogen sulphide[10,11].

Metal replacement method: In this method, different metals or metal alloys of higher electropositivity than silver are used to reduce the silver ions into silver element. This method characterized by its economical advantage and high percentage yield of silver (95-99 %). However, after recovering the silver, the fixer solution cannot be reused. Due to the importance of this process, several patented works have been conducted to determine the optimum conditions for the recovery for silver. For example, steel wool (1-5 mm) was used to reduce silver ions at pH = 2.5[12]. At such low pH conditions the silver thiosulfate may dissociate resulting in precipitation of sulphur, which leads to the formation of the problematic mixture of the reduced with sulphur and the steel powder. Additionally,

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TABLE-1
PHYSICAL PROPERTIES AND THE CONCENTRATION OF SILVER IN THE SAMPLES OF FIXER SOLUTIONS TAKEN FROM HOSPITALS (H) AND PRIVATE CLINICS (C)

Hospital or clinic	Sample code	pH	Density (g/cm^3)	Silver conc. (g/L)	Remarks
Fallooja hospital	H1	5.40	1.058	2.32	Light yellow with a beige precipitate
Ramadi hospital	H2	6.96	1.063	3.1	Yellow to orange
Haditha hospital	H3	5.17	1.119	0.98	Little dark yellow and black precipitate at the bottom
Aana hospital	H4	5.37	1.146	0.82	Brownish yellow and black precipitate at the bottom
Rawa hospital	H5	5.02	1.098	2.92	Yellow slash of green
Karama clinic	C1	5.21	1.074	0.173	Brownish yellow
Fallooja clinic	C2	6.30	1.077	2.81	Light yellow and a white precipitate at the bottom
Baghdad clinic	C3	5.79	1.073	1.5	Little dark yellow
Kortuba clinic	C4	4.85	1.129	2.3	Light yellow and yellow precipitate at the bottom

TABLE-2
VOLUMES OF ACIDS ADDED TO 100 mL OF FIXER SOLUTION FOR THE DISSOCIATION OF THIOSULPHATE IONS AND TO ATTAIN THE REQUIRED pH VALUE

Sample code	pH Original solution	Added 5 % H_2SO_4 Volume (mL)			pH	Added 10 % HCl Volume (mL)			pH
		pH = 4.5	pH = 4	d	d	pH = 4.5	pH = 4	d	d
H1	5.40	3.03	4.80	6.67	3.08	4.97	7.10	8.9	3.38
H2	6.96	5.40	6.89	11.6	2.27	7.34	9.53	15.1	2.26
H3	5.17	2.92 d	-	2.92	4.77	2.90 d	-	2.90	4.90
H4	5.37	3.33 d	-	3.33	5.00	5.60 d	-	5.60	5.00
H5	5.02	3.41	6.37	10.1	3.36	4.89	8.83	14.5	3.14
C1	5.21	4.1	5.62 d	5.62	4.21	4.43 d	-	4.43	4.70
C2	6.30	5.53	7.05	8.34	3.40	7.69	9.68	13.0	3.12
C3	5.79	6.21	8.38	12.2	2.83	8.74	11.66	15.7	3.02
C4	4.85	1.63 d	-	1.63	4.64	1.28 d	-	1.28	4.84

d = decomposition

fixer solution has the potential of corroding the steel wool and, consequently, augments the difficulty of separating the silver metal purely and economically. In another patented work, a rolled string made of different elements was used instead of the steel wool. The string is placed in a devized chamber that allows a continuous flow of the fixer solution[13]. Another invented method indicated the use of the same technique above, but used copper and steel boards placed horizontally to allow flow of the fixer solution. The precipitated silver was collected by specially designed filters[14].

These methods require the manufacture of the reducing agents in a particular pattern and characteristics in addition to the manufacturing cost and the excessive use of the fixer solutions. The recovery of silver and determination of its quantity in fixer solutions is still one of the vital research fields. Research works continues to find the most economical procedure, optimum parameters and environment friendly method of silver recovery.

In a recent research, chitin was used for a quick recovery of silver thiosulphate as a whole from fixer solutions at pH = 2.2[15]. Another research was conducted using a resin containing bisthiourea and formaldehyde[16]. Sodium dithionite compound was used in a different research on the precipitation of silver[17]. However, these methods remain economically impractical as further treatments is required to obtain silver in pure form, in addition to being used only in cases of low concentrations of silver content. However, estimating the concentration of silver in small amounts is still a significant research topic[18-20].

Reaching to the ideal conditions for the recovery of silver from fixer solutions at workplace, without using any energy source and using simple techniques, is one of the main objectives of this research. In addition to seeking the economical feasibility, a substantial consideration was also given to environmental protection through maintaining the concentration of silver ions below the permissible limits set by the environmental protection agency (EPA). The transfer of the used fixer solutions from hospitals and clinics to the silver recovery location, as it is practiced at the present time, is a risky operation that is better avoided and should conform to the standards of environmental safety[21]. Unfortunately, these standards are usually neglected by the workers in this field in most Middle Eastern countries. Thus, further significant is added to the present work in terms of conservation of groundwater and appropriate disposal of harmful solutions into the environment in an orderly manner.

EXPERIMENTAL

Samples collection and characterization: Nine samples of fixer solutions used in radiography sections in (five general hospitals and four private clinics in the province of Anbar) were collected, filtered and their physical properties were estimated. The silver content in each solution was determined using a flame atomic absorption spectrophotometer; model Phoenix-986 (USA), as shown in Table-1.

Acidity adjustments: Acidic medium was chosen for the recovery of silver from the fixer solution, using hydrochloric acid (10 %) and sulphuric acid (5 %) to obtain pH values in the range (4-4.5).

The recovery process was carried out by placing 100 mL of each of the fixer solutions in glass beaker (size 150 mL). The required acid was added dropwise with stirring (using magnetic stirrer) at room temperature and pH values were measured and fixed using a (pH-meter, Sartorius PB-11) as

TABLE-3
RELATIVE AMOUNTS OF METALS FOUND IN BEVERAGE CANS ALLOY

Relative amount of metal (%)						Aluminum (%)
Iron	Chromium	Nickel	Copper	Zink	Manganese	
0.99	0.02	0.01	0.23	0.03	1.02	97.7

TABLE-4
QUANTITIES OF RECOVERED SILVER FROM 400 mL OF THE FIXER (H3) AT pH = 5.17

Reducing agent	Recovered silver (g)					Weight loss in reducing agent in 12 days (g)
	3 Days	6 Days	9 Days	12 Days	Total	
Aluminum platelets	0.3126	0.0202	0.0032	-	0.3360	0.2943
Aluminum cans alloy	0.2951	0.0404	0.0151	0.0152	0.3658	0.246
Copper platelets	0.0273	-	-	-	0.0273	4.5056
Iron platelets	0.2877	0.0199	-	0.4336	0.3076	2.3175
Brass platelets	0.3005	0.0108	0.0017	-	0.3130	3.0543

TABLE-5
QUANTITIES OF RECOVERED SILVER IN 400 mL OF THE FIXER (H4) AT pH = 5.37

Reducing agent	Recovered silver (g)					Weight loss in reducing agent in 12 days (g)
	3 Days	6 Days	9 Days	12 Days	Total	
Aluminum platelets	0.2941	0.0143	–	–	0.3084	0.0599
Aluminum cans alloy	0.1997	0.0187	–	–	0.2184	0.1107
Copper platelets	0.4014	0.0751	–	–	0.4765	3.5701
Iron platelets	0.3656	0.0211	–	–	0.3867	1.8061
Brass platelets	0.3907	0.0224	–	–	0.4131	1.9932

shown in Table-2. The amount of acid required for the dissociation of the thiosulphate complex was fixed by observing the beginning of the turbidity of the solution due to the deposition of elemental sulfur, as well as the emergence of the distinctive smell of sulphur dioxide according to the following equation:

$$2H_3O^+ + S_2O_3^{2-} \rightarrow S + SO_2 + 3H_2O$$

Beverage cans alloy preparation and analysis: A number of beverage cans were collected, appropriately cleaned, melted in a Muffler furnace and cooled. The metal contents of the alloy was directly analyzed using the X-Ray Fluorescence, Model (X-MET 3000TX) and the results were recorded as in Table-3.

For a typical use of beverage cans in the recovery of silver from fixers solutions, samples of such cans were cleaned, melted in a Muffle furnace at 800 ºC and poured into iron molds of the set dimensions (7.5 × 7.5 and 2 mm thickness) that assures complete submersion into the used volume of fixer solutions. All other metals and alloy platelets were prepared and cut in the same way.

On the view of some fixer solutions (C1, C2, H3, H4) being readily dissociated upon the addition of acid, as indicate in Table-1, 400 mL of each of this (Group 1) solutions were placed in 1 L size containers made of opaque plastic to avoid contact with light. Sample C1 was found to contain insignificant amount of silver (0.0692 g/ 400 mL) as shown in Table-1 making the silver recovery results inaccurate and so was neglected.

Reducing platelets preparation and analysis: Five metals and metal alloys from industrial wastes (Beverage cans alloy, aluminum platelet, copper platelet, iron platelet, brass platelet) were used. They were cut to the same dimensions as of the beverage cans alloy. The initial weights of the platelets were taken for later calculations. After a thorough cleaning, each platelet was immersed in the four fixer solutions and the deposited amount of silver was worked out after 3, 6, 9 and 12 days. The total weight loss in each piece was also worked out after 12 days.

RESULTS AND DISCUSSION

Calculation of recovered silver: The quantity of the recovered silver was worked out by combining the weight of silver deposited at the bottom of the used container with the weight of silver deposited on the platelet. The recovered silver was washed with water and washings were poured into the fixer container. The silver was then washed with hot water and with diluted sulphuric acid and washed again with excessive water until acidity was eliminated. The silver product was dried at 200-250 ºC for ½ h and weighed. The platelet was washed, dried, re-weighed to determine the weight loss and was returned to the same fixer solution for further recovery of silver.

The following Tables 4-6 show the quantities of silver recovered from fixer samples taken from hospitals and clinics and weight losses in the used metal platelets (reducing agents).

Considering (Group 2) samples (H1, H2, H5, C2, C3), comparative experiments were conducted on the potential of the reducing agents (metal platelets) in recovering silver using different acidity adjusters, HCl (10 %) and H_2SO_4 (5 %) to attain the set operation (pH = 4-4.5). As an example of this group, the fixer sample C2 was used in a comparative experimentation of silver recovery in different mediums of acidity. Three lots of 400 mL of the original fixer sample (pH = 6.3) were prepared. Into one lot, HCl (10 %) was added to lower the pH down to the operational pH = 4.5. H_2SO_4 (5 %) was added to another lot to attain the same set pH value of 4.5.

Each of the previously experimented platelets was immersed in 400 mL of the original solution (pH = 6.3) and of

TABLE-6
QUANTITIES OF RECOVERED SILVER IN 400 mL OF THE FIXER (C4) AT pH = 4.85

Reducing agent	Recovered silver (g)					Weight loss in reducing agent in 12 days (g)
	3 Days	6 Days	9 Days	12 Days	Total	
Aluminum platelets	0.7566	0.1304	0.0155	0.0042	0.9067	0.4036
Aluminum cans alloy	0.7195	0.150	0.0137	0.0041	0.8873	0.3793
Copper platelets	0.3624	-	0.0069	-	0.3693	6.4530
Iron platelets	0.8186	0.0382	0.0042	-	0.8610	3.4124
Brass platelets	0.5481	-	-	-	0.5481	4.9094

TABLE-7
COMPARATIVE QUANTITIES OF RECOVERED SILVER FROM THE ORIGINAL FIXER SOLUTION (C2) AND FROM THE TWO ACID-ADJUSTED SOLUTIONS (pH = 4.5)

Reducing agent	Recovered silver (g) in 3 days		
	C2 Original solution pH = 6.3	C2 with H_2SO_4 (5 %) pH = 4.5	C2 with HCl (10 %) pH = 4.5
Aluminum Platelets	0.4859	0.5473	0.5105
Aluminum Cans	0.5244	0.5962	0.5671
Copper Platelets	0.7043	0.7161	0.7350
Iron Platelets	0.6429	0.7357	0.6811
Brass Platelets	0.6775	0.6528	0.7284

TABLE-8
QUANTITIES OF SILVER RECOVERED FROM 400 mL OF ALL FIXER SOLUTIONS

Sample code	pH Original	pH Typical	Used acid	Reducing agent	Silver recovered (g/400 mL)	Silver conc. before recovery (g/L)	Yield (%)
H1	5.40	4	HCl (10%)	Copper	1.5151	2.32	163
H2	6.96	6.96	-	Copper	1.8317	3.1	147
H3	5.17	5.17	-	Al Cans	0.3658	0.98	93.3
H4	5.37	5.37	-	Copper	0.4765	0.82	145
H5	5.02	4	H_2SO_4 (5%)	Al Cans	1.1476	2.92	98.25
C1	5.21	5.21	-	-	V. Little	0.173	-
C2	6.30	4	H_2SO_4 (5%)	Al	1.1048	2.81	98.3
C3	5.79	4.5	H_2SO_4 (5%)	A1 Cans	0.5791	1.5	96.5
C4	4.85	4.85	-	Al	0.9067	2.3	98.6

the two pH-adjusted solutions (pH = 4.5) for 3 days. The quantities of recovered silver were recorded (Table-7).

According to the results in Table-7, the most suitable acid was chosen to be used with the reducing agent that would provide the best recovery of silver. A comparative process was conducted on the reducing potential of the five different platelets in duration periods 3, 6, 9 and 12 days. The amounts of recovered silver and weight loss in the reducing agents treated in 400 mL of the different fixer solutions (H1, H2, H5, C2, C3) were recorder in Table-8.

The silver recovered by using the aluminum cans or platelets was in a form of light beige precipitates at the bottom of the recovery container and around the reducing metals. Whereas the silver recovered by using the iron, copper and brass platelets was in a form of blackish colour precipitates toughly attached to the platelets' surfaces.

The results shown in the above tables were summed up in Table-8 and making a comparison between the highest silver quantity recovered from each sample and the quantities of silver measured before recovery (Table-1).

In order to obtain the best results, the purity of silver recovered from the previous fixer solutions was analyzed as follows: An exact weight of silver was reacted with nitric acid until obtaining a clear solution. The solution was heated to rid of the extra nitric acid and was diluted to a definite volume. The purity of silver was determined using Atomic Absorption Spectrometer, as shown in Table-9.

TABLE-9
AVERAGE PURITY OF RECOVERED SILVER USING THE DIFFERENT REDUCING AGENTS

Reducing agent	Silver purity (%)
Aluminum platelets	98.13
Beverage cans alloy	96.21
Copper platelets	27.66
Iron cabinets platelet	90.65
Waste brass platelets	21.59

The concentrations of the remainder silver in the fixer solutions were also worked out after 6, 9 and 12 days of recovery process using all reducing agents and recorded in Table-10.

Despite the development of other accurate and quick methods, such as, the voltametric method for the determination of silver concentration in fixer solutions, the more accurate technique (atomic absorption spectrophotometer) was utilized to measure concentrations at (ppm) level.

The silver recovery process constitutes the replacement of silver ions with other metal ions leading to the anticipation of increased pollution. But, due to the higher molecular weight of silver (107) than that of all the other metals used in the recovery process, the amount of the recovered silver will be

greater than that of the oxidized metals or alloys that form ions of lower concentration than the silver ion. On the other hand, silver ion possesses 1 positive charge, whereas the other ions hold more positive charges, range from (+2) as in copper to (+3) as in aluminum and iron. Evidently, based on the end results, this method was found favourable, both economically and environmentally, as the silver element gets replaced with other worthless elements and of lower molecular weights according to the following chemical equation:

$$n\,Ag^{+} + M \rightarrow n\,Ag + M^{+n}$$

(n = 2,3; M = Al, Fe, Zn, or Cu)

TABLE-35
CONCENTRATION OF SILVER IONS REMAINED IN THE FIXER SOLUTIONS AFTER 6, 9 AND 12 DAYS OF RECOVERY USING THE DIFFERENT REDUCING AGENTS

Reducing Agent	pH	Remainder silver ion concentration in fixer solutions (mg/L; ppm)		
		6 Days	9 Days	12 Days
Aluminum platelets	Original	296	36	2.58
	4.5	496	38	4.11
	4.0	232	41	4.20
Beverage cans alloy	Original	170	20	2.15
	4.5	176	22	3.57
	4.0	146	16	1.68
Waste copper platelets	Original	144	21	0.6
	4.5	148	12	0.76
	4.0	150	14	1.31
Waste iron platelets	Original	182	32	6.89
	4.5	164	42	3.66
	4.0	160	52	3.81
Waste brass platelets	Original	174	35	2.59
	4.5	166	34	0.83
	4.0	190	24	0.86

Table-1 shows that all the collected fixer solutions have an acidity function lower than 7 (pH < 7) and therefore, metals and alloys can be used to recover silver from fixer solutions without the addition of acids to prevent dissociation of the fixers.

The concentration of silver ions in fixer solutions vary between the sources (hospitals and clinics) depending on the differing consumption of radiographic films. The work on Sample (C1) was discontinued as the concentration of silver was too low (0.173 g/ L), which was attributed to the use of fewer radiographic films.

Diluted sulphuric and hydrochloric acids were used rather than acetic acid, as much larger quantities are needed for the adjustment of the acidity of the solutions to the set pH values (4-4.5), besides its pungent odder that is to be avoided inside hospitals and clinics. The use of dilute nitric acid was also avoided as it may react with recovered silver.

The select pH range (4-4.5) was to avoid the dissociation of the fixer solutions at the pH range 2.5-3.5 as shown in Table-2. Concentrated acids must be diluted to avoid the dissociation of the thiosuphate ions[22].

Table-2 also shows that the amounts of acid required for the pH adjustment vary with the different hospitals and clinics. Such variation was attributed to the different preparation procedure of the fixer solutions.

The quantitative analysis of the beverage cans alloy indicated that aluminum was the main constituent as shown in Table 3.

The largest percentage yield of recovered silver (Table-8) were found by using the beverage cans in samples (H3, H5, C3) and in aluminum platelets in samples(C2, C4) and copper platelets in samples (H1, H2, H4) as shown in Table-8.

The purity analysis of the recovered silver (Table-9) indicate that the high values using the copper platelets do not represent the real amounts of silver and can rather be attributed to contamination with sulphide salts of the silver and copper metals. The appearance of black silver precipitates and the distinctive smell of hydrogen sulphide were clear indications to the undesirable contamination.

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