

بسم الله الرحمن الرحيم

SUDAN UNIVERSITY OF SCIENCE AND TECHNOLOGY

College of Graduate Studies

**Analysis of X-ray radiograph developer and fixer solutions
in their waste**

تحليل محاليل المظهرّ والمثبّت لأفلام الأشعة السينية في مخلفاتها

**A thesis submitted in partial fulfillment of the requirements of the
Degree of M.Sc in Chemistry**

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To
My mother and father,
My brothers and sisters

And

To all those without whom I would probably have gone astray. May God bless
them all and provide them with peaceful and prosperous life

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Abstract

Radiography is an important complementary tool used for diagnosis in health centers in many diagnostic laboratories in Sudan. However, during the radiographic processing, effluents are generated (developer, fixer, and wash water) posing an environmental threat, as such effluents contain organic and inorganic compounds that are toxic to the environment which unfortunately is the case in most private practices and teaching institutes where they are inappropriately disposed off. Therefore, this research aimed to determine the chemical parameters of X-ray radiograph developer and fixer in effluent and waste and to estimate the heavy metals present.

Samples of the developer and fixer solutions were taken after they have been used for developing and fixing X-ray radiographic film and subjected to analysis of physicochemical analysis using standard methods, whereas heavy metals were determined by atomic absorption spectrophotometry (AAS) and x-ray fluorescence (XRF).

The physicochemical parameters of developer and fixer were found to be 9.95 pH for developer and 4.90 for fixer, BOD 0.104mg/l for developer and 0.054 mg/l for fixer, COD 8.16mg/l for developer and 0.48 mg/l for fixer, TS 29.3mg/l for developer and 29.5mg/l for fixer, and TDS 29.3 mg/l for developer and 24.3 mg/l for fixer.

Atomic absorption spectrophotometric results showed that the fixer contained higher levels of silver (18 ppm) than that of developer (12.4 ppm). Iron content in developer was (7.2 ppm) and in fixer (6.5 ppm) and lead in developer was (6.5 ppm).

XRF revealed that the silver content in fixer was (16 ppm) whereas lead content was (8.8 ppm).

The results obtained call for development of treatment methods to reduce heavy metals content of radiographic film developer and fixer solution and also to recover their expensive silver content before their discharge.

المستخلص

التصوير الأشعاعي هي أداة تكميلية مهمة تستخدم للتشخيص في المراكز الصحية في العديد من مختبرات التشخيص في السودان. ومع ذلك ، أثناء المعالجة الإشعاعية للفلم (التحميض) ، تنتج نفايات سائلة (المظهر ، المثبت ، مياه الغسيل) و التي تشكل تهديداً بيئياً ، حيث تحتوي المخلفات السائلة على مركبات عضوية وغير عضوية سامة للبيئة والتي هي مع الأسف هو الحال في معظم الممارسات في المؤسسات التعليمية و الخاصة حيث يتم التخلص منها بشكل غير صحيح. ولهذا السبب ، يهدف هذا البحث إلى تحديد العوامل الكيميائية لمظهر و لمثبت أفلام الأشعة السينية في النفايات السائلة وتقدير المعادن الثقيلة الموجودة.

تم أخذ عينات من محاليل المظهر و المثبت بعد استخدامها لتظهير و تثبيت أفلام الأشعة السينية و اخضعت للتحليل الفيزيائي و الكيميائي باستخدام الطرق القياسية ، في حين تم تقدير المعادن الثقيلة باستخدام مطياف الامتصاص الذري و وميض الأشعة السينية.

تم الحصول على المتغيرات الفيزيائية والكيميائية للمظهر و المثبت لتكون ، درجة الحموضة 9.95 للمظهر و 4.90 للمثبت ، وحاجة الأوكسجين الحيوي 0.104 ملجم / لتر للمظهر و 0.054 ملجم / لتر للمثبت ، و حاجة الأوكسجين الكيميائي 8.16 ملجم / لتر للمظهر و 0.48 ملجم / لتر للمثبت ، و العوالق الصلبة الكلية 29.3 ملجم / لتر للمظهر و 29.5 ملجم / لتر للمثبت ، ومجموع العوالق الذائبة 29.3 ملجم / لتر للمظهر و 24.3 ملجم / لتر للمثبت.

أظهرت نتائج مقياس طيف الامتصاص الذري أن المثبت يحتوي على مستويات أعلى من الفضة (18 جزء في المليون) مقارنة بالمظهر (12.4 جزء في المليون). وكان محتوى الحديد في المظهر (7.2 جزء في المليون) وفي المثبت (6.5 جزء في المليون)، وكان الرصاص في المظهر (6.5 جزء في المليون).

كشفت نتائج تحليل وميض الأشعة السينية أن محتوى الفضة في المثبت كان (16 جزء في المليون) في حين أن محتوى الرصاص كان (8.8 جزء في المليون).

النتائج التي تم الحصول عليها تستدعي تطوير طرق المعالجة لتقليل محتوى العناصر الثقيلة من محاليل المظهر و المثبت في أفلام التصوير الإشعاعي و أيضا لاستعادة محتوى الفضة الباهظة في المحاليل قبل تفريغها.

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CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1:INTRODUCTION AND LITERATURE REVIEWS

1-1: Introduction

Radiographs are used for the diagnosis, and/or treatment of patients in the majority of the cases. Even with the advent of digital imaging there are a large number of diagnostic laboratories that use conventional methods to obtain the radiographic images. During the radiographic processing, effluents are generated (developer, fixer, and wash water) posing an environmental threat, as such effluents contain organic and inorganic compounds that are toxic to the environment in cases where they are inappropriately disposed of (Ues K et al, 2008).

Unfortunately, the conventional radiographic procedures generate certain substances that are present as potential challenge to the environment. Although an individual laboratory generates only small amount of environmentally hazardous wastes, the accumulated waste produced by the profession may have a significant environmental impact, which in turn may pose a risk to the human health. Thus, it becomes extremely important for the proper disposal of materials originated from conventional radiographic methods, in order to minimize the negative environmental impact (JyothirmaiKoneru et al, 2014).

A healthy environment is necessary for any organisms, since life depends upon the continuance of a proper exchange of essential substances and energies between the organisms and its surroundings. Water has a unique place on planet as it supports life on earth. The entire fabric of life is woven around it. Man uses this important resource collected in depressions on earth or creates depressions by blocking the streams and constructing reservoirs, because of industrial development and unplanned urbanization.

Health-care activities are a means of protecting health, curing patients and saving lives. But they also generate waste, 20 percent of which entail risks either of infection, of trauma or of chemicals or radiation exposure. The world is generating more and more waste, and hospitals and health centres are no exception. Medical waste can be infectious, contain toxic chemicals and pose contamination risks to both people and the environment.

Many chemicals and pharmaceutical products are used in health-care facilities; most of them entail a health risk due to their properties (toxic, carcinogenic, mutagenic, reprotoxic, irritant, corrosive, sensitizing, explosive, flammable, etc.). There are various exposure routes for contact with these substances: inhalation of gas, vapour or droplets, contact with the skin or mucous membranes, or ingestion. Some substances (such as chlorine and acids) are incompatible and can generate toxic gases when mixed (Medical waste management, 2011).

1-2: Problem

The amount of developer and fixer solutions utilized in radiographic centers varies according to the size of the industrial radiography service and to the number of acquired images. Generally, large industrial radiography receives a large flow of images and consequently utilizes a great amount of developer and fixer solutions, consequently generating a greater volume of radiographic processing effluents.

On the other hand, small industrial radiography performs a lower number of examinations, using a smaller amount of developer and fixer solutions, consequently generating lower amounts of radiography processing effluents. However, as at such small services the generated effluent amount is usually small, many times it is disposed of directly into sinks, thus reaching the sewer system without any previous treatment.

1-3: Literature reviews

1-3-1: Parameter of water quality

Quality of water is important for drinking, irrigation, fish production, recreation and other purposes. The water quality deterioration in reservoirs usually results from acidification, heavy metal contamination, organic pollution, obnoxious fishing practices and excessive nutrient input that leads to nutrients. The effects of these inputs into the reservoir do not only affect the socio-economic functions of the reservoir negatively, but also lead to the loss of structural biodiversity of the reservoir. The physicochemical properties of water quality assessment give a proper indication of the status, productivity and sustainability of a water body (Djukic, N. *et al.*, 1994). The changes in the physicochemical characteristics like temperature, transparency and chemical elements of water such as dissolved oxygen, nitrate and phosphate provide valuable information on the quality of the water.

Hence, the consideration of the physicochemical factors in the study of waste water is a basis for the understanding of trophic dynamics of the water body. The physical and chemical properties of water immensely influence its uses, the distribution and richness of the biota (Unanam, A.E and Akpan, 2006). Each factor plays its own role but at the same time the final effect is the actual result of the interactions of all the factors. These factors serve as a basis for the richness or otherwise biological productivity of any aquatic environment (Imevbore, A.M.A, 1970). The following physico-chemical parameters are considered:

1-3-1-1: pH

Hydrogen ions (acidic) as well as hydroxyl ions (alkaline) are the result of the ionization of water. Any change in the concentration of any one of these ions brings about a change in the concentration of the other. Therefore, the pH scale is used to measure the acidity or alkalinity of water. The pH changes in water are governed by the amount of free CO₂, carbonates and bicarbonate. These changes are accompanied by the changes in other physicochemical aspects that in turn influence quality of water.

1-3-1-2: Chemical oxygen demand (COD)

COD is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. COD measurements are commonly made on samples of waste waters or of natural waters contaminated by domestic or industrial wastes.

1-3-1-3: Biochemical oxygen demand (BOD)

BOD is a chemical procedure for determining the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. Biological Oxygen Demand (BOD) test is useful in determining the relative waste loading and higher degree therefore indicates the presence of large amount of organic pollutant and relatively higher level of microbial activities with consequent depletion of oxygen content.

1-3-1-4: Total solids (TS), total suspended solids (TSS) and total dissolved solids (TDS)

Total solids is the term applied to the materials left in a vessel after evaporation of a water sample on its drying in the oven at a defined temperature. While TSS is the material left in a vessel after filtration of a water sample. Total suspended solids range in size from colloidal to coarse dispersions and range from pure organic substances to those that are highly organic in nature. The TDS consist of the material left in a vessel after evaporation of filtered sample and include different kinds of nutrients and minerals which are considered as useful parameters in determining the productivity of reservoir (Reid GK, 1961).

1-3-2:Health-care waste

Health-care waste includes all the waste generated by health-care establishments, research facilities, laboratories and or diagnostic activities. In addition, it includes the waste originating from “minor” or “scattered” sources. Chemical waste of health-care consists of discarded solid, liquid, and gaseous chemicals, for example from diagnostic and experimental work and from cleaning, housekeeping, and disinfecting procedures (WHO, 1983).

1-3-2-1:Chemical waste

Chemical waste consists of discarded solid, liquid, and gaseous chemicals, for example from diagnostic and experimental work and from cleaning, housekeeping, and disinfecting procedures. Chemical waste from health care may be hazardous or nonhazardous; in the context of protecting health, it is considered to be hazardous if it has at least one of the following properties:

- toxic;
- corrosive (e.g. acids of pH < 2 and bases of pH > 12);
- flammable;
- reactive (explosive, water-reactive, shock-sensitive);
- genotoxic (e.g. cytostatic drugs).

Nonhazardous chemical waste consists of chemicals with none of the above properties, such as sugars, amino acids, and certain organic and inorganic salts (Chih-Shan L and Fu-Tien J, 1993).

The types of hazardous chemicals used most commonly in maintenance of health-care centres and hospitals and the most likely to be found in waste are discussed in the following paragraphs:

1-3-2-1-1: Formaldehyde

Formaldehyde is a significant source of chemical waste in hospitals. It is used to clean and disinfect equipment (e.g. haemodialysis or surgical equipment), to preserve specimens, to disinfect liquid infectious waste, and in pathology, autopsy, dialysis, embalming, and nursing units.

1-3-2-1-2: Photographic chemicals

Photographic fixing and developing solutions are used in X-ray departments. The fixer usually contains 5–10% hydroquinone, 1–5% potassium hydroxide, and less than 1% silver. The developer contains approximately 45% glutaraldehyde. Acetic acid is used in both stop baths and fixer solutions.

1-3-2-1-3: Solvents

Wastes containing solvents are generated in various departments of a hospital, including pathology and histology laboratories and engineering departments. Solvents used in hospitals include halogenated compounds, such as methylene

chloride, chloroform, trichloroethylene, and refrigerants, and non-halogenated compounds such as xylene, methanol, acetone, isopropanol, toluene, ethyl acetate, and acetonitrile.

1-3-2-1-4: Inorganic chemicals

Waste inorganic chemicals consist mainly of acids and alkalis (e.g. sulfuric, hydrochloric, nitric, and chromic acids, sodium hydroxide and ammonia solutions). They also include oxidants, such as potassium permanganate (KMnO_4) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), and reducing agents, such as sodium bisulfite (NaHSO_3) and sodium sulfite (Na_2SO_3) (Halbwachs H, 1994).

1-3-2-1-5: Wastes with high content of heavy metals

Wastes with a high heavy-metal content represent a subcategory of hazardous chemical waste, and are usually highly toxic. Mercury wastes are typically generated by spillage from broken clinical equipment but their volume is decreasing with the substitution of solid-state electronic sensing instruments (thermometers, blood-pressure gauges, etc.). Whenever possible, spilled drops of mercury should be recovered. Residues from dentistry have high mercury content. Cadmium waste comes mainly from discarded batteries. Certain “reinforced wood panels” containing lead is still used in radiation proofing of X-ray and diagnostic departments. A number of drugs contain arsenic, but these are treated here as pharmaceutical waste.

1-3-3: Processing the radiograph

When an X-ray film has been exposed, it must be processed in order to produce a permanent visible radiographic image that can be kept without deterioration for a number of years. Processing transforms the latent image into a visible image. The term for the several procedures that collectively produce the visible, permanent image is processing and consists of developing, rinsing, fixing, washing and drying procedures (Minnesota pollution control agency, June 2011)

1-3-3-1: Exposure (Latent image formation)

The latent (invisible) image formation is the ionization of the exposed silver bromide crystals (by photon energy that emerges from the patient) occurring in the emulsion layer before processing occurs. The primary interaction with the bromide crystals is by Compton and photoelectric interactions, thereby knocking out electrons. Thus, a physical change occurs when the radiograph is exposed. When X-ray photons [or light photons] strike the silver bromide crystals in the emulsion, minute amounts of silver ions are formed on the surface of the crystal and bromine is liberated and is absorbed by the gelatin. Crystals are purposely constructed with electron traps (sensitivity specks) consisting of sulfur impurities but also because of the addition of silver iodide. Electrons are trapped by the sulfur in the sensitivity specks giving it a negative charge. When this situation is created a latent image is produced in the film emulsion.



The latent image is formed by deposits of free (ionized) silver ions that cannot be seen or detected by any physical test devised as yet. It remains in the emulsion of the X-ray film until it is changed into a visible silver image by chemical processing procedures. The free electrons move through the crystal until they are

attracted to a sensitivity site where they become trapped and impart a negative charge to the site.

1-3-3-2: Processing the exposed film

The developer solution is the first solution into which the films are placed. The developer chemically reduces the energized ionized silver bromide crystals by donating electrons, removing the halides and precipitating metallic silver in the emulsion layer. The negative charge attracts positively charged free silver ions and is reduced to black metallic atoms.

This precipitation corresponds to the black (radiolucent) areas on the radiograph. The concentration of the developer slowly weakens due to the number of films processed, [a chemical reaction] and with time by oxidation of the developer by exposure to air. Traditionally, the developer tank is placed on the left side of the other chemicals solutions.

1-3-3-3: Rinsing process

When the film is removed from the developer the gelatin emulsion is soft and swollen and contains chemicals which are removed by placing the film in a water bath. By rinsing the film in the water the soluble chemicals are removed, the development reaction is stopped, and the alkalinity of the residual developer is reduced. The unexposed silver halide crystals are not water soluble and will not be washed away. The film should be rinsed for 10-15 seconds in a bath of fresh, running water. The temperature of the water must be as close as possible to the temperature of the developer and fixer to avoid reticulation - uneven expansion and contractions of the emulsion layer. If this step were omitted, the alkaline developer retained by the film would soon neutralize the acid of the fixer. The fixing and hardening action of the fixer would be impaired and as a result, brown stains will be

produced on the radiograph within a few weeks. Because the emulsion layer (gelatin) is soft when wet, the film scratches easily.

1-3-3-4: Fixing

The acidic fixing solution removes the unexposed and undeveloped silver bromide crystals from the film emulsion and re-hardens the emulsion that has softened during the development process. The gelatin protective coating is hardened by the potassium alum so the film will resist abrasion / scratching.

1-3-3-5: Photo wash

The purpose of the final wash is to remove residual fixer chemicals i.e. acid, thiosulfate and silver salts from the film. Insufficient washing results in the film turning brown as all the chemicals have not been washed away.

1-3-3-6: Drying

In most offices, films are dried merely by hanging them on a rack in the darkroom above a drip tray designed to catch the run-off excess water. Others use a fan to dry the film.

1-3-3-7: Processing chemicals

Table 1-1: Contents of Processing chemicals (developer and fixing solution)

Chemical	Action
Developer (reducing agent)	
Hydroquinone (Elon or metol)	Brings out sharp contrast. The reducer acts slowly is a benzene product and made from dyes acts faster [phenidone - is now often used instead of elon or metol] This reaction can only occur in an alkaline medium
Alkalizer (Accelerator - Na_2CO_3) (The reaction does not occur unless alkalizer is present)	Provides alkaline medium in which the reducer reacts. It softens and swells the gelatin emulsion and attracts the exposed silver bromide crystals
Preservative (Na_2SO_3)	Slows oxidation and therefore preserves the strength of the other chemicals If not present the strength of the other chemicals would rapidly weaken. This explains the darkening of the solution
Restrainer (KBr)	Restrains the developing agent from the strength. The developing agent will deposit silver in the unexposed crystals in the emulsion causing a silver deposit (fogging) on the film if the restrainer is

	not added
Vehicle (water)	Provides a means for the chemicals in the developer to react (Ionize). Water helps to soften gelatin
Fixing solution	
Fixing Agent (Sodium Thiosulfate) (hypo)	Removes unexposed crystals
Ammonium Thiosulfate	Removes all crystals
Preservative (Sodium sulfite)	Prevents deterioration of solution
Hardening agent (Potassium alum)	Shrinks and hardens the gelatin
Acidifier (Acetic acid)	Provides acid medium. Alum reacts better in acid medium. Stops developing process

1-3-4: Radiographic processing effluents

There is a closer link between pollution and health damages. Five million people die each year because of polluted drinking water, poor sanitation and domestic unhygienicity around the world (Anon, 1996).

Radiography is an important complementary tool used for diagnosis in health centers in many diagnostic laboratories in Sudan. However, during the radiographic processing, effluents are generated (developer, fixer, and wash water) posing an environmental threat, as such effluents contain organic and inorganic compounds that are toxic to the environment which unfortunately is not the case in most private practices and teaching institutes where they are inappropriately disposed off.

in a case study developed in a hospital carried out by Carlson, AM. (2007), it has observed that chemical residues such as developer, fixer solutions and xylene leftovers were inappropriately stored in the place where they were generated and were later taken into the basement of the building, where they were left under unsafe conditions, in an unventilated area, without containment means and over permeable floor .

As regards storage time elapsed before the developer and fixer solution wastes were sent for treatment, the respondents revealed that such elapsed time ranged from one week to one year, which is considered a long period as such solutions must be stored for the shortest possible time avoiding accumulation.

As regards radiographic processing effluents treatment and disposal, it was observed that direct disposal of radiographic processing effluents into the public sewer system, without any kind of previous treatment was done by two services (16.66%) for developer, by one service (8.33%) for fixer solution, and by nine other services (75%) for film wash water. Such findings are very worrisome where the film wash water effluents were directly disposed of into the public sewer system without any previous treatment.

1-4: Objectives

- To determine the physicochemical characteristics of X-ray radiograph developer and fixer in effluent.
- To determine the concentration of the heavy metals.

CHAPTER TWO

MATERIALS AND METHODS

2: Materials and Methods

2-1: Materials

2-1-1: Chemicals

All chemicals used were analytical grade; from Sharlauchemie, European Union.

Ammonium chloride, ferric chloride, magnesium sulfate, manganese sulfate, Sulphuric acid (conc.), and potassium dichromate, Potassium dihydrogen phosphate, sodium thiosulphate, sodium thiosulphate, iodine, and salicylic acid.

2-1-2: Standard solutions preparation

2-1-2-1: Preparation of biochemical oxygen demand nutrients

2-1-2-1-1: Phosphate buffer solution

The buffer solution was prepared by dissolving 8.5g of Potassium dihydrogen phosphate (KH_2PO_4), 21.75g of dipotassium hydrogen phosphate (K_2HPO_4), 33.4g of disodium hydrogen phosphate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$) and 1.7g ammonium chloride (NH_4Cl) in about 500ml distilled water and diluting to liter.

2-1-2-1-2: Magnesium sulfate solution

22.5g of anhydrous $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in distilled water and diluted to 1 litre.

2-1-2-1-3: Ferric chloride solution

0.25g of ferric chloride hexahydrate $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water and diluted to 1 liter.

2-1-2-1-4:Manganese sulfate solution

22.5g $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ was dissolved in distilled water, filtered and diluted to 1 liter.

2-1-2-2:Starch indicator

0.25g of soluble starch powder and 0.28g of salicylic acid as preservative in distilled water. Pour this solution in 100ml boiling distilled water. Continue boiling for a few minutes, cool and then use.

2-1-2-3: Standard sodium thiosulphate titrant

6.20g of $\text{Na}_2\text{S}_2\text{O}_3$ dissolved in distilled water. Added 1.5ml 6N NaOH and diluted to 100ml standardize with iodine solution.

2-3:Instruments

- pH meter, Mettler Toledo 320 model according to APHA,
- X-ray fluorescence (XRF),
- Atomic absorption Spectrophotometer

2-4: Samples

Samples of the developer and fixer solutions were taken after been used for developing and fixing X-ray radiographic film in Petroleum training centre (PTC).

2-2: Methods

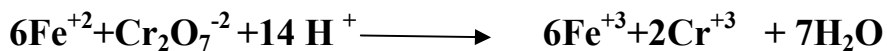
2-2-1:pH

The pH was measured directly in the effluent channel and in the stream using a pH meter.

2-2-2:Chemical oxygen demand (COD)

Most types of organic matter are oxidized by a boiling mixture of chromic and sulphuric acid. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate $K_2Cr_2O_7$. After digestion the excess was determined and the oxidizable amount is calculated in terms of oxygen equivalent.

Ferrous ion from ferrous ammonium sulfate is an excellent reducing agent for dichromate. In solution, however Fe^{+2} is slowly oxidized by oxygen and so standardization must be performed every time prior to titration. The standardization is made with 0.25 N solution of dichromate:



Chemical oxygen demand (COD) is the amount of oxygen required to completely oxidize the organic matter in waste water by use of a strong oxidant and to convert it to carbon dioxide and water. Potassium dichromate was used in this test because of its superior oxidizing ability. A known quantity of water sample was mixed with a known quantity of standard solution of potassium dichromate ($K_2Cr_2O_7$) and the mixture was heated. The organic matter was oxidized by the potassium dichromate in the presence of Sulphuric acid (H_2SO_4) and the oxygen used in oxidizing the water was determined.

2-2-3: Biochemical oxygen demand (BOD)

Biochemical oxygen demand (BOD) was determined by conventional methods according to Association of Official Analytical Chemists (AOAC). A sample of the solution (50 ml) was placed in a 500 ml BOD bottle and filled to the mark with previously prepared dilution water. A blank solution of the dilution water was similarly prepared and placed in two BOD bottles.

A control solution without dilution water was also prepared and placed in a BOD bottle. The bottles were stoppered, sealed and incubated for five days at room temperature. BOD was calculated from the relation:

$$\text{BOD} = (D1 - D2) / P$$

Where:

D1= dissolved oxygen 15 minutes after preparation

D2= dissolved oxygen in diluted sample after incubation, and
P= amount of sample used.

2-2-4: Totalsolids (TS)

Residue left after the evaporation and subsequent drying in oven at specific temperature 103-105°C of a known volume of sample are total solids. Total solids include “Total suspended solids” (TSS) and “Total dissolved solids” (TDS). Whereas loss in weight on ignition of the same sample at 500°C, 50°C, in which organic matter is converted to CO₂ volatilization of inorganic matter as much as consistent with complete oxidation of organic matter, are volatile solids.

2-2-5: Metals analysis

2-2-5-1: Atomic absorption

2-2-5-1-1: Digestion of the samples

100 cm³ of each of the representative water samples were transferred into Pyrex beakers each containing 10 cm³ of concentrated HNO₃. The samples were boiled slowly and then evaporated on a hot plate to the lowest possible volume (about 20ml). The beakers were allowed to cool and another 5 cm³ of conc. HNO₃ was added to each.

Heating was continued with the addition of conc. HNO_3 as necessary until digestion was complete. The samples were evaporated again to dryness (but not baked) and the beakers were cooled, followed by the addition of 5 cm^3 of HCl solution (1:1 v/v). The solutions were then warmed and 5ml of 5M NaOH was added, then filtered. The filtrates were transferred to 100 cm^3 volumetric flasks and diluted to the mark with distilled water. These solutions were then used for the elemental analysis.

A total of eight metallic elements were determined in the pre – treated samples of water using atomic absorption Spectrophotometer as described by Gregg, (1989).

These include gold (Au), iron(Fe), chromium (Cr), Silver (Ag), Bismuth(Bi), Molybdenum (Mo),Zinc (Zn)and lead (Pb).

2-2-5-2: X-ray fluorescence (XRF)

2-2-5-2-1: Digestion of the samples

First we calibrate the equipment by low alloy fabrication block. 30 ml of both developer and fixer solution are put in a sample air free plastic cup and positioning in front of the window of the analyzer then exposed to x-ray fluorescent in a near position to minimize the errors for five seconds with average of three readings.

From the inspection we found gold (Au), iron (Fe), Silver (Ag), Bismuth (Bi), Molybdenum (Mo),lead (Pb), Antimony (Sb), Niobium (Nb), Zirconium (Zr),Stannum(Sn) and Selenium (Se).

CHAPTER THREE

RESULTS AND DISCUSSION

3: Results and Discussion

The results obtained from the analysis of the physicochemical parameters of the samples of wastewater collected are presented in Table 3-1 and the concentrations of heavy metals are shown in Table 3-2, Table 3-3 and Table 3-4.

3-1: Results

3-1-1: pH

pH is a measure of the acid balance of a solution. The pH of water affects the solubility of many toxic and nutritive chemicals. The pH values of the developer solution and fixer solution are recorded in (Table 3-1).

3-1-2: Electrical conductivity

Is an important parameter for determining the water quality for drinking and agricultural purposes.

Many dissolved substances may produce esthetically displeasing colour, taste and odour. The average values of the developer solution and fixer solution are shown in Table 3-1.

3-1-3: Total dissolved solids (TDS)

TDS values are useful to determine whether water is suitable for drinking purpose, agriculture and industrial purposes. The TDS values in the developer solution was 29.3mg/l in the fixer solution was 42.3mg/l. Both values are below the maximum Sudanese standard limit.

3-1-4: Total solids (TS)

Total solids of developer solution were 29.3mg/l and of fixer solution 29.3mg/l. Both values are within the permitted limits of Sudanese standard.

3-1-5: Biochemical oxygen demand (BOD)

BOD is a chemical procedure for determining the amount of dissolved oxygen needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at certain temperature over a specific time period. Biological Oxygen Demand (BOD) test is useful in determining the relative waste loading and higher degree; therefore it indicates the presence of large amount of organic pollutant and relatively higher level of microbial activities with consequent depletion of oxygen content. A high BOD value suggests more waste products or pollutants are present in the effluent. The concentration of BOD in the developer solution and fixer solution was 0.104 mg/l and 0.054mg/l, respectively. Both values are below the maximum effluent limit standard set by Sudanese standard.

3-1-6: Chemical oxygen demand (COD)

COD is a measure of the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic chemicals such as ammonia and nitrite. COD measurements are commonly made on samples of waste waters or of natural waters contaminated by domestic or industrial wastes.

The COD value of the developer solution (8.16mg/l) and fixer solution (0.48mg/l) are below the effluent limit standard (250mg/l) set by Sudanese standard largely as a result of the low COD values of the waste water which was channeled without treatment into the observation ponds.

3-1-7:Heavy metals

Gold, iron,chromium,silver,bismuth, molybdenum, zincand lead heavy metals in developer and fixer solutions were determined by atomic absorption spectrometry (Table. 3-2).

Apart from heavy metal levels in developer and fixer solutions of zinc (4.3ppm and 1.4ppm), the levels of iron (7.2ppm and 6.5ppm),chromium, silver (12.4ppm and 18ppm),respectively, were higher than the maximum limit of Sudanese standard.TheConcentrations in water samples are presented in table (2).Heavy metal concentration in water samples measured in ppm ranges from Nil to 1.42ppm. Generally, the concentrations of heavy metals were within the Sudanese Standard.

Table3-1: physicochemical analysis of parameters of the Developer Solution and Fixer Solution

No	Parameter	Developer Solution	Fixer Solution	Permissible range(maximum)
1	pH	9.95	4.90	6-9
2	E.C (μs)	60.90	85.9	-
3	Total solids (T.S.)(mg/l)	29.3	29.5	200
4	Total Dissolve Solids(TDS)(mg/l)	29.3	42.3	1500
5	Biochemical Oxygen Demand (BOD)(mg/l)	0.104	0.054	100
6	Chemical oxygen demand(C.O.D)(mg/l)	8.16	0.48	250

Table3-2: Meanconcentration (ppm) of heavy metals extracted by aqua digestion from developerand fixer solution and determined by AAS

Elements (PPM)	DeveloperSolution (PPM)	FixerSolution (PPM)	SudaneseStandard (PPM)
Gold(Au)	4.2	1.2	-
Iron (Fe)	7.2	6.5	1
Chromium (Cr)	3.1	11.2	0.1
Silver (Ag)	12.4	18	0.5
Bismuth (Bi)	4.3	2.2	-
Molybdenum(Mo)	4.3	3.5	-
Zinc(Zn)	4.3	1.4	5
Lead(Pb)	6.5	N.D*	0.015

N.D: not detect

Table3-3: Developer solution XRF detection by X-MET5000, amount 30 ml, exposure time 5seconds average of three readings:

Metal	Conc.	S.TD.
Lead(Pb)	47.8%	0.257
Antimony(Sb)	10.8%	0.871
Iron (Fe)	3.3%	0.072
Nubidium(Nb)	2.6%	0.743
Zirconium(Zr)	2.6%	3.296
Gold(Au)	21.7%	0.003
Stannous(Sn)	8.1%	1.421
Molybdenum(Mo)	3.2%	1.538
Bismuth (Bi)	1.3%	1.546
Selenium(Se)	0.3%	0.322

*STD: standerd deviation (tolerance of element detection).

Table3-4:Fixer solution XRF detection by X-MET5000, amount 30 ml, exposure time 5seconds average of three readings

Metal	Conc.	ST.D.
Silver (Ag)	66.9%	0.259
Gold(Au)	8.0%	0.990
Iron (Fe)	3.2%	0.098
Nubideum(Nb)	0.5%	1.040
Lead(pb)	13.6%	3.325
stannous(Sn)	6.8%	1.008
Molybdenum(Mo)	0.6%	1.091
Bismuth (Bi)	0.4%	2.330

*ST.D.: standerd deviation (tolerance of element detection).

Table3-5: Comparison between atomic absorption and x-ray fluorescent (XRF) method

Method	Detection of heavy metals
Atomic absorption	<p>Each element has specific sensor (lamp) for each element detection according to the wave length.</p> <p>Heavy element detected by atomic absorption are : gold (Au), iron (Fe), chromium (Cr), Silver (Ag), Bismuth (Bi), Molybdenum (Mo), Zinc (Zn) and lead (Pb) in both Fixer and developer.</p>
X-ray fluorescent	<p>A characteristic X-ray (X-ray fluorescent) is used as a sensor for detection of element according to the spectra of exposed element.</p> <p>Heavy metals detected by XRF are : gold (Au), iron (Fe), Silver (Ag), Bismuth (Bi), Molybdenum (Mo), lead (Pb), Antimony (Sb), Niobium (Nb), Zirconium (Zr), Stannum (Sn) and Selenium (Se).</p>

Notes:

*All elements detected by atomic are also detected by XRF except Antimony (Sb) Zirconium (Zr), Stannum (Sn) and Selenium (Se) are detected by XRF only.

*From the above result we can say that XRF is more widerange of detection.

3-2: Conclusion

With the exception of the physicochemical properties the developer and fixer solution, the heavy metal content in both solutions of iron, chromium, silver and lead (in developing solution) did not conform to Sudanese standard.

3-3: Recommendations

The heavy metal concentration of X-ray chromatograph and fixer solution necessitates, before its discharge, developments of treatment methods to reduce its heavy metal content and to recover its expensive silver content.

References

Anon, Water and sanitation; WHO fact sheet No.112, World Health Organization, (1996).

APHA standard methods for the analysis of water and waste water, 20th Edition.

Bortoletto EC, Tavares CRG, Barros MASD, et al. Caracterização da geração e da qualidade do efluente líquido gerado no laboratório de raio-x da clínica odontológica do Hospital Universitário de Maringá (HUM). Anais do VI Congresso Brasileiro de Engenharia Química em Iniciação Científica: 1–6; Campinas, SP, Brasil; (2005).

Carlson AM. Gerenciamento de resíduos químicos em ambientes hospitalares: necessidades e dificuldades: estudo de caso: Hospital Universitário localizado no Estado do Rio de Janeiro [dissertação]. Rio de Janeiro, RJ: Universidade do Estado do Rio de Janeiro; (2007).

Chih-Shan L, Fu-Tien J. Physical and chemical composition of hospital waste. Infection control and hospital epidemiology, 14(3):145–150, (1993).

Copenhagen, World Health Organization Regional Office for Europe (EURO Reports and Studies, No. 97). (1985).

Djukic, N., Maletin, S., Pujin, V., Ivanc, A. and Milajonovic, B. Ecological assessment of water quality of Tisza by physico-chemical and biological parameters. Tisza Szeged, 28(1): 37-40, (1994).

Fernandes GS, Azevedo ACP, Carvalho ACP, et al. Análise e gerenciamento de efluentes de serviços de radiologia. Radiol Bras.; 38:355–8, (2005).

Gregg, L.W.: Water analysis Handbook. H.A.C.H Company, USA. Pp. 33 – 39, (1989).

Halbwachs H. Solid waste disposal in district health facilities. World health forum, 15:363–367,(1994).

Imevbore, A.M.A. Some Preliminary observations on the ratios and fecundity of the fish in River Niger. In: S.A Visser (ed) Kainji Lake Studies. Vol. I, Ecology, S.A Visser (ed) 87-88, (1970).

JyothirmaiKoneru ,NehaMahajan , MallikaMahalakshmi. Management of dental radiographic waste. DJAS 2(II), 55-58,(2014).

Managing Photographic and X-ray Waste, Minnesota pollution control agency, June (2011).

Medical waste management, International Committee of the Red Cross, ICRC, Geneva,(2011).

Reid, G. K.,Ecology in inland waters and estuaries. New York.375,(1961).

Sudanese standard SDS 0173-2013, Liquid industrial waste within facility, (2013).

Ues K, Piaia L, Schweickardt M, et al. Uso de processos avançados de oxidação e degradação dos resíduos de revelador e fixador de raio-x. Anais do XVI Encontro de Química da Região Sul; 13 a 15 de novembro de 2008; Blumenau, SC, Brasil; (2008).

Unanam, A.E. and Akpan, A.W Analysis of physicochemical characteristics of some freshwater bodies in EssienUdim Local Government area of AkwaIbom State, Nigeria. In: Proceeding of the 21st Annual Conference of the Fisheries Society of Nigeria (FI50N) Calabar, 13th -17th November, (2006).

WHO.Management of waste from hospitals and other health care establishments.
Report on a WHO meeting, Bergen, 28 June–1 July (1983).