1-Introduction and literature review

1.1Tanning

Tanning is the process of treating skins of animals to produce leather, which is more durable and less susceptible to decomposition. Traditionally, tanning used tannin, an acidic chemical compound from which the tanning process draws its name (tannin is in turn named after an old German word for oak or fir trees, from which the compound was derived). Coloring may occur during tanning. A **tannery** is the term for a place where the skins are processed[(1)].

Tanning leather involves a process which permanently alters the protein structure of skin. Making "rawhide" (untanned but worked hide) does not require the use of tannin. Rawhide is made by removing the flesh and fat and then the hair by use of an aqueous solution (this process is often called "liming" when using lime and water or "bucking" when using wood ash (lye) and water), then scraping over a beam with a somewhat dull knife, then drying. The two aforementioned solutions for removing the hair also act to clean the fiber network of the skin and allow penetration and action of the tanning agent, so that all the steps in preparation of rawhide except drying are often preludes to the more complex process of tanning and production of leather[(1)].

Tanning can be performed with either vegetable or mineral methods. Before tanning, the skins are unhaired, degreased, desalted and soaked in water over a period of 6 hours to 2 days. To prevent damage of the skin by bacterial growth during the soaking period, biocides, typically dithiocarbamates, are used. Fungicides such as TCMBT, 2-(Thiocyanomethylthio) benzothiazole, are added later in the process to protect wet leathers from mould growth. After 1980 the use

of pentachlorophenol and quicksilver based biocides and their derivatives was forbidden[1].

1.1.1 Preparatory steps prior to tanning

1.1.1.1Skinning

The actual tanning process begins with the obtaining of an animal skin. When an animal skin is to be tanned, the beast is killed and skinned before the body heat leaves the tissues. This can be done by the tanner, or by obtaining a skin at a slaughterhouse or farm.[2]

1.1.1.2Curing

Preparing hides begins by curing them with salt. Curing is employed to prevent putrefaction of the protein substance (collagen) from bacterial growth during the time lag that might occur from procuring the hide to when it is processed. Curing removes excess water from the hides and skins using a difference in osmotic pressure. The moisture content of hides and skins gets greatly reduced. In wet-salting, the hides are heavily salted, then pressed into packs for about 30 days. In brine-curing the hides are agitated in a salt water bath for about 16 hours. Generally speaking, curing substantially reduces the chance of spoilage by bacteria. Curing can also be done by preserving the hides and skins at a very low temperature[2].

1.1.1.3 Beamhouse operations

The steps in the production of leather between curing and tanning are collectively referred to as *beamhouse operations*. They include, in order, soaking, liming,

removal of extraneous tissues (unhairing, scudding, and fleshing), deliming, bating (including puering), drenching, and pickling.[3][4]

1.1.1.4 Soaking

In the process known as *soaking*, the hides are soaked in clean water to remove the salt left over from curing and increase the moisture so that the hide or skin can be further treated[4].

1.1.1.5Liming

After soaking, the hides and skins are taken for *liming*: treatment with milk of lime (a basic agent) that may involve the addition of "sharpening agents" (disulfide reducing agents) like sodium sulfide, cyanides, amines etc. The objectives of this operation are mainly to:

- Remove the hairs, nails and other keratinous matter
- Remove some of the interfibrillary soluble proteins like mucins
- Swell up and split up the fibres to the desired extent
- Remove the natural grease and fats to some extent
- Bring the collagen in the hide to a proper condition for satisfactory tannage

The weakening of hair is dependent on the breakdown of the disulfide link of the amino acid called cystine, which is the characteristic of the keratin class of protein that gives strength to hair and wools (keratin typically makes up 90% of the dry weight of hair). The hydrogen atoms supplied by the sharpening agent weaken the cystine molecular link whereby the covalent disulfide bond links are ultimately ruptured, weakening the keratin. To some extent, sharpening also contributes to *unhairing*, as it tends to break down the hair proteins.

The isoelectric point of the collagen in the hide (this is a tissue strengthening protein unrelated to keratin) is also shifted to around 4.7 due to liming[1].

1.1.1.6Unhairing and scudding

Main article: Unhairing

Unhairing agents used at this time are: Sodium sulfide, sodium hydroxide, sodium hydrosulfite, calcium hydrosulfide, dimethyl amine, and Sodium sulfhydrate. The majority of hair is then removed mechanically, initially with a machine and then by hand using a dull knife, a process known as *scudding*[1].

Tanner year 1609

1.1.1.7 Deliming and bating

Main article: Deliming

The pH of the collagen is brought down to a lower level so that enzymes may act on it, in a process known as *deliming*. Depending on the end use of the leather, hides may be treated with enzymes to soften them, a process called *bating*[1].

1.1.1.8 Pickling

Once bating is complete, the hides and skins are treated with a mixture of common (table) salt and sulfuric acid, in case a mineral tanning is to be done. This is done to bring down the pH of collagen to a very low level so as to facilitate the penetration of mineral tanning agent into the substance. This process is known as *pickling*. The common salt (sodium chloride) penetrates the hide twice as fast as the acid and checks the ill effect of sudden drop of pH.Peeling bark for the tannery in Prattsville, New York, during the 1840s, when it was the largest in the world.

1.1.2 Type of tanning :

1.1.2.1Vegetable tanning

Vegetable tanning uses tannin. The tannins (a class of polyphenol astringent chemical) occur naturally in the bark and leaves of many plants. Tannins bind to the collagen proteins in the hide and coat them causing them to become less water-soluble, and more resistant to bacterial attack. The process also causes the hide to become more flexible. The primary barks, processed in bark mills and used in modern times are chestnut, oak, redoul, tanoak, hemlock, quebracho, mangrove, wattle (acacia; see catechu), and myrobalan[*disambiguation needed*]. Hides are stretched on

frames and immersed for several weeks in vats of increasing concentrations of tannin. Vegetable tanned hide is flexible and is used for luggage and furniture[1].

1.1.2.2 Chrome tanning

Prior to the introduction of the basic chromium species in tanning, several steps are required to produce a tannable hide. These steps include: Scudding (removing the hair), Liming (the introduction of alkali agents such as sodium hydroxide), Deliming (restoring neutral pH), Bating (softening the skin with enzymes), and Pickling (lowering pH of the hide with salt and sulfuric acid). The pH is very acidic when the chromium is introduced to ensure that the chromium complexes are small enough to fit in between the fibers and residues of the collagen. Once the desired level of penetration of chrome into the substance is achieved,the pH of the material is raised again to facilitate the process. This step is known as "basification". In the raw state chrome tanned skins are blue and therefore referred to as "wet blue." Chrome tanning is faster than vegetable tanning (less than a day for this part of the process) and produces a stretchable leather which is excellent for use in handbags and garments[1].

1.1.2.2.1 Chemistry of chrome tanning

Chromium(III) sulfate ($[Cr(H_2O)_6]_2(SO_4)_3$) has long been regarded as the most efficient and effective tanning agent.[7][8] Chromium(III) compounds of the sort used in tanning are significantly less toxic than hexavalent chromium. Chromium(III) sulfate dissolves to give the hexaaquachromium(III) cation, $[Cr(H_2O)_6]^{3+}$, which at higher pH undergoes processes called olation to give polychromium(III) compounds that are active in tanning,[4] being the cross-linking of the collagen subunits. The chemistry of $[Cr(H_2O)_6]^{3+}$ is more complex in the tanning bath rather than in water due to the presence of a variety of ligands. Some ligands include the sulfate anion, the collagen's carboxyl groups, amine groups from the side chains of the amino acids, as well as "masking agents." Masking agents are carboxylic acids, such as acetic acid, used to suppress formation of polychromium(III) chains. Masking agents allow the tanner to further increase the pH to increase collagen's reactivity without inhibiting the penetration of the chromium(III) complexes[5].

Collagen is characterized by a high content of glycine, proline, and hydroxyproline, usually in the repeat -gly-pro-hypro-gly-.[5] These residues give rise to collagen's helical structure. Collagen's high content of hydroxyproline allows for significant cross-linking by hydrogen bonding within the helical structure. Ionized carboxyl groups (RCO_2^-) are formed by hydrolysis of the collagen by the action of hydroxide. This conversion occurs during the liming process, before introduction of the tanning agent (chromium salts). The ionized carboxyl groups coordinate as ligands to the chromium(III) centers of the oxo-hydroxide clusters[6].

Tanning increases the spacing between protein chains in collagen from 10 to 17 Å.[6] The difference is consistent with cross-linking by polychromium species, of the sort arising from olation and oxolation[7].

Subsequent to application of the chromium agent, the bath is treated with sodium bicarbonate to increase the pH to 4.0–4.3. This increase induces cross-linking between the chromium and the collagen. The pH increase is normally accompanied by a gradual temperature increase up to 40 °C.[8] Chromium's ability to form such stable bridged bonds explains why it is considered one of the most efficient tanning compounds. Chromium-tanned leather can contain between 4 and 5% of chromium.[7] This efficiency is characterized by its increased hydrothermal stability of the skin, and its resistance to shrinkage in heated water.[9]

A 2013 study by the University of Dhaka found that, boiling and sun-drying can convert other types of chromium into carcinogenic hexavalent chromium. This hexavalent chromium runoff and scraps are then consumed by animals, in the case of Bangladesh, chickens (the nation's most common source of protein). Up to 25% of the chickens in Bangladesh contained harmful levels of hexavalent chromium, adding to the national health disaster.[10]

1.1.2.3 Tanning with other minerals

As chrome tanned hides and skins are called 'wet blue', other forms of tanning like the ones based on alum, zirconium, titanium, iron salts or a combination thereof lead to 'wet white'. Wet white is also a semi finished stage like wet blue, but is much more eco friendly. The shrinkage temperature of wet white varies from 70 to 85 degree Celsius, while that of wet blue varies from 95 to 100 degree Celsius[11].

1.1.3 Anthraquinone

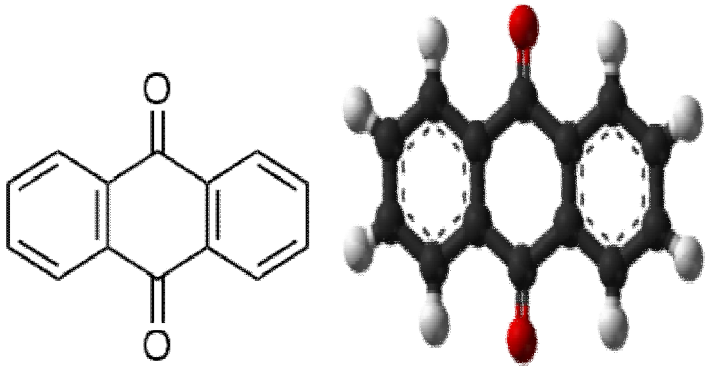


Fig (1) anthraquinone[12]

Anthraquinone, also called **anthracenedione** or **dioxoanthracene**, is an aromatic organic compound everal isomers are possible, each of which can be viewed as a quinone derivative. The term anthraquinone, however, almost invariably refers to one specific isomer, **9,10-anthraquinone** (IUPAC: 9,10-dioxoanthracene) wherein the keto groups are located on the central ring. It is a building block of many dyes and is used in bleaching pulp for papermaking. It is a yellow highly crystalline solid, poorly soluble in water but soluble in hot organic solvents. For instance, it is almost completely insoluble in ethanol near room temperature but 2.25 g will dissolve in 100 g of boiling ethanol[12].

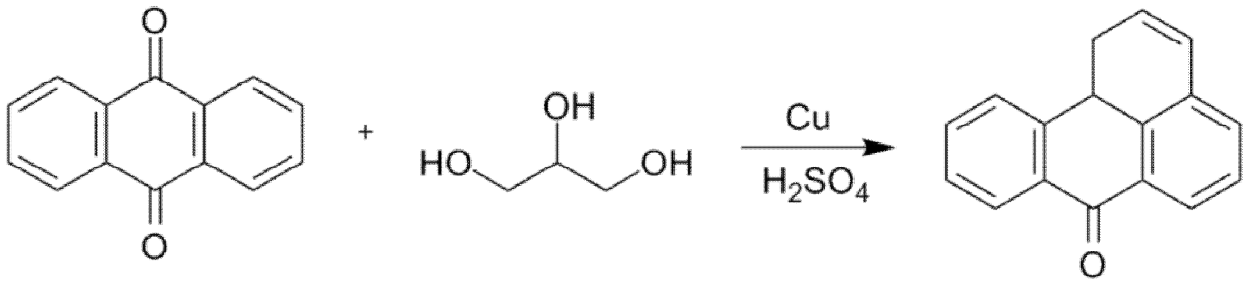
1.1.3.1Properties	
Molecular formula	$C_{14}H_8O_2$
Molar mass	208.21 g mol^{-1}
Appearance	yellow solid
Density	1.308 g/cm^3
Melting point	286 °C (547 °F; 559 K)
Boiling point	379.8 °C (715.6 °F; 653.0 K)

1.1.3.2 Synthesis

9,10-Anthraquinone is obtained industrially by the oxidation of anthracene, a reaction that is localized at the central ring. Chromium(VI) is the typical oxidant. It is also prepared by the Friedel-Crafts reaction of benzene and phthalic anhydride in presence of $AlCl_3$. The resulting o-benzoylbenzoic acid then undergoes cyclization, forming anthraquinone. This reaction is useful for producing substituted anthraquinones. The Diels-Alder reaction of naphthoquinone and butadiene followed by oxidative dehydrogenation will also produce 9,10-anthraquinone. Lastly, BASF has developed a process that proceeds via the acid-catalyzed dimerization of styrene to give a 1,3-diphenylbutene, which then can be transformed to the anthaquinone.[13] It also arises via the Rickert-Alder reaction, a retro-Diels-Alder reaction[13].

1.1.3.3 Some reactions of the anthraquinone

In a classic (1905) organic reaction called the Bally–Scholl synthesis, named after Oscar Bally and Roland Scholl, anthraquinone condenses with glycerol forming benzanthrone.[14] In this reaction, the quinone is first reduced with copper metal in sulfuric acid (converting one ketone group into a methylene group) after which the glycerol is added[14].



Anthraquinone Glycerol benzanthtrone

Fig (2) [14]

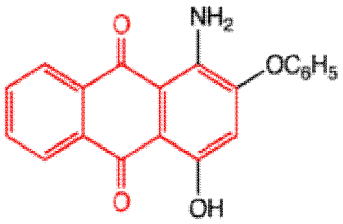
When reduction the anthraquinone yields anthracene, but intermediate reaction products which exhibit trans-annular keto –enol tautomerism can be isolated with ease[15].

When anthraquinone is boiled with mixture of zinc dust and ammonia it gradually dissolves with production of an intense red colour , due to the formtion of the alkali-soluble anthraquinol[15].

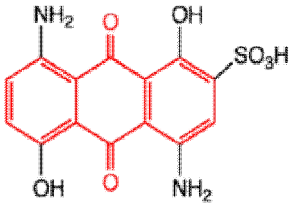
1.1.3.4 Some Applications

1.1.3.4.1Dyestuff precursor

Synthetic dyes are often derived from 9,10-anthraquinone, such as alizarin.[16] Important derivatives are 1-nitroanthraquinone, anthraquinone-1-sulfonic acid, and the dinitroanthraquinone.[15] Natural pigments that are derivatives of anthraquinone are found, inter alia, in aloe latex, senna, rhubarb, and cascara buckthorn, fungi, lichens, and some insects[16].



1-amine, 4- hydroxyl,
anthraquinone octyle ether



4,11-diamine, 1,8-dihydroxy,
anthraquinone, 2-sulfonic acid

Fig (3) (12)

1.1.3.4.2 Digester additive in papermaking

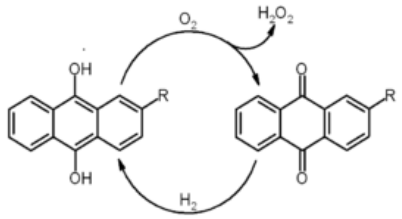
9,10-Anthraquinone is used as a digester additive in production of paper pulp by alkaline processes, like the Kraft, the alkaline sulfite or the Soda-AQ processes.

The anthraquinone is a redox catalyst. The reaction mechanism may involve single electron transfer (SET).[17] The anthraquinone is oxidizing the reducing end of polysaccharides in the pulp, i.e., cellulose and hemicellulose, and thereby protecting it from alkaline degradation (peeling). The anthraquinone is reduced to 9,10-dihydroxyanthracene which then can react with lignin. The lignin is degraded and becomes more watersoluble and thereby more easy to wash away from the pulp, while the antraquinone is regenerated. This process gives an increase in yield of pulp, typically 1-3% and a reduction in kappa number.[18]

Sodium 2-anthraquinonesulfonate (AMS) is a watersoluble anthraquinone derivative that was the first anthraquinone derivative discovered to have a catalytic effect in the alkaline pulping processes.[19]

1.1.3.4.3 In the production of hydrogen peroxide

A large industrial application of anthraquinones is for the production of hydrogen peroxide. 2-Ethyl-9,10-anthraquinone or a related alkyl derivatives is used, rather than anthraquinone itself.[20]



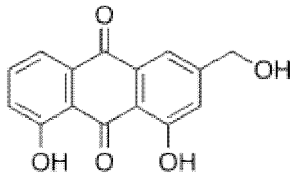
Anthracene Anthraquinone

Fig (4) [20]

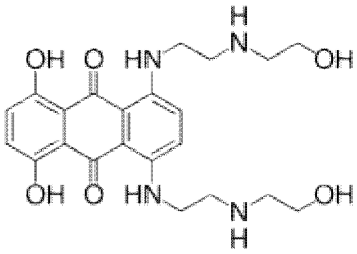
1.1.3.4.4 Medicine

Derivatives of 9,10-anthraquinone include many important drugs (collectively called **anthracenediones**). They include

- Laxatives such as dantron, emodin, and aloe emodin, and some of the senna glycosides
- Antimalarials such as rufigallol
- Antineoplastics used in the treatment of cancer, such as mitoxantrone, pixantrone, and the anthracyclines
- DNA dyes / nuclear counterstains such as DRAQ5, DRAQ7 and CyTRAK Orange for flow cytometry and fluorescence microscopy.



Aloe emodin



Mitoxantrone

Fig (5) [21]

Fig (6) [22]

1.1.3.4.5 Niche uses

9,10-Anthraquinone is used as a bird repellant on seeds and as a gas generator in satellite balloons.[23]

Natural anthraquinone derivatives tend to have laxative effects. Prolonged use and abuse leads to melanosis coli.[24][25] 5 anthraquinones have been shown to inhibit the formation of Tau aggregates and dissolve paired helical filaments thought to be

critical to Alzheimer's disease progression in both mouse models and in vitro testing but have not been investigated as a therapeutic agent[26]

1.1.3.5 Other isomers

Several other isomers of anthraquinone are possible, including the 1,2-, 1,4-, and 2,6-anthraquinones. They are of comparatively minor importance. The term is also used in the more general sense of any compound that can be viewed as an anthraquinone with some hydrogen atoms replaced by other atoms or functional groups. These derivatives include substances that are technically useful or play important roles in living beings[26].

1.1.3.6 Metabolism in humans

The enzyme encoded by the gene UGT1A8 has glucuronidase activity with many substrates including anthraquinones.[27]

1.1.4Senna

Senna (from Arabic *sanā*), the **sennas**, is a large genus of flowering plants in the legume family Fabaceae, and the subfamily Caesalpinioideae. This diverse genus is native throughout the tropics, with a small number of species in temperate

regions. The number of species is estimated to be from about 260[28] to 350.[29] The type species for the genus is *Senna alexandrina*. About 50 species of *Senna* are known in cultivation.[30]

1.1.4.1Chemistry of senna

Senna consists of the dried leaflets or fruits of Cassia senna (C. acutifolia) known in commerce as Alexandrian senna and of Cassia angustifolia commonly known as Tinnevelly senna. The senna plants are small shrubs of Leguminosae cultivated either in Somalia, the Arabian peninsula and near the Nile river. Tinnevelly senna is obtained from cultivated plants mainly in South India and Pakistan. Owing to the careful way in which the plant is harvested, the leaflets of the drug are usually little broken. Damaged leaves and lower quality products are often used for making galenicals. The senna pods (fruits) are collected during the same period as the leaves, then dried and separated into various qualities. The active principle of Senna was first isolated and characterized by Stoll in 1941. The first two glycosides were identified and attributed to the anthraquinone family. These were found to be dimeric products of aloe emodin and/or rhein which were named sennoside A and sennoside B. They both hydrolyze to give the aglycones sennidin A and B and two molecules of glucose. Later work confirmed these findings and further demonstrated the presence of sennosides C and D. Small quantities of monomeric glycosides and free anthraquinones seem to be present as well. The active constituents of the pods are similar to those of the leaves but present in larger quantities. Two naphthalene glycosides isolated from senna leaves and pods are 6-hydroxymusicin glucoside and tinnevellin glucoside. Both compounds can be utilized to distinguish between the Alexandrian senna and the India senna, since tinnevellin glucoside is only found in the latter and the first only in the C. senna[31].

1.1.4.2 Some aglycones of the common anthraquinone glycoside in senna :

1.1.4.2.1 Emodin :

Aloe –emodin (1,8- dihydroxy-3 hydroxy methy1 anthraquinone), occurs in orange red needles (m.p223 °C), solube in acetone , pyripine and glacial acetic acid and less soluble in ethy1 alcooho1, ether and chloroform[31].

It occurs in the free as well as in combined state in senna cascara and aloes[32].

1.1.4.2.2 Chrysophanic acid

Chrysophanic acid (1,8- di hydroxyl-3methyl anthraquinones), occurs in yellow needles (196°C). Soluble in chloroform, springly soluble in alcohol and insoluble in water.

It dissolves in alkalies with red color. Where reduce with zinc dust and dilute acid it is converted into chrysarobin. It occurs in cascara and frangula, rubrab, rhizomes and senna[32] .

1.1.4.2.3 Rhein

Rhein (1,8-dihydroxy anthraquinone 3-carboxylic acid) was first isolated from rubrab rhizomes and was found later to be the parent substance of sennidines in senna[33].

1.1.4.2.4 Sennidine

Sennidines are aglycones of the sennosides, which are the chief glycosides present in senna leaves and pods.

Four sennidines are known A,B,C and D, corresponding to sennosides A,B,C and D. They are dirhein anthrones. The sennidines possess two asymmetric carbon

atoms, at the tow positions number10. The difference between sennidine A and B is stereo chemical.

Sennidine A is optically active, being the laevorotatory isomer, and sennidine B is the meso isomer (being intramolecularly compensated).

In the isomers sennidines C and B sennidine C, is the (-) isomer and sennidine D is the (+) isomer.

Sennidine is a compound having two identical anthrone moieties e.g.sennidine A have two forms (10 S. 10' S and 10 R, 10' R) are possible together with the meso form (sennidine B.). These compounds also occur in the plants as their 1,1 diglucosides[34].

1.1.4.2.5 Sennosides

The sennoside occur as yellow colored crystals. Sennidine A is almost insoluble in water while sennoside B is soluble. Both sennoside are soluble in sodium bi-carbonate and thus solubility is utilized in separating these glycosides containing carboxylic group from other phenolic glycosides present.

It has been shown that aloe-emodin glycoside constituents 12-20% glycoside of the leaves, but constitute only about 2-5 % 0f the total anthracene glycosides of the fruits. Sennoside Aconstitute about 2-5% of the dry leaves and about 3% of the dry fruits. It may be noted here that in the sennosides the anthracene derivative constitute glycones, is in the dianthreone form (diametric form of rhein anthrone) and the two glucose molecules are attached to two different points of the aglycone.

Rhein and rhein -8-glycoside of chrysophanol also occur in senna fruits.

Recently sennoside C and B have been isolated form senna leaves[33].

1.1.4.3 Importance and role of senna glycoside (sennoside) in plants

The glycosides play a vital role in the plant grows. They regulate growth and affect the plant tolerance against insects and pests that infest it[35].

1.1.5 Coordintion compound

Coordination compound or metal complexs are important throughout chemistry and chemical technology.

The first explanation of the bonding in coordination complexes is made by Werner's.

It was put forward before the electronic theory of valenry and for this work Werner won the Noble Prize in chemistry[36].

The chemistry of metallic element , which constitutes80%,of the periodic table , is predominately coordination chemistry[37].

A Coordination compound or complex is formed when Lewis Base called "ligand" is attached to Lewis acid called "accepter" by means of alone pair of electrons.

The ligand may be single negative ion such as halides or may be composed of a number of atoms, the one which directly attached to the accepter is called the donor atom. The metal ion is referred to as the central metal or the coordinated metal. All groups attached directly to central metal atom are coordinating groups or ligands[38].

Ligands are most conveniently classified as mono,bi,tri,tetr,penta and hexa dentate according to the number of donor atoms they contain[39].

Unidentate ligands may be simple monatomic ions suchs as halide ions or polyatomic ions or molecules, which contain donor atom from group(iv),(v),(vi)

such as cyanide ion (CN). This type of ligand (unidentate ligand) forms with a central metal atom or ion a non-chelate complex. Compounds or atom ,which can be used to form a cyclic complex, are called multi dentate ligands. Until recently, progress in the chemistry of d-block or transition elements has occurred a cross two broad fronts classical coordination chemistry and organometallic chemistry . Two separate schools of chemists have tended it. Classical coordination chemistry means, the chemistry of adducts formed by metal in their higher oxidation states bonded to inorganic or organic ions or melcules . Organometallic compound have direct metal –carbon bond with low formal state[40].

1.1.5.1Transition elements and their properties

The three series of elements arising from the filing of the d-orbital are described as transition elements. The transition elements are defined as:

Those elements that have partly filled d-or f-orbitals in any of their commonly occurring oxidation states.[40][41]

The transition elements exbhibt a number of characteristic properties, which together distinguish them form other groups of elements. They are all metals and as such as lustors and deformable . They have high thermal and electrical conductivities. Their melting and boiling points tend to be high .They are generally hard and strong[41].

Most of them display numerous oxidation states.

They have unparalled propensity for forming coordinaton compounds with Lewis bases in general. The tendency to form coordination compounds is shown most strongly by the transition elements but by no means limitedto them.[42][43].

1.1.5.2 Complex formation

The binding of an organic substrate by a metal to form coordination or an organometallic comound often has a powerful influence on the chemical reactivity of the ligand group.

Real “naked” ions exist only in the gas phase at high temperatures. In solutions of metal salts, ions are alwoys solvated although the solvent molecules may be more or less firmly pound to the central ion.

Acomplexation reaction thus involves the replacement of one or several of the solvent molecules by other donor groups. The compexation of a metal ion in aqueous solution .

Here ligand (L) can be either a neutral molecule or a negative ion. Successive replacement of water molecules by other ligand group can occur until the complex (MLn) is formed, where (n) refers to the coordination numbers of the metal ion and represent the maximum number of monodentatee ligands that can bond to it.[43].

1.1.5.3 Stability of the complexes

The stability of a species is a measure of the extent to which this species will be formed from other species under certain condition provided the system reaches equilibrium.

The stability of complex ions varies within very wide limits. It’s quantitatively expressed by means of the stability constant. The more stable the complex, the greater stability constant i.e. the smaller the tendency of the complex ion to dissociate into constituents’ ions. The equilibrium of compex compound in solution can be defined by equations based on the law of mass action. Two groups of reactions may be considered. Reactions leading to mononuclear complex (MLn)

and reactions leading to polynuclear complex (MmLn). The simplest case in-group of mononuclear complexes is represented by n=1 and the stability constant of the reaction M+L--→ ML is defined by the equation.

Kml=[ML]/[M] [L]

But if many ligands are bonud to the central ion, the complex formation will occur stepwise and the equilibrium will be determined, as many constants as there are complexes[43].

1.1.5.4 Anthraquinone complex

Alizarin Lake is an example of anthraquinone complex with metal it is used in paints, printing inks and similar products by dissolving alizarin in a caustic Soda solution and treating with Turkey red oil, Sodium sulfate,aluminum acetate and calcium acetate solution at boiling temperature. By varying the condition treatment lakes of different overtone, undertone, texture and oil absorpation capacity can be prepared

Other anthraquinone mordant and acid dyes are also useful in lake making . turkey red cotanins both aluminum and calcium as part of the the lake produced on the fiber .

The composition varies with the dyeing process and varied structures have therefore been suggested for the alizarin aluminum – calcium complex . Bancroft has made a phase rule study of the reaction between alizarin and alumina and he regarded the lakes as absortion complexes .

The fatty acid used in turkey red dyeing act as dispersing agent for the comlex calcium – aluminm alizarate, and it's not constituents of the complex itself [44] [45].

Fierz-David and Rutis-Nauser regard turkey red lake as a well defined compound isolable in pure form by suitable treatment and contains alizarin, aluminum and calcium in the proportions 4:2:3.The lake crystallizes from pyridine as a pyridine complex.

Calcium may be replace by other metallic radicals including aluminum Geyer and Smith have prepared cobalt,copper and other complexes of 1-hydroxyl anthraquinone and the copper complex of 2-acetylalizarin and have suggested analytical and spectral[44] [45] [47].

1.1.6 Photochemistry

Photochemistry is a science which deals with chemical reactions caused by exposure of reactants to light radiation.

The light radiation of the visible and ultra violet region, lying between 800nm to 200nm wave length, are chiefly responsible of bringing about photochemical reactions.

Photochemical reactions have been defined therefore as those reactions, which occur on the absorpation of light radiation (Photons) [46].

The photons supply the necessary energy to the reactants enabling them to react to yield products.

Photochemical reactions can be classified as oxidation, reduction, decomposition, hydrolysis and polymerization. Some of the photochemical reaction such as conversion of oxygen into ozone and decomposition of ammonia into nitrogen and hydrogen are accompanied by an increace in free energy unlike ordinary ,(or dark) reactions, which are invariably, accompanied by a decrease in free enerqy.

Photosynthesis of carbohydratres from carbon dioxide and water taking place in nature is another reaction, which is accompanied by an increase in energy absorbed by reactants, which is converted into products[46].

1.1.6.1 Some method of photochemical

1.1.6.1.1 Photodissocation

It's the braking of chemical bonds by radiant energy. The importance of photochemical processes can be investigated by considering ozone in the atmosphere.

Ozone prevents ultraviolet radiation being emitted by the sun from reaching the earth surface. The formation of ozone starts with the photo dissociation of oxygen molecules by solar radiation at wavelength below 240nm

The highly reactive (O) atoms combine with oxygen molecules to form ozone as follows:

$O+O2+M \rightarrow O3+M$

Where "M" being some inret substance such as N2. The role of M in this exothermic reaction is to absorb some of the excess energy released and prevent the spontaneous decomposition of the O3 of molecule.

The energy that is not absorbed by M is given off as "M" molecules themselves, become de-excited, they release heat to the surrounding. In addition, ozone itself absorb UV light between 200 and 300nm.

Various optical methods have been applid for the investigation of the empirical formula of coloured complexes[46].

1.1.6.1.2 continuous variation method

was worked out by Denison.[48] in connection with his studies of compound formation in liquid mixtures

Later it was applied by job, to the spectrophotometer determination of the formulaof the complexes that are products of incomplete equilibrium reactions, and modified by Vospurgh and Copper[49].

The equation for such equilibrium reaction may be written as:-

mM+nL=MnLn

A series of the solutions is prepared in which the sum of the total concentration of M and L is constant but their proportions were continuously varied:

Cm+CL= constant

In practice, equimolar solution of the two reactants were mixed in varying ratios and the absorbance of earth mixture was determined at the selected wavelength. The ratio that corresponds to the mole ratio of the components in the complex will have the highest absorbance. Plots of the corrected measured absorbance against the volume of either solution added yield curves with maxima.

From the position of the maximum on the graph one may easily determine the value of n and the formula of the complex[49].

1.1.7 Pollution problems resulting from anthraquinone

As in many other industrial sectoes growing concern about enviroumental issues have prompted the textile industry to investigate more appropriate and environmemtal friendly treatment technologies to meet the discharge consent, as it is becoming stricter everyday.

Textile preparation, dyeing and finishing plants are currently being forced to treat their effluents at least partially prior to discharge publicly owned treatment work due to the high organic load, stronge and resistant color as well as high dissolved solids content of the discharged wastewater.[50][51][52].

The Objective of this work is :

- Extract the anthraquinone from Sudanese senna.
- Prepare metal complexes of sennidine and study their photostability.

2. Experimental

2.1 Preparation of senna

Senna Alexandria (cassia actuifolia) pods were washed, air dried in shade and then turned into fine powder using pistol and mortar. The powder was sieved through a sieve No. 180 (Retch 5657 HAA N Germany), and the fine powder was then kept in drak glass containers appropriately labeled and stored in dry cool place till needed[15].

2.2 Extraction of sennosides (sennedine)

2.2.1 Apparatus

2.2.1.1 Centrifuge

2.2.1.2 Sieves

2.2.1.3 Separating funnal

2.2.1.4 Reflux condenser

2.2.1.5 Volumertic flask

2.2.1.6 Water bath

2.2.1.7 Round bottomed flask

2.2.1.8 Test tube

2.2.1.9 Beakers

2.2.2 Chemical and solvents

2.2.2.1 Distilled water

2.2.2.2 Diethyl ether (Anlar grade)

2.2.2.3 Hydrochloric acid (Anlar grade)

2.2.2.4 Ferric chloride solution (5%)

2.2.2.5 Chloroform (Anlar grade)

2.2.2.6 Sodium hydrogen carbonate

2.2.3 Extraction procedure (extraction of anthraqunione)

A sample of 0.15 g powder senna was taken, 30 ml distilled water were added then the mixture was weighted and heated under reflux condenser in water bath for 15 minutes.

The mixture was allowed to cool and the original weight was with water. Then centrifuged for 10 minutes and 20 ml of the supernatant liquid was transferred to a 150 ml separating funnal.

0.1ml of 2M HCl was added and then shaken three times with 15 ml quantities of chloroform each. The aqueous layer was allowed to separate then the chloroform layer was discharged . 0.1 g of Sodium hydrogen carbonate powder was added and the mixture was shaked for 3 minutes, the aqueous layer was centrifuged. 10 ml of the supernatant liquid was transferred to 100 ml round bottomed flask fitted with a ground glass stopper . 20 ml of ferric chloride solution(5%) was added and heated under reflux condenser in a water bath for 20 minutes.

1ml of HCl (conc) was added to the mixture and heated on a water bath for another 20 minutes and shaked frequently until the precipitate was dissolved.

The mixture was transferred ta a separating funnel.

Then extracted with three quantities each of 25 ml of diethyl ether.

he ether extract were combined and washed twice each time with 15ml 0f distilled water. The ether extract placed in a 100 ml volumetric flask and diluted to 100 ml with ether . 10 ml were taken and evaporated to dryness[15].

2.2.4 Test for anthraquinones in natural extract

0.5g of plant extract is shaken with 10 ml of benzene and filtered. 5ml of 10% ammonia is added to the filtrate. The mixture is shaken and the presence of red or pink or violet colour that detected. They in found anthraquinon.[53] .

2.3 Preparation of the anthraqunione

Was weighted 5.0 g of powdered anthracene and 50 ml 0f glacial acetic acid in a 250 ml two necked round – bottomed flask with a reflux condenser and a dropping funnel. Then mixed the flask contents thoroughly by a swirling action and heat the mixture to reflux when most of the anthracene dissolves. Then was addad 10.0 g of chromium trioxide in 7-8 ml of water , then was added 25 ml of glacial acetic acid and pour the well –stirred mixture into the dropping funnel.Then was removed the heat source from the flask and added slowly the oxidizing reagent at such a rate that the mixture continues to reflux (7-10 minutes) ; then was refluxed for a further 10 minutes when all the anthracene will have reacted completely. Then was cooled the solution and pour into 250ml of cold water. Then stirring the mixture vigorously, then filtered the precipitated anthraquinone with 50ml of hot 1M sodium hydroxide solution and finally with much cold water; drain well. Then was drying the anthraquinone by pressing it between several sheets of filter paper and leave it over night in a desiccator over calcium chloride.[13]

2.3.1 Purification of the anthraquinone

Recrystallise the curde product from boiling glacial acetic acid with the of decolourising charcoal, then was washed the resulting crystals on the Bucher funnel with little cold rectified spirit then was drying in the air.[13]

2.4 Atomic absorpation analysis for tanning solution

2.4.1 apparatus

2.4.1.1 atomic absorpationt spectrophotometer

2.4.1.2 chromium hollow cathode lamp

2.4.1.3 volumetric flask (50ml)

2.4.1.4 volumetric flask (100ml)

2.4.2 metarials

2.4.2.1 tanning solution

2.4.2.2 chromium standared

2.4.2.3 distilled water

2.4.3 atomic spectra

In the first was prepared standared solutions from chromium standared ,

then was putting blank solution in the device , then was putting prepared standared in the device, after that was putting the sample in device, then was being the device working and give result.

2.5 Preparation the chromium(vi)

2.5.1 Apparatus

2.5.1.1 Pippet

2.5.1.2 Beakers

2.5.1.3 Dropper

2.5.2 Metarials

2.5.2.1 chromium (iii) solution(from tanning)

2.5.2.2 Sulforic acid (conc)

2.5.2.3 Sodium sulfate

2.5.3 Prepared procedure

Was taking 30ml of chromium(iii) solution , then was added sulfuric acid drop – drop to convert the colour solution to orange , then was added 0.1g of sodium sulfate.

2.6 Preparation of sennidine and prepared anthraquinone Cr complexes

2.6.1 Apparatus.

2.6.1.1 Water bath

2.6.1.2 Round bottomed flask

2.6.2 Metarials

2.6.2.1 Sennidine powder

2.6.2.2 Distilled water

2.6.2.3 Prepared anthraqunione

2.6.2.4 Chromium (vi) solution(4%)

2.6.2.5 Calcium carbonate(6%

2.6.3 Preparation procedure

0.8 g of pure sennidine extracted from senna or prepared anthraquinone were placed in a round bottom flask and 20ml of distilled water was added, then chromium (vi) solution (4%) was added and the mixture was placed in water bath for minutes, then solution of calcium carbonate(6%) was added , then the mixture was left in a water bath for 30 minutes . after that the complex precipitates in the bottom of the flask [15].

2.7 IR analysis of tanning solution, prepared and extracted sennosidesCr. Prepared anthraqunione Cr complex

2.7.1 Apparatus

2.7.1.1 IR spectrophotometer (shimadzu).

2.7.2 Metarials

2.7.2.1 Senndine powder

2.7.2.2 Prepared antrhaqunione

2.7.2.3 Extracted sennosides and prepaed anthraqunione complexes

2.7.3 Infrared spectra

KBr pellets of sennidine , prepared anthraquinone, and sennidine , prepared anthraqunione complexes,was prepared by finally grinding 2 parts of sennidine sample with about 200 parts 0f dried potassium bromide (spectroscopics grade).

Computerized spectrophotometer was used to obtain the IR spectra.

The computer was switched on IR program was started the menu was displayed and scanned, back ground was done , the sample disc was mounted into the sample cell and was introduced into the instrument sample compartment so the sample was scanned by starting the scan program.

Spectra were printed via the user friendly software interface. [15]

2.8 Determination of some physiochemical properties of sennidine, anthraqunione complexes with Cr

2.8.1 Solubility

The solubility were tested in number of solvents (ether- methanol- water – hydrochloric acid- chloroform) [15]

3- Result and discussion:

3.1 EXTRAVTION of sennidine:

Sennidine was extracted using the procedure mentioned in section 2.2.3.

Senna contained, sterol, carbohydrates, terpinoils, alkaloids, flavanoids tannins, and anthraquinone.

Sudan senna pods which contained sennoside (sennidine) between 2.5%-4.5% in the Alexandrian senna [55] .

The percentage of sennidine content extracted from different Sudanese samples cited above agress wiyh published clader [55] .

However samples collected form medicinal and aromatic plants research institute farm , had higher percentage of sennidine content 6.9%. it has been reported by other researcher that , senna grow in farm usually contain higher sennidine content compared to wildly grow senna [56].

3.2 test for anthraguinones in natural extract

The mixture after skakened give red color, that detected to presances of the anthraqunione [53].

3.3 preparation of the anthraquinone:

This prepared gives yellow crystals, then purification, then reacted was alkali solution and give red colour [53].

3.4 Solubility test:

Solubility test of sennidine sample was carrid out using methanol, water, hydrochloric acid (conc), chloroform.

Result showen in table (1)

No	Solvent	Solubility
1	Diethyl ether	Highly soluble
2	Methanol	Soluble
3	Water	Insoluble
4	Chloroform	Soluble
5	Hydrochloric acid (conc)	Highly soluble

The same above solvents were used to test the solubility of sennidine chromium complex.

They were found to be insoluble in all solvents except in HCl(conc).

3.5 IR spectra characteristic functional group frequency of tanning solution:

Result showen in table (2):

Group fraguency	IR absorption frequencies of sennidine	Absorption frequencies of sennidine functional groups (literature)
O-H	33267.48cm^{-1}	3200-3600cm^{-1}
C=O	1652.88cm^{-1}	1670-1760cm^{-1}

C-H	3078.18cm^{-1}	3000-3100cm^{-1}
C=C	1554.52cm^{-1}	1580-1600cm^{-1}
C-C-O	1128.28cm^{-1}	1000-1260cm^{-1}

Table (2) IR spectra characteristic functional group frequencies often tanning solution in KBr.

Infrared is one of the most important spectroscope tools in structure elucidation.

It provides an excellent means towards identification of the different functional. Groups associated with molecule.

The results were tabulated in the table (2) and TR spectra was given in figure(7) for tanning solution which of the greatest interest lies between 1500-1714cm^{-1} . this part of the spectrum is often called the double bond region were bonds C=O, C=N, C=C shown stronge absorpation[57] .

The group of compounds characteristic by an aromatic ring diplay different absorpation C=O, the phenomena can be explained through electron donating and electron with drawing of the different substituent attached to the aromatic ring . this electron donating properties tend to increase the electron could over the ring system of sennidine causing shift form the standared band for C=O group[58].

M + Formalin + dimethylamine
%T
80
90
100
110
120
3840.69
3737.76
3626.92
3367.48
3174.61
3076.10
2779.23
2349.14
1652.88
1564.82
1463.87
1390.37
1268.36
1128.28
1012.60
4000
3500
3000
2500
2000
1500
1000

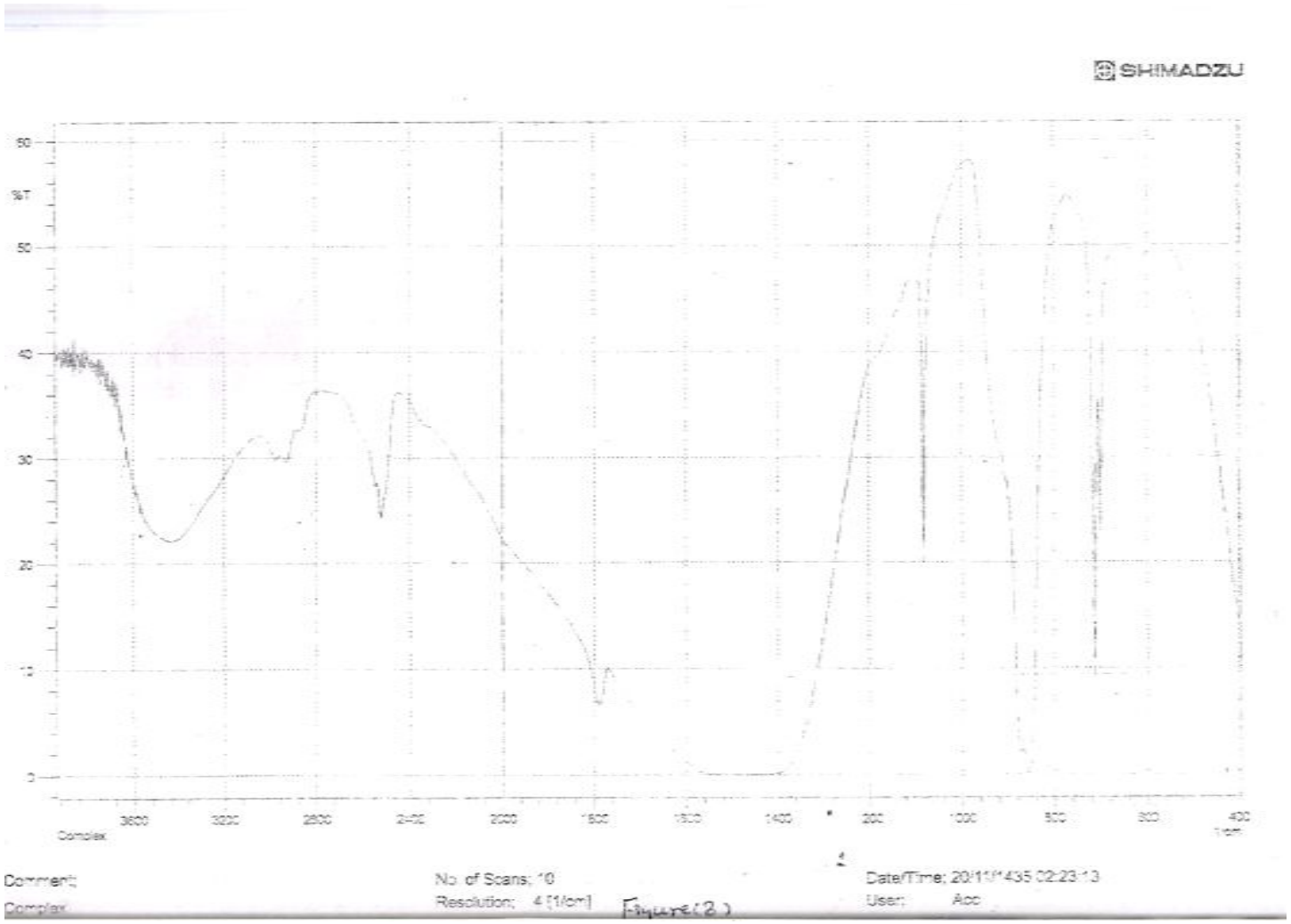
Fig (4)

3.6 IR spectra chromium (vi) sennidine complex:

Charactertristic functional group of chromium (vi) sennidine complex is shown in table (3)

Results showen in table (3)

Group frequency	**Absorpation in cm^{-1} observed**	**Absorpation in cm^{-1} literature**
O-H	3400.62cm^{-1}	3200-3600cm^{-1}
C=C	1558.54cm^{-1}	1520-1600cm^{-1}
C=O	1760 cm^{-1}	1670-1760cm^{-1}
C-C-O	1082.10cm^{-1}	1000-1260cm^{-1}
CH_2	700.18cm^{-1}	600-720cm^{-1}


SHIMADZU
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Complex
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Complex
No. of Scans: 10
Resolution: 4 [1/cm]
Date/Time: 20/11/1435 02:23:13
User: Acc

Figure(2)

The IR spectra of chromium (vi) complex showed the most characteristic bands associated with the sennidine functional group due (O-H, CO, CC, C-C—O, and CH_2).

The band between ($3700cm^{-1}$-$2700cm^{-1}$) correspounds to stretching vibration of (O-H, N-H, C-H)

The band between $2700cm^{-1}$-$3600cm^{-1}$ lies in the band of O-H group and movement of hydrogen caused the stretching.

The aromatic rings give four absorbance bond in ($1580cm^{-1}$- $1600cm^{-1}$) for C=C menthlen group (CH_2) due to:

1-Scissoring.

2- Wagging.

3- Twisting.

4- Rocking.

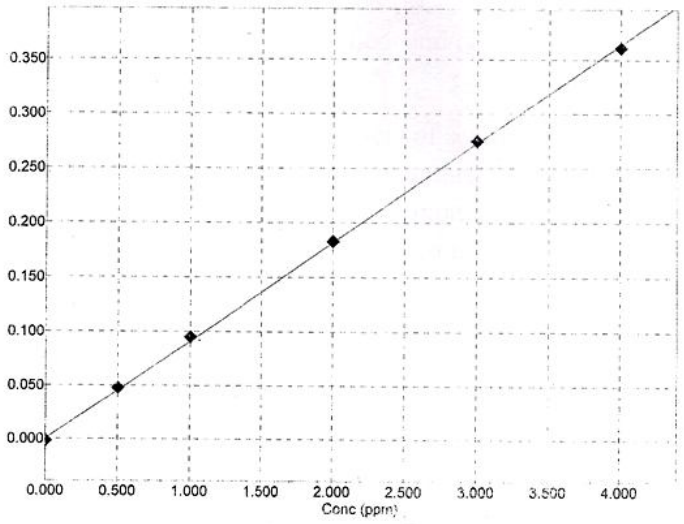
The broad in ($1670cm^{-1}$ -$1760cm^{-1}$) region present in all free ligands was attributed to the ketontic carbonyl [57] [58].

3.7 Atomic spectrum of taning solution:

From this curve they was found the concentration of the chromium in the tanning solution is 0.3608A, also was found the concentration of chromium in the sample 4.0000ppm.

Action	Sample ID	Ture value	Conc ppm	Abs	Df	Actual Conc
BIK				0.0033		
BIK				0.0031		
BIK-AV				0.0032		
STD	STD1		0.0000	-0.0019		
STD	STD1		0.0000	-0.0019		
STD-AV	STD1		0.0000	-0.0019		
STD	STD2		0.5000	0.0494		
STD	STD2		0.5000	0.0458		
STD-AV	STD2		0.5000	0.0476		
STD	STD3		1.000	0.0952		
STD	STD3		1.000	0.0943		
STD-AV	STD3		1.000	0.0948		
STD	STD4		2.000	0.1825		
STD	STD4		2.000	0.1832		
STD-AV	STD4		2.000	0.1828		
STD	STD5		3.000	0.2750		
STD	STD5		3.000	0.2742		
STD-AV	STD5		3.000	0.2746		
STD				0.3602		
STD			4.000	0.3612		
UNK-AV			4.000	0.3607		
UNK-AV				1.7450		
UNK-AV				1.7455		

Calibration Curve(Element:Cr:Flame C#:01)



Abs=0.09692 55Conc+ 0 r=0.9998

CONC	ABS
0.0000	-0.0019
0.5000	0.0176
1.0000	0.0948
2.0000	0.1828
3.0000	0.2746
4.0000	0.3607

Figure(9)

Conclusion and recommendation:

Conclusion:

The fallowing points can be concluded and \ or recommended according to the result of this work:

1. Farm grown senna has higher content sennidine.
2. Anthraquinone can be prepared from anthracene.
3. The study the chemistry of Anthraquionone.
4. Chromium (III) Transfered to chromium (VI) in tanning solution abd prepared complex with sennidine extracted.
5. The complex prepared used to waste treatment tanning.

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