Sudan University of Science and Technology

College of Graduate Studies

Automation of the Treatment of Hexavalent Chromium In Waste Water

اتمتة عملية معالجة الكروم سداسي التكافؤ في المياه العادمــة

A thesis submitted to the Graduate College, in fulfillment of requirement of the degree of Master of Science in chemistry

By

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Detication

This work is dedicated

To my parents, my Brothers, Collogues, and to all those I love

I also dedicate this research to all patient researchers who still working to extract facts.

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Firstly, with full pleasure I would like to send the greatest thanks to Allah almighity in completion of this research in spite of all difficulties that faced me.

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ABSTRACT

There has been great demand for development of technologies that remove toxic heavy metal ions from wastewater. Chemical precipitation operation is known to remove heavy metal ions from water. In this Research studying the reduction and separated of hexavalent chromium (which is very toxic heavy metal) from waste water ,and the automation of the process was undertaken. Reduction process is done by adding suitable quantity of sodium bisulfite solution to waste water in pH range 2.0 - 2.5 after acidifying the media with solution of sulfuric acid. The trivalent chromium ions were then precipitated by adding sodium hydroxide which increases the alkalinity of the solution up to the pH value 10.0.The size of chromium hydroxide crystal enlarged by adding flocculent solution. Then the treated waste water solution filtered to separate chromium hydroxide flocculated crystals. The pH of remaining treated waste water is reduced to pH 7.0 and discharged directly to the sewage.

Experimental works was carried out to determine the exact value of solution potential in ml volts during treatment process steps. The standard solutions after prepared were treated ideally to determine the end points of the reactions in ml volts.

Sepotrrato 100R is one of intelligent systems which were developed for treatment of waste water from electroplating processes. The Electroplating Department,Sudan Currency Printing Press, waste water usually contain many heavy metals ions such chromium, and nickel. This Sepotrrat 100R was recalibrated and programmed according to research finding, for reactions end points.

مستخلص البحث

مع ازدياد الطلب على استخدام التكنلوجيا الحديثة لفصل العناصر الثقيلة من المياه الملوثة بها، هذه الدراسة ركزت على معالجة المياه الملوثه بعنصر الكروم سداسي التكافؤ المعروف بمدى سميته العالية. يتم اختزال الكروم سداسي التكافؤ كيميائياًوترسيبه في شكل هيدركسيدالكروم ثلاثي التكافؤ ومن ثم فصله فيزئيا.

عملية الاختزال تتم باضافة كمية كافية من محلول بيكبريتات الصوديوديم الهيدروجينيه في محلول ذو طبيعة حمضية يتراوح الاس الهيدروجيني pH فيه ما بين (٢-٢,٥) وذلك بعد اضافة كمية مناسبة من حمض الكبريتيك. عملية الاختزال يتم متابعتها عن طريق التغير في جهد الاختزال redox potential التي يتم تسجيلها بواسطة الكترود خاص لعمليات الاكسدة والاختزال redox Electrode . بعد اكتمال عملية الاختزال يتم ترسيب الكروم ثلاثي التكافؤ في شكل هيدروكسيد الكروم وذلك باضافة كمية كافية من محلول هيدروكسيد الصوديوم حتى يكتسب المحلول خاصية قاعدية ويترواح الاس الهيدروجيني pH مابين (١٠-١٠,٥).ومن ثم يضاف محلول الفولكولانت لزيادة حجم جزئية هيدروكسيد الكروم ثلاثي التكافؤ ليرشح بعدها ويفصل من المحلول. بعدها يضاف قليل من حمض الكبريتيك للمحلول حتى يصل الpH الى مابين (٧-٨) ليرسل بعدها مباشرة الى مجاري الصرف الصحي.

كل هذه العمليات تتم في نظام ال100 Septrtato في خطوات منفصله تتم برمجتها حسب طبيعة التفاعل يمكن رصدها اوتوماتيكيابواسطة اجهزة الtransmitter التي زود بها الجهاز وذلك لتسهيل عملية التشغيل.

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List of Abbreviation

No	phrase	Abbreviation
1	The World Health Organization	WHO
2	Environmental Protection Agency USA	EPA
3	Oxidation-reduction potential	ORP
4	SEPOTRATT 100R EFFLUENT TREATMENT PLANT	S100RETP
5	Treatment Tank	TT
6	Collecting Tank	CT
7	Storage Tank	ST
8	Molarity of Oxidizing Agent	M_{Ox}
9	Volume of Oxidizing Agent.	V_{Ox}
10	Number of mole of Oxidizing Agent.	n_{Ox}
11	Molarity of Reducing Agent.	M_{Re}
12	Volume of Reducing Agent.	V_{Re}
13	Number of mole of Reducing Agent.	N_{Re}

Content

CHAPTER ONE

Introduction

1.1Chromium:

Chromium is a hard, brittle, lustrous metal that is very resistant to corrosion. That is why it is used as a protective coating over steel for automobile bumpers. Thin layers of chromium are also deposited by electroplating on brass or bronze for decorative purposes.

One of the principal uses of chromium is in stainless steel, a type of steel that is very resistant to corrosion. A typical stainless steel contains about 19% chromium, 9% Nickel, and rest iron. Unlike ordinary iron and steel, a high quality stainless steel is not ferromagnetic. A small magnet is therefore a handy tool to check whether or not a metal object claimed to be made of stainless steel is, in fact, composed of this alloy.

The principal oxidation states of chromium are (II), (III), and (VI). The (II) state characterized by blue Cr^{+2} ions in aqueous solution is very easily oxidized to the (III) state, which is the most stable oxidation state.

The most important compound of chromium (III) is oxide, Cr_2O_3, the most stable pigment known. It is used for coloring paints, roofing shingles, cements, and plaster. Chromium (III) ion forms many stable complex ions, and in aqueous solutions it actually exists as violet complex ion, $Cr(H_2O)^{+}$.This ion is what that gives many chromium (III) salts their violet color.[1]

Chromium (Cr) exists in several oxidation states, but the most stable are trivalent Cr(III) and hexavalent Cr(VI) species, with different chemical

characteristics and biological effects (Cervantes, 2001).Chromium is an essential trace metal, but overexposure to Cr(VI) produce allergic dermatitis; ulceration in the skin, mucous membranes and nasal septum; renal tubular necrosis; and increase risks of respiratory-trace cancer and cytotoxic and genotoxic effects.[2]

Chromium is naturally found in soils in it's trivalent form Cr(III), but Cr(VI) is widely used in industry such as leather tanning, electroplating, paint pigment and dye manufacturing, and steel and automobile production. Cr (VI) is also found in nuclear waste at Department of energy (DOE) facilities. The hexavalent form of Cr is highly soluble, mobile, and consequently is a high bioavailability in the environment as potential soil, surface water, and ground water contaminant. [2]

Total chromium content typically range from 0.1 to 0.05μg/L in seawater, from 0.3 to 0.6 μ g/L in non-polluted river and surface water, whereas it can reach 200 μ g/L in severely polluted water system.[3]

1.2 Chromium Toxicity:

Chromium contamination of surface and ground water is a persisting problem in many countries[4]. Chromium enters the air, water, and soil mostly in the chromium (III) and chromium (VI) forms. In air, chromium compounds are present mostly as fine dust particles which eventually settle over land and water. Chromium can strongly attach to soil and only a small amount can dissolve in water and move deeper in the soil to underground water. Fish do not accumulate much chromium in their bodies from water.

The most important source of chromium pollution is industrial. Industries that use large amounts of chromium as chromate or dichromate are the textile, leather, and metal finishing (for corrosion protection) industries. [5]

Chromium (III) is an important microelement for plant and animal nutrition and essential for maintenance of glucose as well as for lipid and protein metabolism. With regard to human health, chromium (III) is a required nutrient, with 50 to 200 µg per day recommended for adult. [6]

Exposure to chromium can be by eating food contain chromium(III), Breathing contaminated workplace air, skin contact during use in the workplace, drinking contaminated well water, and living near uncontrolled hazardous waste sites which contain chromium or industries that use chromium. Most research concluded that Chromium has effect on health such as :

- Cr (III) is an essential nutrient that helps the body to use sugar, protein, and fat.
- Breathing high levels of Cr (VI) can cause irritation to the nose, such as runny nose, nosebleeds, and ulcers and holes in the nasal septum. Also Cr (VI) causes inflammation of larynx and liver.
- Skin lesions and kidney damage could be produced as a result of occupational exposure to hexavalent chromium compounds; they are probably carcinogens and the lung is the principal site of action.
- Ingesting large amounts of Cr (VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death.
- Skin contact with certain Cr (VI) compounds can cause skin ulcers. Some people are extremely sensitive to Cr (VI) or Cr(III). Allergic reactions consisting of severe redness and swelling of the skin have been noted.
- Several studies have shown that Cr (VI) compounds can increase the risk of lung cancer. Animal studies have also shown an increased risk of cancer. [14]
- The World Health Organization (WHO) has determined that Cr(VI) is a human carcinogen. [15]

- The Department of Health and Human Services (DHHS) has determined that certain Cr (VI) compounds are known to cause cancer in humans. The Environmental Protection Agency (EPA) has determined that Cr(VI) in air is a human carcinogen.

  Chromium affects children because the exposure to chromium will result in birth defects or other developmental effects in people. Birth defects have been observed in animals exposed to Cr (VI). It is likely that health effects seen in children exposed to high amounts of chromium will be similar to the effects seen in adults.

- USA federal government made recommendations to protect human health. EPA has set a limit of 100 µg Cr (III) and Cr (VI) per liter of drinking water (100 µg/L).The Occupational Safety and Health Administration (OSHA) has set limits of 500 µg water soluble Cr(III) compounds per cubic meter of workplace air (500 µg/m3), 1,000 µg/m3 for metallic Cr (0) and insoluble chromium compounds, and 52 µg/m3 for Cr(VI) compounds for 8-hour work shifts and 40-hour work weeks. [8]

- Result of monitoring drinking water sources by public water system in California show nearly 70 percent of sources with chromium (VI) below the 1 µ g/L detection limit for purpose of reporting; most of report detections are at or below 5 µ g/L. Hence, the determination of chromium traces as well as its expectation in water samples is a very important task because of environmental impact, toxicity and bioavailability of chromium.

1.3 Treatments of Chromium(VI) in waste water:

1.3.1 Biological Treatment:

The conventional remediation process for soil contaminated with Cr(VI) involves physical and chemical removal technologies. Physico-chemical treatment strategies are, however, expensive and produce secondary waste streams that require remediation[9]. Biological remediation using microorganisms offer an attractive treatment option because technology is cost-effective and environmentally compatible. Thus, there is growing interest in the use of microorganism for reduction of Cr(VI) to Cr(III).

The Cr(VI)-reducing capacity of chromate-resistant bacteria (CRB) has been widely reported (Cervantes et al,2001). Many CRB have been isolated from tannery effluent, discharge water (Campos et al.,1995), electroplating effluent (Ganguli and Tripathi,2002), activated sludge (Francisco et al.,1994), evaporating ponds [9]. In many cases, only a single bacterium has been isolated from soil and ground water exposed to Cr(VI), with little or no information available about the microbial communities in these environments.

Unique attempts to study the diversity of population of chromium-resistant and chromium-reducing bacteria were made recently by Francisco et al,(2002). These authors characterized the cultural microbial community of a chromium contaminated industrial site. They used the MIDI system to identify six species never reported as Cr(VI)-resistant and/or Cr(VI)-reducing strains. The dominant species identified was the proteo - bacteria Ocro - bacterium antropi (eight isolated), but those isolated and did not show Cr(VI) resistance. Only two

identified isolated (Aureobacterium estearomaticum and Cellulomonas flavigena) resisted and reduced Cr(VI). The diversity of CRB isolated from Brazilian and U.S soils contaminated with potassium dichromate was studied by Flavio.A.O Camargo et al (2005). They characterized the effect of Cr(VI) exposure on the microbial communities of the two soils and Cr(VI) reduction capacity of the Cr(VI)-resistant bacteria isolates.[9]

1.3.2 Oxidation Reduction process:

Oxidation-reduction potential (ORP) is widely used a control parameter in waste water treatment systems especially in physicochemical treatment such as reduction of hexavalent chromium (Cr^{6+}) by ferrous sulfate. Some favored a process control based on the absolute value of ORP, while other have preferred control strategies based on relative change ORP with time. [10]

In the former control strategy, the set point control where the dosing stopped when ORP value reach certain limit. The deficiencies associated with such method is that ORP is affected by other redox system, ionic strengths of various inorganic salts, and polarization of electrodes which may vary from one batch to another. For this reason, using a preset ORP limit to trigger off the dosing pump can either lead to incomplete reduction of the hexavalent chromium or overdosing. With view of developing a more robust method for controlling this reduction, a paper presented by M.Marzuki Mustafa et al, has concentrated on the feasibly of the later approach using relative change in ORP that has not yet been developed in the treatment process of waste water containing chromium. The latter approach recognizes a general pattern of ORP- time profiles with certain distinctive features, such as the

existence of breakpoints, which can correlated with disappearance of Hexavalent chromium. These findings will enable a real-time control of the reduction process in order to optimize the consumption of the reducing agent. This would significantly reduce the operational cost of the treatment process as a chemical cost is the main expenditure in the physicochemical treatment. [10]

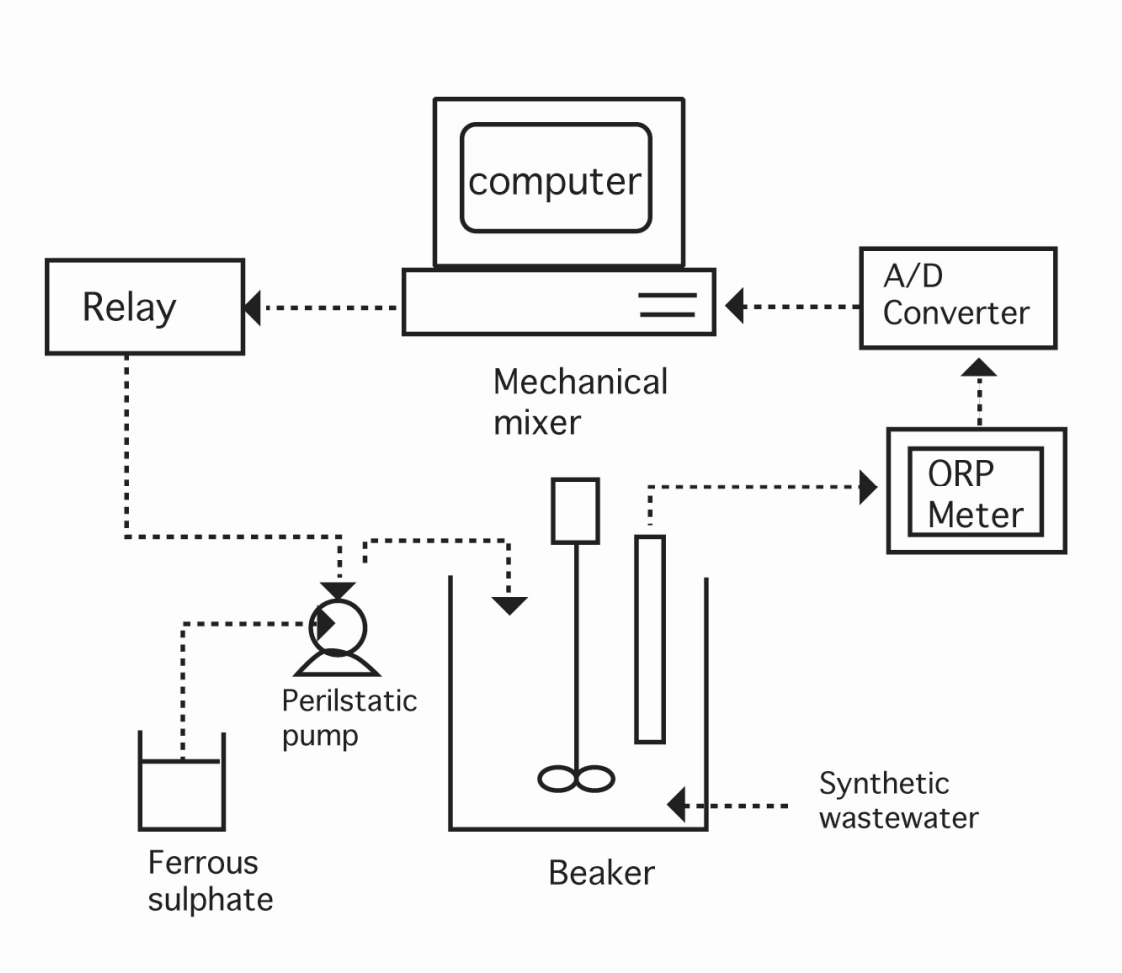


Figure 1

Chapter Two

LITERATURE REVIEW

Effluent treatment plant

2.1 SEPOTRATT 100 System DESCRIPTION:

SEPOTRATT 100R EFFLUENT TREATMENT PLANT (S100RETP) is one of modern systems for electroplating waste water treatment. The plant is manufactured by the Italian company Dalmar. It is almost similar to those systems that depend on oxidation reduction process. The system consist of a collecting tank (CT) (101) which used for collection of chromium contaminated waste water , it is 2000 Liter capacity. It is equipped with a centrifugal pump and many level sensors to adjust the level of the waste water during the operation process. The collecting tank is linked with a PVC pipe to another tank which is called a treatment tank (TT) (401). The (TT) is equipped with stirrer pump to mix the solution during the treating process. Also the TT is equipped with many level sensors to adjust the level of the solution on the treatment tank. Furthermore the TT is equipped with a pH-transmitter to control the pH, and mV-transmitter with a redox probe. the transmitters are very important to follow up the chemical reactions media characteristics. The capacity of the (TT) is approximately about 1000L.[14]

The S100RETP also contains another three storage tanks (ST), (201) (202) (203), all are similar and each one of them equipped with two pumps, a dosing pump for delivering the chemicals to the treatment tank and the other is a loading pump to feed the storage tanks with chemicals when it is empty. The (ST) are also

equipped with sensor level controllers so as to save the maximum and the minimum level for safety operation. The capacity of (ST) is 900 L of consumable raw martial chemicals. The (201) ST is for Caustic soda solution 36 Baumẽ , the (202) ST is for sulfuric acid solution with a concentration of 50%, and the third (203) ST is for the reducing agent, sodium bisulphate of density 1.48.[14]

2.2 S100RETP OPERATION:

2.2.1 GENERAL DESCRIPTION:

Batches of approximately 1000 liters of waste water containing hexavalent chromium at first acidified to a pH value of 2.5 by sulfuric acid in order to help chromium (VI) reduction take place by adding sodium bisulphate until reaching 250mV which detected by the redox electrode transmitter. The pH value is then increased by adding caustic soda up to 10-10.5 to ensure the precipitation of all chromium (III) as a chromium hydroxide. The solution is then flocculated and filtered by a suitable filter press design for a metallic precipitates. The solid waste is discharged whereas clear water is neutralized before discharging. [14]

2.2.2 GROUP DESCRIPTION :

2.2.2.1Group 1: collection of waste water to be treated

Chromium contaminated water plus various residues are collected inside the fiber glass storage tank (101) through an automatic valve which closed when the maximum level is reached. Waste water is transferred to the (TT) through a stainless steel centrifugal pump up to the working level of the (TT).[14]

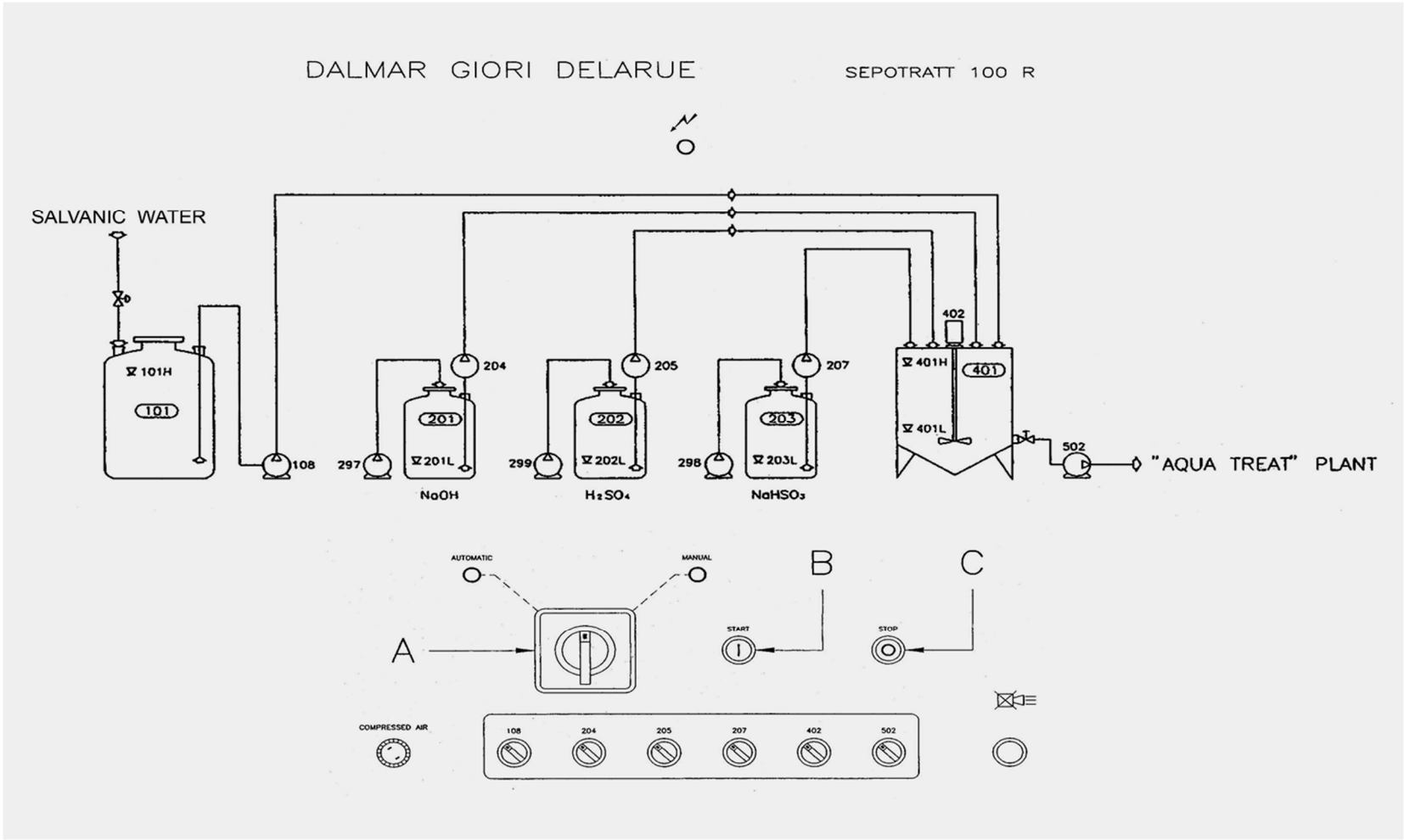


Figure 2: Group Discreption of SEPOTRATT 100 System

2.2.2.2 Group 2: Storage of chemicals

There are three cylindrical phenolic resin tanks for storage of :

- Caustic soda	(201) NaOH	capacity 900 L
- Sulfuric acid	(202) H_2SO_4	capacity 900 L
- Sodium bisulfite	(203) $NaHSO_3$	capacity 900 L

Each tank has:

an external level indicator.

an alarm system indicating minimum level and maximum level.

The set of equipment also includes the dosing pumps which add reactants during treatment.[14]

2.2.2.3 Group 3 Treatment Group

The waste water is treated in the tank (401) which is equipped with redox and pH measuring instruments, with motor stirrer (402) and controller levels the treated water is conveyed to another plant with pump (502). [14]

2.2.2.4 Group 4 Electrical control cabinet

The electrical control cabinet contains the electrical control equipment of the installation and manufactured according to European standers EN 60204-1.Access to inside the cabinet is possible only when the power supply is switched off by means of the main circuit breaker.

The cabinet is provided with frontal display and control panel. On the panel is shown the functional diagram with pilot lights to indicate the operation of the plant alarms. [14]

2.3 OPERATION AND CONTROLS:

The plant can operate either in automatic or manual mode depending on the position of the hand switch (A) (Figure 2). The stand-by mode is also allowed.

In manual mode evenly item can be activated by means of relevant locate on the synoptically panel, regardless of the level control and instruments.

In the automatic mode the plant can operate once reached the working level by turning the automatic hand switch (A) in automatic position, and pushing the start button (B).

The pump (108) transfer the water to be treated to the tank (401). The stirrer (402) starts once reached the working level, while the transfer pump stops. Then the dosing pump (205) for sulfuric acid starts to reduce the pH of the effluent to set value 2.5. after a pre set time of 30 seconds controlled by timer of the dosing pump. Then the dosing pump (207) for sodium bisulphate is activated, until the set point of approximately 150mV. After a pre set time of 15 minutes controlled by timer , the dosing pump of caustic soda is activated, until the set pH value of 10 – 10.5.After a pre set time of 3 minutes, controlled by timer, the transfer pump (502) is activated, until the empting of the treatment tank is completed. In case of stop pushbutton (C), the cycle must manually completed.[14]

2.4 Flow Chart of the treatment process:

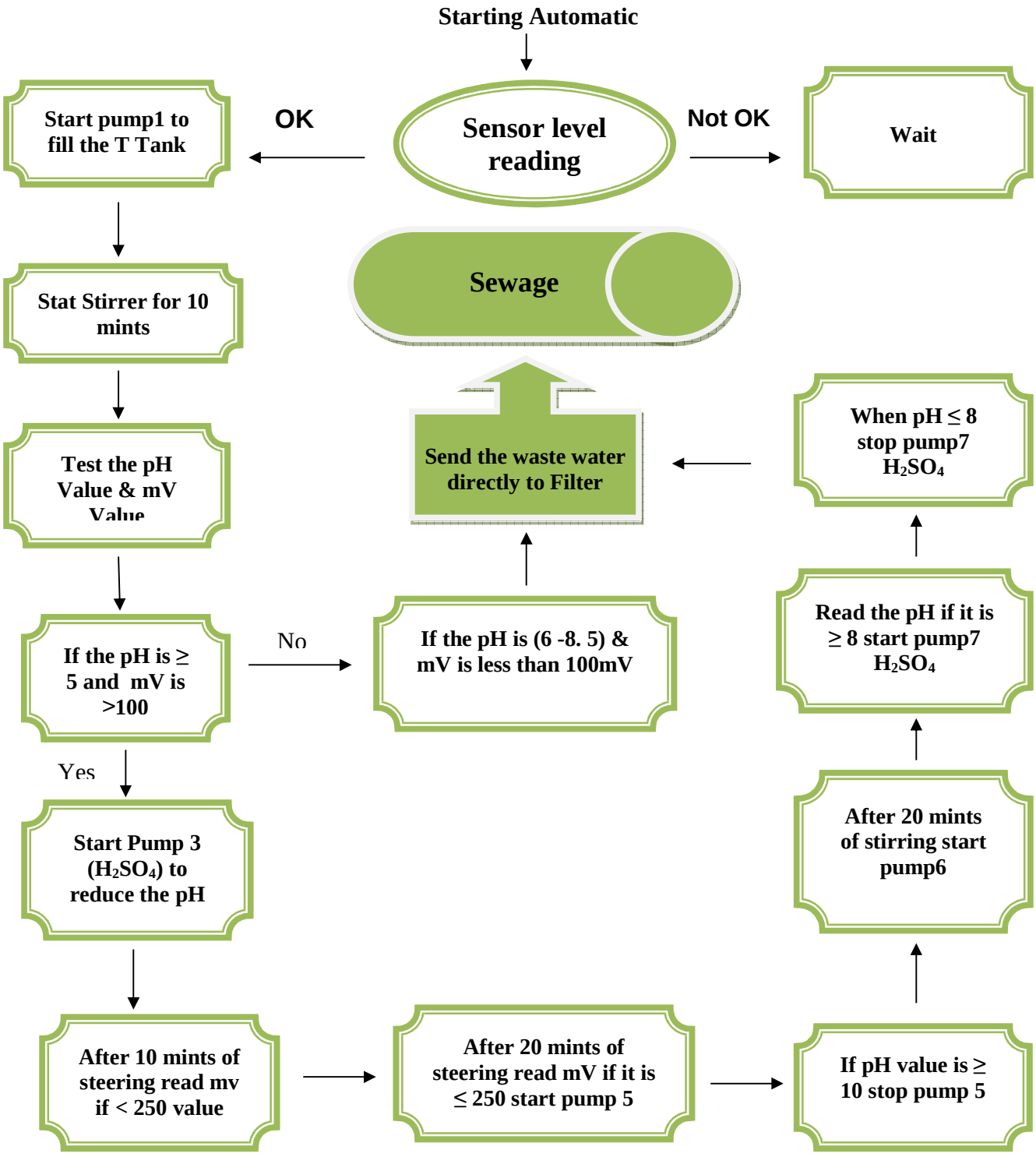


Figure 3:Flow chart of the treatment process

2.5 The chemical reaction theory of S100RETP:

2.5.1 Reduction of Hexavalent chromium:

Chromium tri oxide or chromic acid is one of the best resources for hexavalent chromium in electroplating practices. When chromium tri oxide dissolved in water it gives chromic acid according to the reaction path way below:

$$2CrO_3 + H_2O \rightarrow H_2Cr_2O_7$$

Reduction of hexavalent chromium to trivalent chromium by using sodium bisulfite solution can be summarized by the following reaction equation :

$$H_2Cr_2O_7 + H_2SO_4 + 2NaHSO_3 \rightarrow Cr_2(SO_4)_3 + Na_2SO_4 + H_2O$$

The electron- half- equation of this oxidation – reduction reaction can be shown as follows:

$14\,H^{+} + Cr_2O_7^{=} + 6e^{-} \Rightarrow 2\,Cr^{+3} + 7\,H_2O$ Reduction reaction

$6\,H_2O + 6\,HSO_3^{-} - 6e^{-} \Rightarrow 6\,SO_4^{=} + 18\,H^{+}$ Oxidation reaction

$4H^{+} + Cr_2O_7^{=} + 6HSO_3^{-} \Rightarrow 2Cr^{+3} + 6SO_4^{=} + H_2O$ Electron balance

2.5.2 Precipitation of Trivalent chromium:

The addition of sodium hydroxide is the last step in chromium waste water treatment. The green precipitate of trivalent chromium as a chromium hydroxide. The following equation summarize the reaction path way:

$$Cr^{+3} + NaOH \Rightarrow Cr(OH)_3 \underset{green}{\downarrow} + Na^{+}$$

Processes of recovery of trivalent chromium with alkaline agent of various nature are well known from literature.

At a handicrafts man level, chromium is removed from the diluted chromium containing solution by precipitation of chromium hydroxide by means of various alkaline agent such as calcium oxide, sodium carbonate and bicarbonate, magnesium oxide and like.

Precipitation system by the above mentioned alkaline agent have been the research object of an extensive study of J.C. de Wigs16, “precipitation reuse of trivalent chromium present in the tannery waste waters”, in order to setup a simple and economical process for the recovery of such chromium residues and removing the same from waters.

It has been found that the precipitation carried out with magnesium oxide leads to a chromium hydroxide higher in chromium content and having the best settling characteristics. Settling or sedimentation rates of 250 mm/hour are achieved and wet precipitation at about 10% chromium oxide (Cr_2O_3) is obtained. The preferred pH for the precipitation of Cr_2O_3 from liquid to be treated is about 9 and it allows an almost quantitative precipitation of chromium without formation of chromates.

However, this process requires long operation times (for example, 3 hours) for the treatment of 300 liters of tannery waste liquid with an excess of 30% MgO over the theoretical value and an overnight settling, this leading to a filtered liquid containing 4.6ml/L chromium. [1]

2.6 Reduction of Hexavalent chromium Alternatives:

Many alternatives can be used to reduce hexavalent chromium to trivalent chromium the following table show some of these alternatives:

No	Name	Chemical Formula
1.	Ascorbic acid	$C_6 H_8 O_6$
2.	Sodium thiosulfate	$Na_2 S_2 O_3$
3.	Sodium dithionite	$Na_2 S_2 O_4$
4.	Sodium meta bi sulfite	$Na_2 S_2 O_5$
5.	Iron(II)-sulfate	$FeSO_4 \cdot 7H_2O$
6.	Iron(II)-ammonium sulfate	$(Fe(NH_4)_2(SO_4)_2 \cdot 6H_20$

The most useful and effective chemical agents of the above are the Sodium thiosulfate $Na_2 S_2 O_3$ and Iron (II)-sulfate $FeSO_4 \cdot 7H_2O$.

2.6.1 Sodium Thiosulfate:

Sodium thiosulfate $Na_2 S_2 O_3.5H_2O$ is readily obtainable in a state of high purity, but there is always some uncertainty as to the exact water content because of efflorescent nature of the salt and others. The substance is therefore unsuitable as a primary standard. It is a reducing agent by virtue of the half-cell reaction:

$$2\ S_2O_3^{2-} \Leftrightarrow S_4O_6^{2-} + 2\ e$$

Sodium thiosulfate solutions prepared with ordinary distilled water are unstable. Because distilled water usually contains an excess of carbon dioxide; this may cause a slow decomposition to take formation of sulfur:

$$S_2O_3^{2-} + H^+ \Leftrightarrow HSO_3^- + S$$

Moreover, decomposition may also be caused by bacterial action, e.g. Thiobacillus thioparus, particularly if the solution has been standing for some time. That is why the following recommendations are made:

Preparation of sodium thiosulfate solution must be with recently boiled distilled water.

3 drops of chloroform or 10mgL^{-1} of mercury(II) iodide must be added; this compound improve the keeping qualities of the solution. Bacterial activity is least when the pH lies between 9 and 10. furthermore a small amount of sodium carbonate (0.1 g L^{-1}) must be added also which is advantageous to ensure the correct pH. In general, alkali hydroxide, sodium carbonate (> 0.1g/L - 1g/L) and sodium tetra-borate should not be added, since they tend to accelerate the decomposition:

$$S_2O_3^{2-} + 2O_2 + H_2O \Leftrightarrow 2SO_4^{2-} + 2H^+$$

To hasten the decomposition of sodium thiosulfate solution the solution must not be exposed to the light[12].

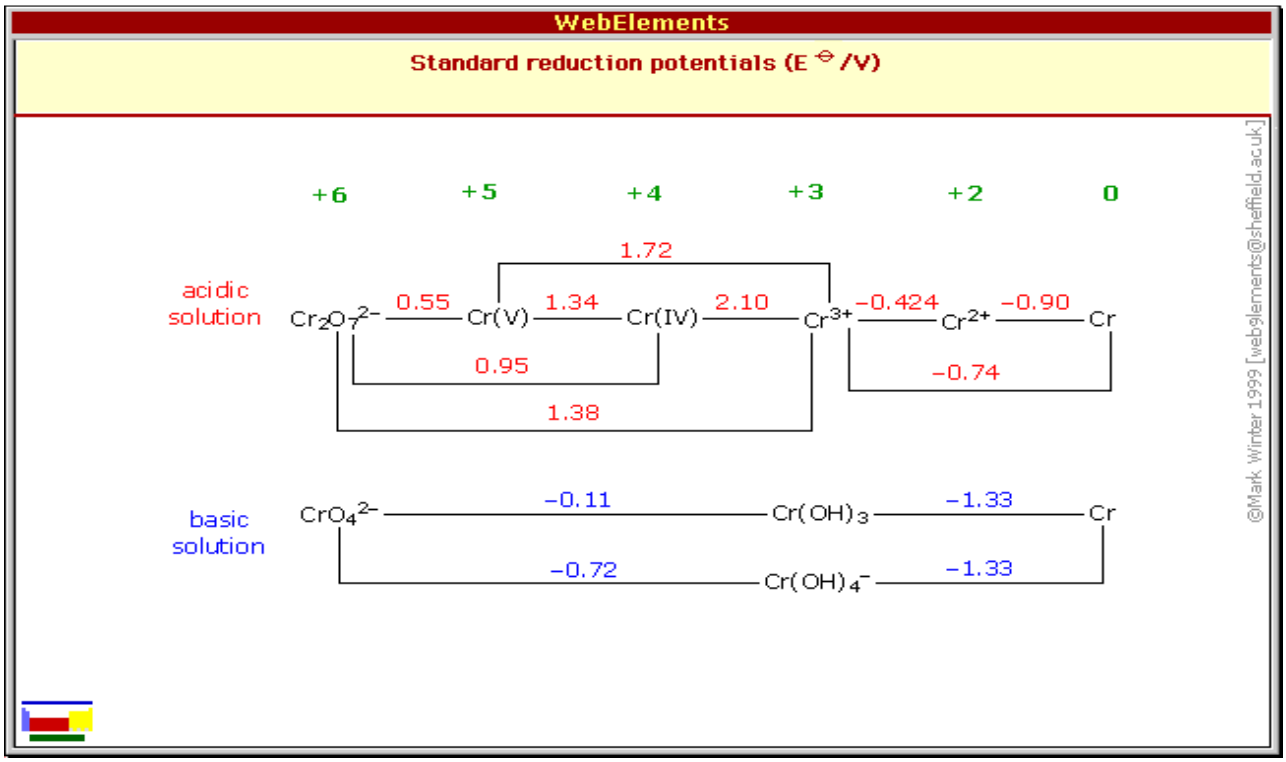
2.6.2 Standard Reduction Potentials:

The standard reduction potential is measured in the following way:

$$Pt, H_2 \left| H^+ (a=1) \right\| \frac{Fe^{3+}(a=1)}{Fe^{2+}(a=1)} \left| Pt \right.$$

It enable us to predict which ions will oxidize or reduce other ions at unit activity (or molar concentration).

2.6.3 Standard Reduction Potentials of chromium:



The standard reduction potentials given here for aqueous solutions are adapted from the IUPAC publication. [17]

CHAPTER THREE

EXPERIMENTAL

3.1 Reagent and Samples:

3.1.1 Prepared samples:

All reagents used were of analytical grade. Chromium (VI) prepared samples were prepared by collecting 500 cm^3 of chromic acid solution from chromium electroplating bath, electroplating Dept, Sudan currency printing press. The concentration of the collected sample was determined. The prepared chromium solution samples was prepared by diluting affixed volumes of the solution according to the table below:

Table1: preparation of prepared Samples

NO	Volume of Cr^{+6} In mL	Dilution in mL	Percentage V/V%
1	0	50	0%
2	0.5	50	1%
3	1	50	2%
4	1.5	50	3%
5	2	50	4%
6	3	50	6%
7	4	50	8%
8	5	50	10%
9	7	50	14%
10	10	50	20%

3.1.2 Random samples:

500 ml of 2 Random samples were also collected during the operation of the system.

3.1.3 Equipment:

1. pH – meter with redox electrode for both pH and mV scale.
2. Digital analytical balance scale four decimal .
3. Automatic dosing system (765-Dosimat – Metrohm).

3.1.3 preparation of reagents:

3.1.3.1 preparation of sodium thiosulfate 0.1M:

25g of sodium thiosulfate crystals ($Na_2S_2O_3.5H_2O$) were weight out. the solid was dissolved into 500 cm^3 beaker with boiled deionized water. the solution was then transferred quantitatively to a 1L graduation flask and made up to 1 liter with deionized water. Sodium carbonate (0.1g) was added to reserve the solution for few days.

3.2 Analytical procedures:

3.2.1 standardization of sodium thiosulfate 0.1M:

3.2.1.1 Materials & Reagents:

Potassium iodate, potassium iodide, sulfuric acid 1M, de-ionized water, and starch solution.

3.2.1.2 procedure[13]:

Accurately 0.15g of a pure dry potassium iodate was weighed. The solid was then dissolved in 25ml of cold de-ionized water to form(0.02M) solution. 2g of iodate –

free of potassium iodide, and 5 ml of 1M sulfuric acid were added. The librated iodine was titrated against sodium thiosulfate solution with constant shaking. When the color of the liquid became pale yellow 200 ml of de-ionized water, and 2 ml of starch solution were added. The titration was continued until the color changed from blue to colorless.

The concentration of sodium thiosulfate was then calculated according to the equation:

$$\frac{M_{Ox} x V_{Ox}}{n_{Ox}} = \frac{M_{re} x V_{\mathrm{Re}}}{n_{\mathrm{Re}}}$$

3.2.2 Standardization of sodium bisulfite solution:

3.2.2.1 Materials and reagents:

sulfuric acid 1M; de-ionized water; potassium permanganate 0.02M solution.

3.2.2.2 procedure[13]:

10 cm^3 of potassium permanganate 0.02M, prepared by dissolving ٠,٨٧٥g of solid potassium permanganate in 250ml of de-ionized water, was pipetted into 250 ml Erlenmeyer flask. 5 ml of concentrated sulfuric acid was added. The solution was then titrated against sodium bisulfite solution until the color changed to colorless. Results was registered and the concentration of sodium bisulfite solution was calculated according to the equation:

$$\frac{M_{Ox} x V_{Ox}}{n_{Ox}} = \frac{M_{re} x V_{\mathrm{Re}}}{n_{\mathrm{Re}}}$$

3.2.3 Determination of hexavalent chromium ions concentration:

3.2.3.1 Reagents:

Potassium iodide; sulfuric acid 20%; sodium Thiosulphate 0.10016M; starch indicator solution; deionizer water.

3.2.3.2 Apparatus:

Beakers; Erlenmeyer flask; Volumetric Flask; Pipettes; Measuring Cylinder.

3.2.1.3 procedure[13]:

500 cm^3 of chromic acid solution were collected from chromium electroplating bath after well mixing and heating. sample was cooled to 20C°. 10 ml of this sample was pipetted into a 500 cm^3 graduated flask and then made up to the mark with deionized water.10 cm^3 of this solution were pipetted into 250 ml Erlenmeyer flask. 2 g of potassium iodide was added followed by 10 ml of sulfuric acid . The solution was then diluted by adding 50 ml of deionized water. The librated iodine was then titrated against standard solution of sodium Thiosulphate until de coloration is maintained, after adding 2 ml of starch indicator, for one minute. The volume of sodium thiosulfate was noted and concentration of samples was calculated according to the redox equation :

$$\frac{M_{Ox} * V_{Ox}}{n_{Ox}} = \frac{M_{re} * V_{\mathrm{Re}}}{n_{\mathrm{Re}}}$$

3.2.4 Determination of Sample's pH and mV:

3.2.4.1Procedure:

For each sample of chromium(VI) pH and mV were measured before treatment.

3.2.5 Treatment of Prepared Samples:

3.2.5.1Reagents:

Sulfuric acid 1M; sodium bisulfite solution 0.5905M; Sodium Hydroxide solution (2M) .

3.2.5.2 Procedure:

20ml of each prepared chromium sample was pipetted into 250ml Erlenmeyer flask. The initial pH and the potential in mV of the solution was determined. 2ml of sulfuric acid 1M was added. The change in pH and mV was registered. Potentiometeric titration of the chromium solution against sodium bisulfite 0.0625M solution was carried out. The reading of the pH and mV was registered. The solution was then titrated against sodium hydroxide solution 2M. The pH and mV values are determined and registered.

3.2.5.3 Treatment of Randomly Selected Samples:

50ml of each contaminated chromium waste water sample was pipetted into 250ml Erlenmeyer flask. 10 ml of deionized water was added. The initial pH, and mV values of the solution was determined. 10ml of sulfuric acid 1M was added. The change in pH and mV values was registered. Potentiometeric titration of the chromium solution against sodium bisulfite 0.0625M solution was carried out. The change in the values of the pH and mV was registered. The solution was then titrated against sodium hydroxide solution (2M). The pH and mV values are determined and registered.

CHAPTER FOUR

Results And Discussion

4.1 Prepared Samples:

Table 2 show the results of calculations of the Standardization of reagents. These reagents used to determine the concentration of the prepared samples.

Table 2: Standardization of Reagents

No	Reagents	Conc. mole/L
1	Sodium Thiosulphate	0.10016
2	Sodium bisulphate	0.5905
3	Solution of Chromium (VI)	0.0629

Determination of the prepared sample concentration is very important in showing how the chromium (VI) behave when it's concentrations increases in solution.

Table 3: Calculation the concentration of prepared samples

Sample NO	Volume of Cr^{+6} In mL	Percentage v/v	Cr^{+6} concentration in mg/L
1	**0**	**0%**	**0**
2	**0.5**	**1%**	**32.71**
3	**1**	**2%**	**65.41**
4	**1.5**	**3%**	**130.82**
5	**2**	**4%**	**163.53**
6	**3**	**6%**	**196.23**
7	**4**	**8%**	**261.64**
8	**5**	**10%**	**327.06**
9	**7**	**14%**	**457.88**
10	**10**	**20%**	**654.16**

The real amount in ml of sodium bisulfite needed to treat 10 ml of chromium (VI) prepared solution are given in table 4.

Table 4: Treatment of prepared samples with Sodium Bisulfite

NO	Conc. of Cr^{+6} in mg/L	Volume Of Sodium bisulfite Needed in ml (for 1L Sample)
1	0	0.00
2	32.70	6.39
3	65.40	12.78
4	1308.06	255.65
5	163.50	31.96
6	1962.31	383.51
7	261.61	51.13
8	327.02	63.90
9	457.88	89.46
10	654.16	89.48

The variation of ORP with concentration is of high significance as it provide a criterion to judge the toxicity of waste water based on whether it contain hexavalent chromium ion or not. Result of variation of ORP with concentration of Cr^{+6} ion are shown in table 4. It is clearly evident from these results ORP increase with Cr^{+6} concentration in solution. Consequently the toxicity of the waste water can be assayed through determination of pH-transmitter with redox electrode.

Table* 5*: pH and ORP Measurement of Prepared samples

NO	Cr+ concentration in percentage	pH reading	ORP in mV
1	0%	7.28	-27
2	1%	3.521	237.6
3	2%	3.417	240.2
4	3%	2.57	243.0
5	4%	2.60	245.5
6	6%	2.31	251.3
7	8%	2.27	258.3
8	10%	2.36	257.7
9	14%	2.32	255.40
10	20%	2.05	270.0

From this table we can indicate that the value of the pH reduced when the concentration of chromic acid increase.

According to Environmental production agency (USA) limits hexavalent chromium must not exceed 100µg/L[25]. So we choose the first prepared sample is less than 100µg/L. The redox potential value of the first sample form table 4 is 237.6 mV that means the first conditions for the waste water need to be treated by the Sepotrato 100R system that the redox potential value must not exceed this value.

Figure 4 below show how the redox potential power is proportional to hexavalent chromium concentration. This indicate that the toxicity of the waste water could be measured by redox electrode ml volts value.

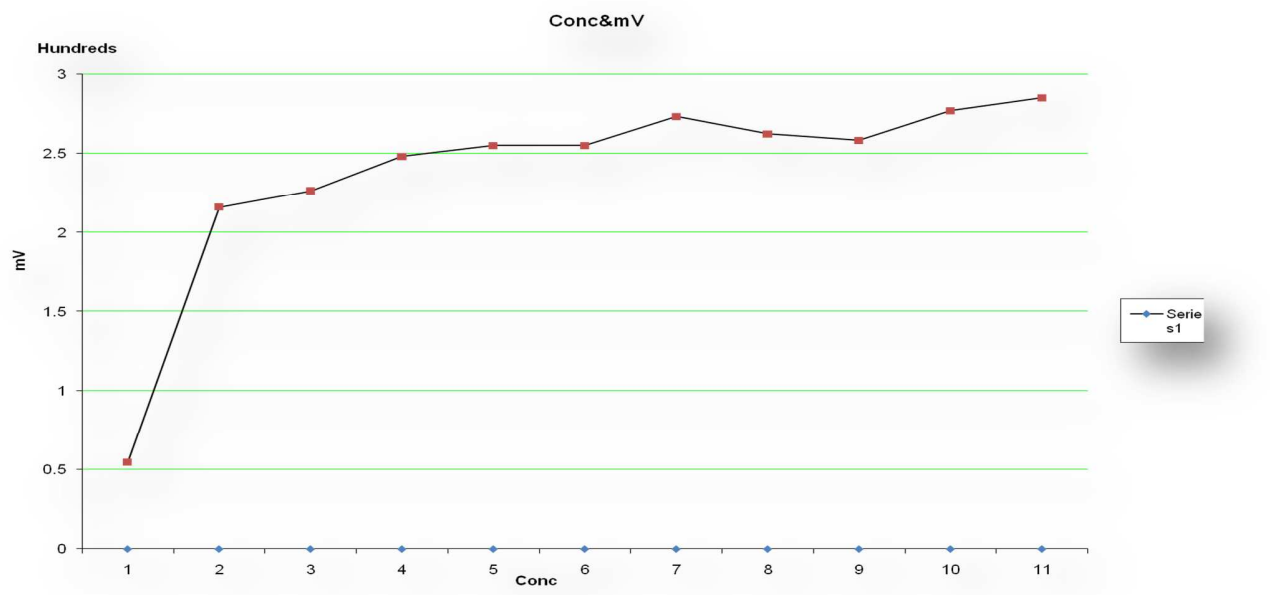


Figure 4: Redox potential power against Concentration of chromium (VI) Ions

Figure 6 illustrate the relation between the concentration of the hexavalent chromium and the pH of the solution. It is so clear that when concentration of hexavalent chromium in the solution increase, the pH of the solution decrease. This result show that in high concentration of hexavalent chromium the pH of the solution decrease to a very law value. This result indicate that it is important to add sulfuric acid for reduction reaction necessity.

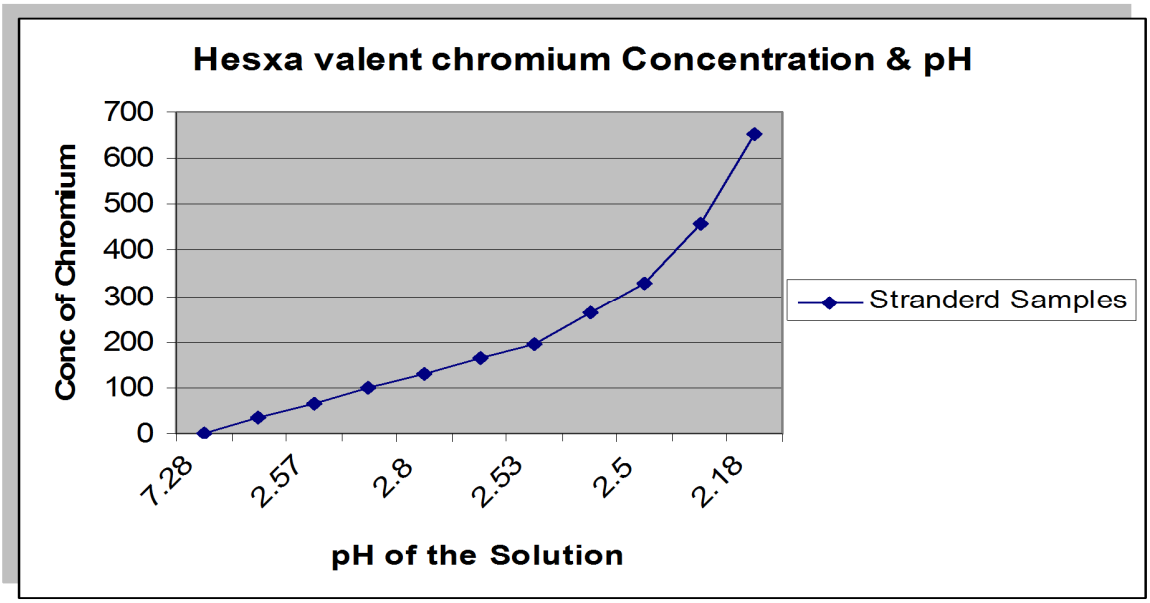


Figure 5: Concentration of chromium (VI) Ions against pH

The result of measuring of ORP for standard samples show that the minimum ORP value, which indicate that the waste water contaminated with hexavalent chromium, is 200mV. This indicate that if the ORP value is greater than or equivalent to 200mV that means this sample is contaminated with hexavalent chromium, so that it need to be treated before sending to sewage.

4.2 Treatment of the Blank Sample:

Table 6a, table 6b and figure 6 show the reading of pH and mV values of the blank sample during the treatment process.

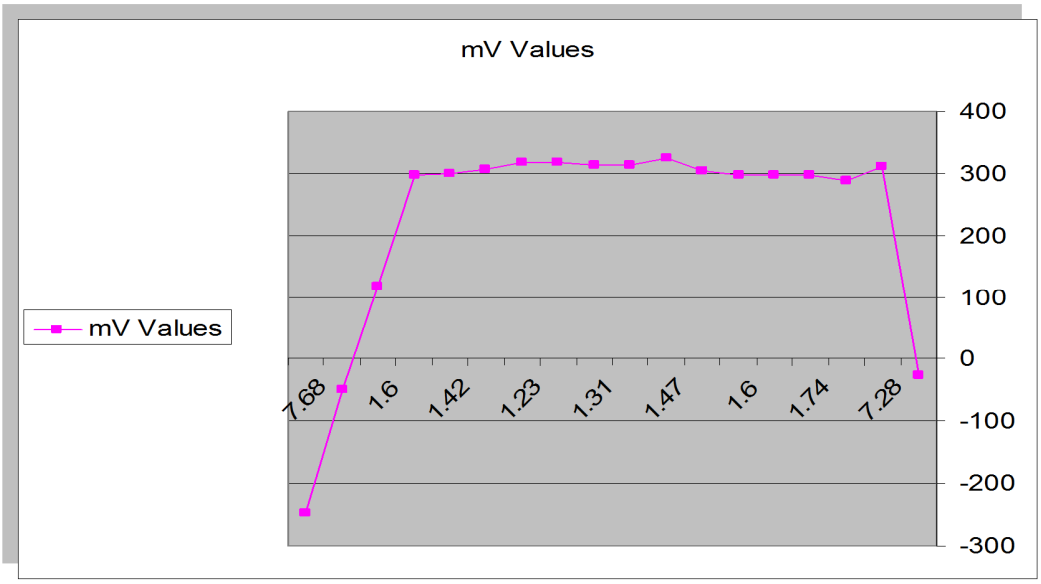


Figure 6: The treatment of the Blank sample

Table 6a below show the reading values of the treatment of the blank sample (0%) with $NaHSO_3$.

Table 6a: Treatment of the Blank sample with Sodium Bisulfite

No	V of $NaHSO_3$ (2ml)	pH	mV
1.	0	1.48	310.4
2.	2	1.74	289.0
3.	4	1.58	297.7
4.	6	1.60	296.8
5.	8	1.58	297.8
6.	10	1.47	303.7
7.	12	1.09	325.6
8.	14	1.31	313.5
9.	16	1.30	313.9
10.	18	1.23	317.6

The follow up of the blank sample treatment conclude the following observations:

1. Addition of sodium bisulphate in the absence of oxidizing agent including cr^{+6} ions doesn't alter to any probable extent the value of ORP, as clearly indicated from table 5a and figure 6.
2. It is also true that addition of successfully increments of the reducing agents, sodium bisulphate, after the completion of the reducing process of Cr^{+6} to Cr^{+3}, does not alter the value of ORP reached at the end of the reduction process and consequently the constant value of ORP thus reached could be used to cancel further addition of reducing agent.
3. It is interesting to note that addition of sodium bisulphate affect the value of the ORP only when an oxidizing species such as Cr^{+6} is present in the system.
4. The addition of the sulfuric acid affect both pH & ORP expected values. While the pH of the solution decrease; the ml volts (ORP values) of the solution increases. Whereas the addition of sulfuric acid is very important for reduction process.
5. The fifth fact is that the addition of sodium hydroxide effect the ORP value by reducing it, While the pH of the solution increase. So in general we conclude that the Acidity of the solution is directly proportional to the value of ORP.
6. Furthermore in the blank sample, concentration of the oxidizing agent (chromiumVI) is zero, ORP value does not have a great deviation when the concentration of the reducing agent (sodium bisulfite) increase. This confirm that the value of ORP in mV does not change by adding excess amount of reducing agent after all hexavalent chromium in solution been treated.
7. From table 5a above it is clear that the change in pH of the blank sample, when treated with sodium bisulphate, is very small so it can be neglected. This means that the addition of the reducing agent, Sodium bisulfite, does not make a great deviation in the pH value which is very important for the reaction progress. Because if the addition of the reducing agent increase the pH of the solution, this

may affect the process of reducing chromium. On the other hand if it decreases the pH of the solution, this may accelerate the process of hexavalent chromium reduction.

8. Also from the same table we conclude that in the absence of oxidizing agent there is no change in the ORP value. So when the concentration of the oxidizing agent is zero the addition of more reducing agent does not affect pH and mV values.
9. Table 5b below show the effect of treating the blank sample with sodium hydroxide solution. There is a great change in both pH & ORP. While the ORP value decrease the pH value increase. So it is very important to add sufficient quantity of sodium hydroxide solution so as to ensure the precipitation of all chromium (III) in the hydroxide form.

***Table 6b : Sample Treatment of the Blank sample with* NaOH**

No	V of NaOH in ml	pH	mV
1.	0	1.23	317.6
2.	2	1.42	306.7
3.	4	1.50	299.1
4.	6	1.60	296.7
5.	8	4.7	116.6
6.	10	7.68	-50.2
7.	12	11.14	-247.3

10. From the above table also it is indicated that neutral waste water with zero concentration of chromium (VI) should be less than zero for ORP value and the pH in range of 6.5 – 8.5.

4.3 The Treatment of Prepared Samples:

4.3.1 Treatment of 1% prepared sample:

The chemical characteristic of the first sample is well summarized in table 5.

Table 5: pH & ORP Measurement of standard samples

NO	Cr^{+} concentration in percentage	pH reading	ORP in mV
1	0%	7.28	-27
2	1%	3.521	237.6
3	2%	3.417	240.2
4	3%	2.57	243.0
5	4%	2.60	245.5
6	6%	2.31	251.3
7	8%	2.27	258.3
8	10%	2.36	257.7
9	14%	2.32	255.40
10	20%	2.05	270.0

The pH value of this sample is equal to 3.52, Acidic, the redox potential value in mV is equal to 237.6mV, and the concentration of Cr(VI) is 1% (32.71µg/L). The addition of sulfuric acid reduce the pH value to 1.2 and increase the redox potential to 319.5 see table 6 below. Measuring the pH & mV values are very important because they help in programming the transmitters. The treatment of this standard sample with sodium bisulfite is well clear from table 7 below:

Table 7 Sample (1%) against $NaHSO_3$

No	V of $NaHSO_3$	pH	mV
1	0	1.20	319.5
2	1	1.05	328.0
3	2	1.06	327.0
4	3	1.08	326.5
5	4	1.09	325.4
6	5	1.11	324.1
7	6	1.14	323.1
8	7	1.16	322.0
9	8	1.17	321.3
10	9	1.19	320.4

The addition of the reducing reagent, sodium bisulfite, results in increasing the redox potential when the pH remains constant or with small neglected deviation. If we compare the treatment of this sample by sodium bisulfite solution with the blank sample we conclude the following:

- The addition of sulfuric acid reduce the pH value and increase the ORP value.
- The addition of reducing agent, sodium bisulfite, reduce the ORP value but it doesn't descend gradually. Because the concentration of oxidizing agent is very little or neglected.
- The addition of sodium hydroxide reduce the ORP value and increase the pH value.

4.3.2 Treatment of 2% prepared sample:

The treatment of the 2% standard sample is well described in table 8a and 8b.

Table 8a sample(2%) against $NaHSO_3$

No	V of $NaHSO_3$	pH	mV
1	0	1.083	326.5
2	1	1.073	327.0
3	2	1.077	326.8
4	3	1.076	326.7
5	4	1.097	325.8
6	5	1.106	325.2
7	6	1.121	324.4
8	7	1.143	323.2

Table 8b sample(2%) against NaOH

No	V of NaOH in ml	pH	mV
1	0	1.143	323.2
2	0.25	1.207	319.0
3	0.50	1.268	316.4
4	0.75	1.360	311.1
5	1.0	1.482	303.6
6	1.25	1.626	295.5
7	1.50	1.811	285.3
8	1.75	2.12	267.3
9	2.0	3.10	214.7
10	2.25	11.5	-272.7

From table 5 it clear that the pH value of the sample 2% is 3.5 and ORP value is 240mV. After the treatment process we conclude:

- The addition of the sulfuric acid reduce the pH value to 1.08 and increase the ORP value to 326.5 mV.
- The titration of the sample against sodium bisulfite solution does not make a great change in the pH and mV values.
- The titration of the last solution against sodium hydroxide solution increase the pH value slowly in the beginning of the titration, but the big change in value appeared clearly after adding 2ml of the NaOH solution.
- The addition of the sodium hydroxide solution decrease the ORP value gradually. After adding 2.25 ml there is also a very clear change in the mV value.
- Figure 8a below illustrate how the potentiometeric titration progress for the sample 2% against the reagents

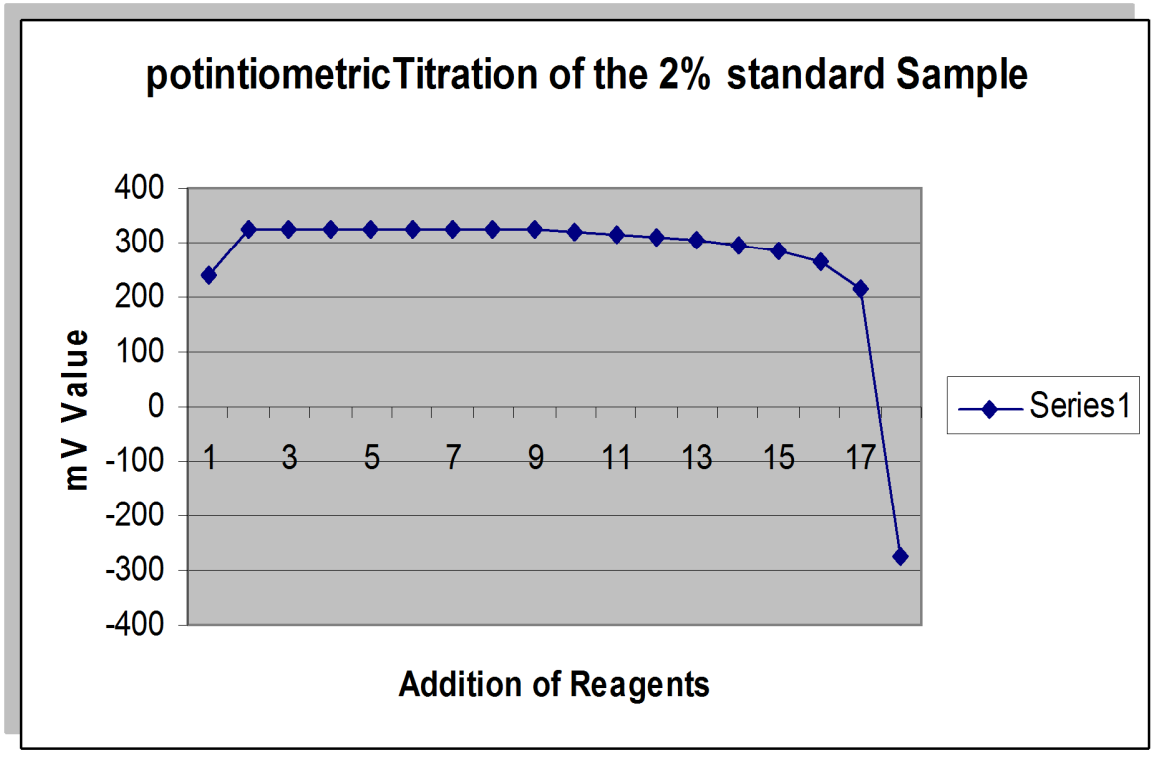


Figure 8a: Illustrate the potentiometeric Titration of the 2% sample:

❖ Figure 8b illustrate how the pH-metric titration progress for sample 2% against the reagents.

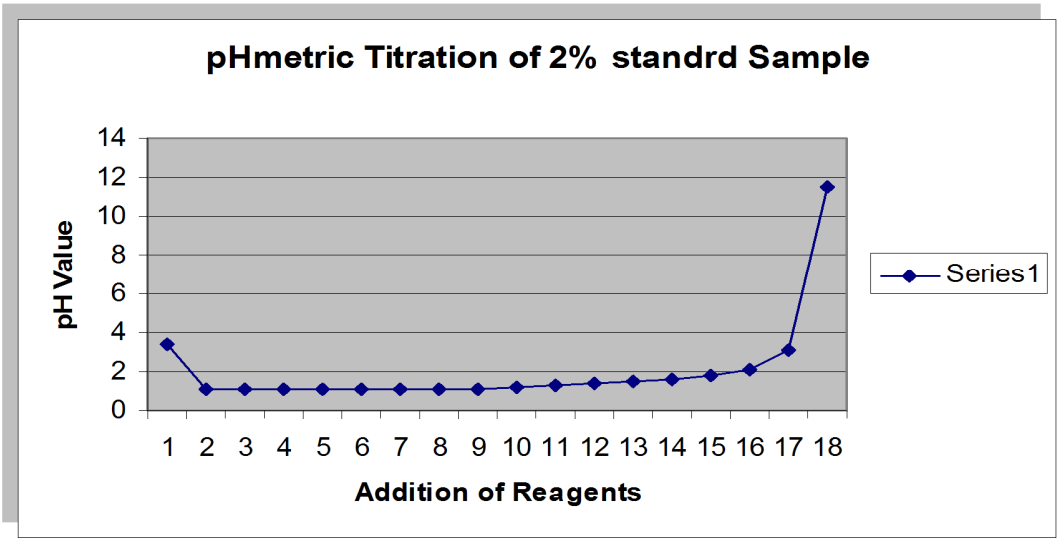


Figure 8: Illustrate the pH-metric Titration of the 2% sample:

4.3.3 Treatment of 3% prepared sample:

The treatment of the 3% standard sample is well described in table 9a and 9b.

Table 9a: Sample (3%) against $NaHSO_3$

No	V of Na_2SO_3	pH	mV
1	0	1.036	328.7
2	1	1.072	328.7
3	2	1.058	327.8
4	3	1.105	325.0
5	4	1.120	324.3
6	5	1.142	321.1
7	6	1.160	321.7
8	7	1.180	320.4
9	8	1.20	319.3

Table 9b: Sample (3%) against NaOH

No	V of NaOH in ml	pH	mV
1	0	1.20	319.3
2	0.25	1.28	315.0
3	0.50	1.36	310.2
4	0.75	1.44	305.7
5	1.0	1.55	299.6
6	1.25	2.07	271.0
7	1.50	2.12	267.0
8	1.75	2.43	249.5
9	2.0	3.11	210.6
10	2.25	11.32	-263.1

From table 4 it clear that the pH value of the sample 3% is 2.57 and ORP value is 243.0 mV. After the treatment process we conclude:

- The addition of the sulfuric acid reduce the pH value to 1.036 and increase the ORP value to 328.7 mV.
- The titration of the sample against sodium bisulfite solution increase the pH and decrease mV values gradually.
- The titration of this sample against sodium hydroxide solution increase the pH value slowly in the beginning of the titration, but the big change in the value appeared clearly after adding 2ml of the NaOH solution.
- The addition of the sodium hydroxide solution decrease the ORP value gradually. After adding 2 ml there also a very clear deviation in the mV value.
- Chart 6 illustrate how the potentiometeric & pH-metric titrations progress for the sample 3% against the reagents.

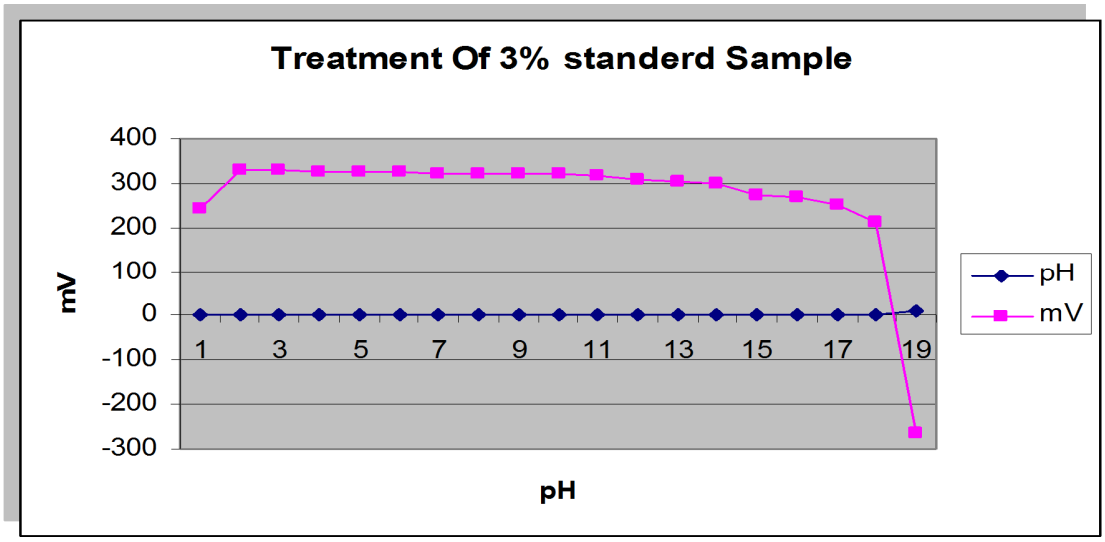


Figure 9 mV and pH trend in treatment of 3% prepared sample

4.3.4 Treatment of 4% prepared sample:

The treatment of the 4% standard sample is well described in table 10a and 10b.

Table 10a Sample (4%) Against $NaHSO_3$

No	Volume of Na_2SO_3	mV	pH
1.	0	307.9	1.40
1.	1	308.4	1.39
2.	2	310.1	1.36
3.	3	310.5	1.36
4.	4	311.2	1.35
5.	5	309.5	1.20
6.	6	319.3	1.20
7.	7	319.1	1.21
8.	8	318.1	1.21
9.	9	317.7	1.23
10.	10	317.1	1.24
11.	11	316.2	1.26
12.	12	315.7	1.27

Table 10b Sample (4%) Against NaOH

No	Volume of NaOH	mV	pH
1.	0	315.7	1.27
2.	0.25	312.7	1.33
3.	0.50	308.7	1.39
4.	0.75	304.8	1.46
5.	1.0	300.4	1.54
6.	1.25	293.5	1.66
7.	1.50	284.6	1.81
8.	1.75	272.4	2.03
9.	2.0	251.1	2.40
10.	2.25	57.5	5.8
11.	2.50	-288.9	11.8

From table 4 it clear that the pH value of the sample 4% is 2.6 and ORP value is 245.5. After the treatment process we conclude:

- The addition of the sulfuric acid reduce the pH value to 1.40 and increase the ORP value to 307.9 mV.
- The titration of the sample against sodium bisulfite solution increase the pH and decrease mV values gradually.
- The titration of this sample against sodium hydroxide solution increase the pH value slowly in the beginning of the titration, but the big change in the value appeared clearly after adding 2ml of the NaOH solution.
- The addition of the sodium hydroxide solution decrease the ORP value gradually. After adding 2 ml there also a very clear deviation in the mV value.
- Figure 10 illustrate how the potentiometeric and pH-metric titrations progress the standard sample 4% against the reagents

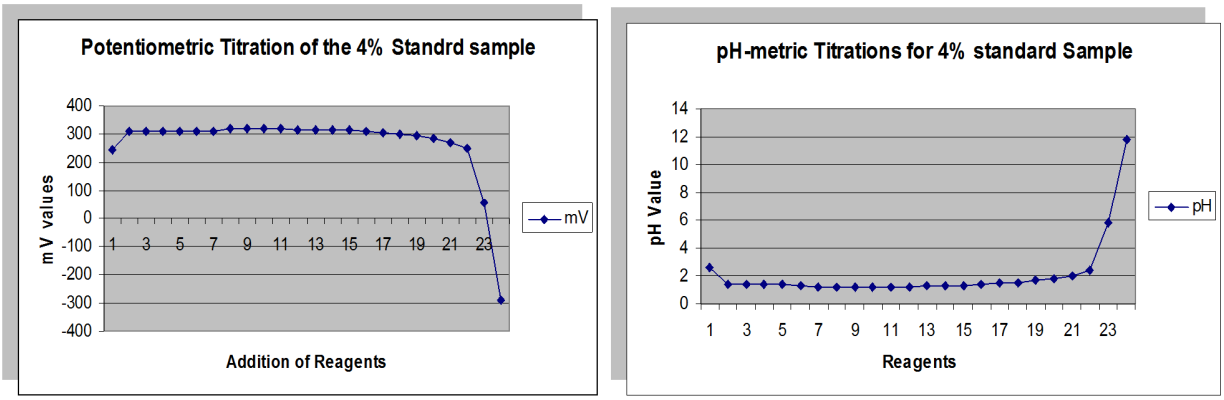


Figure 10: Illustrate the Treatment of the 4% prepared sample

4.3.5 Treatment of 8% Prepared sample:

The treatment of the 8% standard sample is well described in table 11a and 11b.

Table 11a Sample (8%) Against $NaHSO_3$

No	V of Na_2SO_3	pH	mV
1.	0	1.08	326.3
2.	1	1.09	326.0
3.	2	1.10	325.0
4.	3	1.12	323.8
5.	4	1.15	322.4
6.	5	1.21	318.7
7.	6	1.22	318.2
8.	7	1.23	317.7
9.	8	1.24	317.1
1(	9	1.26	316.3
1	10	1.26	315.7

Table 11b Sample (8%) Against NaOH

No	V. of NaOH (0.25) ml	pH	mV
1.	0	1.26	315.7
2.	0.25	1.31	336.3
3.	0.50	1.92	336.2
4.	0.75	1.95	337.1
5.	1.00	2.14	335.5
6.	1.25	2.98	334.8
7.	1.50	12.3	-316.3

From table 4 it clear that the pH value of the sample 8% is 2.27 and ORP value is 258.3mV. After the treatment process we conclude:

- The addition of the sulfuric acid reduce the pH value to 1.08 and increase the ORP value to 326.3 mV.
- The titration of the sample against sodium bisulfite solution increase the pH and decrease mV values gradually.
- The titration of this sample against sodium hydroxide solution increase the pH value slowly in the beginning of the titration, but the big change in the value appeared clearly after adding 2ml of the NaOH solution.
- The addition of the sodium hydroxide solution decrease the ORP value gradually. After adding 2 ml there is also a very clear deviation in the mV value.
- Chart 8 illustrate how the potentiometeric and pH-metric titrations progress for the standard sample 8% against the reagents.

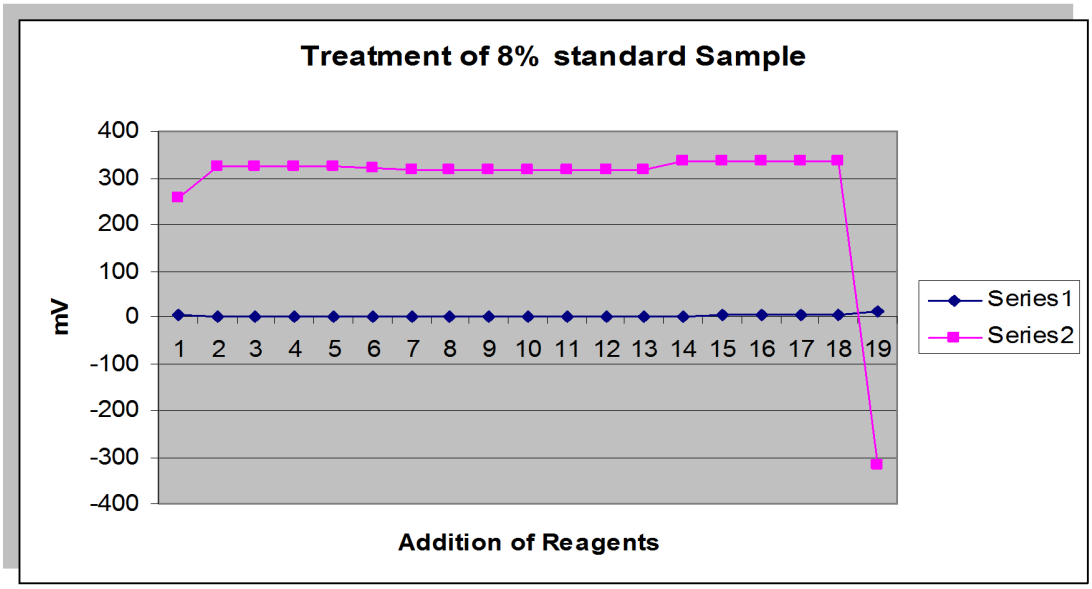


Figure 11: Illustrate the Treatment of the 8% prepared sample

4.3.6 Treatment of 10% prepared sample:

The treatment of the 10% standard sample is well described in table 12a and table 12b.

Table 12a Sample (10%) treatment with $NaHSO_3$

No	V of Na_2SO_3 In Cm^3	pH	mV
1	0	1.29	314.2
2	1	1.30	312.0
3	2	1.37	309.6
4	3	1.399	308.5
5	4	1.439	306.3
6	5	2.10	268.8
7	6	2.4	251.3

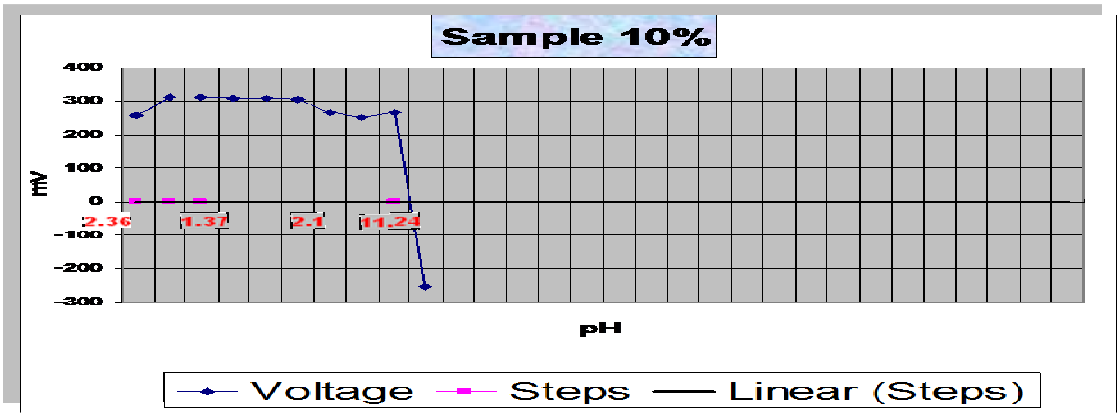
Table 12b the addition of NaOH to sample (10%)

No	V of NaOH	pH	mV
1	0.5	2.10	268.0
2	1	11.24	-255.2

From table 4 it clear that the pH value of the sample 10% is 2.36 and ORP value is 257.7mV. After the treatment process we conclude:

- The addition of the sulfuric acid reduce the pH value to 1.29 and increase the ORP value to 314.2 mV.
- The titration of the sample against sodium bisulfite solution increase the pH and decrease mV values gradually.
- The titration of this sample against sodium hydroxide solution increase the pH value slowly in the beginning of the titration, but the big change in the value appeared clearly after adding 2ml of the NaOH solution.
- The addition of 1 ml of the sodium hydroxide solution decrease the ORP from 268mV to -255mV and increase the pH from 2.10 to 11.24.
- Figure 11 illustrate how the potentiometeric & pH-metric titrations progress for the standard sample 10% against the reagents.

Figure 9: Illustrate the Treatment of the 10% prepared sample



4.3.7 Treatment of 14% prepared sample:

The treatment of the 14% standard sample is well described in table 13a and table 13b.

Table 13a Sample (14%) Against $NaHSO_3$

No	V of Na_2SO_3	pH	mV
1.	0	1.32	326.3
2.	1	1.18	320.8
3.	2	1.18	320.9
4.	3	1.10	325.0
5.	4	1.11	324.3
6.	5	1.13	323.3
7.	6	1.15	322.1
8.	7	1.18	320.9
9.	8	1.20	319.9
1(	9	1.21	318.8
1	10	1.23	317.7

Table 13b:Sample (14%) Against NaOH

No	V. of NaOH	pH	mV
1.	0	1.23	317.7
2.	0.25	1.30	313.9
3.	0.50	1.37	309.9
4.	0.75	1.45	305.5
5.	1.00	1.55	299.5
6.	1.25	1.67	292.8
7.	1.50	1.84	283.6
8.	1.75	2.06	269.0
9.	2.00	2.41	251.4
10	2.25	7.60	-37.8
11	2.50	11.8	-285.0

From table 4 it clear that the pH value of the sample 14% is 2.32 and ORP value is 255.40 mV. After the treatment process we conclude:

- The addition of the sulfuric acid reduce the pH value to 1.32 and increase the ORP value to 326.3 mV.
- The titration of the sample against sodium bisulfite solution increase the pH and decrease mV values gradually.
- The titration of this sample against sodium hydroxide solution increase the pH value slowly in the beginning of the titration, but the big change in the value appeared clearly after adding 2.25ml of the NaOH solution.
- The addition of 2.50 ml of the sodium hydroxide solution decrease the ORP from 317.7mV to -285mV and increase the pH from 1.23 to 11.8.

4.3.8 Treatment of 20% prepared sample:

The treatment of the 20% prepared sample is well described in table 14a and table 14b below:

Table 14a: Sample (20%) Against $NaHSO_3$

No	V of $NaHSO_3$ in ml	mV	pH
1.	0	308.7	1.39
2.	1	307.5	1.41
3.	2	305.4	1.45
4.	3	304.5	1.46
5.	4	303.4	1.48
6.	5	302.0	1.50
7.	6	300.5	1.53
8.	7	299.1	1.56
9.	8	297.6	1.58
10.	9	298.0	1.59

Table 14b: Sample (20%) Against NaOH

No	V of NaOH in ml	mV	pH
1.	0	298.0	1.59
2.	0.25	286.7	1.70
3.	0.50	271.5	2.04
4.	0.75	234.3	2.70
5.	1.0	24.1	6.30
6.	1.25	-290.2	11.8

From table 4 it clear that the pH value of the sample 20% is 2.05 and ORP value is 270.0 mV. After the treatment process we conclude:

- The addition of the sulfuric acid reduce the pH value to 1.39 and increase the ORP value to 308.7 mV.
- The titration of the sample against sodium bisulfite solution increase the pH and decrease mV values gradually.
- The titration of this sample against sodium hydroxide solution increase the pH value slowly in the beginning of the titration, but the big change in the value appeared clearly after adding 1ml of the NaOH solution.
- The addition of 1.25 ml of the sodium hydroxide solution decrease the ORP from 298.0 mV to -290.2 mV and increase the pH from 1.59 to 11.8.

4.4 The Treatment of the Random Samples:

4.4.1 Treatment of Collected sample1:

The treatment of the first random sample is well described in table 15a and 15b.

Table 15a :The treatment of Collected Samples 1 with $NaHSO_3$

No	V of $NaHSO_3$ in ml	mV	pH
1.	0	347.4	0.871
2.	1	342.4	0.869
3.	2	327.6	1.7
4.	3	322.0	1.27
5.	4	314.3	1.29
6.	5	323.6	1.21
7.	6	325.5	1.09
8.	8	322.7	1.14
9.	9	321.5	1.19
10.	10	320.4	1.18
11.	11	319.1	1.22
12.	12	314.1	1.28
13.	13	313	1.33
14.	14	314.2	1.288
15.	15	313.4	1.333
16.	16	312.7	1.32
17.	17	311.7	1.355
18.	18	310	1.36
19.	19	309.7	1.38
20.	20	308.5	1.395

Table 15b:The treatment of Collected Sample 1 Against NaOH

No	V of NaOH in ml	mV	pH
1.	0	306.0	1.46
2.	0.25	299.1	1.55
3.	0.50	289.9	1.73
4.	0.75	267.3	2.11
5.	1.0	231.3	2.76
6.	1.25	115.7	4.77

The initial pH value of this sample is 1.3 and ORP value is 302.0 mV. After the treatment process we conclude:

- The addition of the solution of sulfuric acid reduce the pH value to 0.871 and increase the ORP value to 347.4 mV.

- The titration of the sample against sodium bisulfite solution increase the pH and decrease mV values gradually.
- The titration of this sample against sodium hydroxide solution increase the pH value slowly in the beginning of the titration, but the big change in the value appeared clearly after adding 2ml of the NaOH solution.
- The addition of the sodium hydroxide solution decrease the ORP value gradually.

- Chart 10 illustrate how the potentiometeric & pH-metric titrations progress for the random collected sample1 against the reagents.

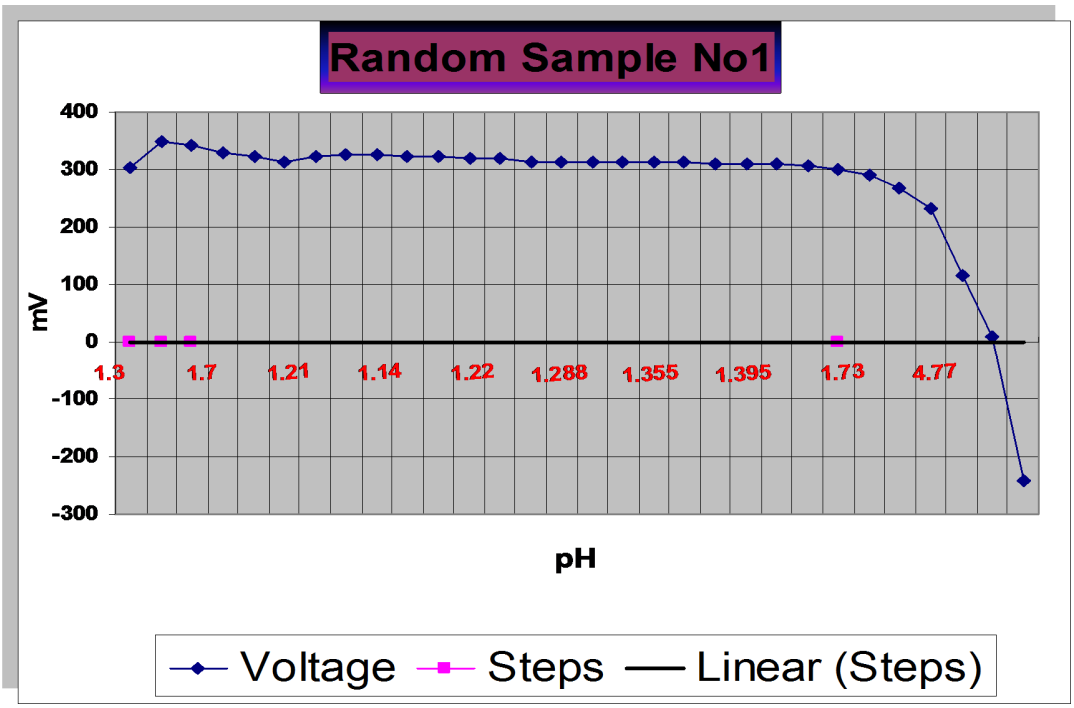


Figure 10: Illustrate the Treatment of the Random sample1

4.4.2 Treatment of Collected sample2:

The treatment of the second random sample is well described in table 16a and 16b as below:

Table 16a:The treatment of Collected Samples 2 with $NaHSO_3$

No	V of $NaHSO_3$ in ml	mV	pH
21.	0	347.4	0.762
22.	1	337.3	0.86
23.	2	333.1	0.96
24.	3	334.5	0.98
25.	4	335.2	0.984
26.	5	328.6	0.955
27.	6	325.5	1
28.	8	325.5	1.099
29.	9	324.3	1.111
30.	10	320.3	1.139
31.	11	316.7	1.25
32.	12	317.1	1.255
33.	13	314	1.26
34.	19	347.4	0.955
35.	20	337.3	1

Table 16b:The treatment of Collected Sample 1 Against NaOH:

No	V of NaOH in ml	mV	pH
1.	0	314.0	1.26
2.	0.25	309.4	1.37
3.	0.50	302.1	1.508
4.	0.75	287.7	1.727
5.	1.0	272.9	1.024
6.	1.25	233.2	2.725

The initial pH value of this sample is 1.53 and ORP value is 314.6 mV. After the treatment process we conclude:

- ❖ The addition of the sulfuric acid solution reduce the pH value to 0.762 and increase the ORP value to 347.4 mV.
- ❖ The titration of the sample against sodium bisulfite solution increase the pH and decrease mV values gradually.
- ❖ The titration of this sample against sodium hydroxide solution increase the pH value slowly in the beginning of the titration.
- ❖ The addition of the sodium hydroxide solution decrease the ORP value gradually.
- ❖ Figure 11 illustrate how the potentiometeric & pH-metric titrations progress for the random collected sample2 against the reagents.

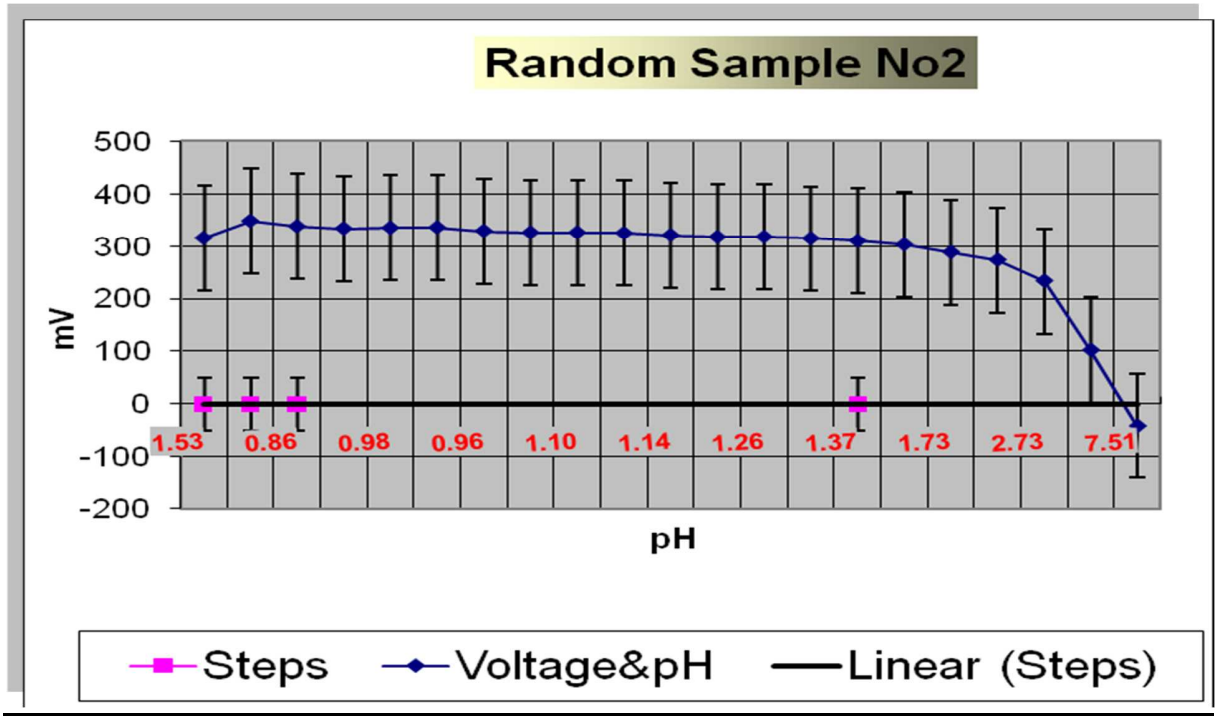


Figure 11: Illustrate the Treatment of the Random sample2

Conclusion And Recommendations

5.1 Conclusion:-

Last but not the least we can conclude the following important remarks:

- The treatment of hexavalent chromium waste water can depend on the potentiometeric titration through the system of Sepotrato 100R.
- The treatment process can not complete without adding suitable quantity of sulfuric acid solution as a reaction catalyst.
- The system can ignore reading the pH value in starting mode.
- For the necessity of the chemical reaction the system must add Sulfuric acid directly in the beginning of the treatment process.
- The addition of sulfuric acid have to be controlled by a timer instead of the pH-transmitter.
- To test the waste water ,if it is contaminated with hexavalent chromium or not, the system can depend on oxidation reduction value after adding the acid.
- If the value of ORP is greater than 200mV, the system can proceed to complete the treatment process by adding the solution of sodium bi sulfite.
- The reduction process must depend on the transmitter of reduction potential.
- The addition of sodium bi sulfite solution affect the value of ORP if waste water contaminated with oxidizing agent such as hexavalent chromium.
- The addition of sodium hydroxide result in lowering the ORP value and increase the pH value too.
- The treated waste water must be colorless, the pH value between 8-10, and the ORP is less than 30mV.
- The ORP value of contaminated waste water is always greater than 200mV.
- The ORP value of the solution is directly proportional to the amount of sulfuric acid added.

- ❖ The ORP value of the acidified hexavalent chromium solution is inversely proportional to the amount of sodium bisulfite solution added.
- ❖ The ORP value of the treated solution is inversely proportional to amount of sodium hydroxide solution added.

5.2 Recommendations:-

Finally, we can summarize our recommendations in the following points:

- ➢ The system of Sepotrato 100R must be reprogrammed according to the resulted value of this research.
- ➢ Complete automation is possible through an interface and simple computer program. So as to manage the process of the treatment of the waste water contaminated with chromium(VI).
- ➢ The Italian system of Sepotrato 100R can be recalibrated and programmed to deal with deferent types of waste water contaminated with heavy metals such as Nickel , and copper.
- ➢ The system can treat the alkaline and acidified waste water which is not contaminated with heavy metals automatically if it is well programmed.
- ➢ The system can pass the good waste water without any treatment or bad consuming of chemicals if it is inelegancy be improved by a computer programming.

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Appendixes

Tables

Table 1:preparations of Prepared Samples

NO	Volume of Cr^{+6} In mL	Dilution in mL	percentage
1	0	50	0%
2	0.5	50	1%
3	1	50	2%
4	1.5	50	3%
5	2	50	4%
6	3	50	6%
7	4	50	8%
8	5	50	10%
9	7	50	14%
10	10	50	20%

Table 2: Standardization of Reagents:

No	Titration	Conc. mole/Liter
1	Sodium Thiosulphate	0.10016
2	Sodium bisulfite	0.5905
3	Standard Solution of Chromium (VI)	0.0629

Table 3: the preparation of standard samples:

NO	Volume of Cr^{+6} In mL	Dilution in mL	percentage	Cr^{+6} concentration in mole/L	Cr^{+6}concentration in mg/L
1	0	50	0%	0	0
2	0.5	50	1%	0.000629	32.71
3	1	50	2%	0.001258	65.41
4	3	100	3%	0.001887	130.82
5	2	50	4%	0.002516	163.53
6	3	50	6%	0.003774	196.23
7	4	50	8%	0.005032	261.64
8	5	50	10%	0.00629	327.06
9	7	50	14%	0.008806	457.88
10	10	50	20%	0.01258	654.16

Table 4:The treatment of standard Samples by *$NaHSO_3$:*

NO	percentage	Conc. of Cr^{+6} in mg/L	Volume Of Sodium bisulfite Needed in ml (10 ml of sample)	Volume Of Sodium bisulfite Needed in ml (for 1L Sample)
1	0%	0	0	0.00
2	1%	32.70	0.06	6.39
3	2%	65.40	0.13	12.78
4	3%	1308.07	2.56	255.65
5	4%	163.51	0.32	31.96
6	6%	1962.31	3.84	383.51
7	8%	261.61	0.51	51.13
8	10%	327.02	0.60	63.90
9	14%	457.88	0.84	89.46
10	20%	654.16	0.89	89.48

Table 5: Prepared Samples pH & ORP Readings:

NO	Cr+ concentration in percentage	pH reading	ORP in mV
1	0%	7.28	-27
2	1%	3.521	237.6
3	2%	3.417	240.2
4	3%	2.57	243.0
5	4%	2.60	245.5
6	6%	2.31	251.3
7	8%	2.27	258.3
8	10%	2.36	257.7
9	14%	2.32	255.40
10	20%	2.05	270.0

Table 6a: Blank sample (0%) treatment with *$NaHSO_3$*:-

No	V of $NaHSO_3$ (2ml)	pH	mV
11.	0	1.48	310.4
12.	2	1.74	289.0
13.	4	1.58	297.7
14.	6	1.60	296.8
15.	8	1.58	297.8
16.	10	1.47	303.7
17.	12	1.09	325.6
18.	14	1.31	313.5
19.	16	1.30	313.9
20.	18	1.23	317.6

Table 6b: Blank Sample (0%) against NaOH:

No	V of NaOH in ml	pH	mV
1.	0	1.23	317.6
2.	2	1.42	306.7
3.	4	1.50	299.1
4.	6	1.60	296.7
5.	8	4.7	116.6
6.	10	7.68	-50.2
7.	12	11.14	-247.3

Table 7a: Sample (1%) against *$NaHSO_3$:*

No	V of Na2SO3	pH	mV
1	0	1.20	319.5
2	1	1.05	328.0
3	2	1.06	327.0
4	3	1.08	326.5
5	4	1.09	325.4
6	5	1.11	324.1
7	6	1.14	323.1
8	7	1.16	322.0
9	8	1.17	321.3
10	9	1.19	320.4

Table 8 a: sample (2%) against *$NaHSO_3$:*

No	V of Na_2SO_3	pH	mV
1	0	1.083	326.5
2	1	1.073	327.0
3	2	1.077	326.8
4	3	1.076	326.7
5	4	1.097	325.8
6	5	1.106	325.2
7	6	1.121	324.4
8	7	1.143	323.2

Table 8b: sample (2%) against NaOH*:*

No	V of NaOH in ml	pH	mV
1	0	1.143	323.2
2	0.25	1.207	319.0
3	0.50	1.268	316.4
4	0.75	1.360	311.1
5	1.0	1.482	303.6
6	1.25	1.626	295.5
7	1.50	1.811	285.3
8	1.75	2.12	267.3
9	2.0	3.10	214.7
10	2.25	11.5	-272.7

Table 9a: Sample (3%) against *$NaHSO_3$*:

No	V of Na_2SO_3	pH	mV
1	0	1.036	328.7
2	1	1.072	328.7
3	2	1.058	327.8
4	3	1.105	325.0
5	4	1.120	324.3
6	5	1.142	321.1
7	6	1.160	321.7
8	7	1.180	320.4
9	8	1.20	319.3

Table 9b: Sample (3%) against NaOH:

No	V of NaOH in ml	pH	mV
1	0	1.20	319.3
2	0.25	1.28	315.0
3	0.50	1.36	310.2
4	0.75	1.44	305.7
5	1.0	1.55	299.6
6	1.25	2.07	271.0
7	1.50	2.12	267.0
8	1.75	2.43	249.5
9	2.0	3.11	210.6
10	2.25	11.32	-263.1

Table 10a: Sample (4%) Against *$NaHSO_3$:*

No	Volume of Na_2SO_3	mV	pH
1.	0	307.9	1.40
1.	1	308.4	1.39
2.	2	310.1	1.36
3.	3	310.5	1.36
4.	4	311.2	1.35
5.	5	309.5	1.20
6.	6	319.3	1.20
7.	7	319.1	1.21
8.	8	318.1	1.21
9.	9	317.7	1.23
10.	10	317.1	1.24
11.	11	316.2	1.26
12.	12	315.7	1.27

Table 10b: Sample (4%) Against NaOH:

No	Volume of NaOH	mV	pH
1.	0	315.7	1.27
2.	0.25	312.7	1.33
3.	0.50	308.7	1.39
4.	0.75	304.8	1.46
5.	1.0	300.4	1.54
6.	1.25	293.5	1.66
7.	1.50	284.6	1.81
8.	1.75	272.4	2.03
9.	2.0	251.1	2.40
10.	2.25	57.5	58
11.	2.50	-288.9	11.8

Table 11a: Sample (8%) Against *$NaHSO_3$:*

No	V of Na_2SO_3	pH	mV
1.	0	1.08	326.3
2.	1	1.09	326.0
3.	2	1.10	325.0
4.	3	1.12	323.8
5.	4	1.15	322.4
6.	5	1.21	318.7
7.	6	1.22	318.2
8.	7	1.23	317.7
9.	8	1.24	317.1
10.	9	1.26	316.3
11.	10	1.26	315.7

Table 11b: Sample(8%) Against NaOH*:*

No	V. of NaOH (0.25) ml	pH	mV
1.	0	1.26	315.7
2.	0.25	1.31	336.3
3.	0.50	1.92	336.2
4.	0.75	1.95	337.1
5.	1.00	2.14	335.5
6.	1.25	2.98	334.8
7.	1.50	12.3	-316.3

Table 12a: Sample (10%) treatment with *$NaHSO_3$:*

No	V of Na_2SO_3 In Cm^3	pH	mV
1	0	1.29	314.2
2	1	1.30	312.0
3	2	1.37	309.6
4	3	1.399	308.5
5	4	1.439	306.3
6	5	2.10	268.8
7	6	2.4	251.3

Table 12b: the addition of NaOH to sample (10%):

No	V of NaOH	pH	mV
1	0.5	2.10	268.0
2	1	11.24	-255.2

Table 13a: Sample (14%) Against *$NaHSO_3$:*

No	V of Na_2SO_3	pH	mV
1.	0	1.32	326.3
2.	1	1.18	320.8
3.	2	1.18	320.9
4.	3	1.10	325.0
5.	4	1.11	324.3
6.	5	1.13	323.3
7.	6	1.15	322.1
8.	7	1.18	320.9
9.	8	1.20	319.9
1(	9	1.21	318.8
1:	10	1.23	317.7

Table 13b:Sample (14%) Against NaOH:

No	V. of NaOH	pH	mV
1.	0	1.23	317.7
2.	0.25	1.30	313.9
3.	0.50	1.37	309.9
4.	0.75	1.45	305.5
5.	1.00	1.55	299.5
6.	1.25	1.67	292.8
7.	1.50	1.84	283.6
8.	1.75	2.06	269.0
9.	2.00	2.41	251.4
10	2.25	7.60	-37.8
11	2.50	11.8	-285.0

Table 14a: Sample (20%) Against *$NaHSO_3$:*

No	V of $NaHSO_3$ in ml	mV	pH
1.	0	308.7	1.39
2.	1	307.5	1.41
3.	2	305.4	1.45
4.	3	304.5	1.46
5.	4	303.4	1.48
6.	5	302.0	1.50
7.	6	300.5	1.53
8.	7	299.1	1.56
9.	8	297.6	1.58
10.	9	298.0	1.59

Table 14b: Sample (20%) Against NaOH:

No	V of NaOH in ml	mV	pH
1.	0	298.0	1.59
2.	0.25	286.7	1.70
3.	0.50	271.5	2.04
4.	0.75	234.3	2.70
5.	1.0	24.1	6.30
6.	1.25	-290.2	11.8

Table 15a :The treatment of Collected Samples 1 with *$NaHSO_3$* :

No	V of $NaHSO_3$ in ml	mV	pH
1.	0	347.4	0.871
2.	1	342.4	0.869
3.	2	327.6	1.7
4.	3	322.0	1.27
5.	4	314.3	1.29
6.	5	323.6	1.21
7.	6	325.5	1.09
8.	8	322.7	1.14
9.	9	321.5	1.19
10.	10	320.4	1.18
11.	11	319.1	1.22
12.	12	314.1	1.28
13.	13	313	1.33
14.	14	314.2	1.288
15.	15	313.4	1.333
16.	16	312.7	1.32
17.	17	311.7	1.355
18.	18	310	1.36
19.	19	309.7	1.38
20.	20	308.5	1.395

Table 15b:The treatment of Collected Sample 1 Against NaOH*:*

No	V of NaOH in ml	mV	pH
1.	0	306.0	1.46
2.	0.25	299.1	1.55
3.	0.50	289.9	1.73
4.	0.75	267.3	2.11
5.	1.0	231.3	2.76
6.	1.25	115.7	4.77

Table 16a:The treatment of Collected Samples 2 with *$NaHSO_3$:*

No	V of $NaHSO_3$ in ml	mV	pH
1.	0	347.4	0.762
2.	1	337.3	0.86
3.	2	333.1	0.96
4.	3	334.5	0.98
5.	4	335.2	0.984
6.	5	328.6	0.955
7.	6	325.5	1
8.	8	325.5	1.099
9.	9	324.3	1.111
10.	10	320.3	1.139
11.	11	316.7	1.25
12.	12	317.1	1.255
13.	13	314	1.26
14.	19	347.4	0.955
15.	20	337.3	1

Table 16b:The treatment of Collected Sample 1 Against NaOH*:*

No	V of NaOH in ml	mV	pH
1.	0	314.0	1.26
2.	0.25	309.4	1.37
3.	0.50	302.1	1.508
4.	0.75	287.7	1.727
5.	1.0	272.9	1.024
6.	1.25	233.2	2.725

Charts

Chart 1: show the descending of standard samples concentration:

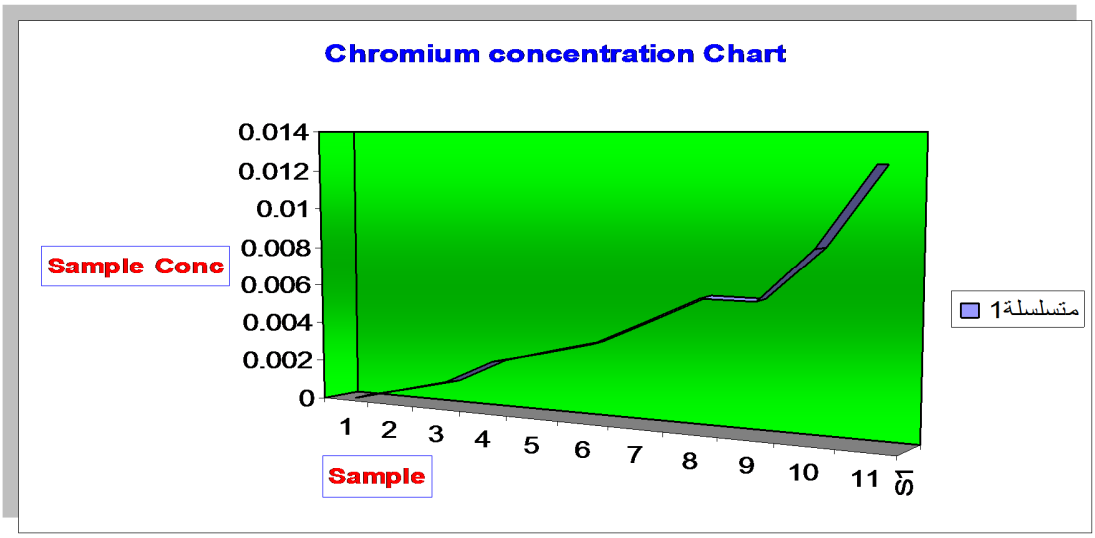


Chart 2:Illustrate the relation between concentrations and redox value of the standard samples

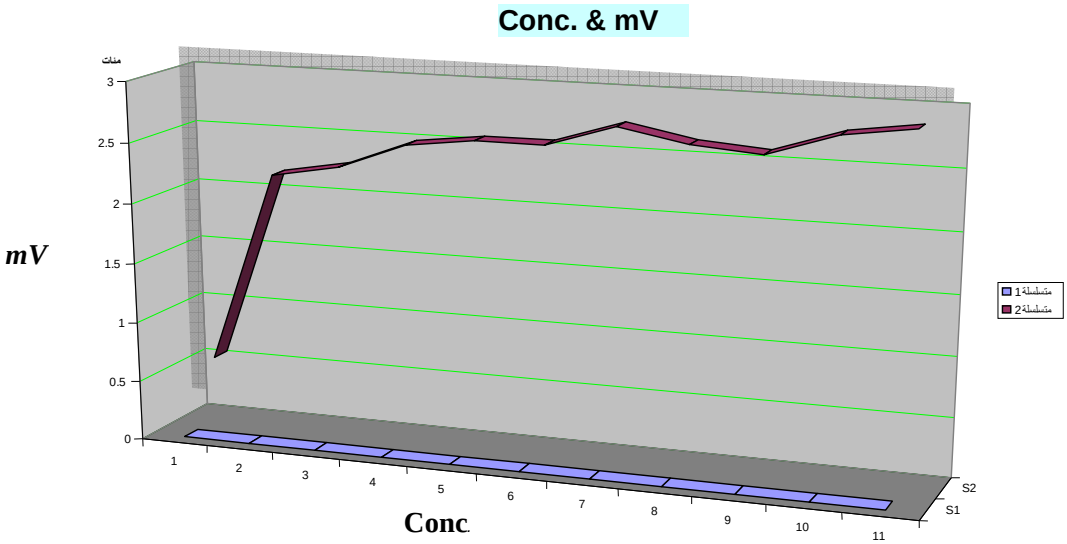


Chart 3: illustrate the relation between hexavalent chromium concentration and the pH of the solution:

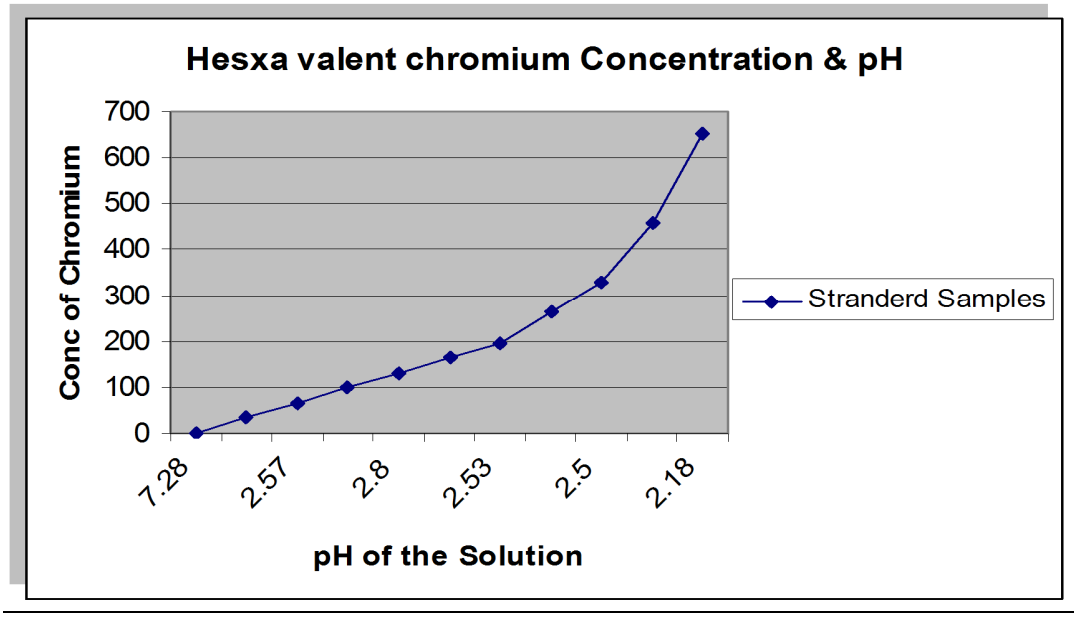


Chart 4. Illustrate the treatment of the Blank sample:

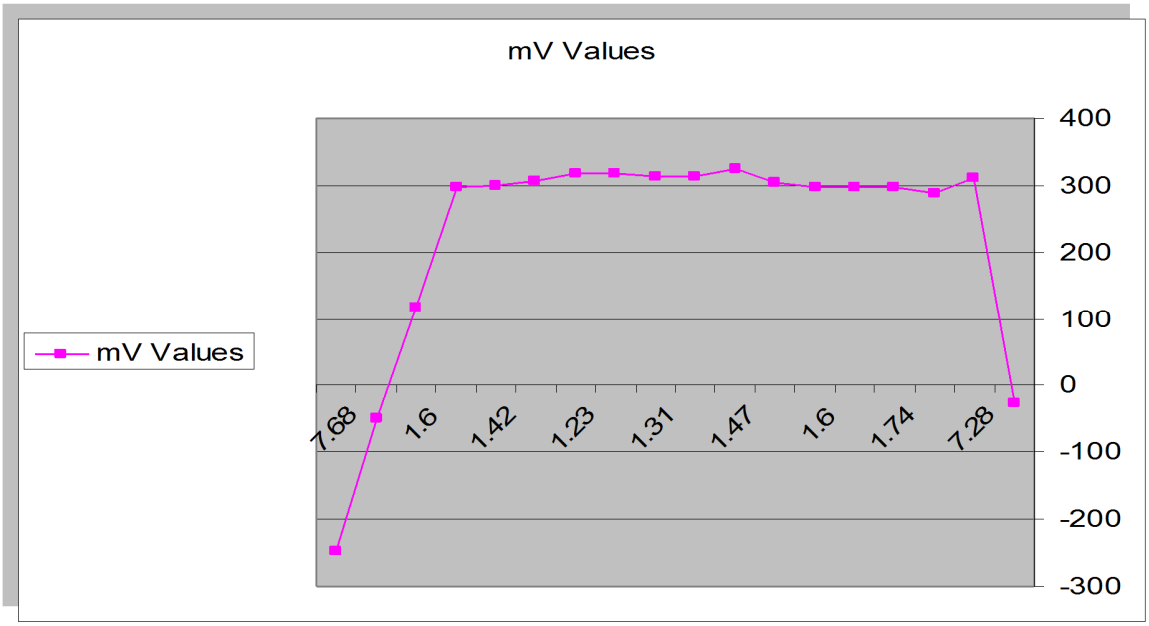


Chart 5a: Illustrate the potentiometer Titration of the 2% sample:

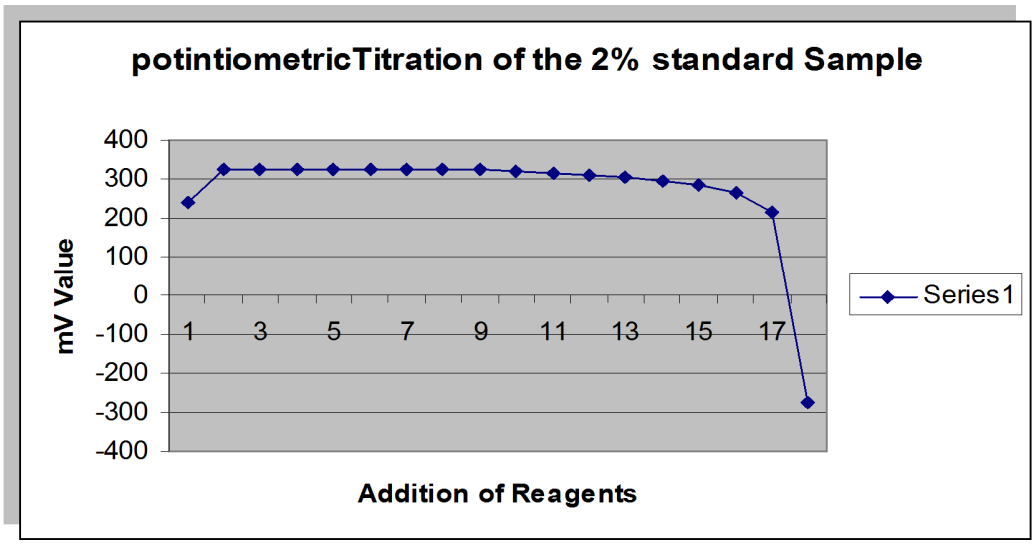


Chart 5b: Illustrate the pH-metric Titration of the 2% sample:

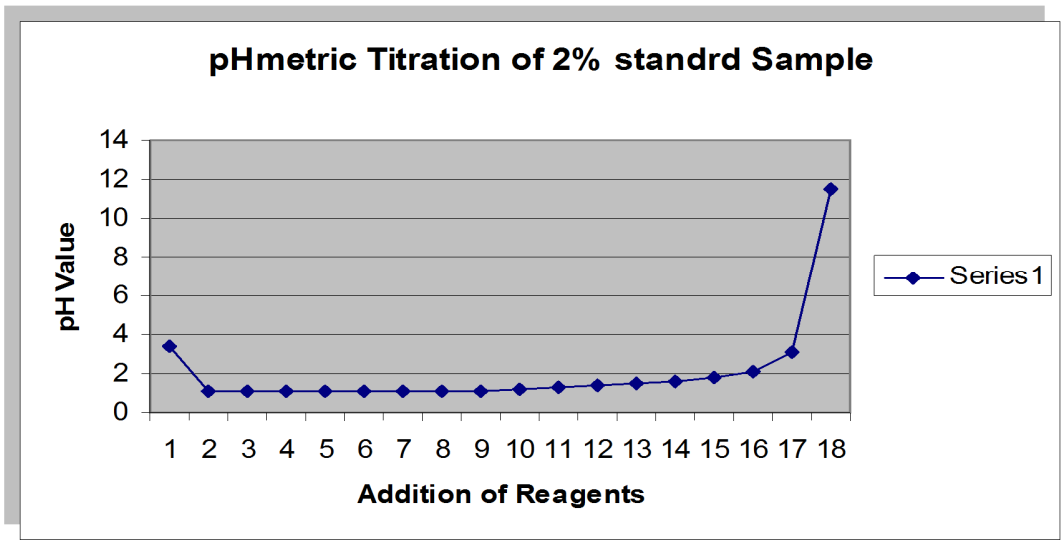


Chart 6: Illustrate the Treatment of the 3% standard sample:

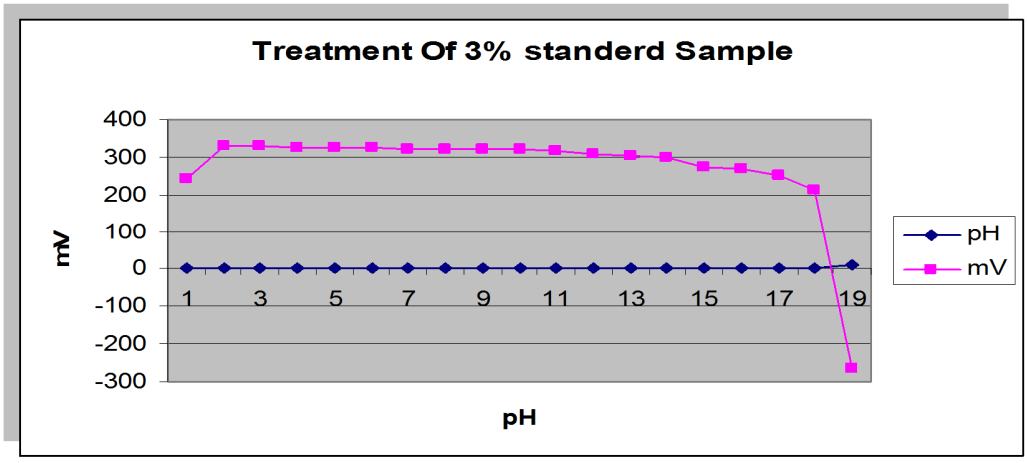
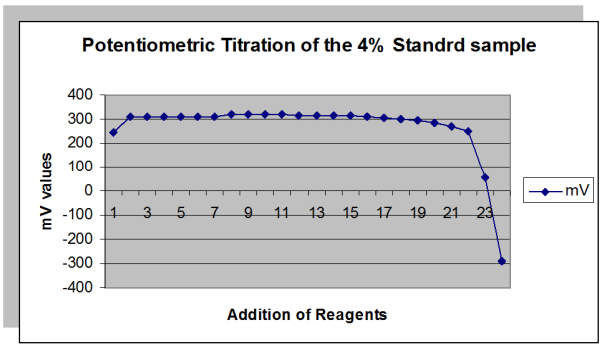


Chart 7: Illustrate the Treatment of the 4% standard sample:



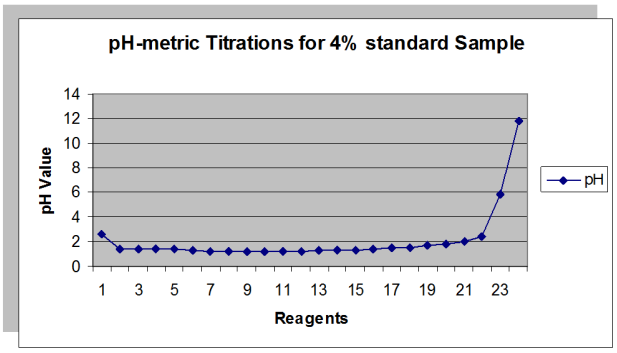


Chart 8: Illustrate the Treatment of the 8% standard sample:

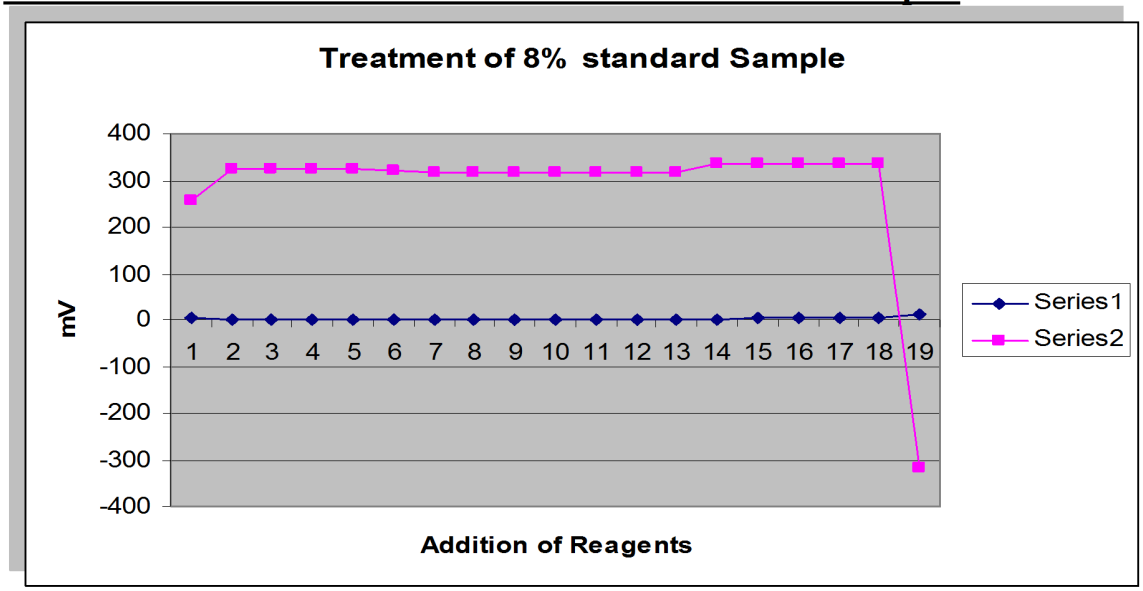


Chart 9: Illustrate the Treatment of the 10% standard sample:

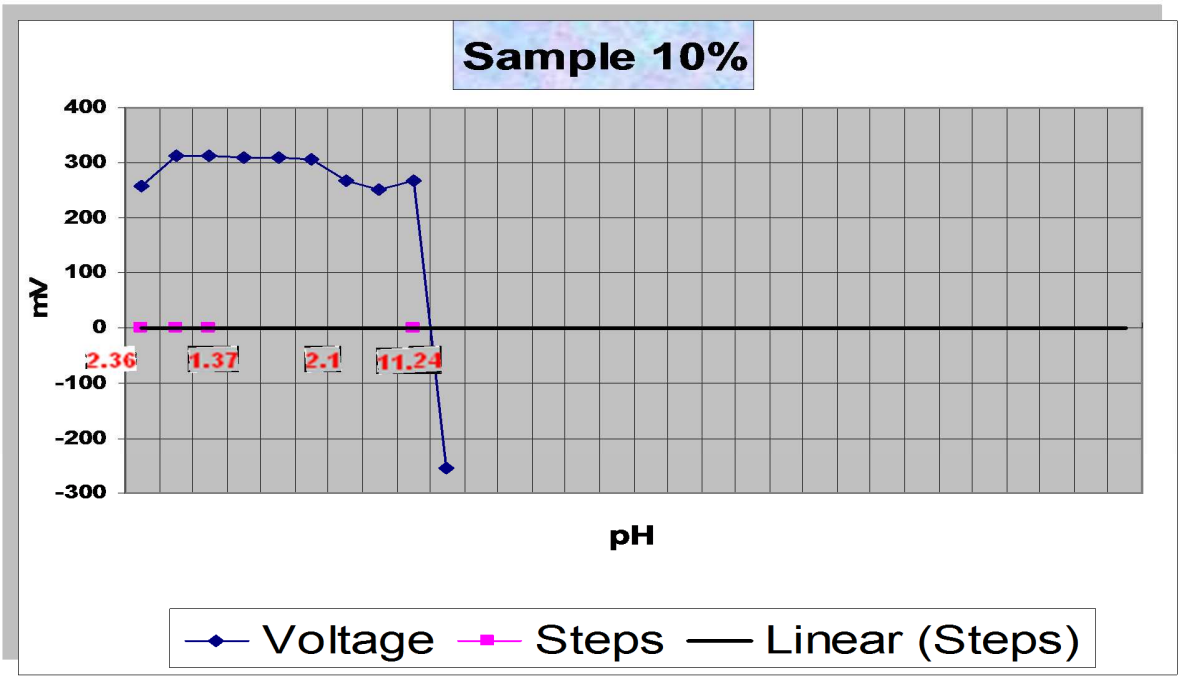


Chart 10: Illustrate the Treatment of the Random sample1:

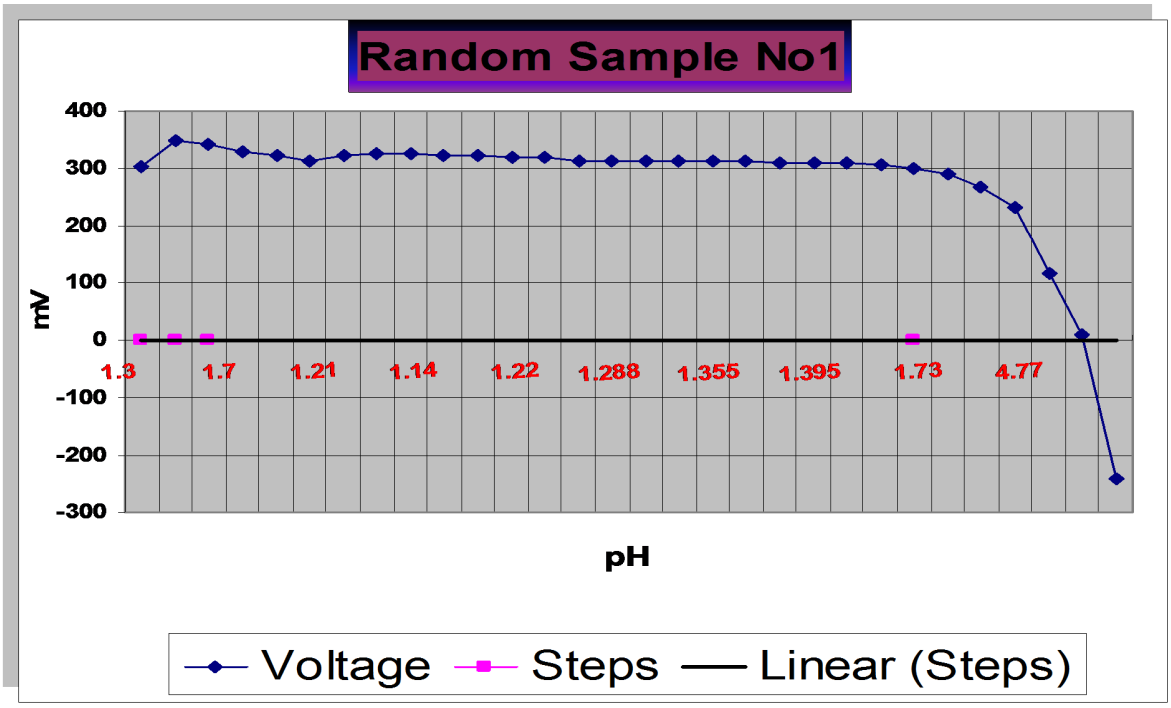


Chart 11: Illustrate the Treatment of the Random sample2: