Chapter one

Introduction

Introduction

Water quality refers to measurement of some constituents in water. It is directly related to health of people. Evaluation of water quality is done by chemical, physical, microbial and radiological analysis.

In this research two samples were collected from two location Dar Almazeed village in each. Contamination of water with iron in one of the major problem facing water quality specially ground water. Many wells in different area in Sudan have a high iron content some of them the concentration exceed the permissible levels. Other have a high concentration which reach up to 15 ppm.

Although it is known that and according of international standards the maximum permissible level for ion is 0.3 ppm, this reflect importance of having a regular analysis and records for all water wells servicing people.

Chapter two

Literature review

2.1 Introduction:

Water is an odorless ,tasteless and colorless liquid made up of combination of hydrogen and oxygen

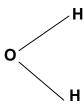
Water which forms rains, moisture, snow, streams, lakes and seas. It occurs in a large quantities in the hydrosphere, atmosphere and liothphere. And have different states (liquid, solid and gas) and it is natural solvent.

Water is of major importance to all living things and essential raw material for life⁽¹⁾.

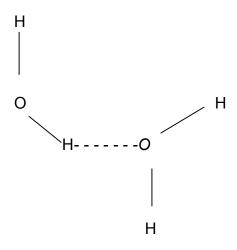
2.2 Chemistry of water:

The structure of water is an important in controlling the chemistry of ground water because it is influence on the solubility of solid and organic liquid.

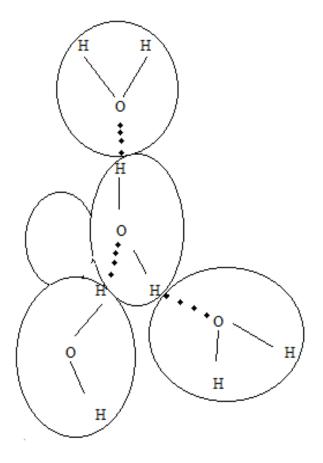
The water molecule is compose of two hydrogen atoms and on oxygen atom, Shared electrons form covalent bond between hydrogen atoms are located symmetrically with respect to the oxygen atom, Because of this structure and covalent bonding; the electrical center of the negative charges (electrons) have different location than positive charges. This separation make the molecule is Polar I n terms of electrical charge.



The water molecules are joined in a series of hydrogen bonds formed by electrostatic interaction between hydrogen atoms and oxygen atom.

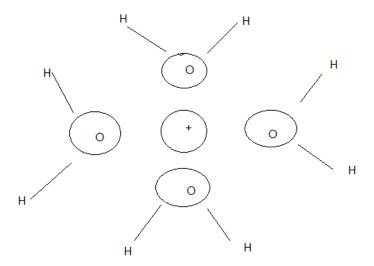


As result of this interaction the water molecules formed octahedral network creating a series of large molecules. And this structure explains some characteristics of water such as freezing point and boiling point.



The structure also contributes to the relative solubility of electrolytes and insolubility of non-electrolytes in aqueous. And the advantages for charges species to be accommodated in water structure overcoming the energy that tends to keep atoms in the solid or another liquid. In water charged species force rearrangement .The water molecules immediately adjacent bind to the charged specie like this

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In the cause of non-polar organic molecule energetically more favorable for mass to remain in an organic liquid rate then the aqueous solution⁽¹⁾.

2.3Anomalous properties of water

The most common physical properties of water that water is a liquid at room temperature, and normal atmospheric pressure .surprising property of water because almost another compound with similar molar mass to water (18 g/mole) are gases under similar condition of temperature and pressure like N₂, and O₂. All these have molar mass lower than water but found in gaseous state

Solubility (ionic /covalent) (bonding /nonbonding), high surface tension, high latent heat of vaporization, high specific heat and low vapor pressure⁽¹⁾.

2.4 Uses 0f water

Domestic (drinking ,cooking ,and sanitation).

Agriculture(plants, animals).

Industry(raw material ,dissolution , transport ,medium, washing ,cooling)⁽²⁾.

2.5 Sources of water

Water that can be made suitable for drinking comes from either surface water or ground water

Surface water; water from lakes, rivers and reservoirs frequently contains substance that must be removed before it can be used as the drinking water

Ground water; water pumped from wells that have been drilled into underground aquifers is usually free from harmful contamination⁽²⁾.

2.6 The significance of various substance found in water:

2.6.1 Acidity

Acid water is one which has pH value less than 7. The most causes of acidity are free carbon dioxide in the water ,organic matter , sulphates which occurs when rain falls through polluted industrial atmosphere or when ground water flow through soils having high sulphate content and some contain iron-bearing formation. Sulfuric acid is produce in the water as a result.

Some treatment processes, notably the use aluminum sulphate as coagulate make water acid. For any treatment works the aim should be to correct the acidity of water and make the pH value slightly above 7.

2.6.2 Alkalinity

Alkalinity of water is due to presence of bicarbonates, carbonates, hydroxides of calcium, magnesium, potassium and sodium. The term alkalinity describes the total amount of those substances which are present in water.

Calcium and magnesium bicarbonate cause temporary hardness and when the hardness is greater.

Than alkalinity this make permanent hardness . The alkalinity of many water 100 -200 ppm.

2.6.3 Aluminum

Not found in natural waters in detectable amount but it may be enter a water from the use of aluminum tanks or pipes. And from over dosing of aluminum sulphate in water supply treatment and the effluent should not contain more than 0.15 ppm⁽³⁾.

2.6.4 Ammonia compounds

There are two main compounds (i) free ammonia called ammoniac ammonia. (ii) albuminoidal ammonia.

When the animal and vegetable matter decays ammonia is produce hence most waters contain at least trace of ammonia⁽³⁾.

2.6.5Arsenic

Is a poison which should not be present to detectable amount in any water supply. It can enter to water from the use of arsenical sprays for weed killing or arsenic solution for sheep dipping⁽³⁾.

2.6.6 Bromine

Sea water contains 50 to 60 ppm ,and some wells contains 2.2ppm. It is not toxic substance in quantities present in water supply⁽³⁾.

2.6.7 calcium

present in water as bicarbonate which is soluble in water and cause water hardness. And also found as sulphate and carbonate⁽³⁾.

2.6.8 carbon dioxide (CO₂)

Free carbon dioxide existing in combination with calcium and magnesium is much important as regarded the corrosive property of water. It is the main causes of acid water. Free CO₂ content up to 10ppm not cause corrosive of water but higher than 20ppm make water corrosive⁽³⁾.

2.6.9 Chlorides

Sodium chloride, calcium chloride and magnesium chloride are present in small quantity in some water but in large quantity in sea water. The amount of sodium chloride present 1.5 times of chloride⁽³⁾.

2.6.10 Chlorine

Is sterilizing gas added to water. The maximum amount of free chlorine which permitted to remain in water depend upon the taste, odor and corrosion that may result. The residual free chlorine content up to 0.20ppm⁽³⁾.

2.6.11Copper

Copper is rarely found in natural waters. But it may in a water supply from use of copper piping or from the dosing of an impounding reservoir with copper sulphate for reduction of algae growths. Water put in distribution system should not contain more than 0.05ppm ⁽³⁾.

2.6.12 Fluorine

It is known that dental decay in children can be reduced by drinking water which contains about 1ppm of fluorine. Excessive quantities of fluorine are toxic⁽³⁾.

2.6.13 Lead

Is accumulation poison and not more than 0.1ppm should exist in a water as drawn from the consumer's tap; preferably none should be detected⁽³⁾.

2.6.14 lodine

Natural waters contain only trace amount of iodine, but this small amount is beneficial to consumers if their diet is over otherwise deficient iodine. Goiter is believed to be an iodine deficiency disease and addition of iodine in some causes give benefit to goiter sufferers⁽³⁾.

2.6.15 Iron

Is frequency found in raw waters and trace usually found in all waters delivered to the consumers when the water has been contact with iron pipes. When iron present above a certain amount it make a water unpalatable, imparting a bitter taste to the water when present in large amounts and make a precipitate when iron present with oxygen and cause brown stains upon laundry and sinks. Iron can be picked up from the many underground formation and when water contain ions is often corrosive. Treatment for removal iron is likely to be necessary when the amount of iron exceeds 0.3ppm⁽³⁾.

2.6.16 Biochemical oxygen demand (B.O.D)

It is measure because it used as an indicator to the degree of pollution. When the organic matter is breakdown by biological organisms uses up oxygen from water; so that the oxygen deficiency when high B.O.D that indicate high pollution and destroyed the fish and plant⁽³⁾.

2.6.17 Magnesium

Magnesium bicarbonate cause temporary hardness in water. The cause of magnesium compounds is much less than the proportion caused by calcium compounds⁽³⁾.

2.6.18 Manganese

Is often associated with iron in water, have the same behavior except that the deposits are accumulative. High quantity of manganese are toxic. Both nor land and wells waters can contain troublesome amount of manganese. In general less amount of manganese can be correlated than iron because the deposition of manganese is slow. And the limits from 0.2 to 0.3ppm⁽³⁾.

2.6.19 Nitrates and nitrites

Cause when organic matter decays. Nitrites appear less than nitrates in water. A deep well water.

Contain about 5ppm and nitrates derived from soil vegetation. But in surface supply or shallow well contain 20ppm⁽³⁾.

2.6.20 Organic matter

Come from plants and animal life the taste for ammonia or nitrates or nitrite are indicate the present of organic matter in water⁽³⁾.

2.6.21 phenois

Are substances in water which originate from trade wasted and creosoted surfaces. There present even in minute quantities of 0.001ppm can make widespread complaints from consumer⁽³⁾.

2.6.22 phosphate

Come from oxidation of phosphorus originating in vegetable and organic matter or from certain rocks⁽³⁾.

2.6.23 Potassium

Potassium phosphate and potassium sulphate are forms of potassium in water⁽³⁾.

2.6.24 silica

Found up to 40ppm as SiO_2 in hard water and in rivers from d5 to 20 ppm⁽³⁾.

2.6.25 Sodium

sodium chloride is usually taken to be evidence of pollution by sea water if quantities found exceeds the normal amount to be expected. When the water come from non dangerous supply source it may be up to 1400ppm⁽³⁾.

2.6.26 Zinc

Is very rarely present in natural water. But not rare in water when it is drawn at consumers taps because of the use of galvanized iron piping and tanks. Zinc dose not exist in water consumed excess than 15ppm⁽³⁾.

2.7 Chemistry of cadmium

Cadmium is a metallic element with atomic number 48 and relative atomic mass 112.41 . In its pure form it's silver white metal and relatively soft .

Cadmium is most often present in nature as complex oxides, sulphides and carbonate in zinc, lead and copper ores and is very rarely present in the elemental form.

Cadmium is obtained during the distillation of crude zinc. It also present as its ions in the zinc sulphate solution from which zinc is obtain by electrolysis; but since cadmium has less negative electrode potential than zinc, it can be obtained by electrolytic method before any zinc is deposited by carful control of voltage used across the cell⁽⁴⁾.

Or by displaced from the same solution by addition of zinc

$$Cd^{2+}(aq) + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + Cd_{(s)}$$

2.7.1 properties and uses of cadmium

Cadmium is white lustrous metal ,soft and more malleable and ductile. It is reactive and when exposed to moist air for any length of time protective layer is formed on their surface; and this is the oxide initially but over period of time the basic carbonate is formed.

About 60 percent of total output of cadmium is used for coating iron and steel. And used in the manufacture of cadmium-nickel alkaline storage batteries which is used in alloys⁽⁴⁾.

2.7.2 Compounds of cadmium

Cadmium exhibit an oxidation state (+2) aqueous solution of it is salts contain $Cd(H_2O)^{2+}_4$ ion. And it is colorless since a full complement of d-electrons is present. There is some evidence suggest the existence of (+1) cadmium compounds e.g the Cd^{2+} ion is analogous to the Hg^{2+} ion has been claimed to exist but it is unstable in the present of water⁽⁴⁾.

Cadmium (II) compound

Cadmium oxide (CdO): this oxide obtain by burning the metal in air or by the thermal decomposition of carbonate or nitrate

$$Cd(NO_3)_2(s) \rightarrow 2CdO_{(S)} + 4NO_{2(g)} + O_{2(g)}$$

It is brown solid .this oxide readily react with dilute acid to give salts

$$CdO +2H^{+} \rightarrow Cd^{2+}_{(aq)} +H_{2}O_{(L)}$$

Cadmium hydroxide $Cd(OH)_2$: obtain as gelatinous white solid when sodium hydroxide solution is add to aqueous solution of cadmium

$$Cd^{2+}_{(aq)} + 2 OH^{-}_{(aq)} \rightarrow Cd(OH)_{2(S)}$$

And this hydroxide is exclusively a basic hydroxide and dissolve in aqueous solution of ammonia with formation of amine complex

Cadmium sulphide (CdS): precipitated when hydrogen sulphide is passed through aqueous solution of cadmium salt

$$Cd^{2+}_{(aq)} + H_2S(g) \rightarrow CdS(g) + 2H^{+}_{(aq)}$$

It is yellow and dissolved when the concentration of acid is increase CdS is used as brilliant and permanent yellow pigment

Cadmium chloride CdCl₂: obtain by reacting the appropriate oxide, hydroxide or carbonate with the dilute hydrochloric acid; partial evaporation followed by crystallization result in the separation of white hydrated chloride

Cadmium sulphate CdSO₄.8/3 H_2O : obtain by reacting the appropriate oxide or hydroxide or carbonate with dilute sulphuric acid followed by partial evaporation and crystallization. Isomorphous double salt of this type K2SO4.CdSO₄.6H₂O are known.

Cadmium nitrate Cd(NO)₃.**XH**₂**O**: obtain by reacting oxide or hydroxide or carbonate with dilute nitric acid followed by partial evaporation and crystallization. When heating this nitrate will decompose

$$2Cd(NO_3)_{2(S)} \rightarrow 2CdO_{(S)} + 4NH_{2(q)} + O_{2(q)}$$

Cadmium carbonate CdCO₃: precipitate when sodium hydroxide solution is add to aqueous solution of the metallic salt

$$Cd^{2+}_{(aq)} + 2HCO_{3} \rightarrow CdCO_{3}(s) + H_{2}O_{(I)} + CO_{2(g)}$$

And this readily decompose in to the metallic oxide and carbon dioxide on heating

$$CdCO_{3(s)} \rightarrow CdO_{(S)} + CO_{2(q)}$$

Some complexes containing cadmium

The majority of the complexes of cadmium have coordination number of 4 and the simple hydrated ions $[Cd(H_2O)_4]^{2+}$ and this complex is poisonous to all living matter. Another example $[Cd(NH_3)_4]^{2+}$, $[Cd(CN)_4]^{2-}$, $[CdCl_4]^{(4)}$.

2.8 effect of cadmium on human health

Cadmium mainly accumulate in the liver and kidney and this make kidney damage. Also cause high blood pressure. Replaces zinc biochemically. Interact with calcium metabolism and can make low calcium level. And distraction of testicular tissue and red blood cell toxicity to aquaticbacota . finally it is carcinogenic⁽¹¹⁾.

2. 9 Iron

2.9.1. Introduction

Iron is the second most abundant metal after aluminum and the fourth most abundant element in the earth's crust. The earth's ore is believed to consist mainly of iron and nickel and occurrence of iron meteorites suggests that it is abundant throughout the solar system. The major iron ore hematite (Fe_2O_3), magnetite (Fe_3O_4), limonite (FeO(OH)) and siderite ($FeCO_3$).

Because of its high abundance iron is often found as an impurity in other materials for example corundum (r. Al_2O_3) and its colors are caused by small of Fe^{IV} .

Chemically pure Fe can be prepared by reduction of pure iron oxide (which is obtained by thermal decomposition of iron (II) oxalate or carbonate or nitrate) with H_2 by electrodeposition from aqueous solutions of Fe salts . Or by thermal decomposition of $Fe(CO)_5^{(4)}$.

2.9.2. Physical properties of Iron:

Boiling point	2887 ⁰ c	
Density	7.87	
Boiling point	3134 K	
Heat of fusion	13.18	
Het of vaporization	340	
Molar heat capacity	25.10 S/mole	
Oxidation stat	{1}2,3,4,5,6,-7,-2	
Electro negativity	1.83	
Thermal conduction	80.4 V	
Crystal structure	low spin 132 ± 3, 152± 6 high sp	in ⁽⁴⁾ .

2.9.3. properties and uses of Iron:

Pure iron is a silvery colored metal with a melting point of 1540 $^{\circ}$ c it is easily magnetized when placed inside a coil carrying an electric current but loses its magnetism when the current is switched off. A number of nonmetals combine with it on heating. e.g. Oxygen forming iron (III) oxide Fe_2O_3 but in the passive form iron is coated with a layer of magnetism oxide of iron Fe_2O_3 . Pure iron dose not corrode significantly of ordinary temperature when exposed either to action of dry air or air- free water. water result in the formation of rust . At red heat iron is attacked by steam with the formation of magnetic oxide of iron and hydrogen.

$$3Fe_{(s)} + 4 H_2O_{(g)} \implies Fe_3O_4_{(s)} + 4 H_2_{(g)}$$

Pure iron is soft but is unobtainable by smelting the material is significantly harder and strength by impurities from the smelting process.

Iron chemical compounds, which include ferrous and ferric compounds have many uses iron oxide mixed with aluminum powder can be ignited to create a thermiterc action, used in welding and purifying ores. It forms binary compounds with halogens⁽⁴⁾.

Iron compounds:-

Iron (VI)compounds:

The ferrate (VI) iron FeO_4^{2-} containing iron in the +6 oxidation state potassium ferrate (VI) K_2FeO_4 can be obtained by fusing mixture of iron filing and potassium nitrate (oxidizing agent).

Iron(III)compounds

Iron(III) oxide Fe₂O_{3:} Occurs naturally as hematite. And by heating Fe(OH₃) or FeSO_{4 (s)}

$$2FeSO_4 \ (s) \ \rightarrow \ Fe_2O_3 \ (s) + S_2O \ (g) + SO_3(g)$$

Iron (III) hydroxide Fe₂O₃.xH₂O: As a green gelatinous precipitate by adding sodium hydroxide solution to an aqueous solution containing Iron II ions

$$Fe^{2+}_{(aq)} + 2OH^{-}_{(eq)} \rightarrow Fe (OH)_{2 (s)}$$

Iron (II) compounds

Iron (II) sulphate FeSO₄: Produce by the action of dilute sulphuric acid on iron .

iron (II) ammonium salphate $FeSO_4(NH_4)_2$ $SO_4.6H_2O$:(double Salt) obtained by crystallizing a solution sulphate containing equivalent amounts of iron (II) sulphate and ammonium sulphate.

iron(II) oxalate Fe C_2O_4 : Is a lemon colored. Due to iron (II) oxalate complex the colored by yellow⁽⁴⁾.

$$Fe(H_2O)_6^{2-} + 2C_2O_4^{2-} \Leftrightarrow Fe(C_2O_4)_2(H_2O)_2^{2-} + 4H_2O$$

Iron II sulphate Fe S: Obtain by heating mixture of iron with sulfur

Fe
$$(s)$$
 + S (s) \rightarrow Fe S (s)

Iron (II) Carbonate Fe CO₃: Occurs naturally as the ore siderite

$$Fe^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow FeCO_3_{(S)}$$

2.9.4 Important role of Iron:

Iron plays an important role in biology forming complexes with molecular oxygen in hemoglobin and myglobin these two compound are common oxygen transport protein in vertebrates .

Iron is also metal used at the active site of many important redox enzyme dealing with cellular oxidation and redaction in plant and animals⁽⁴⁾.

2.9.5. levels iron in water:

The medium iron concentration in rivers has been reported to be 0.7 $\,$ mg/L . In anaerobic grand water where iron is in the form of iron II concentration usually be 0.5 – 10 $\,$ mg/L but concentration up to 50 $\,$ mg/L sometimes be found . Concentration of iron in

drinking water from WHO must not exceed than 0.3ppm but may be higher in countries use iron salt as coagulation agents in water treatment plants⁽⁵⁾.

2.9.6. Iron problem

Groundwater is of a favored some of potable water supplies in rural areas in developing countries because it is generally regarded as unpolluted and can be safely consumed without the need for treatment.

In many rural condition simple well- hand pump systems are use to water . in such circumstances treatment is avoided wherever possible because of the practicalities and costs involved. However ground water may had other properties which can indirectly affect health of people and water use.

Iron in rural ground water supplies is a common problem (concentration rang 0 - 50 mg/L - WHO recommended < 0.3 mg/L). the iron occurs naturally in the aquifer but levels in the ground water can be increased by dissolution of ferrous borehole and hand pump composition.

Iron bearing ground waters are often noticeably orange in color, causing discoloration of laundry and have an unpleasant taste which is apparent in drinking and food preparation⁽⁶⁾.

2.9.7 . the process of biological – enhanced iron removal

Chemical iron removal

Iron is removed from ground water by creating a strongly oxidation environment. this usually achieved by aeration or addition of oxidants such as chlorine or by raising the pH of water using alkaline materials such as limestone. Soluble ferrous ion is oxidized to ferric ion which is subsequently forms a precipitate of ferric hydroxide which may then be removed by filtration .

This technology has been successfully adopted to treated ground waters around the world for many decades .

Biological iron removal filters have been promoted an alternative to the traditional chemical approach. Certain bacteria are capable of oxidizing and immobilsing iron. the bacteria responsible for the process appear to be natural inhabitants of the well environment and therefore the microorganisms necessary to initial the process are carried with the ground water on to the filters. The active pollution of iron – oxidizers, which requires aeration in order to stimulate its growth, grows on the surface of the filter bed in the form of a slimy orange mat. It is within this zone of bacterial activity that iron removed process appears to occur. Proponents of biological iron removed claim that this biologically enhanced process is more efficient that the chemical process⁽⁶⁾.

2.10 Chemistry of lead:

Lead is oldest metals known, the chemical symbol of the element come from Latin name (plumbum), lead was used in ancient Egypt for glazing pottery (7000 - 5000 Bc), the hanging gardens of Babylon were floored with sheet lead to retain moisture and the Romans used lead extensively for water pipes and plumbing.

Lead is now recognized as a poison heavy metal. Because it complexes with oxo-groups in enzymes.

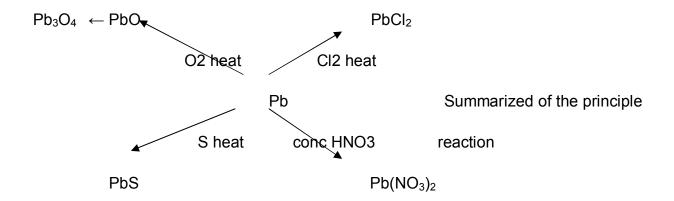
Lead occurs as galena Pbs, often in association with zinc blendes Zns in candy and broken hill in Australia which is that reduced to the metal either by further reduction with galena or with coke

$$\begin{array}{ll} 2 \; PbS_{\;(s)} + 3O_{2(g)} & \rightarrow 2PbO_{(s)} + 2O_{2\;(g)} \\ \\ 2 \; PbO_{\;(s)} + Pbs_{\;(s)} & \rightarrow 3Pb_{\;(L)} + SO_{2\;(g)} \\ \\ PbO_{\;(s)} + C_{\;(s)} & \rightarrow Pb_{\;(L)} + CO_{\;(g)} \end{array}$$

Crude lead is further treated by various processes to remove copper silver, gold, antimony and arsenic⁽⁹⁾.

2.10.1 Properties of lead:

Lead is a very soft metal the principle reaction tends to from covalent compounds since its two electrons are rather inert (the inert pair effect).



The low solubility of PbCl₂ limits the reaction .Hot concentrated a alkalis attack the element and form aplumbate (II) in which it is covalent⁽⁹⁾.

$$Pb_{(s)} + 2OH^{-}_{(aq)} \longrightarrow PbO_{2}^{2-}_{(aq)} + H_{2(g)}$$

2.10.2The structure of lead:

Lead exists in one from which is metallic in nature. The change over from non-metallic to metallic nature with increasing atomic number is thus reflected in the structures of the group 4B element⁽⁹⁾.

2.10.3 Compounds of lead:

Lead is predominately 2-valent and here the 4-valent state tends to be strongly oxidizing⁽⁹⁾.

The halides of lead

Lead forms a tetra fluoride and tetra chloride the former is a solid and appreciably lonic, Pb^{4+} (F-)₄, while the latter is a covalent liquid, $PbCl_4$ and chlorine.

The tetra bromide and tetra iodide do not exist presumably because tetra bromine and tetra iodide do not sufficiently strong oxidizing agents to convert Pb¹¹to Pb^{IV}.

The stable valence state of lead is (II) and all four di halides can be obtained as sparingly soluble solids by adding halide ions to a soluble lead (II) salt e.g the nitrate.

$$Pb^{2+} + 2X^{-}_{(aq)} \longrightarrow pbX_{2(s)} + (X^{-} = CL^{-}, F^{-}, F^{-}Be^{-} \text{ or } I^{-})$$

The fluoride is ionic $Pb^{2+}(F^-)_2$, the chloride, bromide and iodide contain some ionic character which decreases with increasing atomic number of the halogen. Except for the iodide which is yellow, they are white solid.

Lead (II) chloride and lead (II) iodide are of important in qualitative analysis and their formation saves as tests for Pb²⁺ in solution. Both are much more soluble in hot water than in cold and the chloride dissolves in concentrated hydrochloric acid with the formation of the PbCl²⁻₄ complex iron.

The oxide of lead

Lead (IV) oxide PbO_2 , is a brown solid obtained when a soluble lead (II) salt warmed with sodium chlorate (I) which oxidizes it

$$Pb^{2+}_{(aq)} + H_2O + CIO^{-}_{(aq)} \rightarrow PbO_{2(s)} + CI^{-}_{(aq)} + 2H^{+}_{(aq)}$$

It can also be obtained by treating tri lead tetra oxide Pb_3O_4 , with dilute nitric acid (tri lead tetra oxide behaves as if it were mixture of 2 PbO and PbO₂).

$$Pb_3O_{4(s)} + 4HNO_{3(aq)} \rightarrow 2Pb(NO_3)_{2(aq)} + PbO_{2(s)} + 2H_2O_{(l)}$$

lead (IV) oxide is powerful oxidizing agent ($Pb^{IV}_{(s)}$ is unstable with respect to Pb^{II}) for instance, it gives lead (II) oxide and oxygen when heated combine vigorously with sulpher dioxide to give lead(II) sulphate and liberates chlorine from concentrate hydrochloric acid when the mixture is warmed.

$$\begin{split} &2\text{PbO}_{2\,(s)} \ \rightarrow &2\text{PbO}_{(s)} \ + \text{O}_{2(g)} \\ &\text{PbO}_{2(S)} + \text{SO}_{2(g)} \rightarrow \text{PbSO}_{4\,(s)} \\ &\text{PbO}_{2(s)} + 4\text{HCI}_{(aq)} \rightarrow &\text{PbCI}_{2(s)} \ + 2\text{H}_2\text{O}_{(l)} + \text{CI}_{2(q)} \end{split}$$

lead (IV) Oxide is considered to be amphoteric , since it reacts with hydrochloric acid at low temperatures to give lead (IV) chloride (this decomposes readily to lead (II) chloride and chlorine at normal temperatures). And with alkalis to give plumbates (IV) the plumbate (III) Ion is usually written as PbO_3^{2-} but is in fact $Pb(OH)_6^{2-}$.lead II oxide , PbO_2 exits in two forms one of which is a red solid and the other yellow solid, it can be made by the thermal decomposition of lead (II) carbonate, or lead (II) nitrate. Although it is amphoteric , reacting with acids to from lead(II) salt and with alkalis to form plumbates(II) (the plmbate(II) ion is PbO_2^{2-} or $Pb(OH)_4^{2-}$, tri lead tetra oxide Pb_3O_4 can be prepared by heating lead(II) oxide in air at $400c^{\circ}$

$$6PbO_{(s)} \ + \ O_{2(g)} \ \leftrightarrow 2Pb_3O_{4(S)}$$

It decomposes if heat to 500c° into lead (II) oxide and oxygen . X ray examination shows it has a lager structure, each lager of PbO₂ being sandwiched two lagers having the PbO structure. It thus behaves as a mixture of PbO₂ and PbO. It is used in the production of lead(IV) oxide for use in lead accumulators and in the manufacture of red lead paint.

The sulphides of lead

Lead(II) sulphide Pbs can be may by passing hydrogen sulphide through a solution containing lead (II) ions

$$Pb^{2+}_{(aa)} + H_2S_{(a)} \rightarrow PbS_{(s)} + 2H^{+}_{(aa)}$$

It is a black solid and is insoluble in ammonium poly sulphide.

The oxo salts of lead

Only the oxy salts of lead are of any importance. Most of the lead II salts are insoluble in water e.g PbSO₄ (white) , PbCrO₄ (yellow) , lead (II) nitrate and lead (II) ethanoate Pb(CH₃COO)₂ .3H₂O are however freely soluble. The only stable lead (IV) oxy salt is lead ethanoate Pb(CH₃COO)₄, which is obtained as a white solid when treating tri lead tetroxide with hot ethanoic acid. As expected it is an oxidizing agent and used in organic chemistry for oxidizing 1,2 diols to aldenhydes or ketones.

R- CH-OH
$$\xrightarrow{Pb(CH_3COO)_4} 2R CH = O + H_2 O$$
[0]

R- CH-OH

Lead tetra ethyl Pb(C₂ H₅)₄

Lead tetra ethyl poisonous covalent liquid produced by reacting chloromethane vapor with sodium –lead alloy

$$4C_2H_5Cl(l) + 4Na/Pb_{(S)} \rightarrow Pb(C_2H_5)_4(l) + 3Pb_{(S)} + 4NaCl_{(S)}$$

It is an antiknock used in petrol

2.11 lead health effects

Lead is now recognized as a poison heavy metal, because it complexes with ox-groups in enzymes and effects virtually all steps in process of human synthesis and metabolism it also inhibits acetyl chlorine – esterase, acid phosphate ATP use carbonic anhydrate etc. It inhibits protein synthesis probably by modifying transfer- RNA.

Pb¹¹ also inhibit SH enzymes specially by interaction with cytosine residues in proteins, typical symptoms of lead poisoning are colic , an amine headaches, convulsions, chronic nephritis of the kidneys brain damage and control nevus – system disorder⁽⁷⁾.

2.12 Hardness of water

Water is described as being hard if it forms an insoluble scum(precipitate) before it forms a lather with soap . the hardness of natural water is generally caused by the hydrogen carbonates and sulphate of calcium and magnesium but in fact any soluble salts that form as a scum (precipitate):

$$Ca^{2+}_{(aq)} + 2C_{17}H_{35}C00^{-}_{(aq)} \rightarrow (C_{17}H_{35}C00^{-})_{2}Ca^{2+}_{(s)}$$

$$Mg^{2+}_{(aq)} + 2 C_{17}H_{35}COO^{-}_{(aq)} \rightarrow (C_{17}H_{35}COO^{-})_2 Mg^{2+}_{(s)}$$

soap will not produce a lather with water until all the calcium and magnesium ions have been precipitated as octadecanoates, hard water therefore wastes soap.

Water is described as being temporally hard if it contains calcium and magnesium hydrogen carbonates , since this type of hardness is easily removed and permanently hard if it contains calcium and magnesium sulphates . Both type of hardness frequently occur together in hard water⁽⁸⁾.

2.12.1 Temporary hardness in water

Rain water dissolves small quantities of carbon dioxide from the atmosphere and is thus a very dilute solution of carbonic acid. This water attacks calcium and magnesium carbonates in any rocks over which flows and the soluble hydrogen carbonates are formed

$$Ca^{2+}CO_3^{2-}(S) + H_2O_{(L)} + CO_{2(g)} \rightarrow Ca^{2+}(HCO_3^{-})_{2 \text{ (aq)}}$$

The temporary hardness in water is easily removed by boiling as the hydrogen carbonates decompose readily and insoluble carbonate is precipitate.

$$Ca^{2+} CO_3^{2-} (S) + H_2O (I) + CO$$

It can also removed by Clarks process , which involves the addition of slaked lime ${\rm Ca}^{2+({\rm OH}^-)}$

$$Ca^{2+}(HCO_3^-)_2 + Ca^{2+}(OH^-)_{(aq)} \rightarrow 2Ca^{2+}CO_3^{2-}_{(s)} + 2H_2O$$

It is essential to add only the correct amount of slaked lime because any excess will cause artificial hardness⁽⁷⁾.

2.12.2 Perment hardness water:

Perment hardness is introduced when water passes over rocks containing the sulphates of calcium and magnesium. Neither boiling nor the addition of slaked lime will remove this type of hardness it can however be removed together with temporary harness by the addition of washing soda $(Na^+)_2 CO_3^{2+}$ or by the permuted process⁽⁷⁾.

a)Addition of washing soda (sodium carbonate)

The calcium and magnesium ions in the water react with the ions from the sodium carbonate and a precipitate results :

$$Ca^{2+}_{(aq)} + CO^{2-}_{3}$$
 $_{aq} \rightarrow Ca^{2+}CO^{2-}_{3}$ $_{(s)}$

$$Mg^{2+}_{(aq)} + CO^{2-}_{3~(aq)} \to Mg^{2+}CO^{2-}_{3~(s)}$$

The water now contains dissolved sodium salts but these have no effect upon the soap.

b) the ion exchange process

permute is a compound called sodium aluminum silicate (abbreviated here to Na+ Al silicate) is insoluble in water when as low stream of hard water is passed through this material, the calcium and magnesium ions exchange with the sodium ions in the perment it thus.

$$Ca^{2+}$$
 (aq) + $2Na^{+}$ (AL silicate⁻) _(s) \rightarrow Ca^{2+} (AL silicate⁻) ₂ + $2Na^{+}$ (aq)

$$\mathrm{Mg}^{2^+}$$
 (aq) + $2\mathrm{Na}^+$ (AL silicate $^-$) $_{(s)} \to \mathrm{Mg}^{2^+}$ (AL silicate $^-$) $_{(s)}$ + $2\mathrm{Na}^+$ (aq)

Eventually the permuted is converted into a mixture of calcium and magnesium aluminum silicates and has to be regenerated this is achieved by passing a concentrated solution of sodium chloride through it:

$$Ca^{2+}$$
 (AL silicate)_{2(s)} + Na^{+} (aq) $\rightarrow Na^{+}$ (AL silicate $\bar{}$) + Ca^{2+} (aq)

The calcium chloride is then completely washed of the permuted before- use

C) the calgon process

the sodium salt of chain polyphosphate (v) are able to complex with calcium and magnesium ions and so prevent them reaction with soap to form a scum which complexes with calcium and magnesium ions in hard water at the same time releasing an equivent amount of sodium ions into the water

2.13 Hardness health effects:

No health based guideline is proposed for hardness in drinking water (WHO 2004).

Mach research has been done on the relationship between water hardness and cardiovascular disease mortality.

Numerous studies suggest correlation between hard water and lower cardiovascular disease mortality. (Herman et.al 1996).

Research on heart disease and cancer shows healthy water is hard water and moderately high in TDS.

Expire mental evidence shows hard water actually contributes to the prevention of certain type of calculi kidney stones or water belly formation (Sara 2007)⁽¹⁰⁾.

2.14. sampling water:

The sample collection process should be co- ordinate with laboratory so that analyst know many samples will be arriving and the approximate time of their arrival and the analysis that are be carried out, and can thus have appropriate quantities of reagent chemical prepared.

Sample containers that use to vary the sample which contain iron is poly ethylene $(500 - 1000 \text{ ml})^{(10)}$.

Washing procedure:

Rinse three times with tap water . once with chromic acid three time with water.

Once with 1:1 nitric acid and then three times with ultrapure distilled water.

Samples from ground water:

Can be obtained at the point of discharge. The water should flow for several minutes before sampling until it has reached constant conductivity and temperature in order to avoid any water resident in the system piping being taken as sample. The water should be allowed to flow into the bottle for sufficient time to displace the constants of bottle at least three times. Care should be taken to insure that no bubbles are introduce to the sample.

Chapter three

Materials and methods

3.1 MATERIAL:

water samples were collected from two wells in Dar- Almazeed village.

3.1.1 Collection of water samples:

The bottles were washed three times with water then one time with nitric acid And three time with distilled water.

The outside nozzle of the tap was cleaned carefully. The tap was turned on full, and the water was allowed to run to waste for 10 minutes. Sample bottle was filled with water and close immediately. Contamination was avoided by not allowing any surface to touch the screw thread of bottle neck or inside of the tap.

3.2 apparatus and instruments:

- ✓ Conical flask (50 ML ,250 ML)
- √ Beakers
- ✓ Burette
- ✓ Pipette
- ✓ Measuring cylinder
- ✓ Spectrophotometer (DR 5000 HACH LANGE)
- ✓ Atomic absorption spectrophotometer (AA.6800,SHIMDZU)

3.3 Chemicals:

- ✓ Ferrous iron reagent (1.10 phenanthroline)
- ✓ EDTA solution (0.01M)
- ✓ Buffer solution (pH=10)
- ✓ Eiroichrome black T(EBT indicator)
- ✓ Deionized water
- ✓ Stock solution for lead and cadmium (1000ppm)

3.4 Preparation of reagents and standards:

3.4.1 Buffer solution:-

16.9 g of ammonium chloride was weighted and dissolved in 143 ml of ammonium hydroxide solution. Then 1.25 g of sodium salt of EDTA was weighted and added to this mixture to obtain sharp change in colure of indicator and then was diluted to 250 ml of distilled water

3.4.2 Eriochrome black T indicator:-

0.5 g of dye and 100g of sodium chloride were weighted and dissolved in distilled water, Then the solution was transferred to 100 ml volumetric flask and completed to mark.

3.4.3 Standard magnesium solution:-

1 g of magnesium sulphate was weighted in 250 ml beaker and dissolved in Hydrochloric acid (1+1). 200ml of distilled water were added and boil for 20-30 minutes. Then cooled and few drops of methyl red indicator were added .Ammonium hydroxide solution was added drop wise till intermediate orange color develops .Then the mixture was diluted to 1000ml to obtain $1 \text{ml} = 1 \text{mg MgSO}_4$.

Methods of analysis

3.5 spectrophotometric determination of iron content by using 1.10 phenanthroline :

Principle

1.10 phenanthroline will react with iron in water to form an orange complex . This complex can be detected at wavelength 510nm.

3
$$+ Fe^{2+} \rightarrow N$$
 Orange –red complex

Method

10 ml of water sample were placed in 50ml conical flask and 0.28 g of 1.10-

phenanthroline reagent were added to the flask. The content was mixed for three minutes .The absorbance of 10 ml mixture was determined by using 1cm glass cell at wavelength 510nm in the presence of a blank. The result was recorded in table No(1)

3.6 Determination of total hardness (complex metric titration)

Principle:-

sample is buffered to pH = 10, then the EBT indicator is added to solution containing Calcium or Magnesium ion the color will change to wine red .

$$Ca^{2+} + HIn^{2-} \rightarrow CaIn^{-} + H^{+}$$
 $Mg^{2+} + HIn^{2-} \rightarrow MgIn^{-} + H^{+}$

Blue wine red

EDTA, complexes with Magnesium and Calcium ions, remove them from association with the indicator. When all Mg and Ca ions reacted with EDTA the indicator will turn to blue. This is the end point of titration

$$Caln^{-} + H_2Y^{2-} \rightarrow CaY^{2-} + Hln^{2-} + H^{+}$$

$$MgIn^{\text{-}} + H_2Y^{2\text{-}} \rightarrow CaY^{2\text{-}} + HIn^{2\text{-}} + H+$$

Wine red blue

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 \rightarrow MgCO_{3+}H_2O + CO_2$$

3.6.1 Standardization of EDTA:

10 ml of Magnesium sulphate solution (1mg \ml) were transferred to a clean conical flask. 5ml of buffer solution (pH=10) and 2 drops of EBT indicator were added. The solution was titrated against standard EDTA solution (0.01M) solution until the color changed from red to blue. The volume (v_1) was recorded in table No (2).

3.6.2 Determination of total hardness:-

50ml of water sample were transferred to a clean conical flask .5ml of Buffer solution (pH=10) and 2 drops of EBT indicator were added. The mixture was titrated against standard EDTA solution (0.01M) until the color changed from red to blue. The volume (v_2) was recorded in table No (2^*) .

3.6.3 Determination of permanent hardness:-

250ml of water sample were transferred to a clean beaker and heated to boiling for 30 minutes. Then cooled and filtered off. The filtrate was transferred to 250 ml volumetric flask and filled up to the market with distilled water .Then 50ml of filtrate were transferred to a clean conical flask , 5ml of buffer solution (pH=10) and 2 drops of EBT were added. The mixture was titrated against standard E DTA solution (0.01M) until the color changed from red to blue (2**).

3.7 Determination of Cadmium and lead content by Atomic Absorption spectrophotometer:

3.7.1 Preparation of standard stock solutions for Cd and Pb:-

Stock solution for Cd and Pb:

10 ppm of standard solution of Cd were prepared by diluting 100µl of 1000 ppm stock solution to 10 ml in volumetric flask with deionized water. The same method was repeated For lead.

Standard solution of Cadmium:

(0.2, 0.4, 0.6, 0.8,1.0) ppm of standard Cadmium solution was prepared by diluting 100, 400, 600 and 1000µl of 10ppm concentration to 10ml in volumetric flask with deionized water.

Standard solutions of lead:

(0.1, 0.7, 1.0, 2.0) ppm of standard solution of lead were prepared by diluting 100, 700, $1000, 2000\mu$ l of 10 ppm concentration to 10 ml in volumetric flask with deionized water

Method:

Atomic absorption spectrophotometer is calibrated using standard solution for each element.

Each element concentration was measured in water samples. The AAS specific lamp wave change for measuring each ion concentration.

The outmizatio tube was rinsed with deionized water after each sample reading the result was recorded in tube No (3) for cadmium and table No (4) for lead.

3.8 Determination of Cadmium and Lead in water samples :

3.8.1 Standard calibration curve :

calibration curves show in page No (37) for Cd, and page No (39) for Pb.

Chapter four

Results and discussions

4.1 Determination of iron content:

Table No (1)

Note:-

Sample (1) collected from Dar Almazeed well .

Sample (2) collected from pant well.

Concentration of iron:-

Sample No	Concentration of total	
	iron(mg/l)	
1	1.05	
2	0.87	

The results show higher value of iron in sample No(1) compere with sample No(2). These two values are more higher than WHO standard (1983)0.3 mg\l

4.2 Determination of total hardness

Standardization of EDTA

Table No (2)

Initial volume(ml)	Final volume(ml)	Used volume(ml)
0.00	10.40	10.40
10.40	20.80	10.40
20.80	31.50	10.70

Table No (2*):

Total hardness:-

Sample No	Initial	Final volume	Used volume
	volume(ml)	(ml)	(ml)
1	0.00	5.90	5.90
	5.90	11.20	5.30
	11.30	16.60	5.30
2	0.00	6.30	6.30
	6.30	12.50	6.20
	12.50	19.90	7.40

Table No (2**):-

Permanent hardness:-

Sample No	Initial	Final volume	Used volume
	volume(ml)	(ml)	(ml)
	0.00	5.90	4.80
1	4.80	11.20	5.00
	9.80	16.60	4.80
	14.60	19.40	4.80
	0.00	4.00	4.00
2	4.00	8.10	4.10
	8.10	12.30	4.20

Calculations:-

- From table No (2) → v₁ =10.40 ml
- Number of mgs of MgSO₄ equivalent to 1ml of EDTA
- (x mg of MgSO₄ \rightarrow 1ml of EDTA)

10 mg of MgSO₄ \rightarrow 10.40 ml EDTA



X mg of MgSO₄ \rightarrow 1 ml EDTA

→X mg of MgSO₄ =
$$10*1$$
 = $\underline{.961}$ mg

10.40

*Total Hardness:-

From table No (2*)

 V_2^* for sample No (1) = 5.30 ml

 V_2 \for sample No (2) = (6.20 + 6.30)/2 = 6.25 ml

-Sample No (1):-

0.961 mg MgSO₄ \rightarrow 1 ml EDTA

Y mg \rightarrow 5.30 ml EDTA

Y mg = $.961 * 5.30 = \underline{5.0933}$ mg MgSO₄ in 50 ml water sample

No of mgs of MgSo₄ in 1000 ml y*=(y * 1000)/50

For sample (2):-

0.961 mg MgSO₄ \rightarrow 1 ml EDTA Y mg MgSO₄ \rightarrow 6.25 ml

Y =0.961 * 6.25 = 6.006 mg MgSO4 /50ml (water sample)

$$Y' = (6.008 * 1000)/50 = 120.24 \text{ mg/l}$$

*Permanent Hardness:-

From table No (2**):-

 V_3^* for sample No (1) = 4.80 ml

 V_3 for sample No (2) = (4.10 + 4.2)/2 =4.15 ml

For sample No (1):-

0.961 mg MgSO₄ \rightarrow 1 ml EDTA

Z mg MgSO₄ \rightarrow 4.80 ml

Z=.961*4.80 = 4.61 mgs of MgSO₄

Number of mgs $MgSO_4$ in 50 ml = 4.61 mgs

→ Number of mgs in 1000 ml $z^* = (4.61^* 1000)/50 = 92.2 \text{ mg/l}$

For sample No (2):-

0.961 mgs MgSO₄ \rightarrow 1 ml EDTA

Z mgs MgSO₄ \rightarrow 4.15 ml

Z = mgs = 4.15 * 0.961 = 3.98 mgs

Number of mgs of MgSO₄ in 1000 ml $Z^1 = (Z^*1000)50$

 $Z^{1} = (3.98 * 1000)/50 = 79.7 mg/l$

*Temporary water hardness = Total – Permanent

For sample No (1):-

Temporary hardness = $101.86 - 92.2 = \frac{9.66 \text{ mg}}{\text{J}}$

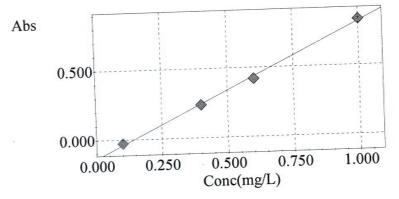
For sample No (2):-

Temporary hardness = $\underline{40.54}$ mg/l

This studied show the water is slightly hard (100-150) mg/l

Calibration curve of Cd (228.8 nm)

Calibration Curve (C#:01)



Conc	Abs
(mg/L)	
0.6000	0.4178
0.1000	-0.0282
0.4000	0.2395
1.0000	0.8335

Abs=0.957415Conc+-0.136993

r=0.9990

Table No (3):-

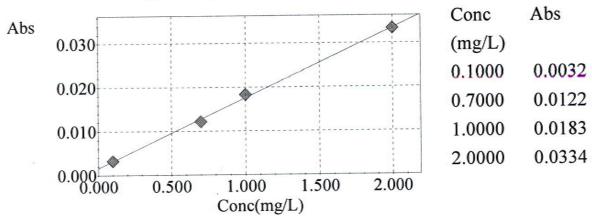
*Concentration of Cadmium by AAs:

Sample No	Concentration of Cadmium (ppm)
1	0.1432
2	0.1435

The studied samples show maximum value of Cadmium than value of 0.003 mg/l Cd Water containing high concentration of Cadmium is more effect on health because Cadmium is carcinogenic.

Calibration curve of Pb (217.0 nm)

Calibration Curve (C#:01)



Abs=0.0159868Conc+0.00158757 r=0.9991

Table No (4):-

*Concentration of Lead :- (by AAS)

Sample No	Concentration of Lead (ppm)
1	0.00
2	0.00

In this studied all samples show zero values of Lead.

The WHO (2011) recorded that concentration of Lead is <u>0.05 mg/l</u>.

When water is free of Lead can be considered good because Lead is poisonous.

Chapter five

Conclusion

Conclusion

According to this analysis these two water samples are not suitable for drinking because there is high concentration of cadmium and iron in the two water samples. The handiness is acceptable and no lead detected.

Suggestions and Recommendation

- 1- Further research may be need to determine other elements such as arsenic (As), mercury (Hg) and iodine (I_2).
- 2- The area may be further studied to include other neighboring village for determination of heavy metals and trace element concentration.
- 3- Further studies can be carried to tend a suitable technique for removing iron and cadmium from water.

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Chapter six

Appendix

The Location of Dar Almazeed Village





