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THEME

Valorization of the dromedary bone as a coagulant
for reduce the turbidity of polluted water

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ملخص

تم بنجاح استخلاص مادة الهيدروكسيباتيت من عظام الجمل كمخثر حيوي تم اختبار قدرته على العمل كعامل تخثير طبيعي للتوضيح باستخدام الماء المقطر الذي قمنا بتعكيره عن طريق خلط 500 مل مع غرام من تربة الحديقة، تم اجراء الاختبارات التجريبية بواسطة تقنية اختبار البرطمان لتقييم تأثيرات التركيز العكارة تمت إزالة العكارة القصوى في الماء عند إضافة الجرعة المثلى 0.8 غرام على اللتر من مسحوق الهيدروكسيباتيت أزال أكثر من 95 % من جميع تركيزات العكارة الأولية أي من 178 إلى 14 وحدة من مقياس الوحدة العالمية. تم تحقيق جودة بكتريولوجية عالية في معالجة المياه الملوثة ما اثبت ان الهيدروكسيباتيت مخثر حيوي صديق للبيئة فعال للغاية في إزالة العكارة لذلك هو مرشح واعد في مجال معالجة المياه.

ABSTRACT:

A biocoagulant was successfully hydroxyapatite extracted from bone of camel. The potential of HAP to act as a natural coagulant was tested for clarification we use distilled water that we did turbidity it. By mixing each 500 ml with 1 g of garden soil. Experimental tests were performed by jar test technic to evaluate the effects of turbidity concentration. The maximum turbidity removal was occurred at water when adding 0.8mg/l the optimum dosage of HAP. Results demonstrated that the HAP removed more than 95% of all initial turbidity concentrations (178–14 NTU). High bacteriological quality was achieved in the treated water. HAP as an eco-friendly biocoagulant was revealed to be a very efficient coagulant for removing turbidity from waters.

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Dedicate

To the one who told me one day when my fire faded

Fatima my dear you should focus on your dream and goal never let laziness affect your mind because it affects mine sometimes that causes my depression and more to it when it start what put me down the most is that I put my mind in something and it doesn't work out for I feel like giving up but my conscience won't let me give so I'm confused from if I should or shouldn't that why in life your yes must be your yes and your no must be your no life is full of challenges but you've to face them head on I like you because you are the type of girl who doesn't give up and i like that and if I'm to advise you like a father pardon I would say is stay clear from romantic relationship for now and put all your mind in achieving what you want to achieve let your hidden light shine Fatima trust me you won't regret your decision try to be workaholic sometimes but not every time that the way business men and women balance their life

In life put work first before yourself and family then you will see how everything works out you will be a boss of your own Every night before you sleep think of what you want think of what you wanna be think of what you will become when you take that certain affect step think of how it will your environment and love one's Study your life like mathematics in school calculate your life like the way you solve the world problem or equations know how to set your compass and measure your limit and with that limit you set find a way to break through that limit mentally and emotionally

More to it be humble at all times always be respectful and humble there is a saying that only when you humble yourself that when you will be lifted up high and higher than you expected,

Fatima we have one life not another so take your life and make it your personal property when you will take responsibility for all the actions you take live your life perfectly so when that final day will come you won't regret anything .Use your mind when it is needed, use your heart when it is needed and more use your brain always, do you understand Fatima.

I want tell you okay my boss just you trust me and believe in me

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ABBREVIATIONS:

Ph: Potential Hydrogen

pHPZC: Zero charge point pH

MV: matter volatile

BOD: Biochemical oxygen demand

COD: chemical oxygen demand

DTO: Distilled Tall Oil

COT: Carbone Organic Total

UV: Ultraviolet is a form of electromagnetic radiation

PACl: polyaluminum chloride

DADMAC: POLYDIALLYLDIMETHYLAMMONIUM CHLORIDE

Hap/ HA/HAP: hydroxyapatite

GPA: A gigapascal (GPA) is a decimal multiple of the Pascal,

Ca/P: calcium/phosphorus (Ca/P) ratio

XRD: X-ray Powder diffraction

FTIR: Fourier Transform Infrared Spectroscopy

SEM scanning electron microscope

EDX: energy dispersive X-ray spectroscopy

NTU: Nephelometric Turbidity Unit

ρ_w : Density of water

W_s : The pycnometer weight with the sample

W_a : the empty pycnometer weight and

W_{sw} : the pycnometer weight with the sample filled with water density of water.

W_2 and W_1 are samples weight before calcinations and the lost weight

GENERALE
INTRODUCTION

GENERALE INTRODUCTION

Water is very important elements that are involved in human life for good health. Portable water is treated from the raw water, Often, the waters from surface water resources have a high level of turbidity and need to be treated with flocculation/coagulation to remove the turbidity. Many flocculants and coagulants are widely used in conventional water treatment processes. These materials can be classified into inorganic coagulants (e.g., aluminum and ferric salts) and synthetic organic polymers (e.g., polyacryl amide derivatives and polyethylene imine). All of them are very efficient at turbidity removal from water [170].

The cost of achieving the desired level of water quality depends primarily on the cost and the availability of the coagulation agents. Aluminum salts are most widely used together with synthetic Organic polymers in water treatments. These coagulants are often expensive, and in many developing countries, they have to be imported. Moreover, the high sensitivity of inorganic coagulants to the water pH and the possibility of secondary contamination of drinking water with traces of toxic synthetic polymeric coagulants or residual iron and aluminum ions are the main challenges of flocculation–coagulation water treatment processes [171]. Further, many researchers have related Alzheimer's disease to the residual aluminum ions in the treated waters [172]. Moreover, as reported by Anastasakis et al. [173], the sludge formed in water treatment plants during flocculation–coagulation with synthetic polymers has a limited potential for recycling because of the non-biodegradability of synthetic polymers. To make the flocculation–coagulation process more attractive, novel low-cost coagulants with higher coagulation capability is required. This has led a growing research interest in the production of natural and food grade coagulants from renewable and relatively cost-effective precursors. It can contribute to achieving sustainable water treatment technologies. Natural coagulants, mainly polysaccharides and proteins, are considered eco-friendly in comparison with inorganic and organic coagulants because of their biodegradability [174]. Recently, the use of some natural polymers for the treatment of various types of water and wastewater as Hibiscus esculentus seedpods, Malva sylvestris , Hercofloc , Purifloc , Grafted Plantago psyllium, mucilage, oleifera, hydroxyapatite

. The most common coagulants are plain or chemically modified and exhibited relatively low turbidity removal of between 50% and 90%. Moreover, most of these natural coagulants changed dissolved organic carbon (DOC), which can cause a concern in the chlorination process [175]. Because of the biomaterials' relatively low efficiency of turbidity

removal, the production and extraction of these biomaterials as coagulants is very expensive, making them impractical for full-scale applications. Regarding the difference in coagulation capacity of various coagulants as well as cheapness, variety and ease of access, the use of regional coagulants is studying to evaluate their applicability.

Hydroxyapatite extracted from nature, such as bones and rocks, is a promising candidate to be a natural coagulant in the process of treating water from turbidity, and this is what we seek through this study. So it was organized as follows

ORGANISATION of these

The study of the problem envisaged and carried out in four chapters and a general conclusion.

The first chapter contains general information on water pollution and source with the types of pollution

The second chapter contains the process of coagulation and flocculation and the mechanism of coagulants and flocculants

The third chapter we define hydroxyapatite and its source, properties and application with preparation method

The fourth chapter contains all the results and interpretations obtained through practical laboratory work to prove that hydroxyapatite can be a bio coagulation agent.

In the end, we ended with a general conclusion which takes up the objectives of our work, and also some proposed perspective.

CHAPTER I

WATER POLLUTION

I. 1- Introduction:

The water is the most important resource on the planet. It is the core of life on earth; So any pollution affects this boon it will cause a big problem in the environment.

Water pollution or aquatic pollution is contamination of water bodies like (Oceans, lakes, rivers, and other inland). It means one or more substances have built up or dissolved, precipitated or remained in the form of suspension in water to such an extent that they cause problems for animals or people.

I.2.-History of water pollution

I.2.1-Ancient Times: Water forms like rivers, lakes and streams were in the ancient times the source of drinking water. However, human waste was deposited in the same water bodies. Therefore, in rivers became so polluted because it passes human waste on its way to rivers and streams that in order to obtain clean drinking water, these ancient cultures needed to build aqueducts [1].

I.2.2-Medieval Times—1800s: During this time, people were unaware of what was good for them and what was bad. Mercury was frequently dumped into water. Most people living in metropolises just dumped their waste and garbage. Civilization made many great strides during the latter half of this period, frequently to the damage of the ecosystem. Individuals even used chemicals at that time

I.2.3-Revolution of the 1800s. At that time, people were not concerned about the environmental impact of their inventions [2]

I.2.4-After World War-II: Besides contaminants such as human waste, composts, leather tanning and slaughtering waste, the development of industries and factories had also resulted in much water pollution problems. As waste from industries dumped into river freely without care about the environment were affecting ecology and humans, including flora and fauna [3].

I.2.5-1969: After a series of fires on the Cuyahoga River in 1969, it was realized that fires were triggered by oil slicks and dumped into it by flammable industrial waste. The government then began the studies that allowed the 1972 Clean Water Act to be enacted [4].

I.2.6-Present Day: Many people still do not know how to guard themselves against chemical toxins and waterborne diseases, even with this act. Many cleanups on a large scale have been going on for years [4] (Fig. 1 represents different studies that had done in different sites to check contamination of water)

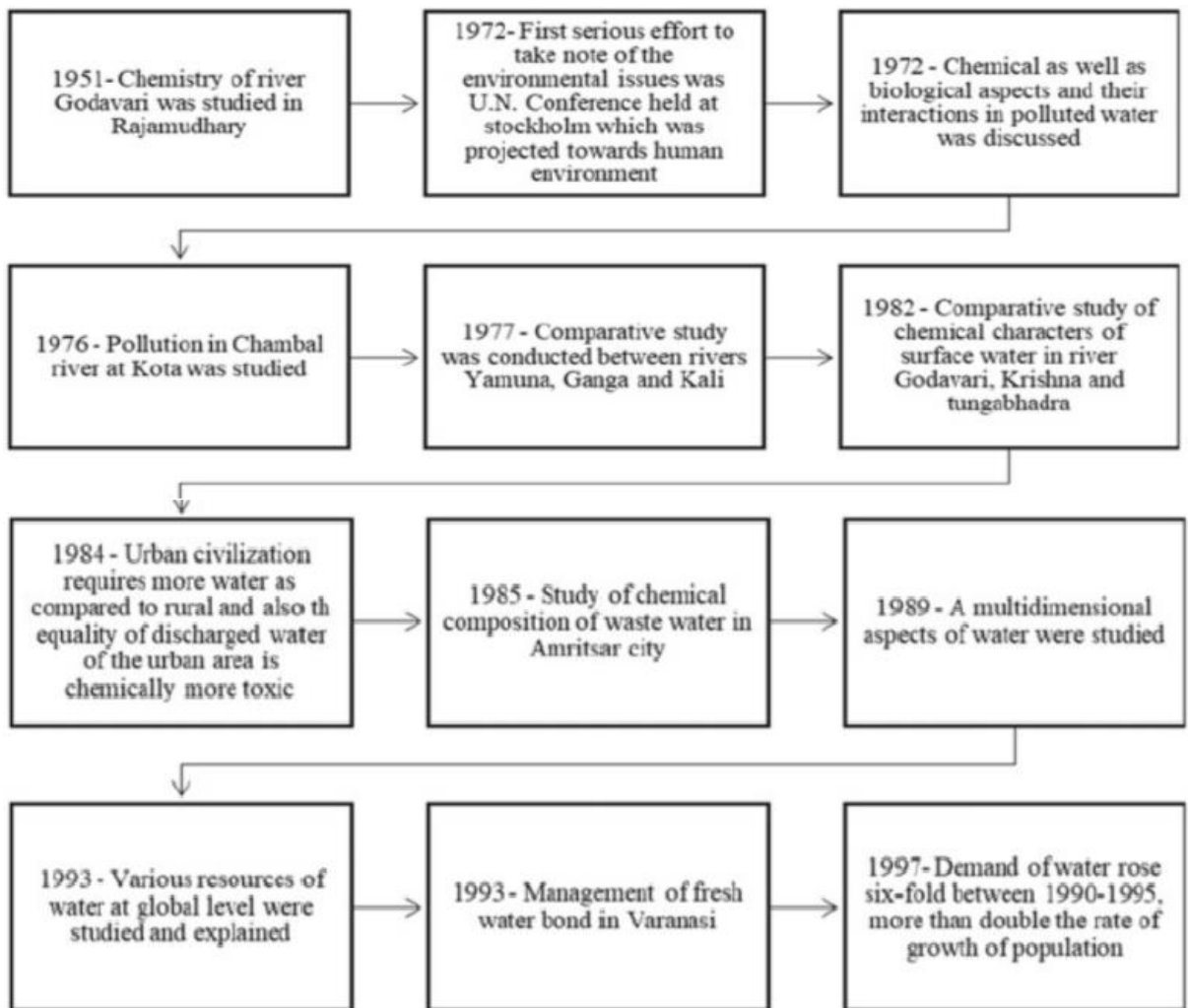


Figure I.1 Flow chart representing different studies on the water contamination at different sites

I.3-Types of wastewater:

There are 3 types of wastewater.

I.3.1-Domestic wastewater:

Domestic wastewater includes domestic water (toilet water, laundry water, cooking water) and black water (urine and feaces), in the so-called “sewerage” system [5]

I.3.2-Urban wastewater:

Urban wastewater includes domestic wastewater and runoff water (rainwater, sprinkling water from public roads, washing water from gutters, markets and courtyards). [6]

I.3.3-Industrial wastewater:

All discharges resulting from the use of water other than domestic are qualified as industrial discharges. This definition concerns discharges from factories, but also discharges from artisanal or commercial activities: laundry, restaurant, medical analysis laboratory, etc. [7]



figure I-2 industriel wastewater

figure I-3 natural pollutant water



I.4-Origin of pollution water

I.4.1-Natural pollutants:

Natural impurities present in water represents natural pollutants: gases like H₂S, NH₃, and Co₂ etc. dissolved in water during raining; minerals such as Ca, Mg, and Ar etc. dissolve in water from soil and various materials such as clay, mud, organic wastes get suspended in water [8]

I.4.2-Man-made pollutant: Water pollutants which are generated by human activity are called man-made pollutants.

Sewage; which contains many pathogenic organisms and decomposable organic wastes Agricultural wastes such as insecticides, pesticides etc.

Get access to water during rain and flooding Industrial waters; contains highly toxic chemicals other pollutants; thermal pollutants, radioactive substances etc. [9]

I.5 Types and sources of Pollutants and pathways their entry into water

All pollutants entering water bodies, are divided into three large groups (Belichenko, Shvetsov ..., 1986).

I.5.1 Mineral pollution is sand, clay, ash and slag, solutions and emulsions of salts, acids, alkalis and mineral oils, other inorganic compounds. They worsen the physical and chemical and organoleptic properties of water, because poisoning of fauna reservoirs. Less dangerous mineral pollution without specific toxic effect - suspended particles of sand, clay, other rocks, but they also worsen the properties of water and contribute to the siltation of reservoirs.

I.5.2 Organic pollution includes a variety of substances plant and animal origin (remains of plants, vegetables, fruits, living tissues, adhesives, etc.). To this group include resins, phenols, dyes, alcohols, aldehydes, naphthenic acids, sulfur and chlorine-containing organic compounds, various pesticides washed into water bodies from agricultural lands, synthetic surfactants and much other.

I.5.3 Biological contamination (pathogenic bacteria and viruses, infectious agents) enter water bodies with household waste waters, as well as wastewater from some industries, including livestock farms and complexes. Using such water for drinking, household needs leads to cholera, infectious hepatitis, dysentery, typhoid fever, various types' helminthes, and etc. [10]

I.6 Characteristics of wastewater

The characteristics of wastewater may vary depending on its origin. The dangers of effluents are of concern because of the many pollutants they contain. These include, among others:

- sand, debris and suspended solids, which can fade the color of the water, make it unsuitable and even suffocate and contaminate plant and animal life; - pathogenic germs which can make the water unfit for consumption; - decomposing organic waste, which depletes dissolved oxygen in water and threatens the survival of fish and other aquatic organisms; - nutrients, which stimulate the growth of algae and other aquatic plants excessively, and thus produce unpleasant odors and create aesthetic problems, which tends to reduce biodiversity; - chemicals, which can cause acute or chronic toxicity in aquatic organisms [8]. These chemicals can have long-term effects on the environment because they do not break down easily and tend to accumulate in aquatic or terrestrial organisms through the food chain.

In general, to assess the quality of the water, various parameters are used, including:

I.6.1- physico-chemical parameters: dissolved gas (oxygen), temperature, pH, conductivity, redox potential;

I.6.2 - Particulate pollution parameters: coarse matter, suspended solids, volatile matter (MV), turbidity;

I.6.3- The parameters of global organic pollution: BOD, COD, DTO, COT (Spectro UV);

I.6.4- parameters of dissolved pollution: nitrogen compounds (NO₃, etc.), phosphorus compounds, other mineral constituents (major elements, heavy metals, etc.), organic compounds (detergents, hydrocarbons, phenols);

I.6.5- Biological parameters: The biological parameters include matter like algae, fungi, viruses, protozoa and bacteria. The life forms present in water are affected to a good extent by the presence of pollutants. The pollutants in water may cause a reduction in the population of both lower and higher plant and animal lives. Thus, the biological parameters give an indirect indication of the amount of pollution in water. [11]

- This study is closely related to **Particulate pollution parameters** for that I will to enlighten about this parameters.

I.7-Impurities present in polluted water:

Impurities present may be of different forms and from different sources. There are several sources of water impurities such as Gases picked up from the atmosphere by rainwater. Dissolvent impurities the get in contact with the water when it touches the ground from precipitation following are the sources of impurities in water.

Remains of decomposed plants and animals produce impurities witching water bodies or when water bodies get in contact with these materials via sub bodies like streams.

Impurities are also introduced in water when it comes in contact with sewage or industrial waste [12]. waste water contains dissolved minerals like sodium bicarbonates, calcium, sulphide, irons, magnesium's and chlorides, and also

contains granular suspended impurities of sand like, rocks, leaves grass and other organic matter, Impurities present in waste water may be classified into two, Suspended impurities and Microscopic impurities

Suspended Impurities are organic and inorganic, while microscopic impurities are fungi, algae and bacteria [12]

Suspended particles affect the flow the transparency of water and the penetration of light into it, the temperature, the composition of the solution surface water components, adsorption of toxic substances, and also on the composition and distribution of sediments and on the rate of sedimentation. [13]

I.7.1-Solids in polluted water

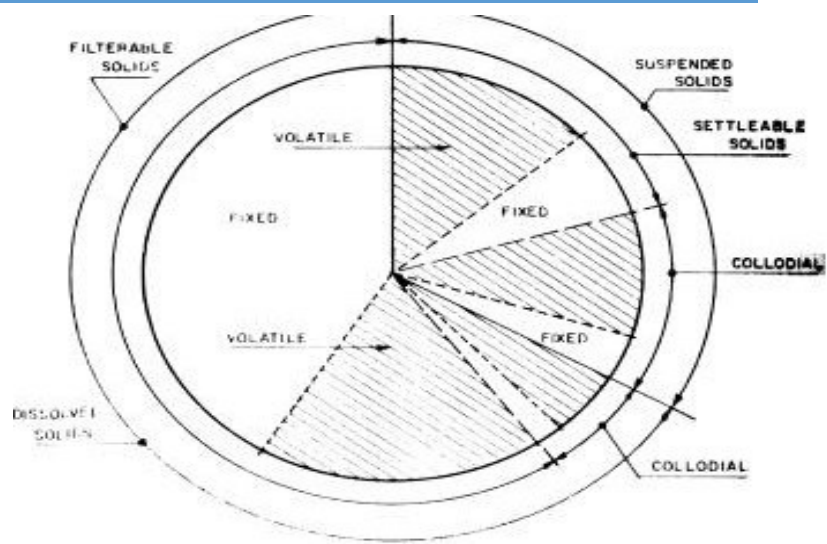
The quantity of solids in polluted water generally represents than a thousand parts of solids per million parts of water (expressed as milligrams per liter, mg/l).

We can classed this Solids as either suspended solids or filterable solids Suspended solids are defined as those retained in a **Gouch** crucible in accordance with a standard test while those not retained are termed filterable solids. Suspended solids are classified further as stable solids which will settle in an **Imhoff** cone.

'Those which will not settle are termed colloidal. Filterable solids are classified further as dissolved solids or Colloidal solids [14]

. All solid classifications may be further described by identifying the organic (volatile) portion and the mineral (fixed) portion. . These main classifications are further divided as shown in Figure No. 4.

figure I-4 classification of solids in wastewater



CLASSIFICATION OF SOLIDS IN

The rate of settling depends on the particle size, weight, shape and on the resistance, or viscosity, of the containing liquid Colloidal Solids Colloids may

be considered as particles which cannot be separated by the force of gravity alone and can remain in suspension indefinitely. [16]

I.7.2-Properties of colloids

The basic physical and chemical characteristics of colloids are important to the understanding of the factors influencing chemical treatment. The five most important properties' of colloids are:

- a).Electrical properties
- b).Brownian movement
- c).Adsorption
- d).Hydration
- 5. Forces of attraction

I.7.3-Stability of Colloidal Dispersions [17].

The factors described above may be classed as those promoting solution stability and those tending to separate the matter from solution. The most important factors are listed as follows:

I.7.3.1-Stability Factors

- a).Electrokinetic charges
- b). Hydration

I.7.3.2-Instability Factors

- a). Brownian movement
- b). Van der Waals forces

I.7.3.3-Factors which may affect either Stability or Instability

- a).Other ions in solute
- b).Amount of kind of matter present
- c).PH
- D).Concentration of dissolved solids
- e).The kind and amount of coagulant.
- f).Order of chemical additions.
- g).Mixing characteristics. [18]
- h).Temperature

I.8-Conclusion:

Water pollution is a serious problem in surface water resources and a growing percentage of its groundwater reserves are contaminated by Biological, toxic, organic, and inorganic pollutants. In many cases, these sources have been rendered unsafe for human consumption as well as for other activities, such as irrigation and industrial needs. This shows that degraded water quality can contribute to water scarcity as it limits its availability for both human use and for the ecosystem.

Extensive studies have been undertaken to find economically feasible alternatives for water and wastewater treatment. A number of methods such as **coagulation**, membrane process, adsorption, dialysis, foam flotation, osmosis, photo catalytic degradation and biological methods have been used for the removal of toxic pollutants from water and wastewater.

CHAPTER II

COAGULATION FLOCCULATION PROCESS

II.1- Introduction:

The stage of water treatment preliminary treatment is any physical or chemical or mechanical process used on water before it put up with the main treatment process. During preliminary treatment:

Screens may be used to remove crags, debris, leaves and other chemicals may be added to control the growth of algae; and a presedimentation stage can settle out sand, grit and gravel from raw water. Coagulation, flocculation and clarification processes are used when a water source contains a large amount of fine suspended matter, for example alluvium or ooze.

If this type of water flows into a sand filter, the filter will soon block and stop working.

II.2-Coagulation:

One of the main stages of preliminary water purification is its coagulation, aimed at reducing coarse and colloidal impurities



figure II-1 treatment water by coagulation and flocculation

Coagulation is a physicochemical process of enlargement colloidal particles into large aggregates (flocules), which ends isolation of the substance into a precipitate, which is removed by precipitation and filtration. . If they clump together and form larger particles, then it would be possible

to removes easily. But a negative charge prevents them to coagulate; as like two same magnetic poles repulse each other [19]

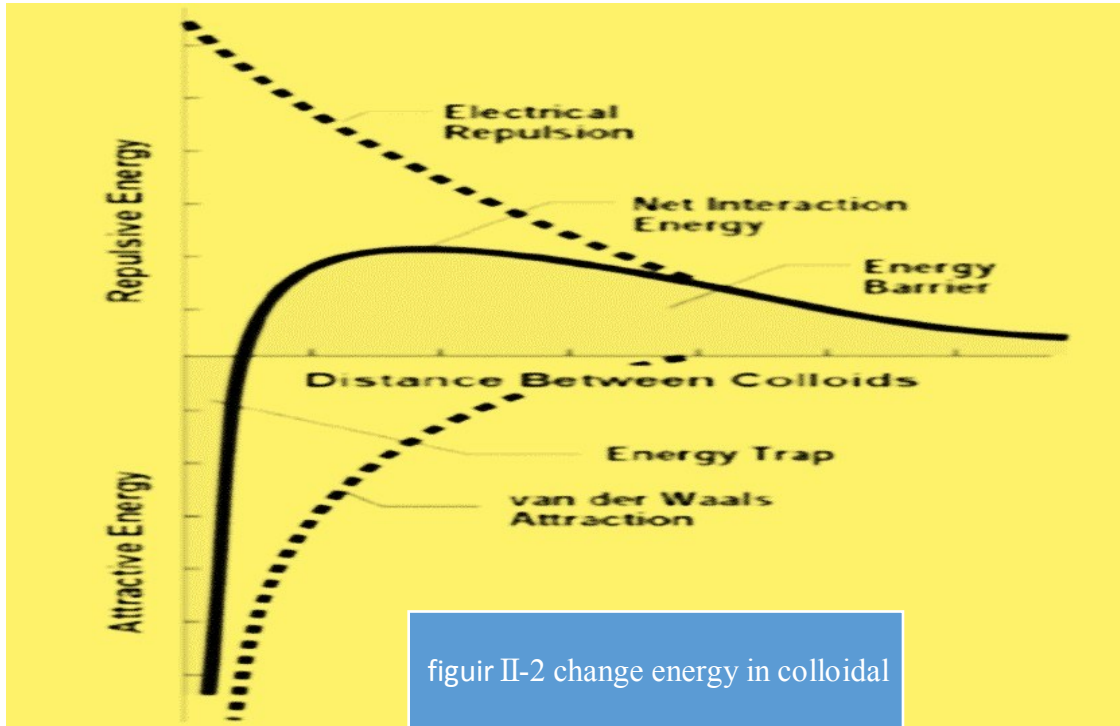
Colloidal particles are very small in size, participate in Brownian motion, have a noticeable diffusion rate, aggregate stability, i.e. the inability to spontaneously enlargement, sedimentation stability (constant concentration impurities throughout the volume of water). Colloidal particles do not settle even with prolonged standing and cannot be filtered, as, for example, coarse water impurities. [25]

The reason for the stability of water colloidal systems is the presence charge on their surface due to the dissociation of surface molecules. So as colloidal substances are amphoteric, the type and degree of their dissociation depend on the pH value of the solution [21] . The pH value at which these substances do not dissociate, have no charge and are able to coagulate, called isoelectric - pH IE Colloidal particles carry the same charge, so between them there are electrostatic repulsive forces (Coulomb interaction) and molecular forces of attraction (van der Waals forces). The stability of colloidal systems is determined by the ratio of these forces. The nature of the change in the repulsive energy and the energy of attraction shown in the figure above [20]

The figure represent for different distances between the particles "x" there are two energy minima in the region attraction, when the force of attraction prevails between the particles, and one energy maximum (potential barrier) when between particles repulsive force prevails. This potential barrier prevents adhesion of particles when they approach and is responsible for aggregate colloidal systems. Since there are no forces in natural water, allowing to

overcome the potential barrier, water coagulation carried out with mutual coagulation of dissimilar dispersed systems. [22]

For this purpose, mineral salts are specially introduced into the treated water. The process of consolidation of colloidal particles by neutralizing the charges with a coagulant, so that they can remove from the treated water by sedimentation or filtration is called coagulation. It is a vital part for drinking water and wastewater treatment. [23].



figuir II-2 change energy in colloidal

II.3-flocculation

Flocculation, a gentle mixing stage, increases the particle size from submicroscopic microfloc to visible suspended particles. Microfloc particles collide, causing them to bond to produce larger, visible flocs called pinflocs. Floc size continues to build with additional collisions and interaction with added inorganic polymers (coagulant) or organic polymers. Macroflocs are formed and high molecular weight polymers, called coagulant aids, may be added to help bridge, bind, and strengthen the floc, add weight, and increase settling rate. Once floc has reached it optimum size and strength, water is ready for sedimentation. Design contact times for flocculation range from 15 or 20 minutes to an hour or more, and flocculation requires careful attention to the mixing velocity and amount of mix energy. To prevent floc from tearing apart or shearing, the mixing velocity and energy are usually tapered off as the size of floc increases. Once flocs are torn apart, it is difficult to get them to reform to their optimum size and strength. The amount of operator control available in flocculation is highly dependent upon the type and design of the equipment. [25]

II.4-Factors affecting coagulation water treatment

The process of coagulation of water depends on various indicators such as pH of the medium, temperature of water, coagulant feed concentration, coagulant

dosage, and type of coagulant, mass and initial turbidity. Moreover it is also depends on pre-treatment and type of pollutants present. [24].

II.4.1-Effect of pH on coagulation

PH effects on the activities of coagulants. The optimum pH for alum coagulation is 6 to 7.5 whereas 5.0 to 8.0 are for iron. If the alkalinity is lower or higher, then the floc does not form properly. As a result, more coagulant is consumed. In this case, it is beneficial to correct the pH by adding acid or base.

II.4.2-Temperature

Temperature is another factor for coagulation water treatment process. It is more significant at lower turbidity. In case of alum, at low temperatures aluminum hydroxide form a strongly hydrated and very stable sol. So in winter season high coagulant are consumed. When the temperature becomes below the 5⁰ C, then alum or ferric salts do not work properly. So it should be consider another coagulant like polyaluminum chloride (PACl).

II.4.3-Type of pollutants

The salt composition of soft water and hard water are not the same. Hard water contains Ca²⁺and Mg²⁺ ions. They can alter the charge on the colloidal particles.

II.4.4-Optimum dosage

It is very significant to determine the optimum dosage of a coagulant which will give the maximum clarifying effect. Insufficient amount of coagulant cannot be able to destabilize properly of the colloidal particles. On the other hand higher dosage can cause excessive sludge production, corrosion and loss of money.

II.4.5-Type of coagulant

All the coagulants are not suitable for all cases. Different temperatures, pH, type of medium may vary the effectiveness of the coagulant. At lower temperature the polyaluminum chloride (PACl) may be more effective than the traditional coagulants like alum or iron salt. Same way, some pH range can be beneficial to use iron salt instead of alum. [26].

II.5-How Coagulants and Flocculants Work?

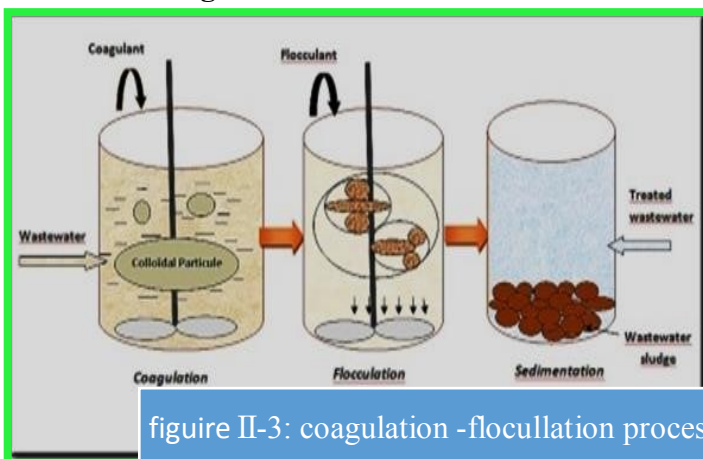


figure II-3: coagulation -floculation process

II.5.1-Coagulants

For any wastewater pretreatment program that deals with suspended solids, coagulants can consolidate suspended contaminants for easy removal. Chemical

coagulants used in industrial wastewater pretreatment fall into one of two categories: organic and inorganic coagulants.

Inorganic coagulants are cost-effective and can be used in a wider variety of applications. They are especially effective on any raw water with low turbidity, an application not fit for organic coagulants. When added to water, inorganic coagulants form aluminum or iron precipitates that absorb the water's impurities, thus cleaning it. This is referred to as the "sweep-floc" mechanism. While effective, this process adds to the overall sludge volume that needs to be removed from the water. Frequently used inorganic coagulants include aluminum sulfate, aluminum chloride, and ferric sulfate. [27].

Organic coagulants offer the advantages of lower dosages, lower volumes of produced sludge, and no effect on the pH of the treated water. Examples of common organic coagulants include polyamines and polyDADMACs, as well as melamine formaldehydes and tannins.

In different spheres of the economy and everyday life, different types of coagulants are used. They can be divided into two large groups: **mineral** and **organic**.

II.5.1.1-Organic coagulants are more expensive and are most often used for the purification of drinking water. They demonstrate slightly better performance than inorganic compounds, however, their use is often less cost-effective. [28].

In the case of cleaning industrial effluents, various coolants and circulating media, swimming pools and reservoirs,

II.5.1.2-Inorganic coagulants are used: Ferric chloride. Strong corrodant and toxin, used in industry. Iron sulfate. Used in industry for sewage treatment, in municipal services for water treatment, as well as in medicine for stopping blood. Aluminum sulfate. Suitable for purification of drinking, household and industrial water of various Purpose. Aluminum oxychloride. This salt - hydroxychloride - is good for the treatment of waste water, tanks, swimming pools, reservoirs. Aluminum hydroxochlorosulfate. It is a mixture based on aluminum sulfate. It is an excellent preparation for the treatment of dirty flood waters at temperatures below + 12° C.

These substances are distinguished by their relatively low price, availability, safety and ease of use. [30].

II.5.2-Flocculants

Used in a wide range of industries and applications, flocculants help to remove suspended solids from wastewater by aggregating contaminants into flakes or "flocs" that float to the surface of the water or settle at the bottom. They can also be used for lime softening, sludge thickening, and solids dehydration. Natural or mineral flocculants include activated silica and polysaccharides, while synthetic flocculants are most commonly based on polyacrylamide. [31].

Depending on the charge and chemical composition of your wastewater, flocculants can either be used on their own or in combination with coagulants. Flocculants differ from coagulants in that they are often polymers, whereas coagulants are typically salts. They can range in molecular size (weight) and charge density (% of the molecule with either anionic or cationic charges), which

Figure II-4 :exempel of coagulant

Aluminiumsulphate (Alum) $Al_2(SO_4)_3 \cdot 15H_2O$
Sodium Aluminate $Na_2Al_2O_4$
Polyaluminium Chloride (PAC) $Al_{13}(OH)_{20}(SO_4)_4Cl_{15}$
Ferric Sulfate $Fe_2(SO_4)_3$
Ferric Chloride $FeCl_3 \cdot 6H_2O$
Ferrous Sulfate (Copperas) $FeSO_4 \cdot 7H_2O$
Lime $Ca(OH)_2$

is used to “balance” the charge of the particles in the water and cause them to come together and dewater. Generally speaking, anionic flocculants are used to catch mineral particles while cationic flocculants can capture organic particles. [29].

Example of flocculants (Al_2SO_4 , CaO , CaCO_3 , FeCl_3 , Fe_2SO_4)

II.6-Should you trust folk methods of coagulation?

Despite the fact that a sufficient number of coagulants are now produced for open and closed reservoirs at completely affordable prices, many are trying to use and promote strange remedies from pharmacies and garden shops. For example, hydrogen peroxide, brilliant green, potassium permanganate occupying the first places in home methods of cleaning the pool. And if there are reservations and even doubts about the last two, then peroxide is considered the best, most effective and safe. Proof of this is the dirty foam and build-up on the walls of the pool.

II.7-Conclusion:

Chemical coagulant used in the coagulation process [32, 33] may cause several health hazards. Aluminum is characterized in poisoning factor for encephalopathy, study of various reports on impact of aluminum on human health; it is strongly evidenced aluminum based coagulants linked in the development of neurodegenerative ill-nesses as Sesil dementia [34] and with Alzheimer's disease [35]. Synthetic polyelectrolytes are questioned due to the toxicity and carcinogenic potential of the monomers used for their synthesis [36]. Therefore, it is need to progressively replacement of these inorganic and organic coagulants with alternative natural coagulants. Natural coagulants (bio-polymers) would be of great interest since they are natural low-cost products, characterized by their environ-mentally friendly behavior, and presumed to be safe for human health [37].

CHAPTER III

HYDROXYAPATITE (HAP)

III1-INTRODUCTION:

There has been considerable interest in development and usage of plant based natural coagulants [38] Use of Plant based material for water treatment agents have long history, particularly wood charcoal are considered as an excellent adsorbents.[39] . Natural polyelectrolyte of plant origin has been used for many centuries in developing countries for purification of turbid water [40]. For home water treatment, the materials have to be used in the form of powder or paste, 90% of which consists of substances other than the polyelectrolytes. Even under such conditions, a few plant seeds make effective coagulants [41]. Several plant based material were identified as a natural coagulants such as *Moringa oleifera* [40-42], *Nirmali* [43], *cactus* [44].

Recently tannin based coagulants have been utilized in coagulation/flocculation processes for water purification. Tannins are high molecular weight polycyclic aromatic compounds, general name given to large polyphenol compounds. Tannins are widely distributed in the plant kingdom obtained from natural materials, for example, the organic extract from bark and wood of trees such as *Acacia*, *Castanea*, or *Schinopsis* and hydroxyapatite .

Using the hydroxyapatite as a coagulation that have been extracted form animals bones on water treatment that is goal of this study.

III2-Histoire: The era of hydroxyapatite (HA) in regenerative science dates back to 1950s1 when bioceramics were used as an inert scaffold for filling of the bone defects. The history of calcium orthophosphates dates back to 1770; the early history till 1950 can be read elsewhere in the published literature [45]. On the basis of the exhaustive literature available on HA from 1950 in relation to its composition, properties, production, and its uses, [46].

III2.1-name :Named hydro-apatite in 1856 by Augustin Alexis Damour from the *ἀπατάω* (apatao), to deceive as Apatite was often confused with other minerals (e.g. Beryl, Milarite), plus the "hydro-" prefix for the water-rich (as hydroxyl) nature of the mineral. Waldemar Schaller changed the name slightly to hydroxyl-apatite in 1912 and the one-word, hydroxylapatite, was introduced by Burri, Jakob, Parker, and Hugo Strunz in 1935. Additional names applied to this mineral include: pyroclastite, ornithite, monite, etc. Much "carbonate-apatite" is hydroxylapatite, including some dahllite, collophane, etc. Apatite Group. The hydroxyl analogue of fluorapatite (much more common) and chlorapatite (rare) [47].

III3-Hydroxyapatite (HAp)

It is a member of calcium phosphate, similar to the human hard tissues in morphology and composition1. Particularly, it has a hexagonal structure [48]-[49]. and a stoichiometric Ca/P ratio of 1.67, which is identical to bone apatite. [48], [50], [51]

The common mineral apatite has formula $\text{Ca}_5(\text{PO}_4)_3\text{X}$, where X is F, Cl, OH, or a mixture; but the general formula is $(\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2)$.



Figure III-1 hydroxyapatite

Hydroxyapatite if the extra ion is mainly hydroxide. Up to 50% by volume and 70% by weigh of human bone is a modified form of HAp, known as bone mineral. The main substance of our teeth is HAp (97 % of enamel and 70 % of dentin) [52]. Due to its similarity in size, crystallography and chemical composition with human hard tissue, HAp is one of the most widely studied materials for orthopedic and dental implants. HAp could be prepared from natural or synthesized sources via several processes, and can be made as a powder. Is a naturally occurring mineral of biological and agricultural importance is identical to bone apatite an important characteristic of hydroxyapatite is its stability when compared to other calcium phosphates. Thermodynamically hydroxyapatite is the most stable calcium phosphate compound under physiological conditions as temperature, pH and composition of the body fluids [48].

III4-Sources:

III4.1-Natural hydroxyapatite can be prepared

Biological sources, such as mineral (rocks, plants...), and more importantly from waste, among which essentially figure **animal bones** (fish bones, chicken bone ...), as well as **biogenic products** (eggshells, mussel shells ...) etc. [53]. Recently, hydroxyapatite has attracted interests because of its hemostatic properties, and bone healing function [54]. [55]. [56].

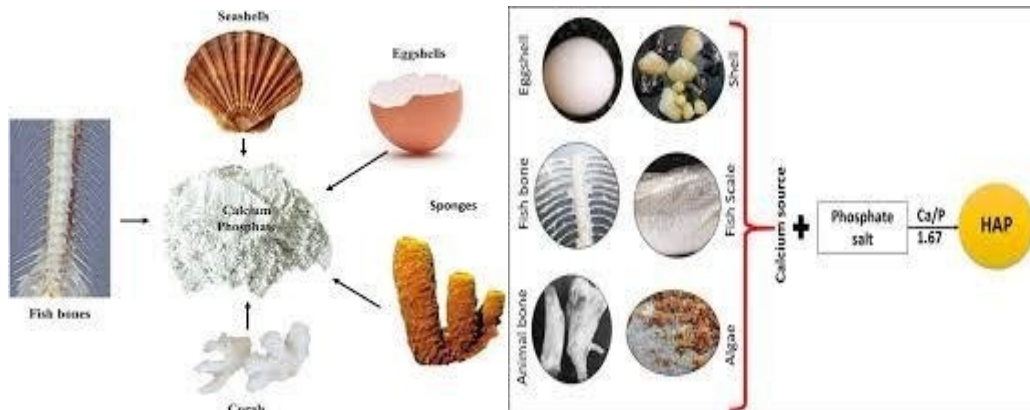


Figure III-2: natural source of HAP

III.4.2-synthetic hydroxyapatite (industrial)

Synthetic hydroxyapatite (HA) is of importance as a biomaterial as it is chemically similar to the mineral component of mammalian bone.

- HA is sometimes used in powder form, but in most cases it is used as a bulk material. To produce bulk samples generally requires sintering at elevated temperatures, usually in excess of 1000°C. High temperature exposure is often required in the production of HA coatings, another common application of the material.
- Dehydroxylation HA is a hydrated calcium phosphate material. It begins to dehydroxylate at about 800°C to form oxyhydroxyapatite, or $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{O}_x$, where x =vacancy. This process is gradual and takes place over a range of temperatures.
- Furthermore, HA also decomposes to form other calcium phosphates at elevated temperatures. Two mechanisms have been proposed for the decomposition as follows[57]

III.5-Structure and form:

Hap crystallizes in the hexagonal symmetry (P63/m space group) and the convergent parameters are: $a = b = 9.418 \text{ \AA}$ and $c = 6.884 \text{ \AA}$. [58] there are two crystallographically different Ca atoms. So we can rewritten the general formula of the Hap as $\text{Ca(I)}_4\text{Ca(II)}_6(\text{PO}_4)_6(\text{OH})_2$ (seen in Figure 1), the framework of hydroxyapatite can be described as a compact assemblage of tetrahedral PO_4 groups where each PO_4 tetrahedron is shared by one column, and delimit two types of unconnected channels. The first channel has a diameter of 2.5 \AA and is bordered by Ca^{2+} ions (denoted Ca (I)). The second type, which plays an important role in the acid-base and electrical properties of apatite type solids, has a diameter of around 3.5 \AA , is bordered by triangular Ca^{2+} ions (denoted Ca(II)), and hosts the OH groups along the c- axis in order to balance the positive charge of the matrix [59]–[60].

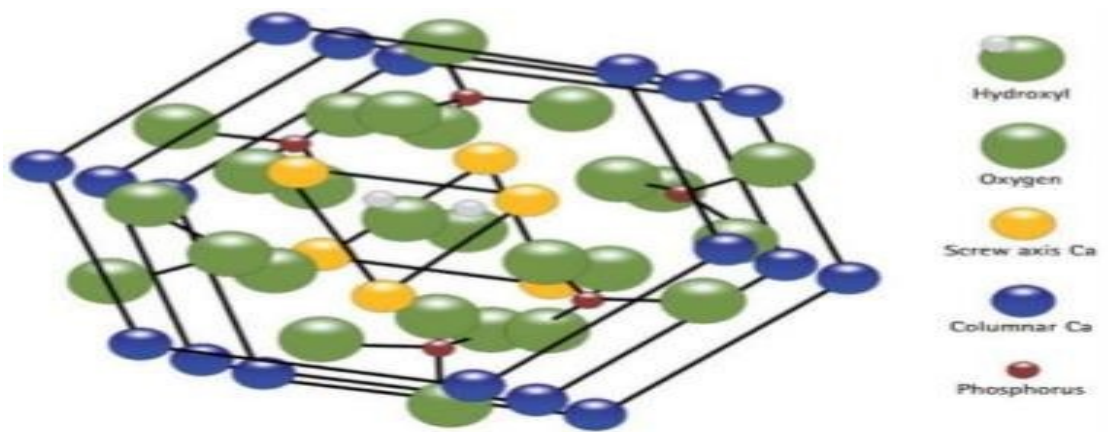
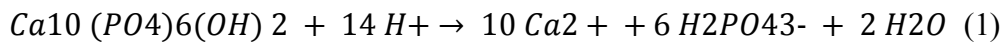


Figure III-3. Lustration of the structure of hydroxyapatite. From reference [61].

The aforementioned Hap allows large variations in compositions, and, as a matter of fact, can be a highly non-stoichiometric solid. Stoichiometric Hap (Hap-S) has the chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ where the ratio Ca/P is of 1.67. Calcium deficient Hap (Hap-D) has a Ca/P ratio less than 1.67 and its chemical formula is $\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}$ with $0 < x < 1$, and finally carbonate-rich hydroxyapatite (Hap-E) with the chemical formula $\text{Ca}_{10-x}(\text{PO}_4)_{6-x}(\text{CO}_3)_x(\text{OH})_{2-x}$, or $\text{Ca}_{10-y} \text{Na}_y[(\text{PO}_4)_{6-y}(\text{CO}_3)_y][(\text{OH})_{2-2x}(\text{CO}_3)_x]$ in case sodium is present, has a Ca/P ratio higher than 1.67 [62], [63].

Furthermore, Hap is poorly soluble in water and insoluble in alkaline solutions. It is, however, soluble in acids because both PO_4^{3-} and HO^{\bullet} react with H^+ [64], [65]:



III.6 Properties of HA

III.6.1 Chemical properties of HA

HA with a general formula of $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ The pure HA powder is white, whereas naturally occurring HA can also have brown, yellow, or green colorations, HA is used as a bone substitute because of its chemical similarities with the natural bone. The major composition of bone is a mineral phase (69 wt %), an organic matrix (22 wt %), and water (9 wt %). [68] [67] and is a ceramic–organic bionanocomposite, that has a complex structure.

HA is one of the most stable and less-soluble calcium phosphate bioceramics with Ca/P ratio of 1.67. [66], [68]

HA occurs as the principal inorganic constituent of normal (bone, teeth, fish enameled, and some species of shells) and pathological (dental and urinary calculus and stones). [67]

III.6.2 The mechanical properties of HA depend on porosity, density, sinter ability, crystal size, phase composition, and so on. The bending, compressive, and tensile strength values of HA ceramics lie in the range of 38–250, 120–150, and 38–300 MPa, respectively. [66], [68] Young's modulus of dense HA ceramics varies from 35 to 120 GPa, depending on the residual porosity and impurities. [66], [67], [68]

The mechanical properties of HA bioceramics strongly depend on the microstructure and sintering ability; densely sintered bodies with fine grains are tougher and stronger than porous ones with larger grains. [66] [67] [68]

III.6.3 Biological Properties of HA favorable biological properties, which include biocompatibility, bioaffinity, bioactivity, Osteoconduction, [66] osteointegration, [67] no adverse local or systemic toxicity. Newly formed bone binds directly to HA through a carbonated calcium deficient apatite layer at the bone–implant interface. [68], [69] HA surface supports osteoplastic cell adhesion, growth, and differentiation, and new bone is deposited by the creeping substitution from the adjacent living bone, In general, the mechanism of action of a biomaterial is considered to be biocompatible, bio inert, bio tolerant, and bioactive, and includes bioresorbable materials.

The use of HA with Ca/P ratio of 1.0–1.7 is nontoxic and neither has it induced any foreign body reaction. The nature of healing mimics fracture healing. [68] HA has displayed an ability to directly bond with bone. [69], [70], [71], [72] – [82]. The mechanism of bone induction by a synthetic material is still not clear, but various factors such as micro porosity, surface area, geometry, and topography are important, [82]– [84] of which micro porosity has a positive effect on increasing bone formation. Biodegradation of HA is usually initiated by changes in the surrounding biofluids and adsorption of biomolecules. The physicochemical dissolution process depends on the surface area to volume ratio, fluid convection, acidity, and temperature. [85], [86].

III.7- Application of HAP:

III.7.1. Biological and medical applications

As mentioned previously, HAP as the main mineral constituent of bone and tooth enamel, have very good biocompatibility properties and in particular the specific adsorption properties of cells or proteins [87], [88].

They are therefore frequently used in the field of medicine and pharmacy. HAPs, for example, serve as substitute materials for replacement or regeneration of diseased or damaged tissue. By coupling a HAP to a polymer it is possible to create bioactive and better tolerated ceramic-polymer composite implants by the body. [89]

HAPs are also frequently used as a "coating" on prostheses in titanium to facilitate Osseointegration [90] or to prevent wear due to oscillatory micro-movements at the interface between the implant and the bone, sometimes even leading to rupture of the prosthesis. [91]

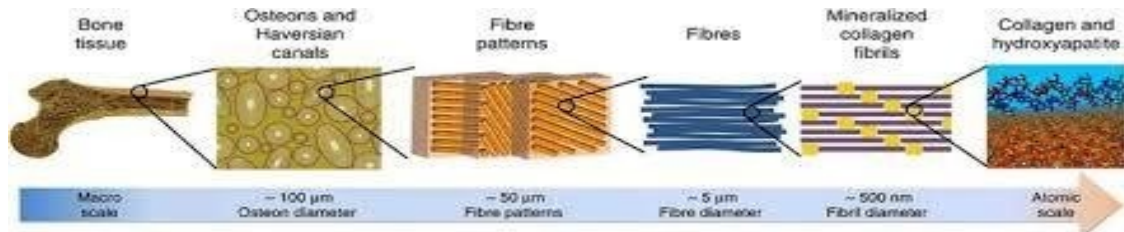


Figure III-4 biomedical application

There are some examples of use as a cement used in facial surgery to replace autogenous bone grafts [92] and a growing number of applications as a vector of drugs thanks to a structure presenting interconnected micro pores. [93]

However, under certain conditions, this same material may present a character pathogenic for the organism [94]: following dysfunctions, the body can produce HAP of particular morphologies which may be the cause of kidney stone formation or calcification of cartilage [95] which is dangerous for the body.

In all these applications, it is ultimately the surface reactivity of HAP with the biological environment which is the key point. This is the reason why many studies fundamentals deal with the interaction of biological molecules (often amino acids) with HAP, the objective being to rationalize the adhesion properties of proteins on this support (at the

origin of its biocompatibility). Without going into the details of these studies, we can underline the link that is made between the adsorption or desorption capacity of proteins according to the pH of the medium [96], which not only affects the speciation of the biological molecule, but also on the surface charge of the HAp. However, while these interactions translate at the molecular level of acid-base interactions (as will be seen for the catalytic applications), few studies pose the problem in these terms.

III.7.2-Applications in archeology and climato-paleontology

HAp are materials that are also studied in archeology and in paleontology. Analysis of HAp from human or animal remains (teeth, bones), allows a reconstruction of the eating habits of the time in question, and thereby to reconstitute the flora and thus to go back to the climate [97]. Indeed it has been proven that the strontium to calcium ratio (Sr / Ca) makes it possible to identify the type of diet of the animal and even makes it possible to distinguish between carnivores, herbivores and omnivores [98]. Of the same way, it is reported that the quantity and distribution (site A or B) of carbonates within these fossil apatites should make it possible to identify, by studying the isotopic ratios of these carbonates, the nature of the plants ingested by the animals, and here again and therefore to deduce data climatological studies at the time in the place where they lived. [99]



Figure III-5: archeology Applications of HAP

III.7.3- Other chemical applications

Other specificities than the biocompatibility of HAp can also be put to benefit such as its ability to substitute which allows it to clean up water contaminated by metal cations by acting as an inorganic cation ex They are also used very frequently in chromatography to separate the proteins and other biomolecules. HAp are effective due to the combined effects of calcium and phosphate groups exposed on the crystal surface which give the material a high selectivity allowing the separation of complex mixtures. [101], [102]

III.7.4-Catalysis applications

For a relatively recent period, HAp have been a very popular material in the field of heterogeneous catalysis.

They are for example used in the selective oxidation of alcohols [103] or methane

[104], but in co-action with a metal of the ruthenium or nickel type. In this type of reaction the active species are the metallic species ($\text{Ru}(\text{OH})_2$ or Nickel in partially form metallic and oxidized and the HAp simply serves as a support which proves to be highly stable both textural and also in terms of the interaction between these metals and the apatite structure, and this even under the conditions of catalysis. Likewise, in the water gas shift reaction, the Hap is used as a carrier for gold particles (the HAp having no activity in itself in this reaction even for temperatures above 400°C), and this combination

Au / HAp allows good activity in this reaction for temperatures as low as

110°C . [105]

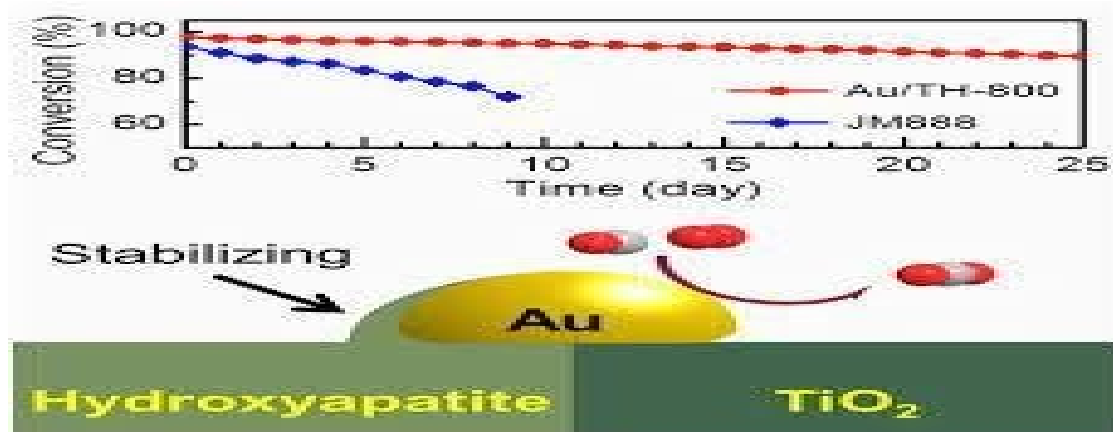


Figure III-6: catalyze in HAP

III.7.4.1-In acid catalysis, HAp can be used as a substitution for AlCl_3 in reactions

Friedel-Crafts [106] in order to make the process less polluting. Although the best activity is reached for ZnCl_2 supported on HAp (97% conversion of toluene in 2 minutes), the HAp alone is also active (95% conversion of toluene in 120min). Here the properties

Intrinsic acids of HAp are used in addition to its function as a simple carrier.

III.7.4.2-In basic catalysis, the intrinsic acid-base properties of HAp are brought to light. Profit. In some cases these properties can be doped, as in the reaction of Knoevenagel [107], where the addition of potassium fluoride will increase the basicity which pre-exists before doping. The authors attribute this upsurge in activity to a change in morphology induced by KF doping, which is not surprising since fluorine easily substitutes for hydroxyl groups and that substitutions by ions of different charge (such as K^+) have already been reported and translate into often by reorganizing the material to compensate for the load.

Likewise, without any doping, HAp turns out to be a very good basic catalyst in certain fine chemical reactions: in Michael's addition, for example, it allows to obtain high yields while avoiding undesirable reactions, in changer [100]. Relatively mild conditions [106].

The reaction takes place at the surface of the HAp and not within the channels present in the structure and that the excellent activity of these materials is due to the acidic and basic nature of this surface: the character acid induces a polarization of the C = O bond of the reagent while the basic sites go increase the nucleophilicity of thiol, thereby accelerating the formation of the S-C bond of the final product.

The Guerbet reaction is another convincing example of the particular basic activity of HAp: unlike other basic oxides such as CaO or MgO, HAp has the particularity selectively form n-butanol from ethanol [104]. The authors highlight light the importance of stoichiometry: the selectivity of the different products will vary in function of the Ca / P ratio of the Hap used. Although stoichiometry is a property of heart, we see that it has an impact on the surface properties and therefore on the basic activity of the HAp.

To understand the atypical behavior of HAp in this Guerbet reaction, but also more generally its good performances in several reactions in particular basic, and rationalize the impact of stoichiometry, a mass property, on reactivity basic, we must ask ourselves the question of the nature of the basic sites active on the surface of this material and how they work.

So far, few studies have been conducted to identify the basic and acidic sites that are involved in the reactivity of HAp. In view of the structure of the HAp it is possible to imagine two species that could potentially play the role of basic sites: on the one hand, hydroxyl groups which, as mentioned above, are weak bases liable to present an interesting reactivity and, on the other hand, the PO₄ groups, are also potential weak bases. With regard to acidic sites likely to be involved, two types can a priori be considered Lewis acid-type sites that are the ions calcium and Bronsted acid-like sites represented by P-OH. [100],[107]

III8-The features that and characteristic make HAP an environment-friendly material:

- **So in this point I tried to combine the most prominent properties of HAP and its application in correspond with this study**

In the first Hydroxyapatite is among which figure its non-toxicity, inexpensive and readily available, high adsorption capacity, low water solubility, and have high stability under reducing and oxidizing conditions. And biocompatibility this latter, combined with its excellent osteo conductive property, it mine Hap playing a vital role in clinical applications such as drug delivery, bone tissue regeneration [108], And capacity to be derived from natural sources, and more precisely from waste. Indeed, Hap has been successfully obtained from animal waste such as fish bones [109]–[111], chicken bone [112], fish scales [110], [113]–[116], eggshells [117]–[119], and mussel shells [120], all of which were found to constitute important bio resources for hydroxyapatite production

This, makes calcium phosphate compound particularly attractive from an environmental point of view, besides its intrinsic properties and its environmental applications.

It is important to mention that hydroxyapatite derived from natural sources differ from synthetic Hap in terms of lower purity, higher degree of substitution and deficiency, lower specific surface area value (4.49 m².g⁻¹ for natural phosphates [121] while that of synthetic Hap can attain 100 m².g⁻¹ and more) and consequently, poorer sorption capacities [121]–[128].

Indeed, bio-sources of Hap contain small amounts of inorganic compounds other than Hap, such as Ca₄O (PO₄)₂, NaCaPO₄, Ca₃ (PO₄)₂, CaO, and MgO. In addition, through Hap's substitution ability, natural apatite contains some fluoride or chloride in place of hydroxide and some metal ions (aluminum, iron, copper, zinc...) in place of Ca²⁺.

Finally, organic matters are also present within natural apatitic materials. All of these alterations in the compound's purity and therefore in the obtained Ca/P value [121] - [128], can have a direct influence on the efficiency of hydroxyapatite used in environmental remediation applications. This is why, a pre-treatment of naturally derived Hap is usually conducted before its use, in order to eliminate remaining organic matter and attain a pure hydroxyapatite phase, which would result in a Hap material with comparable properties and efficiency as synthetic hydroxyapatite.

What is important of Hap from waste does not only offer economic benefits since it relies on the use of cheap, natural and undesirable materials, but also, contributes in achieving a sustainable development by being an active part in the global waste management process. In other words, solids which would have accumulated, creating thus a pollution source, endangering human, animal and vegetation's health, are in this way being utilized for the production of very sought-out product.

- And without forgetting we can use Hap as:

Adsorbent for wastewater and soil treatment very efficient in immobilizing metals such as: Cr, Pb, Cd, Ni, Zn, Al, Cu, Fe, Co, Mn, and Fe [129]–[150], as well as many others with 2 mechanisms Dissolution-precipitation [132], [146], [147], [150], [151]. And Ion exchange [152]. [153], **or Nuclear waste management** its use as radionuclide sorbent seems like a cost-effective choice of PRB [154]–[157]. In fact, hydroxyapatite was found to exhibit a higher activity towards uranium removal compared to granulated activated carbon based sorbents confirming its great potential in the treatment of uranium contaminated sites [159] adding **Inorganic elements removal** and **Organic compounds adsorbent** because have high adsorption capacities and has no unfavorable effect on water quality [160]- [166]

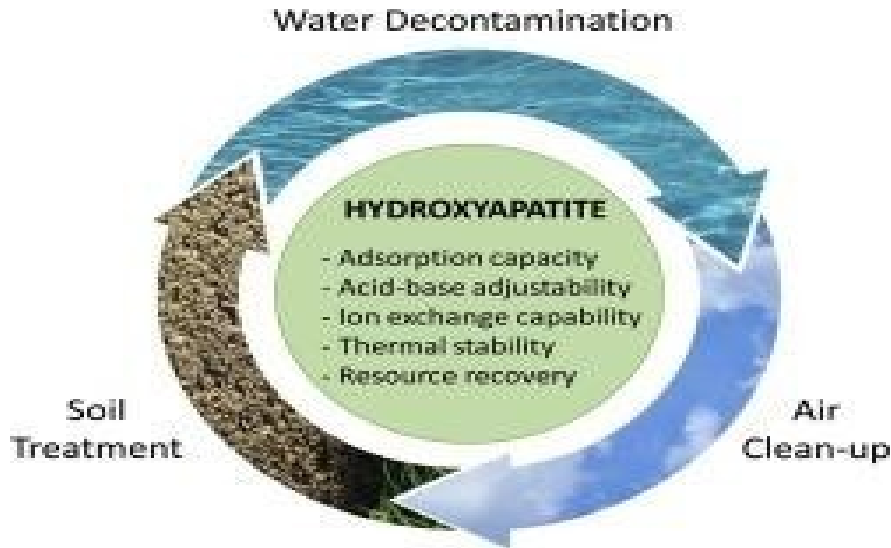
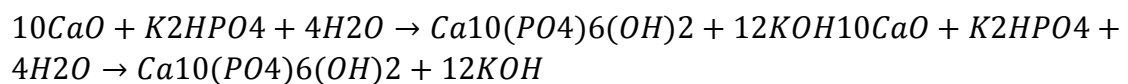


Figure III-7: utilization HAP in environment

III9-Different methods preparation of hydroxyapatite

Hydroxyapatite can be prepared by different methods such as sol-gel process, chemical precipitation, etc. prepared the HAP by applying the following reaction.



III9.1-Wet Chemical Method

The wet method utilizes either precipitation from mixed aqueous solutions or the hydrolysis of calcium phosphates. Many experiments on the preparation of HA by this method have been reported in order to investigate the formation mechanism of calcium phosphates in vitro and in vivo. HA is usually prepared by precipitation under the very basic conditions and sintering the precipitate at 950° to 1100° C. However, the powders prepared by this method usually are poorly crystallized, inhomogeneous in composition and irregularly formed. HA powders produced by the wet process also possess a high surface area and fine particle size. However they are non-stoichiometric (Ca-deficient) and are of low crystallinity. [167]

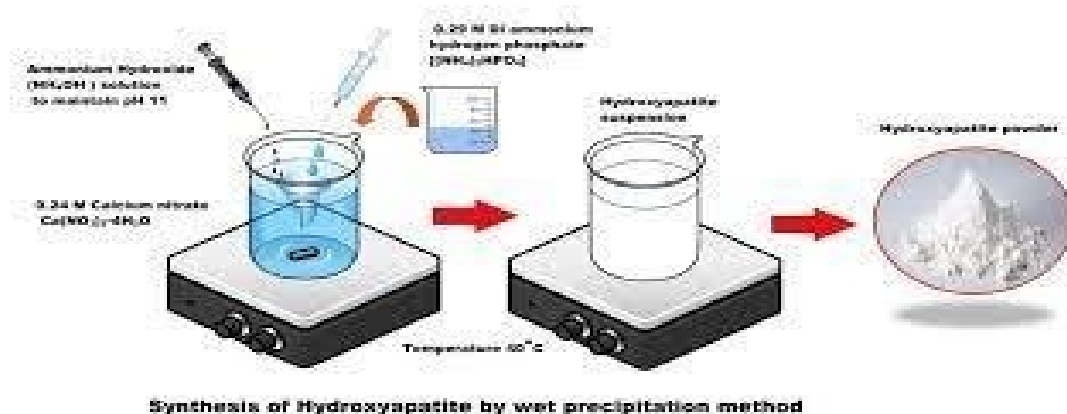


Figure III-8: Wet Chemical Method for prepared HAP

III.9.2-Hydrothermal Method

Another method to produce hydroxyapatite is by a hydrothermal. The hydrothermal method involves reactions in an aqueous environment, conducted at relatively high temperatures and pressures with respect to the ambient conditions. The hydrothermal fluid environment is thus created in a pressurized and heated sealed system where the reactants are housed. The temperature and pressure can vary in the range of 80° to 400°C (in some cases even higher) and small autogeneous pressures of up to 100 MPa or more, respectively had produced a well-crystallized HA powder by using hydrothermal treatment at 109 °C in a pressurized pot for 3 hours. However, all samples had a Ca/P molar ratio of 1.64-1.643 which were slightly calcium – deficient than the stoichiometric HA.

This calcium – deficient HA could transform into other phases such as TCP which later could weaken the strength of dense specimens. [168]

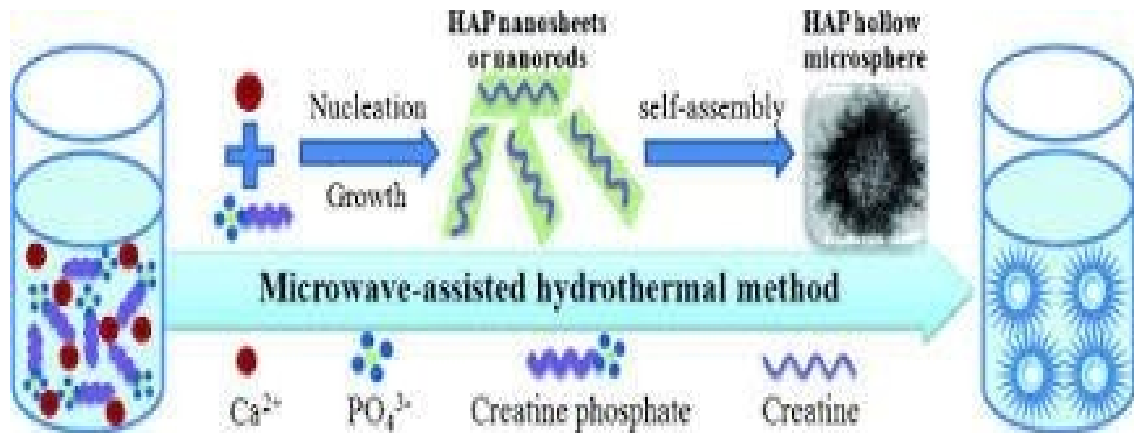


Figure III-9: Hydrothermal Method for prepared HAP

III.9.3-Solid-State Reaction

Mechanical alloying and mechanical milling have been the most popular methods for producing powders in the solid state. A characteristic feature of all solid-state reactions is that they involve the formation of product phases at the interfaces of the reactants. The solid-state reactions initiated by intensive milling in high energy ball mills could be a good choice for ceramic powder preparation. An important criterion for intensive milling is the mechanical activation of highly dispersed materials or the formation of new product because of a solid-state reaction (mechanochemical reaction).

A solid-state reaction which is usually a dry process has generally been used for the processing of ceramic powders and for studying phase stabilities. The powders prepared by this method however, usually have irregular forms with a large grain size and often exhibit heterogeneity in composition due to incomplete reaction resulting from small diffusion coefficients of ions within solids. [169]

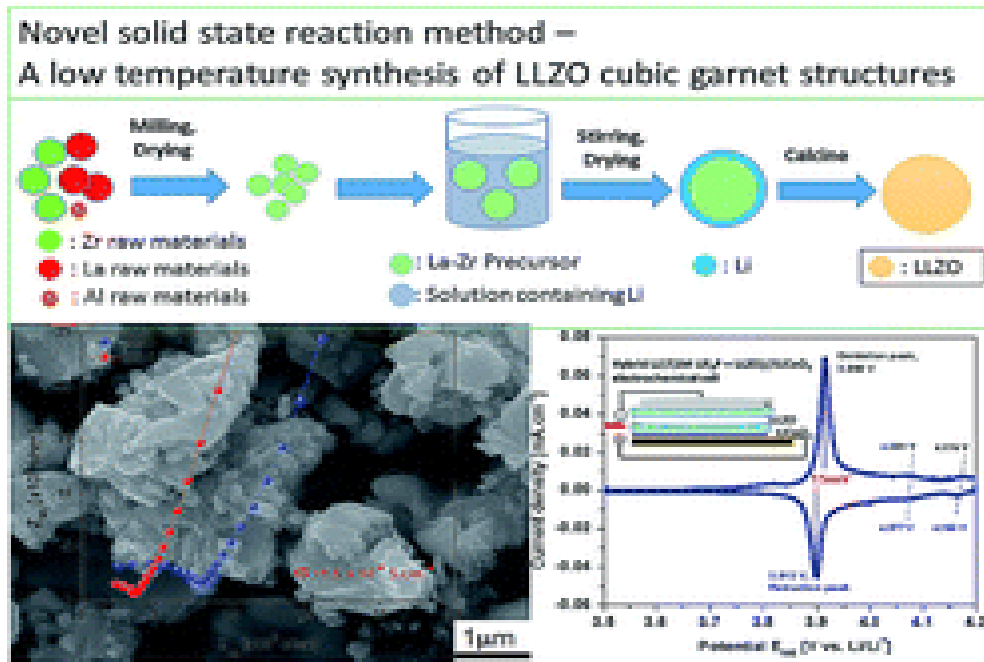


Figure III-10: solid state method for prepared HAP

III.10-Conclusion:

Natural Hydroxyapatite, is very promising candidate for the treatment of air, water and soil pollution. Indeed, hydroxyapatite (Hap) can be extremely useful in the field of environmental management, due in one part to its particular structure and attractive properties, such as its, its acid-base adjustability, its ion-exchange capability and its good thermal stability. Moreover, Hap is able to constitute a valuable resource recovery route in addition to great **adsorption capacities** that what inspired us to idea of using it as a **biocoagulant** in polluted water.

CHAPITRE IV

EXPERIMENTAL PROCEDURE & RESULTS AND DISCUSSION

IV.1-Introduction

After we got to know hydroxyapatite and studied its properties, as well as after its great success in the adsorption process, all this prompted us to apply it to polluted water, but this time as a coagulant, and this is what we will try to confirm out through these experiments.

- ✓ **Remark:** Due to the lack of time allocated for the completion of laboratory work related to this memorandum. We used hydroxyapatite prepared by my co-promoter so we was resumed the mechanic processor of preparation in the first part of this chapter.

IV.2-1. Preparation hydroxyapatite powder

The first step is to obtain the camel bones (biowastes) from an Abattoir. Extraction of the bone mineral is carried out from the dromedary femur bones by the calcination method. Figure 2 presents the steps process used to obtain HAp. The preliminary stage of preparation is the treatment of bones by a gas torch to remove all the fat that is present in their surface and to reduce the smell of gas evolution during their calcination. After that, the bones are crushed into small pieces to ensure effective calcination. The bone pieces are calcined in the oven air (Nabertherm) at 900°C during 12 h with a heating rate of 10 °C/min. After calcination, the prepared powder is cooled slowly inside an oven. To determine the yield of Hap prepared, the raw bone is weighed at room temperature and after heat treatment. The percent yield is evaluated according to the following equation:

$$\Delta W = \frac{(W_1 - W_2)}{W_1} * 100$$

W2 and W1 are samples weight before calcinations and the lost weight.



Figure IV.1- HAP powder

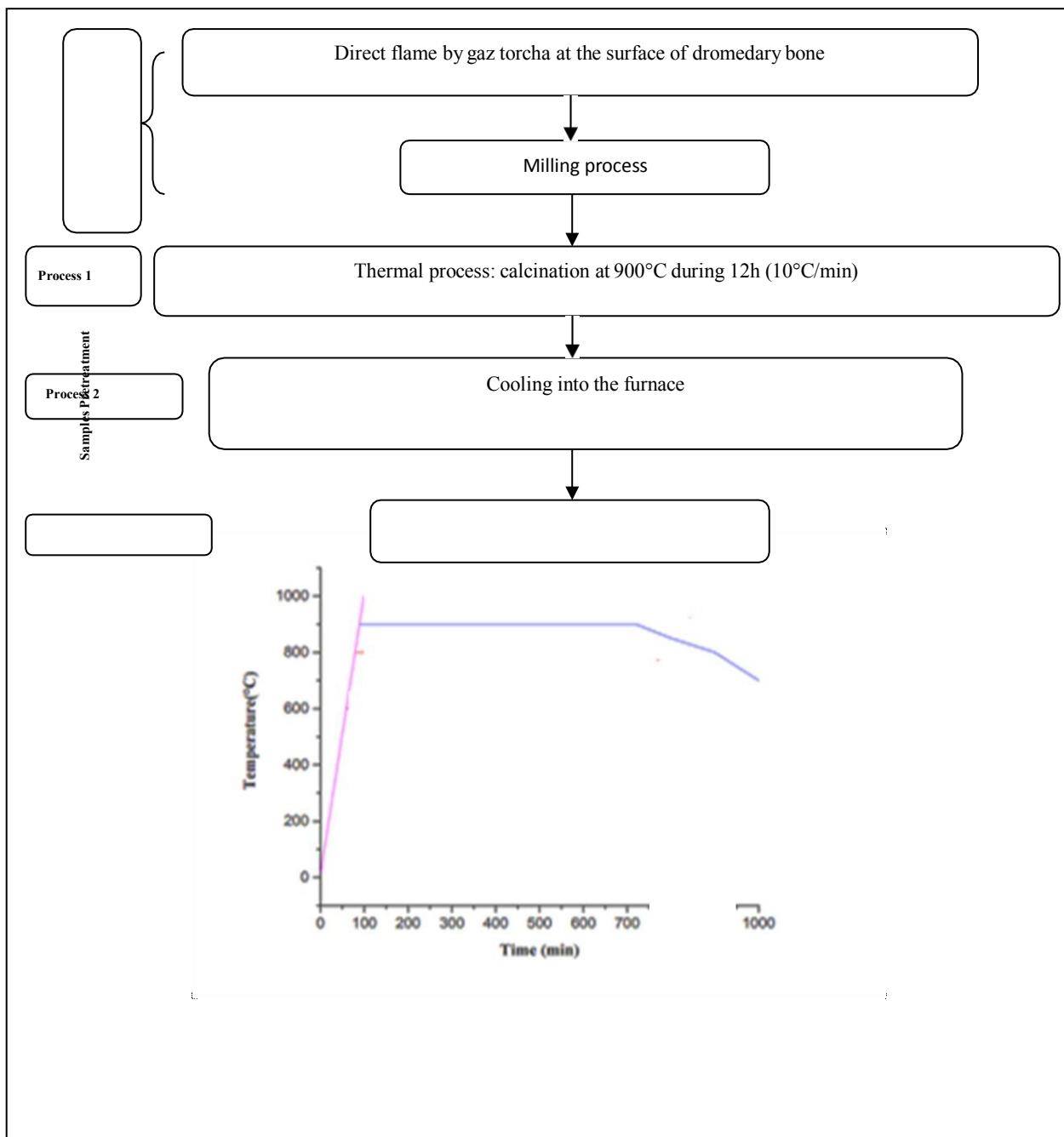


Fig IV. 2- Diagram of the process to produce natural Hap from dromedary bone and its thermal history

IV.2.2. Physico-Chemical characterization

IV.2.2.1 Fourier transform infrared (FTIR)

The FTIR method (KBr pellet method, FTIR-8400s SHIMADZOU) is used for the analysis of samples in the 400-4000 cm^{-1} wavelength range in order to determine the optimum temperature and time for extraction of pure hydroxyapatite.

IV.2.2.2 X-ray diffraction (XRD)

The Diffractograms are acquired with copper $\text{K}\alpha$ radiation ($\text{CuK}\alpha$ 1, 54056 Å) with a Bruker D8 Advance diffractometry, where the spectrum is taken at 20: 20°-60° with a pitch of 0.02. The size of the crystals was determined according to the equation Scherrer [176]: $D = \frac{k\lambda}{\beta \cos\theta}$, where D is the crystallite size, $k = 0.9$

is a correction factor to account for particle shapes, β is the full width at half maximum (FWHM) of (002) peak, λ the wavelength of the radiation and θ is the Bragg angle.

IV.2.2.3 SEM

Morphologic analysis of the samples prepared from dromedary bone was realized out in a Leo 1530 Carl Zeiss Scanning Electron Microscope. The electron acceleration voltage was 20 kV. First of all, the sample was covered with a thin layer of gold using a CRESSINGTON SPUTTER COATER 108 AUTO.

IV.2.2.4 X-ray fluorescence spectrometer

The oxide elements present in the sample are analyzed by XRF X-ray fluorescence spectrometer (Bruker AXS GmbH).

IV.2.2.5 Laser granulometry

The powder prepared is milled by a ball mill (Retsch) at a ratio of 1/10 of the powder to the bead. The grinding speed used is 300 rpm for one hour. These crushed powders are analyzed by laser granulometry (Cilas, Particle Size Analyzer 1090) their particle size distribution.

IV.2.2.6 Pycnometer

The use of the pycnometer allows to measure the density of the HAp powder using the following formula Eq. (2):

$$\rho_s = \frac{(W_s - W_a)}{[W_{sw} - (W_s - W_a)]}$$

Where: ρ_w : density of water, W_s : the pycnometer weight with the sample, W_a : the empty pycnometer weight and W_{sw} : the pycnometer weight with the sample filled with water density of water.

IV.3- pH_{ZPC} determination:

The pH_{ZPC} was made using the reported pH technique (Vieira *et al.* 2009). For this purpose, six solutions of distilled water are prepared by adding HCl or NaOH solution (0.1M) from pH 2 to 12. To 100ml of each of these solutions is added 0.1 g of bio adsorbent. The suspensions obtained are left stirring for 24 hours at room temperature ($28 \pm 2^\circ C.$), then the pH of the solutions is determined. In practice, the pH_{ZPC} is the point of intersects resulting $\Delta pH=0$ for which curve of the $pH_{initial} - pH_{final} = f(pH_{initial})$.

IV.4- Application: as Coagulant

IV.4.1.-Jar test

Coagulation is the important method utilized to take away of color, turbidity, microorganism, suspended matter, and odor producing matters. Adding the coagulant to bring down the small destabilized particles to form large matter then they are automatically settle with the help of gravity and separated from the waste water. We put with every 500 ml of distilled water 1 g of sifted garden soil into fine granules. Then we mix it well for a few minutes and add hydroxyapatite in varying quantities and add $CaCO_3$ with it (calcium carbonate (PCC) as a means to ameliorate process water stickies.) First quick mixing is carried out for 3 minutes at 150 rpm along with add flocculation a slow mixing for 25 minutes at 40 rpm. The samples are permitted to settle for 30 minutes. Then the supernatant water was filtered and their parameters were find out. Same procedures are followed by HAP powder.

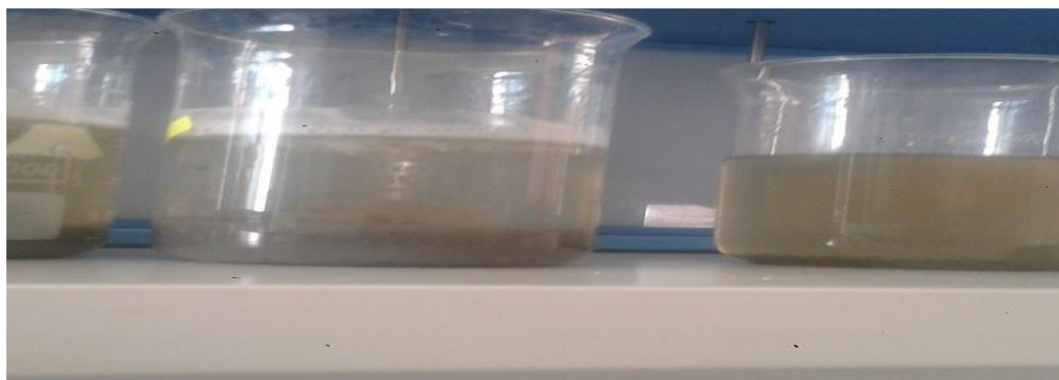


figure IV.3: polluted water in jar test beaker

B.1-RESULTS AND DISCUSSION:

B.1. General observation and Weight changes

The powder of the calcined dromedary bone remains grey after 9 hours heating at 900°C. It is only after 12 hours of calcination that it becomes white. The change of the grey to white color that means a removal of organic matter.

Table 1 shown the extraction yield of HAp prepared from dromedary bones 900 °C during 12h (69%),it was approximately equal to that found [2, 22] from bovine bones.

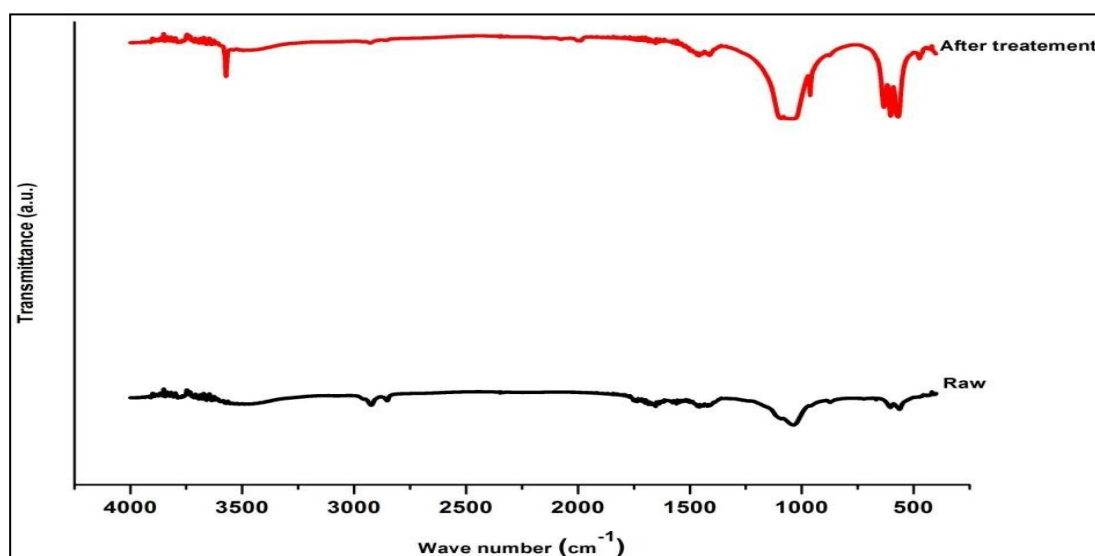
B.2 Physico-Chemical characterization

B.2.1 FTIR analysis

Figure 4 shows the spectra resulting from the FTIR analysis of dromedary bone before and after calcination. In order to examine the degree of removal of organic matter, the appearance or disappearance of the characteristic bands of organic matter has been verified [14]. The bands from the amide functional groups (CH, NH) are 2860, 2929 and 2913cm⁻¹[6, 28]. They are present in the bone

spectrum at 2854 cm^{-1} and 2924 cm^{-1} . As a result of calcinations during 12h (Fig. 1) shows the organic matter in the powder is removed at 900°C except carbonate groups (871 , 1460 and 1417 cm^{-1}), that have been inserted into the phosphate and hydroxyl site, which explains the change of black to white. The presence of carbonate group in HAp has an influence mainly in the behavior of HAp in biological

Medium [29].

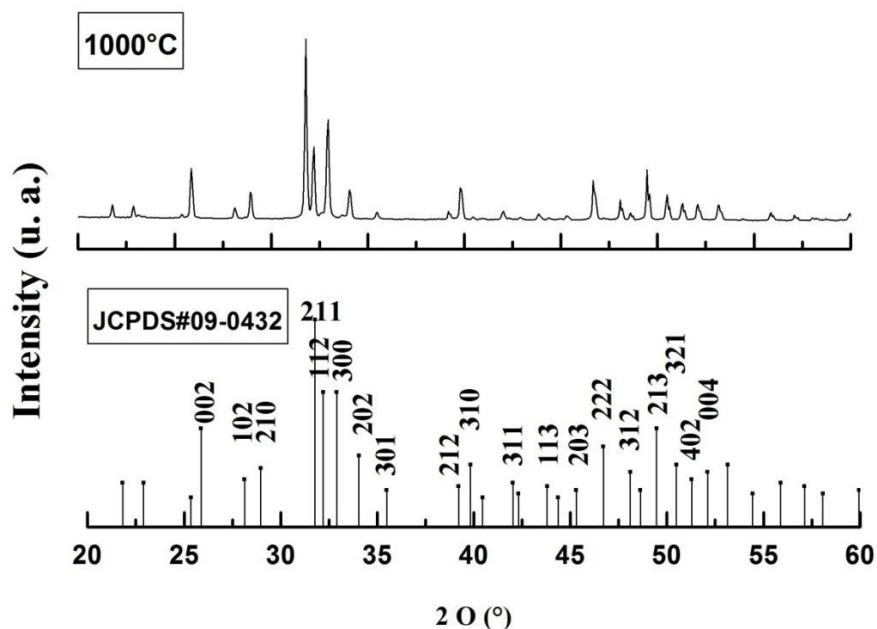


FigureIV.4-: FTIR spectrum of heat-treated camel bone.

B.2.2 XRD analysis

The diffractogram of the bone treated are shown in Fig.5. These results were compared to the Joint Committee on Powder Diffraction Standards (JCPDS) reference 00-009-0432 of HAp. All the peaks presented in the calcined bone diffractogram correspond to the HAp. No presence of another phase was observed. The results of other work practised revealed the presence of their impurity phases (CaO , NaCaPO_4 and MgO) in bovine bone treated at a temperature above 800°C .

From the results of XRD and Scherrer's equation, we have calculated the size of the HAp crystals prepared from dromedary bone at plans (002). Additionally, the crystalline size of HAp prepared at 900°C is 74 nm.



FigureIV.5-: DRX diffractogram of dromedary bone after heat treatment

B.2.3 SEM analysis

The morphology of the treated HAp at different temperature has been illustrated in the fig. 4. As shown in this figure, Furthermore, the HAp prepared from dromedary bone apparea a non-regular shape. This result is in disagreement with finding of researcher.

B.2.4 XRF analysis:

As seen in Table 2, calcium and phosphorus are the major constituents with other minor components such as sodium and magnesium as well as sulfur, strontium, zinc and potassium as traces in the Hap. This minor and trace element such as strontium plays a very important role in the biocompatibility of the HAp.

The comparison between the results of the chemical compositions of hydroxyapatite extracted from dromedary bone (Table 2) and the results of other studies of the chemical compositions of hydroxyapatite extracted from bovine

bone shows that there is a small difference. It is noted the rate of strontium obtained is relatively high in the dromedary bone 0.131% against 0.053% in bovine bone. Strontium is naturally present in the structure of the bone. Its behavior in the body is very close to that of calcium. The substitution of dental enamel calcium by strontium improves resistance to chemical attack.

Research has shown that this mineral element enhances the mechanical properties of bone and allows in vivo a better link between hydroxyapatite coatings and surrounding tissues. The crystals HAp enriched by strontium are more stable. The introduction of strontium into the composition of some ionomer glasses and dental filling cement increases the radiopacity of these materials and acts on the bacterial activity present in the oral cavity. In vitro studies, comparing calcium silicate ceramics substituted with Mg^{2+} , Zn^{2+} , or Sr^{2+} have shown that the presence of strontium stimulates the differentiation of osteoblasts and increases significantly the expression of osteoplastic markers such as alkaline phosphatase and osteopontin, compared to magnesium or zinc doping.

The molar ratio Ca/P (1.62) of HAp obtained from dromedary bone at 800°C during 12h is in accordance with the research on bovine bone[42] and it is lower than the molar ratio of HAp obtained from pig bone (1.95), human teeth (1.84) and bovine bone (2.23) and theoretical HAp (1.67). This difference may be due to biological factors such as nutrition, sex, age, race of the animal, site dietary history and the presence of disease.

Table 2: Principal inorganic constituents (wt %) of the studied hydroxyapatite and hydroxyapatite extracted from bovine bone

Element	Dromedary bone	Bovine bone [7]	Bovine bone [6]	Bovine bone [25]
CaO	54.192%	53,698%	52.25	51.51
P2O ₅	41.842%	42,701%	38.37	44.68
Na2O	1.258%	1,708%	—	<0.1
MgO	1.195%	1,769%	0.41	1.63
SO ₃	0.159%	0,25%	—	0.25
K ₂ O	0,021%	0,072%	—	—

B.2.5. Laser Granulometry

The distribution of particle size of the HAp powder (Fig.1) is multimodal with a grain size between 0.5 and 80 μm. The majority population is centered on 1.5 μm.

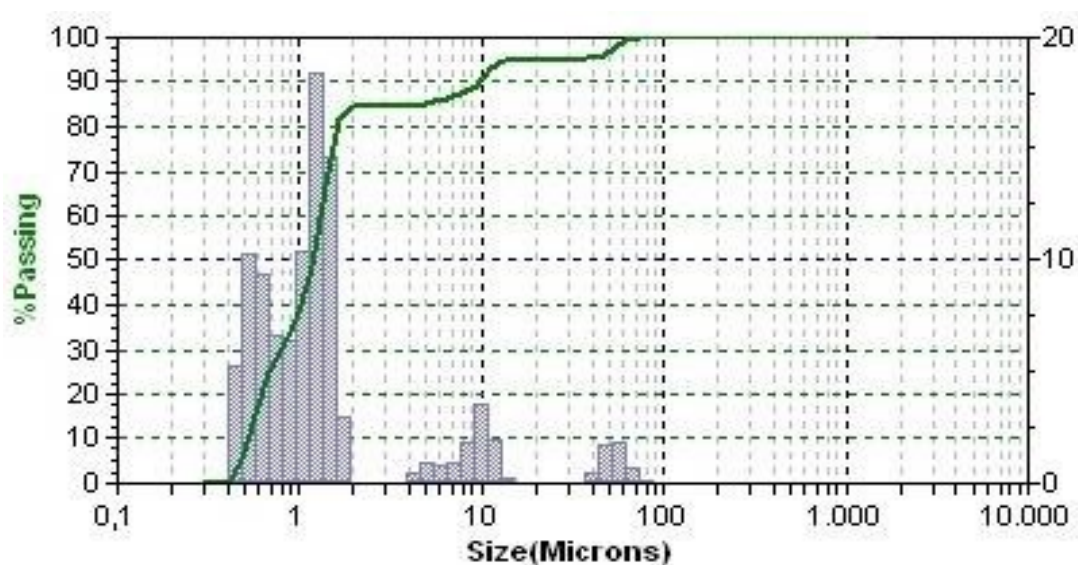


Figure IV.6-. Particle size distribution of hydroxyapatite

B.2.6 Density

The density of hydroxyapatite prepared from dromedary bone at 900°C during 12h was found to be 3.178 g/cm³, these results corroborate with those of the studies carried out. The density of the synthetic hydroxyapatite is 3.16 g/cm³. These results show that there is no significant difference between the density of natural hydroxyapatite and synthetic hydroxyapatite.

B.3- Zero charge point pH:

The zero load point (pHPZC) is used to characterize an adsorbent material at this pH, the surface has no charge and the total of negative charges is equal to the total positive charges. Indicating, when the pH of the solution is greater than pHPZC,

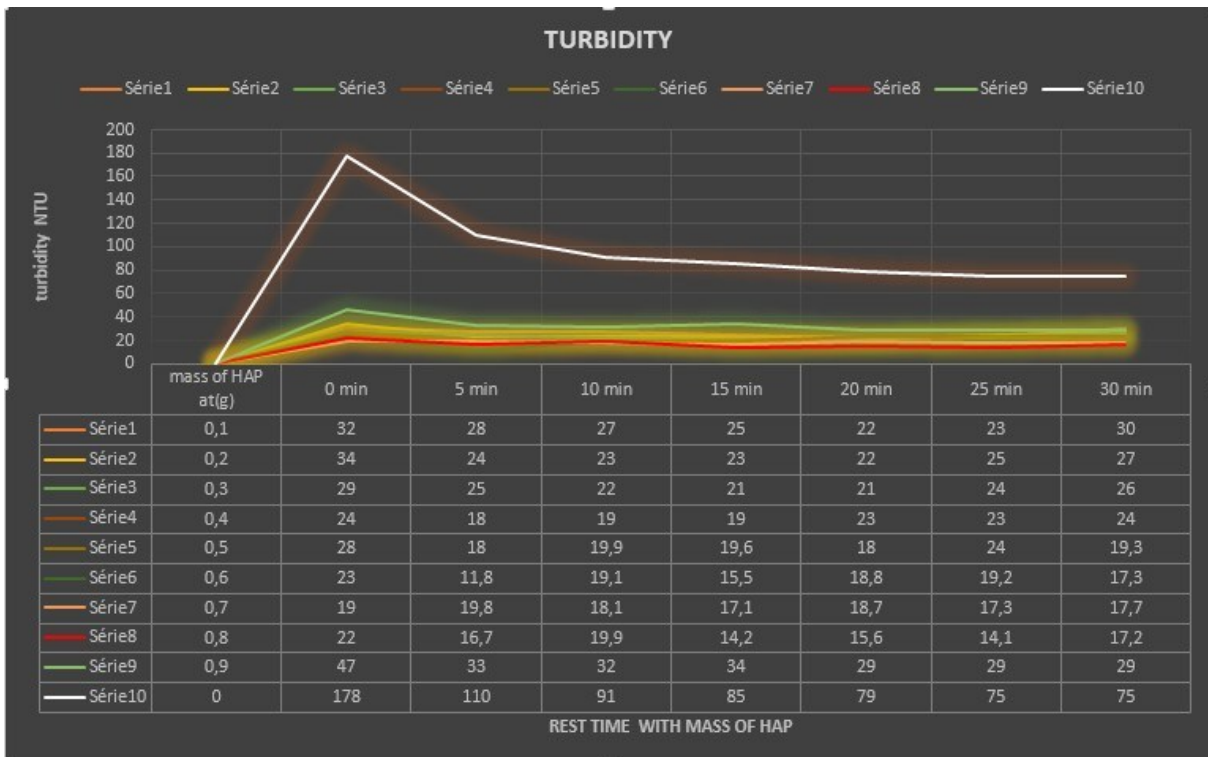
The adsorbent has a negatively charged surface which can attract charged dyes positively. The zero charge point value of hydroxyapatite prepared from the camel bone is 10, this result is higher than that of synthetic hydroxyapatite (7.2) (7.4).

Table 03:

PH	2	4	6	8	10	Temperature
experience01 pH _f -pH _i	3.3	10.03	10.02	10.02	10.4	25.5C°
Experience02 pH _f -pH _i	4.002	10.10	10.23	10.25	10.33	29C°



FigureIV.7-graph Zero charge point pH

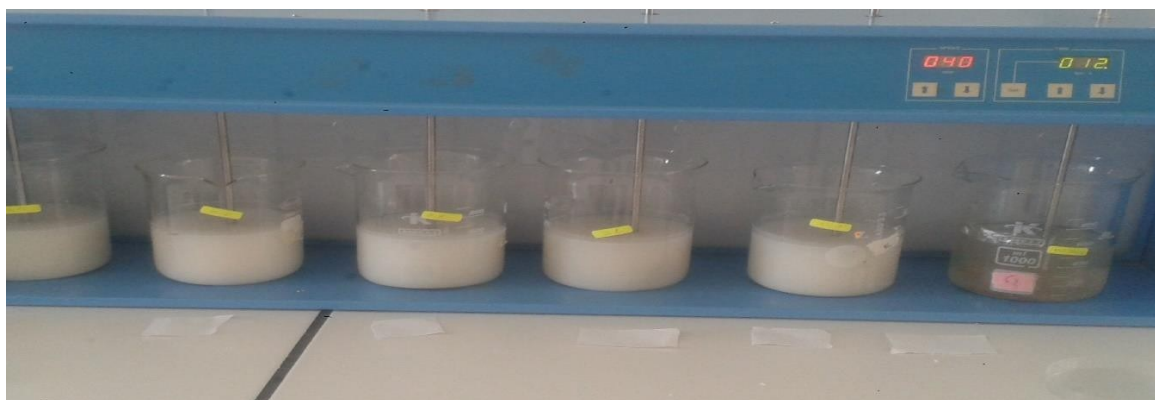


FigureIV.8-: result of coagulation with rest time and deferent dosage Ideal bio-coagulant dosage was calculated from different dosage of bio- coagulant as 0 to 1 g/L for waste water. Nephelometric turbidity meter is utilized to calculate the turbidity is the white curve represents turbid water without adding anything (**witness**).

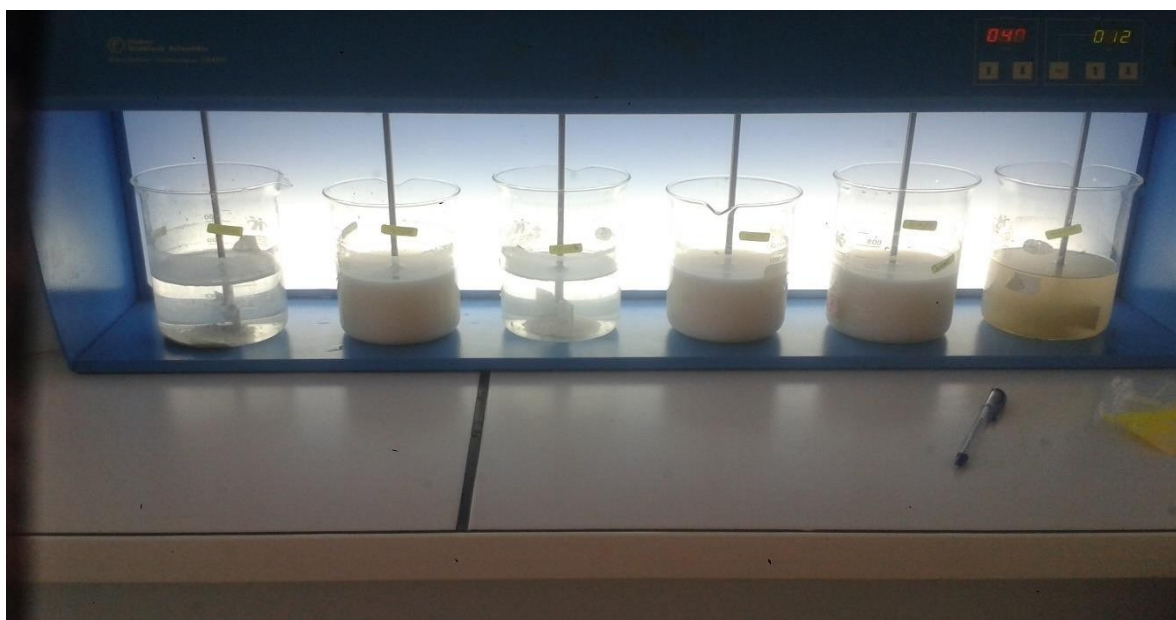
The red curve represent **ideal bio-coagulant dosage is 0.8 g/L** of waste water. Turbidity decreases about 95%.

B-4 Visual observations of coagulation process and effects of HAP dose

when the coagulation experiments were started, the first dramatic observations indicative of coagulation process were the visual observations. As soon as the low HAP value, 0.1 g/L, was dosed, the formation of large flocs was observed. The flocs looked strong and heavy and they settled rather quickly as soon as the mixing was terminated.



FigureIV.9- during the mixing process in jar test



FigureIV.10- after the mixing process jar test

The coagulation process is generally a surface phenomenon; therefore, coagulation performance can be significantly affected by the charge due to the

mass of the coagulant. Thus, from an economic point of surface view, the optimization of the coagulant dosage and the best-required mass of the coagulant for the scale-up and design of large-scale equipment is necessary. Hence, the obtained results are plotted in Fig. 9 from the perspective of the turbidity removal efficiency. As can be inferred from Fig. 9, for the two lowest HAP quantities, i.e., 0.1–1 g/L, the final turbidity was low, less than 11,8 NTU, which is soon as the standard for drinking water 5 NTU. Further, the results of the effect of the coagulant dose on the turbidity removal exhibited the following trend: First, the turbidity removal efficiency decreased from 98% to 26% as the coagulant mass increased from 0.1 to 1 g/L. Then, the turbidity removal efficiency increased with an increase in the HAP dose from 0.4 to 0.8g/L. Finally, the turbidity removal efficiency decreased when the HAP dose was more than 1 g/L this phenomenon could be attributed to a couple of reasons. On one hand, at a lower coagulant concentration, its long chain adsorbed on the surface of one colloid particle was adsorbed onto the surfaces of the others, and thus two or more particles aggregated by bridging flocculation. However, when the coagulant concentration was increased to a certain value (here, 1 g/L), the adsorbed aggregation completely covered the particle surface and prevented the particles from flocculating. The obtained result is valid only under the considered conditions. For each natural coagulant and natural water, the optimum dose and the other optimum factors that influence the coagulation process have to be found.

With condition in my laboratory I found 0.8g/l is optimum dosage, the turbidity decreased at 14,1NTU.

GENERAL

CONCLUSION

GENERAL CONCLUSION

The present work is based on the utilization of biological waste (camel bone) to produce hydroxyapatite for bio-medical applications. The camel bone seems to be a promising source of calcium for preparing hydroxyapatite with excellent properties.

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), a calcium phosphate biomaterial, is a very promising candidate for the treatment of water pollution. Thanks to its feature, its particular structure and attractive properties, such as its great adsorption capacities, its acid-base adjustability, its ion-exchange capability and its good thermal stability. Moreover, Hap is able to constitute a valuable resource recovery route.

This study mainly focuses on the removal of turbidity by jar test method. We get a magnified successful and good result: make larger flocs with the suspended particles in the wastewater by bridging mechanism, finally settle them down and can be easily removed from turbid waters. In the rate of 95% from 178 NTU to a 14.1 NTU with an ideal dosage in 0.8 mg/l, but still some experiments are needed to know why the turbidity values are increasing, still some studies are needed to complete this experiment successfully.

Finally, it is a nontoxic and eco-friendly way of treatment of wastewater, and subsequently, it is being suggested for large-scale water treatment. So that leaf powder is an alternative coagulant of water treatment plant.

Prospect:

We cite here some themes that we will propose for future work.

- ✓ Do the same work for various terms of pH
- ✓ Do the same work with industrially polluted water and analyze BOD COD.....
- ✓ Finding solutions and causes of instability of turbidity after sedimentation time
- ✓ Study what types of pollutants do they remove it?
- ✓ Calculate reduction of turbidity
- ✓ Do studies about Active sludge of hydroxyapatite
- ✓ Study remove nano particles by HAP

This is for the field of coagulation water treatment. We can use HAP in other procedures: water treatment or soils pollution and air.

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ANNEXES

pH meter:

A pH meter is a scientific instrument that measures the hydrogen-ion activity in water-based solutions, indicating its acidity or alkalinity expressed as pH. The pH meter measures the difference in electrical potential between a pH electrode and a reference electrode, and so the pH meter is sometimes referred to as a "potentiometric pH meter". The difference in electrical potential relates to the acidity or pH of the solution. The pH meter is used in many applications ranging from laboratory experimentation to quality control.



Turbidity Meter

Turbidity meter for the detection of turbidity of liquids and aqueous solutions can be found here. The accurate turbidity meter is used in suspensions. There are hand-held turbidimeters or bench-top units. The turbidity meter for water works by infrared method or with the USEPA measuring technique. Turbidity is caused by undissolved, finely dispersed substances in a liquid. A turbid liquid has the property of scattering and reflecting light incident on it. The intensity of the reflected light provides information about the degree of turbidity.

The turbidity meter indicates the turbidity in FTU (Formazine Turbidity Unit), this unit is identical to NTU (Nephelometric Turbidity Unit). The turbidity meter is often used in drinking water treatment. From a hygienic point of view, the limit values today are below 1 FTU.



Jar test

Jar test for coagulation

The dose of the coagulant to be used can be determined via the jar test. The jar test involves exposing same volume samples of the water to be treated to different doses of the coagulant and then simultaneously mixing the samples at a constant rapid mixing time. The microfloc formed after coagulation further undergoes flocculation and is allowed to settle. Then the turbidity of the samples is measured and the dose with the lowest turbidity can be said to be optimum.





FTIR: Fourier Transform Infrared Spectroscopy

FTIR analysis is used for the identification of organic, inorganic, and polymeric materials utilizing infrared light for scanning the samples. Alterations in the characteristic pattern of absorption bands clearly indicate a change in the material composition. FTIR is useful in identifying and characterizing unknown

materials, detecting contaminants in a material, finding additives, and identifying decomposition and oxidation.

A typical FTIR spectrometer includes a source, sample cell, detector, amplifier, A/D convertor, and a computer. Radiation from the sources reach the detector after it passes through the interferometer. The signal is amplified and converted to a digital signal by the A/D convertor and amplifier, after which the signal

is transferred to the computer where the Fourier transform is carried out. Fig. 7 shows the schematic diagram of FTIR spectrometer.



DRX:

X-ray crystallography, radio crystallography or X-ray diffractometry (XRD, also often used the English abbreviation XRD for X-ray diffraction) is an analysis technique based on the diffraction of X-rays by matter, particularly when that - this is crystalline. X-ray

diffraction is elastic scattering, that is to say without loss of photon energy (unchanged wavelengths), which gives rise to interference that is all the more marked as the matter is ordered. For non-crystalline materials, we speak rather of diffusion.