

**Sudan University of Science and Technology**

**College of Graduate Studies**

**Hardness Removal of Industrial Water by some  
Clays in Sudan**

إزالة العسر من المياه المستخدمة في الصناعة بواسطة بعض أنواع  
الطين في السودان

**Athesis submitted for fulfillment for the degree of  
Doctor of Philosophy in Chemistry**

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# DEDICATION

*This work is dedicated to*

*My  
Family*

## Abstract

The industrial water is the water used to generate steam to be used in many industries. The tap water contains salts, minerals, ions, organic material and micro organisms. The ions of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  are most common ions present in the tap water; they make a problem of hardness and scales deposit on the electrical pipes of the boilers. The scales are building up through time to the limit of total coverage of the pipes and even materials that can make unavoidable blocks. The mechanical removing of the salts result into many difficulties; moreover, the exploitation of energy with poor efficiency of the generation of the steam. The general practice used industrially is that, they use HCl to remove scales, in addition to small amounts of organic materials to clean the pipes after mechanical removal of the deposits.

Here in this research we adopted five types of earths available in the Sudan. They are: West Nile Clay, East Nile Clay, Blue Nile, Soba, and in addition to famous Jurdiga. By treating the earths with 0.01, 0.02, 0.05, 0.07, 0.1 and 0.2M NaOH and with the same concentrations of KOH. Usually 50g of these earths were treated with  $150\text{cm}^3$  of the alkali solutions. The treated clays were calcined to  $400^\circ\text{C}$ . A pilot plant was developed to test the efficiency of large scale production of soft water by passing tap water continuously through the treated clays.

The experimental part used the ordinary glassware, for activation, then the technique of grain size distribution. The flame photometer, the X- ray fluorescence, the X- ray diffraction were used for samples characterization, in addition to wet chemical analysis. The statistical product and service solution (SPSS) was used to evaluate the results obtained from the laboratory.

The following results were obtained according to the efficiency of hardness removal by different alkali concentrations. For NaOH the efficiencies were in the range 50% to 80% for Jurdiga sample, then West Nile Clay in the range 18% to 70%, East Nile Clay 13% to 70%, Blue Nile 8% to 62% and West Soba 18% to 48%. The pilot results gave efficiency of scale removal of 40% when (250 g earths were treated with 0.1M NaOH ), to give 18 liters of soft water; while the calcined samples gave only 8 liters. The SPSS results showed that the independent sample T- test prove that there was no difference in using NaOH or KOH. The

difference is that in concentration of the base as given by ANOVA. The chemical analysis of the samples showed that the samples were aluminium silicates. The results of chemical analysis were reviewed by X- ray fluorescence of same constituents while the X- ray diffraction showed the dominant constituents of hematite, of West Nile clay while feldspar of East Nile clay, Blue Nile and Soba sample, while Jurdiga was plagioclase feldspar. The grain size distribution ranges from silty clay to fine sands of West Nile clay, East Nile clay and Blue Nile samples respectively. 50% silt and 50% fine sand of Soba sample. Usually it was noticed that the sample contains clays and feldspar was the best one.

The used earths contain amounts of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  as waste products, then for further research work, the waste could be moulded, calcined and material impact tested as ceramic bricks.

The research findings could be directly reflected to the industries to solve the problems of hard water and to save energy with high degree of safety to the boilers and the workers. It is the utilization of our local resources using science innovation.

## المستخلص

تستخدم المياه من الشبكات العامة أو المصادر لإنتاج البخار الذي يستخدم في الصناعات المختلفة. إن المياه العادية تحتوي أملاحاً ومعادن وأيونات ومواد عضوية وأحياء دقيقة. أيونات الكالسيوم والماغنيزيوم هما أكثر الأنواع وجوداً في مياه الشبكات وهذه بدورها تنتج عنها مشاكل في عسر الماء وأيضاً تترسب هذه المواد على الأنابيب الموصلة للكهرباء في القيزانات. فهذه المواد المترسبة تتراكم بمرور الزمن حتى تغطي الأنابيب تماماً ثم تتراكم أكثر فأكثر حتى تنتج كتلاً لا يمكن إنتاج البخار معها بالصورة المطلوبة. إن إزالة هذه الكتل ميكانيكياً تؤدي إلى صعوبات كبيرة علاوة على ذلك فإن استخدام الطاقة يكون بكفاءة متدنية وكميات البخار الناتج ضعيفة. هذا وكان الناس يمارسون علاج هذه المشكلة صناعياً باستخدام حامض الهيدروكلوريك مخففاً مع إضافة كميات صغيرة من المواد الكيميائية العضوية وذلك لتنظيف الأنابيب والقيزانات بعد استخدام الإزالة الميكانيكية للرواسب.

في هذا البحث استخدمت خمس أنواع من الأطيان الموجودة في السودان وهي عينة طينة غرب النيل وطينة شرق النيل والنيل الأزرق وطينة منطقة سوبا بالإضافة لأطيان الجردقة المشهورة. هذه الأطيان خضعت لتفاعل التراكيز التالية من هيدروكسيد الصوديوم 0.01، 0.02، 0.05، 0.07، 0.1، 0.2 مولار وخضعت لنفس التراكيز من هيدروكسيد البوتاسيوم. عموماً فإن 50 جراماً من الأطيان اضيفت لها 1 50 سم<sup>3</sup> من محاليل الهيدروكسيدات بعد ذلك تم معالجة هذه النواتج من الطين حرارياً في درجة 400° م لإنتاج ماء يسر. فإن المياه من الشبكة العامة تمرر خلال هذه الأتربة المعالجة حيث يمكن الحصول على ماء يسر تستخدم لملء القيزانات.

ثم اجراء البحوث التجريبية لمعرفة كفاءة الأطيان المعالجة في إزالة عسر الماء ولتغطي صورة أكبر من الاستخدام الصناعي الواسع لها.

في الجانب العملي استخدمت في التجارب المختبرية الأجهزة الزجاجية العادية لتنشيط الأطيان ثم استخدام تقانة التوزيع الحجمي الحبيبي وجهاز مطياف اللهب وجهاز فلورة الأشعة السينية وجهاز حيود الأشعة السينية وذلك لمعرفة طبيعة وأنواع الأطيان والتحليل الكيميائي لها.

ثم استخدام التحليل الاحصائي لتقييم النتائج التي تم الحصول عليها مختبرياً. النتائج الآتية تم الحصول عليها باستخدام كفاءة إزالة العسر من الماء باستخدام التراكيز المختلفة للقلويات ولهيدروكسيد الصوديوم فإن الكفاءة في مدى 50-80% وذلك لعينات الجردقة ثم عينات غرب النيل في مدى 70-18% وشرق النيل في مدى 70-13% أما عينات النيل الأزرق فإنها أعطت كفاءة في مدى 62-8% وغرب سوبا. 48-18% أما نتائج البحث التجريبي فإنها كانت بكفاءة 40% إزالة عسر وذلك عند استخدام 250) جرام من الأطيان معالجة بواسطة هيدروكسيد الصوديوم بالتركيز 0.1 مولار (والتي نتج عنها 18 لتراً من المياه الصالحة للاستخدام بينما العينة التي تم معالجتها حرارياً نتج عنها 8 لترات.

إن استخدام آلية الإحصاء نتج عنها عدم وجود فروقات في استخدام هيدروكسيد الصوديوم أو البوتاسيوم ولكن الفرق يمكن أن يكون ملحوظاً في تراكيز القلويات، والذي ظهر في تحاليل التباين. أظهرت التحاليل الكيميائية أن هذه العينات هي سليكات الامونيوم وجاء هذا مطابقاً مع نتائج فلورة الأشعة السينية أما تجارب حيود

الأشعة السينية فأظهرت أن هذه العينات هيما تيت لعينة غرب النيل. أما عينات شرق النيل والنيل الأزرق فهما من فصيلة الفلسبار أما عينة الجردقة فإنها بلاجوكليز وعينة سوبا هي دايبوسيد مع ميكروكلين. إن نتائج تجارب حجم التوزيع الحبيبي فأظهرت ان العينات تتراوح بين طفل سلتي إلى رمل ناعم لعينات غرب النيل وشرق النيل والنيل الأزرق أما عينة سوبا فإنها ذات طبيعة 50% سلت و 50% رمل ناعم. وعموماً فإن العينة التي تحوي طفل وفلسبار هي من أفضل العينات. أن الطين الذي أستخدم في تنقية الماء يحتوي كميات من أيونات الكالسيوم والماغنيزيوم كمخلفات صناعية. لأمتداد هذا البحث أن هذه المخلفات يمكن أن تصب على هيئة قوالب وتعالج حرارياً ثم تجري عليها إختبارات قوي الكسر لأنتاج طوب طيني. ان نتائج هذا البحث يمكن أن تستفيد منه الصناعة لحل مشاكل الماء العسر وهو يوفر الطاقة لإنتاج البخار بتكلفة أقل مع درجة أمان كبيرة للقيزانات والمستخدمين لها من العمال. إن هذا البحث يمثل استغلال الموارد المحلية باستخدام التطور العلمي والمعرفة.

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## **A-Introduction**

The tap water is used in large quantities as industrial water to provide the steam, to fill the steam tanks (boilers). The boilers are designed to serve huge quantities of steam to provide it in many industries like soaps and oils, beverages, dairy products, food industries, iron and steel industries, grain milling industries... etc. The boilers are equipped with electrical pipes to provide energy for steam generation.

The tap water is usually hard water, i.e., it contains particles; among them are  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  that are responsible for hardness. The cations are distributed in all boilers system including the surfaces. The steam can not pass easily, since those cations scales as considered as inorganic solutes preventing the full scale generation of the steam to outside flow.

Another problem to the scales is that, they are depositing on the heating pipes and accumulating on time to make unavoidable problems of low efficiency of generating the steam (quality and quantity) that leads to energy disposal with generation of high cost. At the end of that, the boilers might explode with a lot of damage in lives and materials.

The industry was practicing the commercial scale removal of “Cleansol” that is the dilute hydrochloric acid with some organic species as additives to coat the pipes from acid attack, and then flushing with water. This is somewhat a solution, especially in the early stages.

The better solution is suggested here in this study to prevent scale formation by an effective removal of the cations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from tap water at the beginning by reacting some clays and earths available in the Sudan with standard caustic soda KOH and then passing the tap water over the modified clays to fill the boilers by soft waters.

## **B-Literature Review**

The ion exchange process is extensively used and also the most effective methods to remove hardness in water, it consists of resin that calcium and magnesium can be exchanged for sodium and potassium ions (Alley et al. 2007). The ion exchange resins are (functionalized porous or gel polymer), zeolites, montmorillonite, clay and soil humus. Clays can be modified by treating with bases such as NaOH or KOH (Yoder 1957). Natural molecular sieves such as modified clays contribute to a cleaner, safer environment in a great number of ways. Orumwense (1996) studied the removal of lead from water by adsorption on a kaolinitic clay. Smith (2000) said that clays remove metals in a variety of ways. Konta (1995) studied clay minerals in rivers, both in suspension and settled in muds, as important adsorbents of toxic substances in solution. Rob et al. (2003) used ceramic filter for water purification. Naddafi et al. (2005) showed that clay pipes were not successful in removing total hardness and permanent hardness. Parapat et al. (2011) showed that the hardness removal efficiency of ground water with waste poly-styrene plastics was higher than with no added resin (43% vs 12%). Bulut and Baysal (2006) and Malakootain et al. (2009) have investigated various low-cost locally available adsorbents for the removal of  $Pb^{2+}$  ions from wastewater. The phase composition of raw brick clays and fired bricks are generally complex due to the use of highly heterogeneous soil. The major phases found in the raw soil materials, however, included quartz, calcite, chlorite and albite. In slight fired bricks, illite is the most persistent of the clay minerals (Ahmed et al. 2008).

The range of minerals contained in most natural waters is quite limited (Arden 1968, Metuchen 1961). The cations present are normally of calcium, magnesium and sodium, while anions are mainly chloride, sulphate and bicarbonate, with lower concentration of nitrate, phosphate and silica.

There are also traces of organic matter; the analysis of the ions mentioned above will give the total dissolved solids in the water (Arden 1968).

The water molecule is made up of two hydrogen atoms bonded to an oxygen atom. The three atoms are not in straight line, they form an angle of 105. Because of water bent structure and the fact that the oxygen atom



attracts the negative electrons more strongly than do the hydrogen atoms, the water molecule behaves like a dipole having opposite electrical charges at either end. The water dipole may be attracted to either positively or negatively charged ions. This kind of attraction for ions is the reason why water dissolved many ionic compounds and salts that do not dissolved in other liquids

A second important characteristic of the water molecule is its ability to form hydrogen bonds, which hold the water molecules together in large groups. Hydrogen bonds also help to hold some solute molecules or ions in solution. Water is an excellent solvent for many materials. It has the highest heat capacity of any liquid or solid,  $1 \text{ cal.g}^{-1} \cdot \text{Deg}^{-1}$ . The extremely high heat of vaporization of water,  $585 \text{ cal/g}$  at  $20^\circ \text{ C}$ , likewise stabilizes the temperature of bodies of water and the surrounding geographic regions. Water has its maximum density at  $4^\circ \text{ C}$ , a temperature above its freezing point (Skooge 1995).

It is customary to refer to waters as “hard” or “soft” the former are waters containing appreciable concentrations ( over 50 ppm ) of calcium and magnesium ( in Great Britain) which are acquired through contact with rock and sediments in the environments.

### **1-1 Hardness:**

Calcium ion, along with magnesium and sometimes iron (III), account for water hardness. The most common manifestation of water hardness is the curdy precipitate formed by soap in hard water. Temporary hardness is due to the presence of calcium and bicarbonate ions in water and may be eliminated by boiling the water



Increased temperature may force this reaction to be right by evolving carbon di oxide gas, and a white precipitate of calcium carbonate may form in boiling water having permanent hardness. Water containing a high level of carbon di-oxide readily dissolves calcium from its carbonate minerals.



When this reaction is reversed and carbon dioxide is lost from the water, calcium carbonate deposits are formed. The concentration of carbon dioxide in water determines the extent of dissolution of calcium carbonate (Skooge1995). Hard drinking water may have moderate health benefits, but compose seriously problem in industrial setting, where water hardness is monitored to avoid costly breakdown in boilers, cooling towers and other equipment that handle water. In domestic setting, hard water is often indicated by a lake of sud formation when soap is agitated in water, and by the formation of lime scale in kettles and water heaters (American Public Health Association 1966).

### **1-2 Boiler scales :**

The deposition of solids within boilers under steaming conditions results in an accumulation of sludge or in the production of scale (American Public Health Association1966, Lower, Stephen 2007). The deposits in the form of scale are highly objectionable, since they are poor conductors of heat and causes reduced efficiency, and are after responsible for burned tubes or plates(Ppcoetzee 1998).

The scale resulting from deposition of mineral constituents in boilers consists not of single salt but of a number of compounds (Powell and Sheppard 1945). But calcium carbonate is the principal scale – former in condensers and other water - jacketed equipment(Metuchen 1961). The damage caused by calcium carbonate deposits varies in the crystalline form, for example, calcite or aragonite (Sorg et al. 1999). The presence of ions in an electrolyte, in this case hard water, can also lead to galvanic corrode in which one metal will preferentially when in contact with another type of metals, when both are in contact with an electrolyte(Ppcoetzee 1998) .

### **1-3 water softening methods:**

The most common means for removing water hardness rely on ion exchange polymers or reverse osmosis; other approaches include precipitation methods and sequestration by the addition of chelating agents. Devices which use magnetism or electrolysis as water softening technique claim to inhibit scale buildup without actually removing hard ions from the water. Such devices have been marketed to consumers since the early 20<sup>th</sup> century but are fraudulent (Mellor 1941).

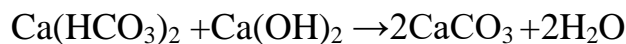
#### **1-3-1 Lime softening:**

A technique known as Clark's process, in which lime softening involves a relatively complicated series of chemical reaction. The goal of all of these reactions is to change the calcium and magnesium compounds in water into calcium carbonate and magnesium hydroxide.

The first step in lime softening is to addition of lime to water

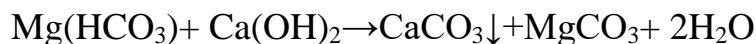


Once carbon dioxide demand has been met, the lime is free to react with and remove carbonate hardness from water.

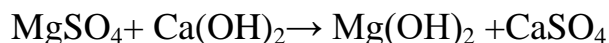


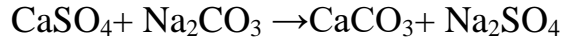
We have focused on calcium bicarbonate since it is the most common calcium compounds in water but other calcium based hardness compounds have similar reaction. In any case the calcium carbonate produced is able to precipitate out of solution.

Magnesium compounds have a slightly different reaction

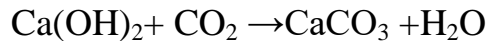


In many cases, only the carbonate hardness needs to be removed, requiring only the addition of lime. However if non carbonate hardness also needs to be removed from water, then soda ash must be added to the water along with lime.





The reactions which remove carbonate and non carbonate hardness from water require a high pH and produce water with a high concentration of dissolved lime and calcium carbonate. If allowed to enter the distribution system in this state, the high pH would cause corrosion of pipes and the excess calcium carbonate would precipitate out, causing scale. So the water must be recarbonated, which is the process of stabilizing the water by lowering the pH and precipitating out excess lime and calcium carbonate(epa. Gov 2013).



In the process both of calcium (and to extent magnesium) in the raw water as well as the calcium added with the lime are precipitated.

Lime softening produces large volumes of a mixture of calcium carbonate and magnesium hydroxide in a very finely divided white precipitate which may also contain some organic matter flocculated out of raw water processing or disposal of this material may be a cost to the process.

### **1-3-2 Chelating agents:**

Chelators are used in chemical analysis as water softeners, and ingredients in many commercial products a commonly used synthetic chelators are ethylene di amine tetra acetic acid (EDTA) (American Public Health Association 1966).

### **1-3-3 Reverse Osmosis:**

Reverse osmosis (RO) is a water purification technology that uses a semipermeable membrane to remove large particles from water. In RO an applied pressure is used to overcome osmotic pressure. A colligative property, which is driven by chemical potential, a thermodynamic parameter.RO can remove many types of molecules and ions from solutions, including bacteria, and is used in both industrial process and the production of potable water. The result is that the solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. To be “selective”, this membrane should not allow large

molecules or ions through the pores (holes) but should allow smaller components of the solution (such as solvent) to pass freely.

Reverse osmosis is the process of forcing a solvent from a region of high solute concentration through a semipermeable membrane to a region of low solute concentration by applying pressure in excess of the osmotic pressure.

The membrane used for RO has a dense layer in the polymer matrix- either the skin of an asymmetric membrane or an interfacial polymerized layer within a thin – film – composite membrane –where the separation occurs(Aruidhas 2004).

The latest development when it comes to drinking water includes Nano scale and graphene membranes (Selley 1982)

### **1-3-4 Distillation:**

Since  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  exist as non volatile salts they can be removed by distilling the water. Distillation is too expensive in most cases. Rain water is soft because it is naturally, distilled during the water cycle of evaporation, condensation and precipitation.

### **1-3-5 Ion exchange:**

Conventional water softening appliance intended in household uses depend on an ion-exchanged for sodium ions. As described by NSF/ANSI standard 44(24, ion-exchange device reduce the hardness by replacing magnesium and calcium (or toxic heavy metal cations). With sodium or potassium ions ( $\text{Na}^+$  and  $\text{K}^+$ )(Bulut andBaysal2006). Although the phenomenon of ion-exchange was noted and vaguely reported early but it was placed on a firm and practical basis since 1905. This development was due to Robert Grans(Sorg et al. 1999), who produced synthesized ion-exchange minerals by Fusion clay, sand, and sodium carbonate (soda – ash). He called this product “permutits” from the latin permute, which means interchange.

Zeolite has been much widely used to describe such water – softening mineral (Metuchen 1961, Powell and Sheppard 1954, Sorg et al. 1999).

### **1-4Molecular sieves:**

They constitute a member of adsorbent materials such as charcoal, (activated carbon) and silica gel (Bulut and Baysal 2006). They are crystalline structures in which the molecules are arranged in a definite pattern. The most common molecular sieve is based on anhydrous aluminosilicate. It is also common to refer to molecular sieve as zeolites. Molecular sieves are most often found in granular form held together by a binder having regularly spaced cavities with interconnecting pores of a known and definite size. Typical surface areas are on the order of 1200 m<sup>2</sup>/g. With an effective pore diameter of 13Å. Other materials used for molecular sieves include anhydrous sodium aluminosilicate and anhydrous calcium aluminosilicate .The average pore diameter of anhydrous sodium aluminosilicate is 4Å and for anhydrous calcium aluminosilicate is 5Å (Bulut and Baysal 2006) .

### **1-5 Zeolites:**

Zeolites are a large group of aluminosilicates with interesting structural complexities, formed by diagenesis or the very lowest temperature of metamorphism. They have wide industrial application as molecular sieves, ion exchangers , and catalysts .As with Garnets and Spinel's , industrial interest has led to synthesis of numerous molecular sieves with no natural counter parts (Deer et al. 1992).

#### **1-5-1 Occurrence of Zeolites**

Zeolites have long been found in amygdaes and fissures in basic volcanic rocks where they often form well - developed crystals. More recently they have been recognized as being important and often abundant authigenic constituents in

sedimentary rocks. They have been found as major constituents of volcanic tuffs in metamorphic rocks, they occur as a result of hydrothermal activity and by burial metamorphism (Deer et al. 1992).

### **1-5-2 Synthesis of Zeolites:**

There are about forty -five natural zeolites, they offer only a limited range of atomic structure and properties .The synthetic production of zeolites is largely aimed at tailoring their properties to specific industrial needs.( Malakootian et al. 2009).Synthesis of zeolites was first conducted through mimicking of geothermal conditions for natural zeolites formation, i.e., high - temperature hydrothermal reactions. Although, compared to natural zeolites, synthesized zeolites have many advantages such as high purity, uniform pore size, and better ion-exchange abilities (Ruren et al. 2007)

Zeolites are manufactured in a number of ways : one important technique, involves mixing sodium, aluminum and silica chemicals with steam to create a gel ( an amorphous ; non crystalline ,water - rich solid) .The gel is aged ,then heated to about 90° C . Another technique uses kaolin clay that has been heated in a furnace until it begins to melt ,then chilled and ground to powder .The powder is mixed with sodium salts and water ,aged ,and heated .In all the synthesis methods , the zeolites produced depends on the compositions of the starting materials and the reaction conditions ,including acidity ,temperature, water and pressure (Malakootian et al. 2009).

### **1-5-3 Structures of Zeolites:**

The atomic structures of zeolites are based on three -dimensional frameworks of silica and alumina tetrahedra (primary building), that is silicon or aluminum ions surrounded by four oxygen ions in a tetrahedral configuration. Each oxygen is

bonded to two adjacent silicon or aluminum ions, linking them together. Clusters of tetrahedra form box like polyhedral units that are further linked to build up the entire framework (secondary building unit) SBU is a double four - membered "ring" .Six SBUs surround a cage of a truncated octahedron .This cage has an internal diameter of 112 pm (11.2 Å), with 42- pm (4.2Å) channels connecting the cages.

The aluminosilicate, framework of a zeolite has a negative charge, which is balanced by the cations housed in the cage like cavities. Zeolites have much more opened, less dense structures than other silicate; between 20 and 50 percent of the volume of a zeolite structure is voids. Silicates such as zeolites that have three - dimensional frameworks of tetrahedra are termed tectosilicates (Deer et al. 1992, Klein 2001).

#### **1-5-4 Application of Zeolites:**

Zeolites are widely used as ion - exchange beds in domestic and commercial water purification, softening. In chemistry, zeolites are used to separate molecules (only molecules of certain sizes and shapes can pass through) and as traps for molecules so they can be analyzed.

Zeolites are also widely used as catalysts and sorbents. Their well - defined pore structure and adjustable acidity make them highly active in a large variety of reactions (Vivnov et al. 2014)

Zeolites have the potential of providing precise and specific separation of gases including the removal of H<sub>2</sub>O , CO<sub>2</sub> and SO<sub>2</sub> from low - grade natural gas streams .Other separation include noble gases ,N<sub>2</sub>,O<sub>2</sub>, freons and formaldehyde .

On-Board oxygen Generating systems (OBOGS) use zeolites in conjunction with



pressure swing adsorption to remove nitrogen from compressed air in order to supply oxygen for aircrews at high altitudes. Synthetic zeolites are widely used as catalysts in the petroleum and petrochemical industry.

Zeolites have uses in nuclear industry, for example, in the aftermath of the Fukushima Daiichi nuclear disaster, sandbags of zeolites were dropped into the sea water near the power plant to adsorb radioactive cesium which was present in high levels (Associated press 2001)

Zeolite substance developed for use in biogas industry for long-term storage of energy at density 4x more times than water

Zeolites can be used as solar thermal collectors and for adsorption refrigeration. They are also used as a molecular sieve in cryosorption style vacuum pumps (Guglielmo et al. 2012) Zeolites are used in detergent. They are also used as sand additive in the production process of warm mix asphalt concrete (Dypayan 2013)

Naturally zeolites are used in many biochemical and biomedical applications (Scott et al. 2003) In agriculture, it is used as a soil treatment.

Zeolites are used as a filter additive in aquariums.

## **1-6 Clays:**

Clay, according to the definition put forward by the American Ceramic Society, is "a fine grained rock which, when suitably crushed and pulverized becomes plastic when wet, leather hard when dries, and on firing is converted to permanent rock-like mass; it is essentially hydrated aluminum silicate (Stephen and Martin 1995, Weaver and Pollard 1973, Grim 1962, Zoltai 1984).

Clay minerals typically form over long periods of time from the gradual chemical

weathering of rocks and hydrothermal activity.

There are three or four main groups of clays: kaolinite, montmorillonite - smectite, illite and chlorite (not always, sometimes classified as a separate group within the phyllosilicates). Most natural clays are mixture of these different types.

The clay minerals are built up of tetrahedrally (Si, Al, Fe<sup>3+</sup>) and octahedrally (Al, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>), coordinated cations organized to form either sheets or chains all are hydrous. The basic structural units in layer silicates are silica sheets and brucite or gibbsite sheets. These sheets are combined so that the oxygens at the tips of the tetrahedra project into a plane of hydroxyls in the octahedral sheet and replace two-thirds of the hydroxyls. This combination of sheets form a layer (Weaver and Pollard 1973, Putnis 1995, Pitty 1979, Lewis and M 1994, Gill 1996).

### **1-7 Properties of the Clay:**

The main properties of clay minerals are:

#### **1-7-1 Grain Size:**

Grain size of a soil refers to the diameters of the soil particles making up the soil mass. These particles varying in size from stones and gravels down to the submicroscopic particles of colloidal clay (Brady 1974, Frye 1993). To study successfully the mineral particles of soil, they are usually separated into convenient groups according to size. The analytical procedure by which the particles are separated is called mechanical analysis; it is a determination of the particle size distribution (Frye 1993).

As might be expected a number of different classifications have been devised. The size ranges for four of these systems are shown in table (1).

This classification established by the U.S Department of Agriculture.

Table (1) classification of soil particles ( Frye 1993).

British Standards Institution International Society of Soil Science	Particle size mm	0.002	0.006	0.02	0.06	0.2	0.6	2.0mm
	Clay	Fine	Medium	Coarse	Fine	Medium	Coarse	Gravel
		Silt			Sand			
	Clay				Sand			
Fine					Coarse			
		0.002	0.05	0.10	0.25	0.5	1.0	2.0

US Department Of Agriculture	Clay	Silt	Very Fine	Fine	Med	Coarse	V.Coarse	Gravel
			Sand					
US Publinstration	Clay	Silt	Sand				Gravel	
			Fine		Coarse			

### **1-7-2 Surface area:**

All clay particles, because of their fineness of division must expose a large amount of external surface (Frye 1993). The surface area is that inversely proportional to particle diameter and the surface area of the tiny but innumerable clay particles is huge (Petti 1975).

### **1-7-3 Cation exchange:**

Many of the important properties of clay minerals are related to the positive charge deficiency in the mineral resulting from broken bond at the edges of the tiny crystal (activity) and isomorphism substitution within the crystal lattices.

In minerals of a high charge deficiency (7 Ca 0.8/unit cell). The inter layer ions that are tightly held, tend not to exchange with other ions, except when the charge deficiency is between about 0.2 and 0.7 / unit cell.

The bonding is weak and cation exchange commonly results when there is a change in the relative ion concentration in the water surrounding the minerals. When the charge deficiency is low and the crystals are relatively coarse in size there is a low exchange capacity because there are few charge sites on which the exchange can take place

The exchangeability of ions depends on several factors including the type of clay, the size of the clay crystallites, the type and availability of ions, the EH and pH condition of the solution, temperature, and time. In general, the smaller the hydrated ion size, the more tightly the cation will be held by the clay, but this rule does not always strictly apply (Petti 1975, Vogel's 1989). Most of the cation exchange capacity -(C.E.C)-(80%) is due to the substitution with the structure, but a lesser amount (20%) is due to the charge at the edge of the sheet (Weaver and

Pollard 1973).

The ionic diameter largely governs the substitution which occurs. The edges of all the clay minerals have net negative charge resulting in attempts to balance the charge by cation attraction which is in proportion to the net charge deficiency and may be related to the activity of the clay.

Percent clay is taken as the soil fraction < 2 $\mu$ m

Typical activity values based on the statement above are as follows:

Typical activity values based on the statement above are as follows:

No	Type	Activity	
1	Kaolinite	0.4 -0.05	Least active
2	Illite	0.5 – 1.0	Intermediate activity
3	Montmorillonite	1.0 – 7.0	Most active

Better particle indicator of activity is the shrinkage limits from a practical stand point, the higher the exchange capacity, the more cations ( in some form of admixture ) will be required to effect a change in activity ( Lewis and M 1994 , Brown 1977 ) .

#### **1-7-4 Hydration:**

Clay particles are always hydrated .i.e., surrounded by layer of water molecules called adsorbed water (diffused layer). This layer of water maybe lost at temperature higher than 60 to 100 $^{\circ}$  C and will reduce the natural plasticity of the

soil ( Lewis and Mc Conchie 1994).

## **1-8 Clay modification:**

Typical ion-exchangers are ion-exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay and soil humus.

Clay minerals play a pivotal role as cation exchangers in soil; of considerable significance are the characteristics of clay mineral, viz., not only their nature and proportion, exchange capacity charge density but also ion – selective adsorption sites ( preferential pockets), which govern the distribution of cations between the exchanger and the equilibrium solution (Weigartiner 2006).

Ion-exchangers can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge or their structure.

Since the first cation exchanger used in water softening was a synthetic zeolite and for the next, was other silicious minerals or mineral product resembling the zeolites in their properties.

Sodium cation exchanger will soften water, it is not such a serious matter to call it a zeolite; after all, it works like a zeolite even if it is unlike a zeolite in composition.

The first commercial zeolites were made by a fusion process from materials such as clay, sand and soda ash. Its capacity was about 4.5 kg/cu ft and its salt consumption was originally 400g/kg (Metuchen 1961). Another technique uses kaolin clay that has been heated in a furnace until it begins to melt, then chilled and ground to powder. This powder is mixed with sodium salts and water, aged and heated (Malakootain et al. 2009).

Clays can be modified by treating with bases such as NaOH or KOH (Ahmed et al. 2008), by heating with bases in heater for about half an hour at 100° C and then cleaned with distilled water and dried. In the modification process,  $K^+$ ,  $Na^+$  cations of bases takes place in clay at the edges of crystals and at interlayer ( between layers) . When hard water containing  $Ca^{2+}$ ,  $Mg^{2+}$  cations passes through the modified clays those cations of  $K^+$ ,  $Na^+$  in clay replace the  $Ca^{2+}$ ,  $Mg^{2+}$  cations in hard water due to ion – exchange process and so the hard water is softened.

## **1-9 Water Hardness Analysis**

Hardness is the characteristic of water which represent the total concentration of just the calcium and magnesium ions expressed as calcium carbonate equivalent, part per million, grain per US gallon, partper hundred thousand, or grains per imperial gallon(Metuchen 1961,American Public Health Association 1966) .

Two approaches are presented for the determination of hardness. Method A, hardness by calculation, is applicable to all waters and is considered to yield the high accuracy. If a complete mineral analysis is performed, the hardness can be reported by calculation. Method B, the EDTA titration method, the ethylene diamine tetra acetic acid and its sodium salts form a chelated soluble complex when added to water. EDTA will complex first with  $\text{Ca}^{2+}$  and then with the  $\text{Mg}^{2+}$ . To remove hardness ( American Public Health Association1966, USGS.Gov).

### **1.10 Gravimetric Methods of Analysis:**

Any analytical result can only be as accurate as the sample that was used for the determination of its constituents .The sampling procedure actually constitutes part of the analytical process ,and as such it will affect both the, precision and the accuracy of the results .Good precision therefore ,does not necessarily imply good accuracy(Wainerda and Uken 1971) .When preparing materials for chemical analysis it is not only essential to attain a homogenous sample from which representative portions may be taken ,but the material must also be sufficiently fine. The finer the material is ground, the more readily it will be subject to chemical attack.

The sample has to be brought into solution before a wet chemical analysis can be performed. There is no universal method for obtaining a solution of the sample, since the procedure to be adopted will depend on the nature of the material to be analyzed .This method includes:

1. Acid digestion.
2. Sample fusions.

In a platinum crucible .Once the sample to be analyzed has been obtained in solution ,the constituent to be determined must often first be separated from the other components by precipitation methods and then determination of the interest elements by gravimetric or volumetric procedures .

Gravimetric encompasses all techniques, which measure mass ,or a change in mass .Measuring mass is the most fundamental of all analytical measurements ,and gravimetry is unquestionably the oldest analytical technique (Skoog et al. 1997).

There are four types of gravimetric methods:-

- \* Precipitation gravimetry, the method in which the signal is the mass of a precipitate,
- \* Electro gravimetry,
- \* Volatilization gravimetry,
- \* Particulate gravimetry.

Precipitation gravimetry is based on the formation of insoluble compound following the addition of a precipitating reagent or precipitant, to a solution of the analyte .The precipitate must be separated from the supernatant solution .These tasks are accomplished by filtering, washing, and drying .Precipitate containing volatile ions or substantial amounts of hydrated water is usually dried at a temperature that is sufficient to completely remove the volatile species.



## 1.11 Flame Emission Spectroscopy (FES)

There are two main methods used for flame emission spectroscopy. The original method, known as flame photometry, is now used mainly for the analysis of alkali metals. Flame photometers are intended primarily for analysis of sodium and potassium and for calcium and lithium, i.e. elements that have an easily excited flame spectrum of sufficient intensity for detection by photocell (Johnstone and Johnstone 1961).

Flame spectrometry is one of the most rapid and sensitive techniques for qualitative analysis, each element has its characteristic spectrum, which can be identified by a few lines.

If a solution containing a metallic salt is aspirated into a flame (e.g. of an acetylene burning in air), a vapour which contains atoms of the metal may be formed. Some of these gaseous metal atoms may be raised to an energy level, which is sufficiently high to permit the emission of radiation characteristic of the metal (Johnstone and Johnstone 1961).

The sample must be prepared in the form of a suitable solution.

### **Instrumentation:**

Involves a burner which operates at such a temperature that the emission lines of the elements under study are excited, an optical system that will disperse the radiation from the flame and a receptor (Petti 1975).

## 1.12 X – Ray Fluorescence (XRF):

An X ray is a high frequency electromagnetic radiation of energy from perhaps

$10^{-5}$  Å to about 100 Å .The X –ray arises from electron transitions between discrete orbital shells of an atom, X-ray spectroscopy, is based upon measurement of emission, absorption scattering, fluorescence and diffraction of electromagnetic radiation .The processes will usually lead to determination of element in a sample or, in the case of diffraction to determination of its crystal structure ( Harvey 200) (Potts 1992) (Putnis 1995).

For analytical purposes X- rays are obtained in three ways, namely:

- By bombardment of a metal target with a beam of high – energy electrons.
- By exposure of a substance to a primary beam of X –ray in order to generate a secondary beam of fluorescent X-rays.
- By employment of a radioactive source whose decay process results in X- ray emission.

X – ray emission is the characteristic line for each element in the sample; electrons are dislodged from the innermost shells. An expelled electron must be replaced ,and it is highly probable that the vacancy will be filled from the next outer shell (L-shell) rather than from a more remote shell (Klein and Hurlbut 1999).This creates a new vacancy ,which is filled from the next shell and so on .Electrons that “fall into “ inner electron shells move from higher to lower energy levels and as a result emit energy in the form of characteristic X radiation .These generated the emission phenomenon called X ray fluorescence each elements has characteristic spectral lines with specific wavelength. Qualitative X –ray fluorescence analysis

involves identification of the various spectral lines with the elements responsible for them. X-ray spectra are that the magnitude of the split into sub-orbitals increases as the number of electrons on the atom increases. Thus low-atomic-number atoms will have relatively simple X-ray spectra, whereas a large number of X-ray lines are likely to be distinguishable in the spectra of the heavier elements. Three series of analytically important lines are identified. The K-series, the L-series, the M-series, each series correspond to an X-ray emission derived from a transition required to fill a vacancy in the K-, L-, M- shells respectively. Within each series, X-ray lines are sub-classified according to their observed relative intensity,  $L_{\alpha}$  lines being more intense than  $L_{\beta}$  lines, which are more intense than the  $L_{\gamma}$  lines. Selection of an emission line in the XRF analysis depends upon the most intense emission line (Asheoft and Mermin 1967).

Quantitative analysis is more involved because each X-ray intensity must be quantitatively compared to that of standard (of known composition) of the same elemental makeup. The relative intensities of lines depend on quantum mechanical selection rules, and the relative intensities are influenced by the probability of internal conversion of the X-ray by the Auger effect (Klein and Hurlbut 1999).

X-ray spectra is that the minimum acceleration voltage required for the excitation of the lines for each element increases with atomic number. For all but the lightest elements, the wavelength of characteristic X-ray line is independent of chemical combination because the transitions responsible for these lines involve electrons that take no part in bonding (Potts 1992). The wavelength of the fluorescent lines are always somewhat greater than the wavelength of the corresponding absorption edge, however, because absorption requires a complete removal of the electron (Brown 1977).

( that is ionization ) where as emission involves transitions of electron from a higher energy level within the atom .The measured intensity of the fluorescent X - ray depends both on the particle size distribution in the powder sample and compression pressure used for making the pellet .

Samples must be ground to flour – like consistency to ensure that the sample presented for analysis is homogeneous and representative of the original specimen .This powder must pass a 200 –mesh sieve having a nominal sieve opening size of  $74\mu\text{ m}$ ; it is in fact impractical to crush powders routinely to a much finer grain size , because of the reduction in efficiency of the milling equipment and the increased degree of contamination introduced into the sample .Then the powder composed into a crucial pellet .Critical depths of penetration in powder pellet vary from element to element ,being dependent on both the penetration power (i.e. energy of the corresponding X –ray photon ) and sample composition .This sample preparation problem is likely to be particularly serious in samples that contain flaky minerals such as biotite ,which tend to align preferentially parallel with the pellet surface during compression. The principle method of overcoming mineralogical effects to permit reliable determination of light elements is to break down the rock matrix by fusion with a suitable flux prior to analysis .The molten mixture, which is then cast as an amorphous glass disc is stable for analysis(Asheoft and Mermin 1967).

The radiation intensity, which is lost within the sample, is absorbed or scattered by three principle phenomena:

- Photoelectric absorption: this effect is the dominant form of interaction between X-ray beam and sample in the energy range under consideration.

- Rayleigh scatter: result from the interaction of radiation with inner orbital electrons that are also so strongly tended to the nucleus that electron excitation is not possible. High atomic-number element be more efficient in promoting, Rayleigh scatter than lighter elements.
- Compton scatter: results from interaction of radiation with the more loosely bound outer electrons of an atom, sample like light matrices (such as silicate rocks) are much more effective in scattering. Rayleigh or Compton scatter processes are the main fundamental limitation to the detection limits that may be achieved by XRF analysis. There is a second competing route by which an atom may de-excite. The X-ray energy is totally reabsorbed by the atom may result in the ionization of the second electron and causing a second orbital vacancy in the atom (Auger effect). This effect is undesirable phenomenon, as it reduce the intensity of observed X-ray emission. This effect is encountered in light elements where, in consequence, Auger losses are significant.

The most serious drawbacks to X-ray fluorescence analysis is that the intensity of an observed fluorescence lines is not directly proportional to concentration but is effected by concentrations of all other elements present in the sample, this is called matrix –inter element effect. The choice of correction procedures, for absorption enhancement effects in rock samples is influenced by mineralogical effects and sample preparation procedure designed to reduce the magnitude of these phenomena.

### **Instrumentation of XRF:**

There are three types of instrument wavelength dispersive, energy dispersive and non-dispersive. The latter two can be further subdivided depending upon whether an x-ray tube or a radioactive substance serves as a radiation source. Wavelength dispersive instruments are of two types, single channel or sequential and multi channel or simultaneous. Multi channel dispersive instrument is large which permit the simultaneous detection and determination of as many as 24 elements. The principle components of wavelength dispersive instruments are:

- \* Source of x-ray radiation, the most widely used in the x-ray tube. Materials most commonly used for analytical work include chromium, molybdenum, rhodium, silver, gold tungsten and scandium.
- \* An x-ray spectrum excited within the sample. The spectrometer consists of various collimators to maintain adequate spectrum resolution.
- \* x-ray diffracting crystal.
- \* Detector.
- \* Normally gas flow proportional counters or a scintillation counter.
- \* Goniometer(Potts 1992, Asheoft and Mermin 1967).

### **1.13 X – ray diffraction method (XRD):**

The spacing of the layers of atoms in solid crystals is usually about 2 to 20Å. The wavelength of x-ray are also in this range. Thus, a crystal can serve as an effective diffraction grating for x-rays. x-ray diffraction results from the scattering, of x-rays by regular arrangements of atoms, molecules or ions. Much of what we know about crystal structures have been obtained by studies of x-ray diffraction by crystal, a technique known as x-ray crystallography(Frye 1993). There are two ways to view the scattering of x-rays by a perfect periodic structure

due to Bragg and to Von Laue. The Von Laue approach, which is closer to the spirits of modern solid-state physics, but the Bragg approach is still in wide use by x – ray crystallographers. Bragg showed that in order to observe any intensity in the emerging x- ray, a relatively simple relationship had to be fulfilled. This relationship known as Bragg equation is:

$$2d \sin\theta = n\lambda \quad .$$

Where d is the spacing between the successive layers that are reflecting the x- rays,

$\theta =$  the angle at which the x- rays enter and leave the particular set of layers.

$\lambda =$  The wavelength of the x- ray.

$n =$  an integer ( $n=1,2,\dots, etc$ )

The Bragg equations serve as the basis for the study of crystalline structure by x- ray diffraction. Bragg law shows that the waves from different planes of atoms are in phase only when  $2d \sin\theta = n\lambda$  (Skoog 1995, Aruidhas 2004, Selley 1982).

The crystalline sample is ground to a fine homogeneous powder. Sample may be held in the beam in dim walled glass or cellophane capillary tubes. Alternatively, specimen may be mixed with a suitable non crystalline binder and molded into an appropriate shape. In such a form the enormous number of small crystallites are oriented in every possible direction, thus, when, an x – ray beam traverses the material , a significant number of the particles can be expected to be oriented in such ways as to fulfill the Bragg condition for reflection from every possible inter spacing(Potts 1992, Aruidhas 2004).

## **XRD Instrumentation:**

Diffraction patterns are generally obtained with automated instruments similar in design to that shown in XRF instruments. The source is an X-ray tube with suitable filters. The powdered sample, however, replaces the single crystal on its mount.

The diffraction pattern, which is then obtained by automatic scanning instrument of this type, offers the advantage of high precision for intensity measurements and automated data reduction and report generation.

The classical method for recording powder diffraction patterns that still finds wide application, particularly when the amount of sample is small, is photographic. The most common instrument for this purpose is the Debye Scherer powder camera, which is cylindrical and equipped to hold a strip of film around its inside wall.

The identification of species from its powder diffraction pattern is based upon the position of the lines (in terms of  $\theta$  or  $2\theta$ ) and their relative intensities. The diffraction angle  $2\theta$  is determined by the spacing between a particular set of planes; with the aid of the Bragg equation, this distance  $d$  is calculated from the known wavelength of the source and the measured angle. Line intensities depend upon the number and kind of atomic reflection centers in each of planes. (Potts 1992, Skoog 1995).

Identification of crystal is by using a powder diffraction file that contains powder diffraction patterns for over 50000 compounds. Computer search programs are now available to relieve the tedium of the search process. By measuring the intensity of the diffraction lines and comparing with standards, a quantitative analysis of crystalline mixtures is also possible.



## **The Objective:**

The aim of this work is to:

- a- Attempt to make natural molecular filter by modifying some Sudan clays to remove hardness from water, to generate soft water suitable for most industrial.
- b- Maximize competence of molecular filter by changing the parameters of the clay.
- c- Suit industrial application and try make beds (if possible).

The great economic and scientific importance of water softening has created a large and thriving industry because of low energy spending.