1.Introduction

1.1. Water Supply in Egypt

According to the data recently issued by the world health organization, (WHO) an average of 50000 people die each day from diseases associated with bad water; one person about every two seconds [1].

Drinking water can come from either ground water sources (via wells) or surface water sources (such as rivers, lakes, and streams). The main difference between ground water and surface water is presented in table (1). Nearly one-fifth of all water used in the world at present is obtained from groundwater [2].

Table (1) **The main difference between the ground and surface water [3]**

Characteristics considered	Surface water	Groundwater
Temperature	Varies with season	Relatively constant
Turbidity, suspended solids	Level variable, sometimes high	Low or nil
Mineral content	Varies with soil, rainfall, effluents etc.	Largely constant, generally appreciably higher than in surface water from the same area
Divalent iron and manganese (in solution)	Usually none, except at the bottom of the lakes or ponds in the process of eutrophication	Usually present
Aggressive carbon dioxide	Usually none	Often present in large quantities
Dissolved oxygen	Often near saturation level	Usually none at all
Ammonia	Found only in polluted water	Often found, without systematically indicating pollution
Hydrogen sulfate	None	Often present
Silica	Moderate proportions	Level often high
Nitrates	Level generally low	Level sometimes high; risk of methemoglobinaemia
Living organisms	Bacteria (some pathogenic), viruses, plankton	Ferro-bacteria frequently found

Groundwater quality is usually superior to that of surface water with respect to bacteriological content, turbidity, and total organic matter concentrations. On the other hand, the mineral content (hardness, iron and

manganese) of groundwater may be inferior and requires additional treatment. Groundwater supplies are frequently pumped into the distribution system with minimal treatment [4].

Currently, the quality of groundwater with respect to trace concentrations of organic chemicals, such as pesticides, herbicides, and solvents, is of great concern. Concentration of the location of landfills, buried storage tanks, etc., should be a part of the groundwater source evaluation [4].

Finally, some communities have the option of using both surface and groundwater supplies. Use of these supplies can be optimized to provide a more reliable water source that uses the best features of both supplies[4].

In Egypt, the conventional water resources are limited to the River Nile, groundwater in the deserts and Sinai, rainfall and flash floods, and desalinization of seawater. Each resource has its limitations on use. These limitations relate to quantity, quality, space, time and/or use cost. [5-7].

The Nile River is the main and almost exclusive source of fresh water in Egypt, supplying approximately 95% [7] of the country's water needs.

According to the 1959 Nile Agreement, Egypt's stable share is fixed at 55.5 billion cubic meters annually [5-6].

Water resources in Egypt are becoming scarce. surface water resources originating from Nile are now fully exploited, while ground water sources are being brought into fully into full production. Egypt is facing increasing water needs [5-6].

In Egypt table [2] indicates the distribution of water supply and demand for years 1995/1996. However, it is predicted that by the year 2017, the water demand will reach 97.79 billion m^3/year, while the water supply will reach 95.24 billion m^3/year, thus indicating the occurrence of a deficit in the water supply amounting to 2.55 billion m^3/year [5-6].

Table (2) The Distribution of water supply and demand in Egypt [6]

Category	**1995/1996**	**Forecasted for 2017**
Water Supply (Unit: billion m^3/year)		
Nile River	55.50	57.50
Groundwater in the Nile Valley and Delta	4.80	7.50
Recycling of agricultural wastewater	12.92	16.92
Recycling of domestic wastewater	1.14	13.62
Recycling of industrial wastewater	0.70	1.70
Rain and floods	1.00	1.00
Loss due to evaporation in the water network	(3.00)	(3.00)
Total of supply	73.06	95.24
Water usage		
Agriculture	60.73	75.53
Industry	7.53	15.44
Domestic	4.54	6.82
Navigation	0.26	
Total of usage	73.06	97.79
Supply of usage	0.00	-2.55

Fresh groundwater resources in Egypt contribute to some 20 % of the total potential of water resources in Egypt. The main challenge facing Egyptian national development is limited water resources. Water is the main factor, which determine the size, type and location of many economic activities. Egypt is a very arid country, where the average annual rainfall seldom exceeds 200 mm along the northern coast. [7,8].

Ground water found in aquifers ,which have the capability of both storing and transmitting ground water. An aquifer is defined formally as a geologic unit that is sufficiently permeable to supply water to a well [9], the water undergoes a natural filtering process as it trickles through layers of soil and sand particles before collecting in the aquifers [9].

In Egypt groundwater can be classified into two categories. The first comprises groundwater in the Nile Valley and Delta system. The total storage capacity of the Nile Valley aquifer system is about 200 billion m^3, with an average salinity of 800 ppm. Another 300 billion m^3 is the storage capacity of the Delta aquifer. The current annual rate of groundwater withdrawal from the Valley and Delta aquifers is 6.13 billion m^3/y.

The second category is the nonrenewable type, which is located in the Western Desert in the Nubian Sandstone Aquifer. Where the groundwater exists in the Western Desert, it is deep seated. Use of this fossil water depends on the cost of pumping and potential economic return over a fixed time period [7,8].

The El Moghra aquifer system, located west of the Cairo Alexandria Desert Road with an average thickness of 300 m is also considered as a non-renewable aquifer system.

The Fissured Aquifer system covering more than 50 % of total area of Egypt, is considered as one of the poorest aquifer in the country.

The limestone aquifer thickness. is about 200 m at El Farafra oasis to 900 m at Siwa [8].

Table (3) Hydro geological characteristics of main aquifers [7,8]

Aquifer	Location	Top aquifer, m-msl	Saturated thickness, m	Dept to ground water level, m	Transmissivity, m/d	Salinity, ppm
Nile Valley and Delta	Nile Valley South Nile Delta North Nile Delta	0-20 0-20 0-100	10-200 100-500 500-1000	0-5 0-5 0-3	5000-10,000 5000-10,000 5000-250,000	<1500 <1500 <5000
Coastal Aquifer	Med. Coast Qaa Plain Arish	0 50-100 15-30	<5 60-80 40-50	15 50-70 0-30	300-800 200-1000	1000-6000 600-2500
Nubain	Western Desert	50-200	500-700	0-30	1000-3000	<1000
Sandstnne Aquifer	Kharga Dakhla Bahariya Farafra E. Oweinat Eastern Desert Aish El Malha Sinai Nakhl Ain Mussa	200 150-300 200-500 100-300 0-30 1000 100-500	500-100 100-1500 1500-2000 100-300 <200 2000 1500	0-20 0-20 Flowing 20-30 Flowing 200 Flowing	2500-4000 900-15,000 5000-10,000 100-2500 — — —	<1000 <1000 <1000 <1000 3000-4000 1500-2000 1000-4000
Moghra Aquifer	W. El Natrun Qattara Depr.	0-200	500-900	100	—	1000-12000
Fissured carbonates	Helwan/Wadi Araba	0-100	500	Flowing	—	1000-12000
Hard rncks	South Sinai Eastern Desert	0-50	—	+50	—	1000-2000

Table (4) Distribution of groundwater abstraction (million m^3/y) [8]

Nile Valley and Delta		Western Desert		Eastern Desert	Coastal Aquifers	Sinai
Valley	Delta	Nubian	Moghra			
1932	4195	1000	200	8	2	89

So the most common sources of underground water are Valley and Delta due to difficult attaining of water from other sources [8].

1.2. Ground water pollution

The term "water pollution" is referred to the addition to water of an excess of material (or heat) that is harmful to humans, animals or desire able aquatic life or otherwise causes significant departures from the normal activities of various living communities in or near bodies of water. It was stated " water gets polluted if it has been not of sufficiently high quality to be suitable for the highest uses people wish to make of it at present or in the future". A precise definition is " water pollution is every impact which changes the quality of our surface and subsoil waters to such a degree that

its suitability either for human consumption or for the support of man's natural life processes will decrease or cease" [10].

The major of water contamination have been domestic, industrial and agricultural waste, as well as solid waste, thermal pollution, shipping water pollution and radioactive waste [11].

Despite rapid population growth in Egypt there are many sources of contamination. Water during its passage through ground acquires various types of dissolved and suspended impurities. In addition to this, the ever-increasing environmental pollution substances. The main sources of water pollution are sewage, industrial, agricultural, radioactive wastes and chemical wastes. The large-scale use of insecticides, pesticides and other agrochemicals is gradually contaminating the water-resources with toxic chemicals. Effluent from many industries are discharged into rivers and canals, without proper treatment to conform to the regulatory requirement. Similarly, untreated municipal effluents are dumped into water bodies [12-15].

1.3. Ground water major problems

Basic groundwater quality problems are topically associated with high hardness .iron and manganese [4].

1.3.1.Hardness

Hardness is generally defined as the sum of the polyvalent cations present in water and expressed as equivalent quantity of calcium carbonate ($CaCO_3$). The most common of such cations are calcium and magnesium.

Although no distinctly defined levels exist for what constitutes a hard or soft water supply, water with less than 75 mg/l $CaCO_3$ is considered to be soft and above 150 mg/l $CaCO_3$ as hard [16].

$$\text{Total hardness} = 2.5\,(Ca^{+2}) + 4.1\,(Mg^{+2}) \quad \ldots\ldots\ldots\ldots\ldots\ldots(1.1)$$

An inverse relationship has been postulated between the incidence of cardiovascular disease and the amount of hardness in the water, or, conversely, a positive correlation with the degree of softness. Hypotheses outline below suggest a protective effect from either the major or minor constituents of hard water, or, conversely, a harmful effect from elements more commonly found in soft water (National Academy of Sciences Safe Drinking Water Committee, 1980b) [17].

Many investigators attribute a cardiovascular protective effect to the presence of calcium and magnesium (reviewed by Marx and Neutra, 1997; McCarron, 1998b). A moderate increase in calcium in the diet has been observed to lower levels of circulating organ cholesterol; this is speculated as possible factor in relating water hardness and cardiovascular disease. Magnesium is theorized to protect against lipid deposits in arteries, to reduce cardiac irritability and damage, and may also have some anticoagulant properties that could protect against cardiovascular diseases by inhibiting blood clot formation [17].

A limited number of studies have been carried out which showed that minor constituents often associated with hard water may exert a beneficial effect on the cardiovascular system. Candidate trace element include vanadium, lithium, manganese, and chromium. On the other hand, other investigators suggest that certain trace metals found in higher concentrations in soft water, such as cadmium, lead, copper, and zinc, may be involved in the induction of cardiovascular disease. However, USEPA strongly support corrosion-control measures (some of which add hardness)

to reduce exposure to lead. WHO set MCL of 500 mg/l (as calcium carbonate) for hardness [4,18-19].

1.3.2.**Iron**

Iron is one of the most abundant metals in the Earth's crust fourth most abundant element about (4.5%) [20-22]. Water percolating through soil and rock dissolves iron and many others minerals, and these minerals subsequently enter groundwater supplies. iron is required for the growth of microorganisms, it is one of macronutrients, along with calcium, magnesium and potassium, it is found throughout the plant and animal kingdoms [22].

In deep wells and springs, where both the oxygen content and pH tend to be low, water containing dissolved iron or manganese appears colorless [22].

Soluble iron, referred to as "clear water" iron (referred to as Fe^{2+}) and insoluble iron, also referred to as "red water" iron (referred to as Fe^{3+}) are the most available iron forms in drinking water supplies [18,19].

Because iron can combine with other elements, it also can be present in an organic complex, then it can appear as colorless, yellow or brown. A more daunting problem is when iron bacteria may also be present, which can create reddish brown or yellow slime, clog plumbing and cause a nasty odor that's fishy or oily. Iron, in general is nuisance chemical with characteristic staining properties, although high level can impart a bittersweet or metallic taste to drinking water [18,19].

Iron is an essential element in human nutrition. Estimates of the minimum daily requirement for iron depend on age, sex, physiological status and iron bioavailability and range from about 10 to 50 mg/day[4, 18].

Iron may be found in natural fresh waters at levels ranging from 0.5 to 50 mg/l. Typical values of dissolved iron in groundwater are generally less than 10 mg/l. Iron may also be present in drinking water as a result of the use of iron coagulants in water treatment plants or the corrosion of steel and cast iron pipes during water distribution. Iron stains laundry and plumbing fixtures at levels above 0.3 mg/l; there is usually no noticeable taste at iron concentrations below 0.3 mg/l, and concentrations of 1-3 mg/l can be acceptable for people drinking anaerobic well water [20].

WHO established no health based guideline value for iron in drinking water in the 1993 Guidelines, but it was mentioned that a value of about 2 mg/l can be a precaution against storage in the body of excessive iron [18,19].

The US EPA established no MCL value for iron in drinking water, however, US EPA secondary drinking water standards for public water supplies (nonobligatory) has been set to 0.3 mg/l for iron. According to the US EPA, private water supplies are not subject to this federal regulation[18,19].

The Egyptian Authorities, has set the value of iron content in "domestic" water supplies to 0.3 mg/l. Egyptian standards allow for 1 mg/l of iron content in underground well water supplies [18,19].

1.3.3.Manganese

Manganese is the seventeenth most abundant element 0.1 %[20-22] in earth crust which is known as, lithosphere. Manganese is used principally in the manufacture of iron and steel alloys, dry batteries, glass , fire works as an oxidant for cleaning, bleaching and disinfection as potassium permanganate and as an ingredient in various products. More recently, it

has been used in an organic compound. Manganese greensands are used in some locations for potable water treatment [4].

Manganese is required for the growth of microorganisms, it is one of micronutrients, along with cobalt, cupper and molybdenum, it is found throughout the plant and animal kingdoms [22].

The most important oxidation states for the environment and biology are Mn^{2+}, Mn^{4+} and Mn^{7+} [23].

Occurrence levels in fresh water typically range from 1 to 200 µg/l, although levels as high as 10 mg/l in acidic groundwater have been reported; higher levels in aerobic water is usually associated with industrial pollution.

The presence of manganese in drinking water will be objectionable to consumer if it is deposited in water mains and causes water discoloration. Concentrations below 0.05- 0.1 mg/l are usually acceptable to consumers but may sometimes still give rise to the deposition of black deposits in water main over an extended period; this may vary with local circumstances [4].

Manganese is an essential element for humans and other animals. Adverse effects can result from both deficiency and overexposure. Manganese is known to cause neurological effects following inhalation exposure, particularly in occupational settings, and there have been epidemiological studies that report adverse neurological effects following exposure to very high levels in drinking water [4].

Manganese is an essential nutrient, fulfilling a catalytic role in various cellular enzymes. the national Research Council (1989) recommended from 2 to 5 mg/day as safe and adequate for adults, on anther hand. The total daily intake of manganese is 0.06 mg/kg of body weight, based,compared with 0.3 to 5 mg/day for infants .It has been

regarded as nontoxic and naturally occurring however is removed due to aesthetic reason [4, 24 -25].

The WHO (2003)Guidelines for Drinking Water Quality, proposed a health based guideline value of 0.4 mg/l for manganese. Egyptian standards allow for MCL 0.5 mg/l for underground water. The US EPA allows for MCL of 0.05 mg/l [18,19].

Table (5) Maximum contaminant levels (MCL)for Fe^{2+} and Mn^{2+} (µg/l) in different countries [3,18,19]

Contaminant	WHO	USA	Japan	Germany	Canada	Egypt
Fe (µg/l)	300	300	300	200	200	1000
Mn ((µg/l)	100	50	300	50	50	500

1.3.4. Iron and manganese in groundwater supplies

Iron is present in many groundwater supplies, whereas manganese is present only occasionally, and then usually along with iron. Usually the manganese is the minor constituent; it is considerably less abundant in the lithosphere [21-22].

Groundwater, which is frequently high in carbon dioxide and low in dissolved oxygen, will readily dissolve or convert insoluble iron and manganese-bearing minerals to soluble ferrous and manganous bicarbonates [20] having, respectively, the divalent ferrous iron, Fe^{2+}, and the divalent manganous manganese ion, Mn^{2+}. It has been established that inorganic [22], carbonate and bicarbonate iron complexes are not a constituent of most groundwater, meaning that the ferrous ion, Fe^{2+}, is the only inorganic form of iron of any significance in carbonate-bearing groundwater [22].

The carbon dioxide found in groundwater probably originated in the decomposition of organic matter in the soil. Ferric iron, a constituent of many iron-bearing minerals, is reduced to ferrous iron through the action of

microorganisms in the anaerobic environment of a deep well. Similarly, there is evidence that manganese of higher valences than two, a constituent of many manganese-bearing minerals, such as the tetravalent manganese in manganese dioxide, MnO_2, is reduced to manganous manganese through the action of microorganisms in the anaerobic environment of a deep well [22] .

Although iron and manganese are normally present in groundwater as soluble bicarbonates, soluble ferrous and manganous sulfate, with their respective ferrous iron ion, Fe^{2+}, and manganous manganese ion, Mn^{2+}, are to be found in groundwater containing sulfur, particularly hydrogen sulfide. In a recent survey, 52 percent of the untreated groundwater supplies had iron concentrations greater than 0.05 mg/L and 26 percent exceeded 0.26 mg/l. Also, organically bound iron and manganese can be found in some groundwater. For example, humic acids, sometimes called "the yellow acids", derived from humus of the organic portion of the soil resulting from the partial decay of leaves and other vegetation, react with the ferrous iron ion to form colored organic complexes [26].

Records on the concentration of iron in groundwater indicate that it normally ranges from a few hundredths to about 25 mg/l and. manganese is usually present in groundwater in a concentration of less than 1.0 mg/l however, there are exception [22,27].

A more general observation is that water of high alkalinity often has a lower iron and manganese concentration than water of low alkalinity. Also, the iron concentration of water from gravel wells is often less than that of the water from rock wells because the gravel wells often draw water from a single aquifer rather than multiple aquifers. Any colloidal or precipitated iron, if formed, is removed by underground filtration [28].

1.3.5 The iron and manganese problems

The presence of significant iron and manganese in water supply can create several problems as follows [4,17,22,29-34]:

1- Promote the growth of gelatinous masses of iron and manganese bacteria :this may cause partly or completely clogging of pipes
2- Neither iron nor manganese posses health risks, in small concentration is essential for human health.
3- Higher concentration will give water a medicinal or metallic taste
4- Long time consumption of drinking water with high concentration of iron causes liver diseases.
5- Cause corrosion and pipe blockages either directly, precipitating deposits or indirectly by providing favorable condition for growth of specific bacteria [3].
6- Large concentration of iron and manganese in water can cause trouble in domestic and industrial uses.

In this concern iron and manganese produce ugly and insoluble rusty brown, yellow, gray, or black stains, blotches, and streaks on clothing during laundering, on plumbing fixtures, and on everything they touch. Manganese is particularly tenacious. In extreme cases, iron and manganese interfere with culinary use, turning tea black and darkening boiled vegetables, for example.. Iron also imparts a state described as a bitter, sweet, astringent, or "iron" taste, detectable by some persons at levels of 1 to 2 mg/l [20,22,35-37].

Sometimes the presence of iron and manganese becomes a disaster in industrial wet-processing operation, water containing iron and manganese promotes the growth of iron and manganese-tolerant bacteria in mains, with accompanying increases in friction loss and power consumption. When large masses of bacteria break loose, they clog nozzles, lines, and valves.

Also, precipitation of iron in distribution systems causes the familiar red water problems in home and industry uses. If consumers have water softeners, they become fouled and must be repeatedly cleaned to prevent an excessive loss in efficiency. In addition, as the bacteria decay, they impart a particularly bad taste and odor to the water, making it objectionable to drink or use for sanitary purposes [22,35-37].

Because iron and manganese are chemically similar, they cause similar problems. Iron will cause reddish-brown staining of laundry, porcelain, dishes, utensils, and even glassware. Manganese acts in a similar way but causes a brownish-black stain. Soaps and detergents do not remove these stains, and the use of chlorine bleach and alkaline builders (such as sodium carbonate) can actually intensify the stains.

Iron and manganese deposits will build up in pipelines, pressure tanks, water heaters, and water softeners. This reduces the available quantity and pressure of the water supply. Iron and manganese accumulations become an economic problem when water supply or softening equipment must be replaced. There are also associated with increased energy costs, like pumping water through constricted pipes or heating water with heating rods coated with iron or manganese minerals.

Iron and manganese are concentrated in water by contact with rocks and minerals, and occasionally man-made materials like iron and steel pipes. It is usually groundwater supplies that may require treatment for high levels of iron and manganese. Generally speaking, few surface water supplies have high enough levels of ether to cause problems. Occasionally discharge of acid industrial wastes or mine drainage may increase iron or manganese to problem levels in surface water[38-42].

1.4. Common methods of iron, manganese and hardness removal

Iron and manganese can be present in water in one of the three basic forms [30-34].

1- dissolved : ferrous (Fe^{2+}) and mangnous (Mn^{2+})
2- particulate ferric (Fe^{3+}) and manganic (Mn^{4+})
3- Colloidal very small particulate (difficulties to settle and filter and presence of one over another is dependent on pH, redox potential and temperature of water [30-34].

There are many methods of iron and manganese removal, summarized report is discussed below.

1.4.1.Poly phosphate Treatment

Poly phosphate react with dissolved iron and manganese by trapping them in a complex molecule that is soluble in water. Poly phosphate protect dissolved iron and manganese from reacting with oxygen and precipating on household appliances, bath/plumbing fixture, and laundry and manganese are not available to react with oxygen and precipitate. Polyphosphate can be fed into the water with controlled injection equipment. Poly phosphate is not stable at high temperature. If water treated prior to heating in a water heater the polyphosphate will release iron and manganese in a heater as they break down. The released iron and manganese will then react with oxygen and precipitate[38-42].

1.4.2.Ion exchange

A typical ion exchange softening process is shown in Fig. (1). Pretreatment to remove iron and manganese, if they are present in the

source water, should precede ion exchange. High organic content can also foul certain ion exchange resins.

The most common ion exchange softening resin is a sodium cation exchange (zeolite) resin that exchanges sodium for divalent cations. After the resin has reached its capacity for hardness removal, it is backwashed, regenerated with a sodium chloride solution and rinsed with finished water. This places the resin back in the sodium and rinsed with finished water. This places the resin back in the sodium form so that it can resume softening. A portion of the source water is typically bypassed around the softening vessel and blended with softened water. This provides calcium ions to help stabilize the finished water [4, 22].

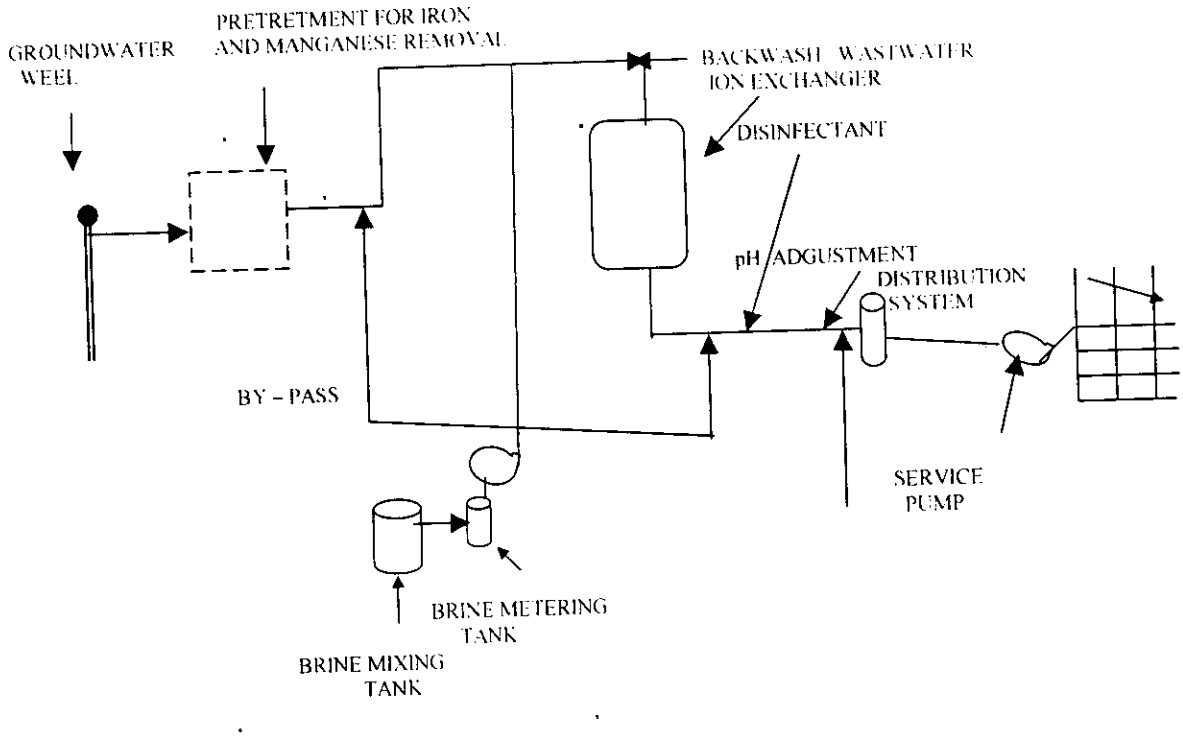

Fig (1) Removal of hardness. iron and manganese [4, 22].

1.4.3. Greensand (adsorptive / oxidative) filtration

The active material in greensand is glauconate. Glacunate is a green clay mineral that contains iron and has ion exchange properties. Glucanate

is mined, washed, screened, and treated with various chemical to produce a durable greenish –black that capable of adsorb soluble iron and manganese. As water is passed through the filer, soluble iron and manganese are pulled from solution and later react to form insoluble iron and manganese. Eventually the greensand must be regenerated by washing with potassium permanganate solution. Regeneration will leave the greensand grains coated again with manganese material that absorbs soluble iron and manganese. Frequency of regeneration will depend on the level of iron, manganese, oxygen in water, and size of filter .If pH is lower than 6.8 the greensand will probably not adequately iron and manganese [38-42].

The regeneration follows the reaction:

$$Mn_2O_3 + MnO^-_4 + 2H_2O \longrightarrow 5MnO_2 + 4H^+ \text{[3]} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1.2)$$

1.4.4. Chlorination (oxidation) plus filtration

· Chemical oxidation followed by filtration is accepted method of iron and manganese removal There are a number of strong oxidant that have been used in this procedure (oxygen, chlorine dioxide, potassium permanganate and ozone) however, chlorine generally used in house hold systems. A chlorine solution is injected with a chemical feed pump ahead of a sand filter. Soluble iron and manganese begin to precipitate almost immediately after contact with a chlorine solution. However, approximately 20 minutes of contact time is needed for precipitate to form particles that can be filtered. An additional advantage of using the chlorination system is its bacterial effect. Iron and manganese bacteria, along with other bacteria, are destroyed. Chlorination does produce trihalomethanes (THM) when organic matter is present in the water. THMs are considered to be carcinogenic (maximum contaminated level permissible in public water systems is 0.1 ppm) and if necessary can be

filtered out with an activated charcoal filter.The optimum rate of oxidation of iron and manganese by chlorination is at pH of about 8.30- and 8.5 respectively [38-42].

Concentration of iron and Manganese when using the last methods of treatment as follow:, ploy phosphate treatment [0-3] ppm, ion exchange (softener)[0-10ppm], green sand filter [0-10ppm] and chlorination [0->10ppm] [38-43].

Table (6) Reactions of iron with alternative oxidants and theoretical reaction stoichiometry [43].

Metal	Oxidant	Reactions	Stoichiometry
Fe^{2+}	O_2 aq	$2\,Fe^{2+} + \frac{1}{2}\,O_{2(aq)} + 5\,H_2O \rightarrow 2\,Fe(OH)_3(S) + 4\,H^+$	0.14mg O_2/mgFe
	O_3 aq	$2\,Fe^{2+} + O_3 + 5H_2O \rightarrow 2\,Fe(OH)_3(S) + 4\,H^+ + O_2$ aq	0.43mg O_3/mgFe
	HOCL	$Fe^{2+} + HOCL + 5\,H_2O \rightarrow Fe(OH)_3(S) + 5\,H^+ + Cl^-$	0.64mg HOCL/mgFe
	CL O_2	$2Fe^{2+} + CLO_2 + 3\,H_2O \rightarrow 2Fe(OH)_3(S) + 3\,H^+ + Cl\,O_2^-$	1.2mgCL O_2/mgFe
	$KMnO_4$	$2Fe^{2+} + MnO_4^- + 2H_2O \rightarrow 2Fe(OH)_3(S) + 5H^+ + MnO_2$	0.94mg$KMnO_4$/mgFe

Table (7) Reactions of manganese with alternative oxidants and theoretical reaction stoichiometry [43].

Metal	Oxidant	Reactions	Stoichiometry
Mn^{2+}	O_2 aq	$Mn^{2+} + \frac{1}{2}\,O_{2(aq)} + H_2O \rightarrow MnO_2(S) + 2\,H^+$	0.29mg O_2/mgMn
	O_3 aq	$Mn^{2+} + O_{3(aq)} + H_2O \rightarrow 2\,MnO_2(S) + 2\,H^+ + O_2$ aq	0.88mg O_3/mgMn
	HOCL	$Mn^{2+} + HOCL + H_2O \rightarrow MnO_2(S) + 3\,H^+ + CL^-$	1.3mg HOCL/mgMn
	CL O_2	$Mn^{2+} + 2CL\,O_2 + 2\,H_2O \rightarrow MnO_2(S) + 4\,H^+ + CL\,O_2^-$	2.45mgCL O_2/mgMn
	$KMnO_4$	$3\,Mn^{2+} + MnO^{-1}_4 + 2\,H_2O \rightarrow 5MnO_2(S) + 4\,H^+$	1.92mg/mgMn

1.4.5. Traditional method of iron and manganese removal plus desinfection

If the minerals in the aquifer include iron or manganese, these inorganic constituents may be found in groundwater. For removal of iron and manganese, oxidation, precipitation, and filtration are commonly employed. Fig.(2) shows processes for iron and manganese removal. Presence of organics in the source water can impair removal of iron and manganese by oxidation and filtration. Iron can be oxidatized in many instances by aeration. Treatment at a pH of 8 or higher promotes a more rapid oxidation of iron by aeration, if natural organic matter (NOM) is not present in significant concentrations. Chlorine, potassium permanganate, chlorine dioxide, or ozone can be used to oxidize iron and manganese. Potassium permanganate is commonly used for manganese, which is more difficult to oxidize than iron. Greensand has been used in conjunction with potassium permanganate for iron and manganese removal in numerous treatment plants, especially for small- or medium-sized systems. Greensand can adsorb excess permanganate when it is overfed and later remove iron and manganese when permanganate is underfed, allowing operators to attain effective treatment without continuously matching the permanganate dosage to the iron and manganese content of the raw water. When chemical oxidants are used rather than aeration, pressure filters are sometimes used to accomplish iron or manganese removal without the need for repumping following treatment [22,44-57].

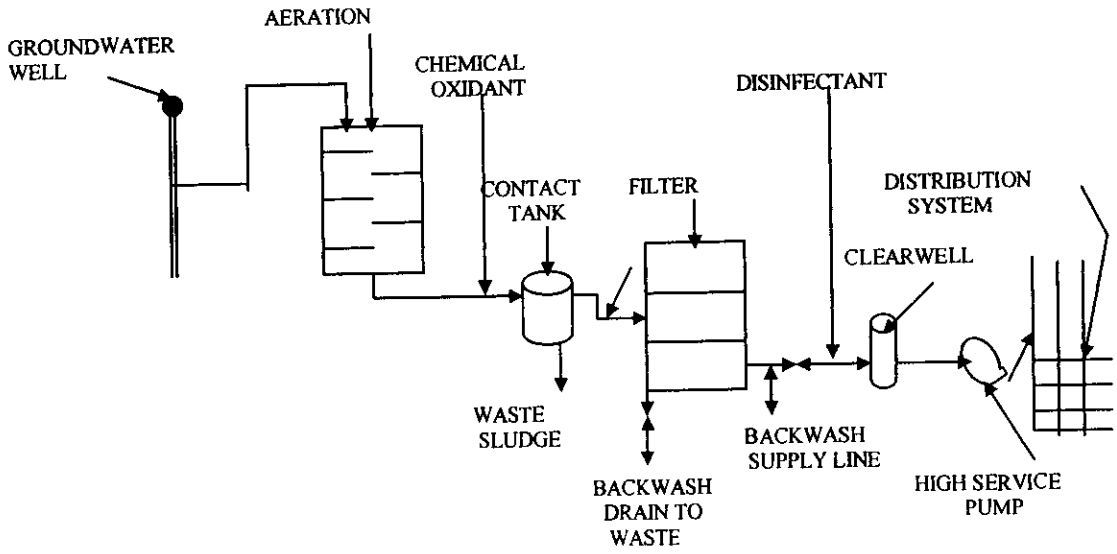

Fig.(2) Iron and manganese treatment, groundwater[22,44-57].

Groundwater supplies have only three forms of iron and manganese that must be removed to their SMCL or less. They are the ferrous iron ion, Fe^{2+}, and its usually colored organic complexes, in significant concentrations up to a normal maximum of 25 mg/l; the manganous manganese ion, Mn^{2+}, and its organic complexes, in concentrations that rarely exceed 1 mg/l; and the color, only a small fraction of which is complex with iron and possibly manganese [4].

When the colored groundwater contains 5 to 10 mg/l of iron, treatment can take place in an iron and manganese removal plant, where it consists of aeration, detention, and filtration with chlorine, chlorine dioxide, or ozone as a part of the pretreatment. (Note: chlorine alone may be adequate). However, with lower concentrations of iron, treatment preferably takes place in the solids-contact type of plant, except that 1 to 3 grains of ferric sulfate per gallon is added as a floc former. As an oxidant for color removal, chlorine dioxide is more effective than chlorine, and ozone is more effective than chlorine dioxide [22].

The ferrous iron ion, Fe^{2+}, and the manganous manganese ion, Mn^{2+}can be simultaneously removed with the other hardness in

groundwater using zeolite water softeners. Care must be taken to prevent air from entering the water softener. If this occurs, iron precipitates form, resulting in clogging or fouling of the ion-exchange resin bed. The iron and manganese leakage will not average more than 1 percent of the influent, or either 0.1 mg/l of iron or 0.05 mg/l of manganese, whichever is greater. The ion-exchange capacity of the resin must not exceed 50 percent of the raw water's total hardness, up to 50 mg/l maximum iron. Records indicate that water containing several milligrams per liter of iron and manganese has been treated in zeolite water softeners to obtain an essentially iron-free and manganese-free soft water [22].

However, removing iron and manganese by other methods, such as aeration, detention, and filtration, prior to utilizing ion exchange for softening, is now a more common municipal water treatment practice [22]. Water softeners remove hardness to a desired minimum level; in municipal supplies the standard is 3 to 5 grains per gallon. Part of the unsoftened water must bypass the softeners and be reblended with the treated water [22].

If the blended finished water contains iron and manganese in excess of their SMCLs, manganese zeolite units are placed in the bypass line to remove the iron and manganese but not the other hardness. This is a very simple and effective way to treat groundwater containing 1.0 mg/l or less iron and manganese [22].

The ferrous iron and manganous manganese ions in anaerobic carbonate-bearing water can be almost completely precipitated as carbonates at pH of 8.0 and 8.5, respectively, by addition of lime or soda ash. When this anaerobic water is softened by the lime-soda process, where the pH is about 11.0, the ferrous ion and the manganous manganese are precipitated as their hydroxides, $Fe(OH)_2$ and $Mn(OH)_2$ [22].

Much less soluble iron and manganese compounds result when the ferrous iron ion, Fe^{2+}, is oxidized to the ferric ion, Fe^{3+}, precipitated as ferric hydroxide, $Fe(OH)_3$, and the manganous manganese ion, Mn^{2+}, is oxidized to the tetravalent (quadrivalent) manganese ion, Mn^{4+}, and precipitated as manganese dioxide, Mno_2; through their agglomeration, they are readily removed from the water by filtration [22].

Using two of the most frequently quoted solubility equilibrium constants, the solubility of ferric hydroxide at a pH of 6.0 is about $3.3x10^{-9}$ mg/l, and the constant indicates that the insolubility increases 1000-fold each unit increase in pH. Manganese dioxide is just as insoluble. Thus, the solubility of the precipitates is so negligible as to be of academic interest only [22].

The actual precipitation and agglomeration of the iron and manganese are not instantaneous. Important to the design and operation of a treatment plant including iron and manganese removal are the condition under which these hydrous derivatives can be completely precipitated in a reasonable period of time. The time required to accomplish this is dependent on the oxidant and on the chemical environment in the water in which oxidation and precipitation occur. Information related to this, along with information on the application of the oxidants, is presented below [22].

1.5 Adsorption in water treatment

Adsorption is a process in which the molecules or atoms of one phase interpenetrate nearly uniformly those of another phase to form a solution with it. The material that concentrated or adsorbed to surface is called the adsorbate while the adsorbing phase is termed the adsorbent. There are many substances which can be used as adsorbents such as fly ash, metal oxides, zeolites, biomass, goethite, pyrite fines, hydroxides, clays, peanut

hulls, coral, sand and active carbon. Because of their large surface area and their high degree of surface reactivity, active carbons are regarded as very good adsorbents for the removal of both organic and heavy metal contaminants

In this context , it is desirable to distinguish between three principal types of adsorption :

A. Adsorption of the first type falls within the realm of ion–exchange and is often referred to as exchange adsorption. Exchange adsorption is, as the term implies, a process in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface. For two potential ionic adsorbates in like concentration and in the absence of other specific sorption effects, the charge on the ion is the determining factor for exchange adsorption. In a system containing a monovalent ion under the stated conditions, the influence of kinetic energy to remain in solution phase is the same for each, but the trivalent is attracted much more strongly toward a site of opposite charge on the surface of the adsorbent. For ions of equal charge, molecular size (hydrated radius) determines order of preference for adsorption, the smaller ion being favored .

B. Adsorption occurring as a result of van der Waal s forces is generally termed " *physical adsorption* " a term which has come to represent cases in which the adsorbed molecule is not affixed to a specific site at the surface but is rather, free to undergo translational movement within the interface. Physical adsorption is usually predominant at low temperature, and is characterized by a relatively low energy of adsorption, that is the adsorbate is not held as strongly to the adsorbent as for chemical adsorption. Adsorption of this type is sometimes referred to also as " *ideal adsorption* "

C. If the adsorbate undergoes chemical interaction with the adsorbent, the phenomenon is referred to as " *chemical adsorption* ", " *activated adsorption* " or " *chemisorption* ". Chemically adsorbed molecules are considered not to be free to move on the surface, or within the interface.

Chemical adsorption processes exhibit high energies of adsorption because the adsorbate forms strong localized bonds at active centers on the adsorbent. Chemical interaction between the adsorbent and the adsorbate is favored at higher temperature because chemical reactions proceed more rapidly at elevated temperatures than at lower temperatures

Most adsorption phenomena are combinations of the two forms of adsorption, that is, the several forces which influence the different types of adsorption often interact to cause concentration of a particular solute at interface. Thus, it is generally not easy to distinguish between physical and chemical adsorption .

1.6 Activated Carbon in Adsorption

Activated carbon functions by adsorption, i.e. by the adhesion of certain substances to the internal substances constituting the walls of the pores. Therefore, the greater the adsorption surface available, the better is the adsorption function [1]. Adsorption occurs because of an imbalance of forces upon the carbon atoms constituting the surface of the pore wall, a phenomenon inherent in all surfaces.

In general, the factors that influence the adsorptive behavior of activated carbon from aqueous solution are temperature (adsorption generally decreases with increasing temperature), the pH value of the solution (carbon generally has a low affinity for ions, especially those with a high charge to surface ratio, and pH can affect ionicity), the nature of the species present, their relative concentration and the nature of the activated

carbon and its particle –size distribution. For the molecules to be adsorbed, they must reach the internal surfaces of the micropores by diffusion. Therefore, the reaction time will depend on the length of the diffusion path, and the kinetics of adsorption will increase with decreasing particle size.

Once molecules have been adsorbed within the pores of granular activated carbon, which is then saturated or spent, it is frequently desirable for one to remove the adsorbate from the carbon matrix, thus renewing the carbon for re-use in the process, and possibly also to recover the adsorbed material.

1.6.1. Raw materials for activated carbon

Any cheap material with a high carbon content, low in inorganics, can be used as a raw material for the production of activated carbon. In early production procedures, preference was given to younger fossil materials such as wood, peat and wastes of vegetable origin, which included fruit stones, nut shells and saw dust.

In practice, five different types of carbonaceous materials are being used for industrial–scale production of activated carbons. These raw materials in the order of their importance and in terms of activated carbon production capacity world wide are as follows [58].

1- Wood 130,000 tone/year.
2- Coal 100,000 tone/year.
3- Lignite 50,000 tone/year.
4- Coconut shells 35, 000 tone/year.
5- Peat 35, 000 tone/year.
6- Others 10, 000 tone/year.

Low inorganics are essential to keep ash content low in the final product because the ash content in terms of percentage of the final product can increase many times after activation.

1.6.2. Preparation of activated carbon

According to R.C. Bansal (1988) and Sai et al (1997), [59,60] the preparation of activated carbons involve two main steps; *carbonization* of the carbonaceous raw material at temperature below 700 ^{o}C in the absence of oxygen, and *activation* of the carbonized product. During carbonization most of the non-carbon elements such as oxygen and hydrogen are first removed in gaseous form by the pyrolytic decomposition of the starting material. The free atoms of elementary carbon are grouped into sheets of condensed aromatic ring systems with a degree of planar structure. The mutual arrangement of these aromatic sheets is irregular and leaves interstices between them, which may, filled with tarry matter or products of decomposition or at least blocked partially by disorganized carbon. The important parameters that determine the quality and the yield of the carbonized product are: (i) rate of heating, (ii) final temperature and (iii) soaking time.

Carbonization does not give rise to products that have adsorption capacity because of their less developed pore structure and low surface area. This pore structure is enhanced during the activation process, which convert the carbonized raw material into a form that contain the greatest possible number of randomly distributed pores of various shapes and size giving rise to an extended high surface area of the product [59].

The objective of the activation process is to enhance pore volume and to enlarge diameter of the pores, which were created during carbonization process, and to create new porosity. Activation removes the disorganized

carbon, exposing the aromatic sheets to the activation agent in the first phase and leads to the development of microporous structure. In the later phases of the reaction the significant effect is widening the existing pores or the formation of large-sized pores by complete burn-off of the walls between the adjacent pores [59-61].

Thus, the large internal surface area of activated carbons is the result of the activation process; there are mainly two different methods for activation, namely physical and chemical. In both methods there is a reaction of the precursor with the activating agent (gas or liquid) to develop the porosity, they differ not only in the practical procedure but also in the mechanism by which the activating agent develops such porosity [62].

1.6.2.1. Physical activation

Physical activation is the most common method, and involves gasification with oxidizing gases. Commonly used gases are carbon dioxide, steam and air. They can be used singly or in combination. The term "thermal activation" is recently introduced [63].Two physical activation methods, namely, two-steps procedure and one-step procedure, are normally used for the preparation of activated carbon

1.6.2.2. Chemical activation

The second commercial route to producing porous carbons involves the reaction of the precursor with chemical reagents. The chemical is introduced into the precursor, where it produces physical and chemical changes, modifying the thermal degradation process. As consequence, the temperature of the process range (500-900 ^{0}C).

The most commonly used activating agents are phosphoric acid, $ZnCl_2$, sulfuric acid. Sometimes potassium sulfide, potassium thiocyanate,

hydroxides and carbonates of alkali metals, calcium and magnesium chlorides, and other substances are used. The precursors are usually cellulosic materials [63-65].

The pore–size distribution of these carbons is reported to be dependent on the ratio of chemical activant to precursor. A high ratio leads to wider micoporosity and more developed meso-and macroporosity [64-68] The optimum ratio of reagent to precursor with respect to adsorptive properties and yield is dependent on the precursor composition.

The manufacture of activated carbon involves two main steps;[58] carbonization of the carbonaceous raw material at temperatures below 700 ^{0}C in the absence of oxygen, and activation of the carbonized product. During carbonization most of the non-carbon elements such as oxygen and hydrogen are eliminated as volatile gaseous products by the pyrolytic decomposition of the starting material .

Carbonization does not give rise to products that have adsorption capacity because of their less developed pore structure and low surface area. This pore structure is enhanced during the activation process, which converts the carbonized raw material into a form that contains the greatest possible number of randomly distributed pores of various shapes and sizes giving rise to an extended and extremely high surface area of the product. Activation is an oxidation reaction at elevated temperatures where the oxidizing agent is usually steam and carbon dioxide and sometimes only air. The objective of the activation process is to enhance pore volume and to enlarge diameter of the pores which were created during carbonization process and to create new porosity . Steam is the preferred activation gas because the water molecule has smaller dimensions than the CO_2 molecules and consequently the use of steam leads to faster diffusion into the pores network, easier access into microspores, and a faster

reaction rate (approximately three times faster than the CO_2 reaction at a temperature of 800 ^{0}C and a pressure of 10 kpa) [69-70].

1.6.3Removal of heavy metals by activated carbon

Anthropogenic sources of heavy metals include wastes from the electroplating and metal finishing industries, metallurgical industry, tannery operations, chemical manufacturing, mine drainage, battery manufacturing, leachates from landfills, and contaminated ground water from hazardous waste sites .

Factors affecting heavy metal removal by activated carbon include: pH of solution, metal type and concentration, surface loading, presence of complexing ligands, competing adsorbates, ionic strength, temperature and carbon type.

In systems with more than one adsorbate, competition between the adsorbates for surface sites may occur. The degree of competition is dependent on the type and concentration of the competing ions, number of surface sites and the affinity of the surface for adsorbate. The presence of second adsorbate does not always decrease metal removal [71]. reported that the presence of organic adsorbates did not adversely affect the removal of several heavy metal .

1.7. Equilibrium adsorption models

The common manner to predict the adsorption equilibrium between the two phases is to express the amount of substance adsorbed per unit weight of adsorbent, q_e , as a function of the residual equilibrium concentration, c_e, of substance remaining in the solution phase. An expression of this type, termed an adsorption isotherm, defines the

$b \alpha \ (\exp^{(-\Delta H/RT)})$ [81].

Two convenient linear forms of the Langmuir equation derived :

$$\frac{C_e}{q_e} = \frac{1}{bq^0} + \frac{C_e}{q^0} \qquad \text{.....(1.4)}$$

$$\frac{1}{q_e} = \frac{1}{q^0} + \left(\frac{1}{bq^0}\right)\left(\frac{1}{C_e}\right) \qquad \text{.....(1. 5)}$$

form chosen usually depends on the range and spread of the data and on the particular data to be emphasized. For very small amounts of adsorption, that is, when $b\ C_e << 1$, the specific adsorption is proportional to the final concentration of adsorbate in solution, yielding a linear adsorption relationship [73] :

$q_e = q^0 b C_e$ .....(1.6)

For large amounts of adsorption:

$bC_e >> 1$ and $q_e \simeq q^0$ .....(1.7)

1.7.2. Freundlich isotherm

The Freundlich or Van Bemmelen equation is basically empirical formula, has been used for many years [73].The equation is a special case for heterogeneous surface energies in which the energy term, b, in the Langmuir equation (1.1) varies as a function of surface coverage, strictly due to variations of heat adsorption [81].

The Freundlich equation has the general form [82-85].

$$q_e = K_f . C_e^{1/n_f} \qquad \text{.....(1.8)}$$

Where

q_e is the amount of solute adsorbed per unit weight of adsorbent .

C_e is the equilibrium concentration of the solute .

K_f is a constant related to adsorption capacity, and

n_f is a constant related to the adsorption intensity .

n and K_f are constants, can be determined from the slope and intercept from linear form of equation (1.6) by ploting log q_e versus log C_e.

$$\log q_e = \log K_f + 1/n \log C_e \qquad \text{.....(1.9)}$$

1.8. Contacting systems and modes of operations

Of particular importance in the application of carbon for large–scale treatment of water and waste water is the manner in which the carbon contacts the solution to be treated. Rates of adsorption from solution on granular adsorbents have been found to be strongly dependent upon the particle size of the adsorbent [86]. It would therefore appear desirable to employ particles of as small a diameter as condition of efficient operation allow, so that high rates of adsorption may be obtained.

1. 8.1. Batch system

In batch type contact operation, a quantity of carbon is mixed continuously with a specific volume of water or waste until the pollutant in

that solution has been decreased to a desired level. The carbon is then removed and either discarded or regenerated for use with another volume of solution. If finely powdered carbon is used in this type of system, separation of the spent adsorbent from the water is generally difficult. Conversely, the use of large particles of carbon, which may be removed more readily when exhausted, requires long periods of contact between solution and adsorbent, necessitating large basins or tanks in which to retain the water or waste during treatment.

1.8.2. Continuous - flow system [87-89]

Column–type continuous – flow operations appear to have distinct advantage over batch-type operations because rates of adsorption depend on the concentration of solute in the solution being treated. For column operation the carbon is continuously in contact with a fresh solution. Consequently, the concentration in the solution in contact with a given layer of carbon in a column is relatively constant. For batch treatment, the concentration of solute in contact with a specific quantity of carbon steadily decreases as adsorption proceeds, thereby decreasing the effectiveness of the adsorbent for removing the solute.

Most continuous – flow adsorption systems are operated as fixed – bed adsorption column. These systems are capable of treating large volumes of waste water and are widely used for both municipal and industrial applications. Fixed–bed adsorber may be operated as simple columns or as multiple columns in series. Furthermore, they may be operated in either the upflow or downflow mode. In downflow system the carbon can serve for adsorption and for filtration of suspended solid, however, adsorption is more efficient and the beds are less expensive to operate if suspended solids are removed in advance.

Upflow columns may be operated either as packed or expanded beds. Packed beds require a high–clarity influent to prevent clogging; whereas expanded beds are capable of handling waste water high in suspended solids, since the solids will move through the void spaces between the carbon particles and not clog the bed .

The use of upflow and downflow columns in series has been reported to optimize carbon usage reduce operating costs [90]. The Upflow bed is placed first in sequence and serves as a roughing contactor, while the down flow filter in the second position can be functioned as a polishing unit.