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DEPARTMENT OF CHEMISTRY

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OPTION: INORGANIC CHEMISTRY

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SORPTION OF HEAVY METALS(NICKEL,LEAD,CHROMIUM) IONS BY USING PINE TAR

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شكر و عرفان

قـال رسول الله صلى الله عليه و سلم'' :من لم يشكر الناس لم يشكر الله ''صدق رسول الله صلى الله عليه و سلم

الحمد لله على إحسانه و الشكر له على توفيقه و إمتنانه و نشهد أن لا إله إلا الله وحده لا شريك له تعظيما لشأنه و نشهد أن سيدنا و نبينا محمد عبده و رسوله الداعي إلى رضوانه صلى الله عليه و على آله و أصحابه و أتباعه و سلم .بعد شكر الله سبحانه و تعالى على توفيقه لنا لإتمام هذا البحث المتواضع أتقدم بجزيل الشكر إلى الوالدين العزيزين الذين أعانوني و شجعوني على الإستمرار في مسيرة العلم و النجاح، و إكمال الدراسة الجامعية و البحث؛ كما أتوجه بالشكر الجزيل إلى من شرفتني بإشرافها على مذكرة بحثي الأستاذة الدكتورة"ميلودي صفية" التي لن تكفي حروف هذه المذكرة لإيفائها حقها بصبرها الكبير علي، ولتوجيهاتها العلمية التي لا تقدر بثمن؛ و التي ساهمت بشكل كبير في إتمام و إستكمال هذا العمل؛ كما أتوجه بخالص شكري و تقديري إلى كل الأساتذة الذين اشرفوا على تصحيح وتقيم هذا العمل وهم : البروفيسور قايد محمد والبروفيسور مصطفاي أسماء والدكتورة زاوي فتيحة والدكتورة رمضاني أمينة وكل ساعدني من قريب أو من بعيد على إنجاز و إتمام هذا العمل. **'' رب أوزعني أن أشكر نعمتك التي أنعمت علي و على والدي و أن أعمل صالحاً ترضاه و أدخلني برحمتك في عبادك الصالحين''**

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ABREVIATIONS LIST

ΔS^0: the standard molar entropy

ΔH^0: The standard enthalpy

ΔG^0: the Gibbs free energy

Kj :kilojoule

^{0}C: Celsius degrees

Trn: turns

T: temperature

t: time

pH: potential of Hydrogen

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Diverse amounts of heavy metals may be found everywhere; in soils, water, sediments, plants, and the Arctic. The emission sources of these xenobiotics have been studied for several years in order to reduce pollution.[1]

Control of water pollution has reached primary importance in developed and a number of developing countries. The prevention of pollution at source, the precautionary principle and the prior licensing of wastewater discharges by competent authorities have become key elements of successful policies for preventing, controlling and reducing inputs of hazardous substances, nutrients and other water pollutants from point sources into aquatic ecosystems.

In a number of industrialised countries, as well as some countries in transition, it has become common practice to base limits for discharges of hazardous substances on the best available technology. Such hazardous water pollutants include substances that are toxic at low concentrations, some water pollutants which become extremely toxic in high concentrations are, however, needed in trace amounts. Copper, zinc, manganese, for example, can be toxic or may otherwise adversely affect aquatic life when present above certain concentrations, although their presence in low amounts is essential to support and maintain functions in aquatic ecosystems. The same is true for certain elements with respect to drinking water. Selenium, for example, is essential for humans but becomes harmful or even toxic when its concentration exceeds a certain level. The concentrations above which water pollutants adversely affect a particular water use may differ widely. Water quality requirements, expressed as water quality criteria and objectives, are use-specific or are targeted to the protection of the most sensitive water use among a number of existing or planned uses within a catchment.

Water quality criteria are developed by scientists and provide basic scientific information about the effects of water pollutants on a specific water use. They also describe water quality requirements for protecting and maintaining an individual use. Water quality criteria are based on variables that characterize the quality of water and/or the quality of the suspended particulate matter.

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[1] A. Dube R. Zbytniewski1 T. Kowalkowski1 , E. Cukrowska, B. Buszewski1Department of Environmental Chemistry and Ecoanalytics, 87-100 Torun, Adsorption and Migration of Heavy Metals in Soil .2000.

Most industrial processes pose less demanding requirements on the quality of freshwater and therefore criteria are usually developed for raw water in relation to its use as a source of water for drinking-water supply, agriculture and recreation, or as a habitat for biological communities. Criteria may also be developed in relation to the functioning of aquatic ecosystems in general. The protection and maintenance of these water uses usually impose different requirements on water quality and, therefore, the associated water quality criteria are often different for each use.[2]

There are many methods for depollution of water, this method divided into synthetic and natural method; in this research we use pine tar as natural substance for depollution of water from heavy metals such as nickel, lead and chromium.

This research divide into two part theorical and experimental part. the theorical part contain three chapters:

Pine tree and pine tar.

Water pollution and heavy metals.

Adsorption and method analyses.

And experimental part contains also three chapter:

Extraction of pine tar.

Thermodynamic and kinetic study.

Comparison between the spectrum of the tar before and after adsorption for three metals.

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[2] Richard Helmer and Ivanildo Hespanhol book :Water Pollution Control - A Guide to the Use of Water Quality Management Principles First edition 1997

I. Tree pine and wood tar:

I.1 Generality on wood[1]:

Wood is an important source of raw materials widely used in the chemical industry. Wood is mainly composed of three natural polymers (cellulose, hemicellulose and lignin) constituting the cell wall and which form the largest part of the wood, but there is also a variable amount, according to wood species, of low molecular weight organic compounds called extractables. They are of various natures and consist mainly of terpenes, constituting the majority of essential oils and tannins (chemical compounds of phenolic nature). The economic and industrial interest of this fraction makes these compounds high value-added products that are highly sought after in various sectors such as perfumery, cosmetics, pharmaceuticals and agrifood.

In a world where oil resources are becoming scarce and polymeric materials are very important, obtaining polymers from natural products is proving to be most interesting.

I.1.1 Introduction:

Wood is a noble material, a composite of plant origin, produced by living trees[2]. The chemical compositions of different varieties of wood can be seen in Table I.1.1

Table I.1.1: Chemical compositions of different varieties of wood.[3]

wood	resinous		hardwood	
	fir	maritime pine	beech	oak
cellulose%	48.2	47.1	44	44.8
hemicellulose%	20.5	25.2	19	38.2
lignin%	26.9	25.6	20	22.5
protein substance%	0.6	0.9	--	1.1
resins%	1 a 1.8	2 a 4	0.7	0.3 a 0.9
hot water extract%	3.7	1.3	13.5	2.8
ash%	0.66	0.3	0.4	0.83

I.1.2 Family of Pinaceae tree family (Pine tree):

These are usually tall trees with long cones. This family is represented in Algeria by three types:

- Genus Abies (the fir tree)
- Cedrus genus (cedar)
- Pinus genus (pines).

Pinus genus (pines).

- **The genus Pinus** comprises about 800 species worldwide, concentrated mainly in the northern hemisphere. In Algeria, we find Aleppo Pine, Maritime Pine, Djurdjura Black Pine, Brutia Pine, Notable Pine, Pinion Pine, Seed Pine and Canary Pine. The first three pines are spontaneous in Algeria, while the others are of great importance in the reforestation.[4]

Figure I.1.2 Photograph of maritime pine, tree, thorns and fruits, bark and heartwood[13]

Table I.1.3: Characteristics of Aleppo pine in Algeria[5].

<table>
<tr><th colspan="2">Aleppo pine</th></tr>
<tr><td colspan="2">
A grove of Aleppo pine</td></tr>
<tr><td>Botanical name</td><td>Pinus halepensismill</td></tr>
<tr><td>Vernacular names</td><td>Senouber, raouraizgougou (seed), Radjina (resin), qat'ran (tar), zeft (tar), azenbi, azouber (bark), taïda (bark), aïdha (bark), igengen, taila, ouazouri (the resin), Chelouda (bark)</td></tr>
<tr><td>Family</td><td>Pinaceae</td></tr>
<tr><td>Odour</td><td>Softwood, aromatic, pleasant.</td></tr>
<tr><td>Flavor</td><td>Young shoots: resinous, a little bitter.</td></tr>
<tr><td>biotope</td><td>Common in Algeria, especially in the mountainous areas large settlements, it prefers hot and dry places, it can be grown</td></tr>
<tr><td>Harvest</td><td>The bud harvest takes place immediately before hatching (April). Drying in the shade.</td></tr>
<tr><td>Parties to use</td><td>Bark, small twigs, buds, resin.</td></tr>
<tr><td>Chemical components</td><td>Tannin, resin, primaric acid, primarinic acid, pinipicrine,terpene.</td></tr>
<tr><td>properties</td><td>Expectorant, balsamic, mild diuretic, antiseptic, astringent "especially buds</td></tr>
</table>

I.1.4 Some types of pines[6]: Some types of pine trees can be mentioned in the following table:

Table I.1.4: Some types of pines and their characteristics.

The pine tree	Scots pine	Maritime pine	Parasol pine	Pin laricio
Habitat	Essence of light	limestone soils	Mediterranean rim	Mediterranean rim
Maximum size	35m	35m	30m	40m
Lifetime	500 years	500 years	250 years	-
Bark	detaching in gray-brown scales, giving off lighter, orange-pink areas at the top.	cracked thick, red-purple on the lower part of the trunk, pink-orange to ferruginous red on the top	cracked brown-red with large vertical gray plates	clear veined deep black cracks
points	4-8 cm, twisted, bluish green, grouped in pairs on the branch	10-20 cm, straight or slightly curved, grouped in pairs, semicircular section	8-10 cm, bluish green, not pungent, inserted in pairs on the branch.	12-18 cm, green, grouped by two
cones	3-8 cm long	18 cm long, grouped by two or more	8-21 cm long	9 cm long
Picture				

I.1.5 Utility of pine resin[7]:

With the campaign of afforestation of the Landes plains by Napoleon III in 1857, the pine was an important economic stake for the department at that time. The resin of the pines was very used formerly. Resiners harvested the resin by practicing the gemmage, that is to say by breaking the bark of the pine to recover the precious nectar, from where the nickname of "tree Golden ".

Hard resins can be classified into two categories: rosin ester derivatives and polymers derived from petroleum chemistry. Rosin is extracted from conifers (pine) and can come from gum, wood or tall oil.[8]

The first uses of the resin were used to make torches or candles. Then we began to distil it to obtain turpentine, which is found in particular in paints, varnishes but also rosin, necessary for the manufacture of glues, paper or adhesives. Today, the maritime pine is no longer used for its resin but for its wood.

I.1.6 Barks:

I.1.6.1 Definition:

The bark comprises all the so-called cortical tissues produced towards the outside of the stem by the operation of the phellogen or suberophelodermic generating seat on the branches, the trunk, but also the roots of the trees. It is a layer of generative cells, secondary meristem, which produces cork (or suber or phelleme) to the outside, and phelloderm (sometimes called "living bark") inwards. The phelloderm ensures the continuity of the external protection, in spite of the increase in diameter of the stem. To summarize, the bark in the common sense of the term is constituted by the epidermis, the cortical parenchyma, and the suber (or cork).

The bark of trees is often rich in toxins (phenols) and bitter principles (tannins) which makes it more protective, but actually also a source of medicinal principles.[9]

Figure I.1.6.1: Bark, pine tree.[10]

I.1.6.2 General chemistry of bark:

The bark is generally composed of a thin inner layer (phloem) and an outer layer (rytidom) separated by an intermediate layer (periderm). The thickness of the bark varies according to the tree and its age. The cell walls that make up the phloem are mainly rich in starch, fatty acids and tannin. The resins circulate inside tiny channels. The peridem is composed of three layers whose thickness varies with the species. The list of compounds found in the bark.

is very long; the main families of compounds that can be mentioned are: carbohydrates (cellulose, hemicellulose), pectins, lignins, terpenes (flavonoid, tannins, stibenes and others), and poly-flavonoids. we know about the bark chemistry, we can consider that the bark could be used as matrix "ion exchanger". The important content of functional groups, mainly the presence of hydroxyl, carboxylic and phenolic groups, makes the shell interesting for ionic fixations.[11]

The chemical composition of pine bark is summarized in Table I.5. the extracts amount to 19.1% and mainly comprise polar compounds extracted by ethanol and water (14% of the gold bark); about half of the extractives (7.2% of the gold bark) are phenolic and correspond to tannins which represent 96% of the total phenolic Table I.1.6.2. [12]

Table I.1.6.2.a: Average chemical composition of the bark of Pinus Pinea.

compound	Percentage of kiln dried weight
Ash	2.3
Total extractions	19.1
dichloromethane	2.1
Ethanol	12.1
Water	4.9
Suberin	2.5
Lignin and polyphenol	37.5
polysaccharides	36.8

Table I.1.6.2.b: Phenolics and total tannins of Pinus Pinea.

compound	Percentage of kiln dried weight
Phenolic total	7.5
tannins	7.2

I.1.6.3 Pine bark: use, interest and inconvenience[13]:

Pine bark is a very popular material used in public and private gardens, to mulch the rosebushes and other perennials, and to cover the earth with potées and jardinières. Be careful, however, not to use it anyhow, because these barks have some disadvantages.

a. Pine bark mulch trade[14]:

The pine bark used in gardens as mulch is mainly derived from the maritime pine (Pinus pinaster). It is at the time of their slaughter that the logging pines are debarked. The bark, considered as a production waste, is recycled in the form of mulch: pieces of bark washed and calibrated, then packaged in a bag of 5 to 100 L (for individuals). These bags are available in most garden centers.

II.1 Description of pine tree:

The sizes are 5/10 mm or 5/15 mm, 10/25 mm, 25/40 or 20/40 mm and 40/60 mm. The destination of the pine bark depends on the choice of caliber.

Figure I.4 : Ecorce de pin :Calibre 10-25 et 20-40.

I.1.6.4 Characteristics of pine bark

Pine bark is a rather heavy organic material (compared to other organic mulches: hemp, flax, straw, shearing ...) which decomposes very slowly, especially the maritime pine (life span of large mulch estimated between 6 and 7 years, 5 years for medium sizes) .The puffed structure of the bark gives it a very high water absorption capacity (80% of its weight). [14].The acid pine bark is said . In reality, its acidity does not last in time: its pH can vary from 4 to 8 depending on the degree of composting. Finally, the bark of maritime pine has a beautiful red-brown color.

I.1.6.5 Uses of pine bark

Of organic origin and split into pieces, pine bark is a good mulch material. And like all mulches, its use allows:

- Avoid soil erosion and compaction, and thus maintain their aerated and drained structure;
- To limit the evaporation of water and the development of weeds;
- Provide plants with good protection against the cold;
- In the long term (because it only deteriorates very slowly), contribute to improving soil humus levels.

I.9.5.1. Benefits of a pine bark mulch

- Its ability to keep water keeps the soil cool and wet for a long time;

- Its airy structure does not block the penetration of water and promotes gas exchange;

- Its color is aesthetic; it highlights the green foliage. In addition, the visual effect is different according to the caliber used;

- Its weight gives it good resistance to the vents.

I.1.6.6 Disadvantages of pine bark

- The use of pine bark on acidic soil (pH between 4.5 and 5.5) and only in this case, accentuates its acidification. In the case of a neutral or calcareous soil, the latest studies show that there is no significant acidifying effect that would be detrimental to crops.

- Its slow decomposition does not allow it to be used to improve soil quality, as is the case with organic mulches used in vegetable gardens

I.2 Wood Tar - Pine Tar :

I.2.1 General:

Wood Tar is a viscous, blackish brown liquid, translucent in thin layers. It has an empyreumatic odor and sharp taste. The chief constituents are volatile terpene oils, neutral oils of high boiling point and high solvency, resin and fatty acids. The proportion of these vary in the different grades of tar, also according to tree species and the part of the tree used, type of carbonization oven ect.... Fat wood tar made from stumps of the pine tree has always been recognized as the best tar, since it contains much of the ingredients which protect the living tree. However, stumps are hard to find and expensive, so ordinary pine wood is mostly used nowadays.

is very long; the main families of compounds that can be mentioned are: carbohydrates (cellulose, hemicellulose), pectins, lignins, terpenes (flavonoid, tannins, stibenes and others), and poly-flavonoids. we know about the bark chemistry, we can consider that the bark could be used as matrix "ion exchanger". The important content of functional groups, mainly the presence of hydroxyl, carboxylic and phenolic groups, makes the shell interesting for ionic fixations.

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I.2.2 Genuine Pine Tar 588:

General: A dark colored, old fashion type of pine tar obtained as a byproduct throughdestructive distillation of pine wood in the manufacture of charcoal. Thinned withturpentine to a standard viscosity.

- **Technical data**
- Density at 20°C 1.05
- Water content: max. 0.5%
- Volatile matter max. 6.0%
- Ash content: max. 0.5%
- Viscosity at 50 °C
- C approx. 380 °C
- Acidity (as acetic acid) max. 0.3%
- Flash point: approx. 120°C

Thinner: Turpentine

I.2.3 Kiln burned Pine Tar 773:

General: Golden brown pine tar produced according to the old kiln method from stumps of the pine tree Pinus Silvestre’s,. Also known as "peasant made" tar. This type of tar is characterized by high resin content (rosin acids and retene), low content of pitch and high purity, i.e. free from soot and other impurities.

- **Technical data:**
- Density at 20°C approx. 1.05
- pH value: approx. 3.5
- Reaction with Ca
- $(OH)_2$ positive
- Water content: approx. 1%
- Solubility: soluble in ethanol, ether and in fixed and volatile oils; slightly
- soluble in water[8]

II. Water pollution and heavy metals

II.1 Water pollution:

II.1.1Environmental Concerns:

Environmental concerns associated with water result from natural events and human activities. Our towns and cities were developed near sources of drinking water and along rivers for transportation. Past policies favored “reclaiming“ lands for agriculture and the consumption of water without much concern for the environment. These past decisions are reflected in the existing conditions of our water resources. Natural events, such as floods, droughts and changes to water quality, may cause problems for humans. Many human water uses require changes to the natural flow of water through the construction of dams, canals, and by the pumping of groundwater. These changes bring benefits to people, but they also affect natural Environments. Municipal, industrial, or agricultural uses of water may degrade water quality and cause environmental problems. If anything happens to disrupt our water supply or degrade the quality of our water, we become concerned. Changes to the water regime can impact human habitation, Agriculture , sensitive ecosystems, economic development, and land-use decisions.[16]

II.1.2 Chemistry of Water:

The chemical formula for water is H_2O. Water contains strong covalent bonds that hold the two hydrogen atoms and one oxygen atom together. The oxygen can be regarded to be at the center of a tetrahedron, with a bond angle of 105 between the two hydrogen atoms in liquid water and a larger angle of 109 between the hydrogen’s in ice[17] .

II.1.3 Water pollution[18]:

Water resources are special. In their natural states they are beautiful. People like to live and vacation near rivers, lakes and coasts. Water is also powerful. Water can erode rock, alter existing landscapes and form new ones. Life on this planet depends on water. Most of our economic activities consume water. All of the food we grow, process and eat requires water. Much of our waste is transported and assimilated by water. The importance of water to our wellbeing is beyond question. Our dependence on water will last forever.

Water is essential for the existence of all life forms. In addition to household uses, water is vital for agriculture, industry, fishery and tourism etc. Increasing population, urbanisation and industrialisation has led to the decreased availability of water. The quality of water used is also being deteriorated as it is getting more and more polluted. You may be aware of at least some health hazards and harmful effects of water pollution.

II.1.4 Water Resources on Earth:

You may be aware that about three fourths of our planet earth's surface is covered by water. However, very little of it is available for consumption. Most (about 97%) of the water on earth is present in the seas and oceans. It is too salty to be of any use for drinking, agriculture and industrial purposes. The remaining 3% is fresh water; 75% of which is locked up in the polar ice caps and in glaciers and quite deep under the earth's surface as underground water. The fresh water, which we can use, comes to us from two sources:

- Surface water
- Ground water

a. Surface Water:

Surface waters include streams, rivers, lakes, reservoirs, and wetlands. Rain and snow are good natural resources of fresh water[16]. It is estimated that of all the precipitation (rain water and snow) that falls on the earth, about one-third is absorbed by the plants and another one-third seeps down into the soil and the remaining one third runs off the surface into streams and rivers. This part of precipitation, which runs off to form streams, rivers and lakes, is called the surface water.

b. Ground Water:

Groundwater occurs almost everywhere beneath the land surface. Although surface water is currently the most commonly used water source[16] .The part of precipitation that seeps into the ground as a result of gravity and fills the pores between soil particles and rocks under it is called groundwater. The water bearing layers of soil and rocks are called aquifers. Ground water is very important for agricultural and industrial purposes. Ground water in the form of wells and springs is often the only source of water supply especially in villages and small towns. In spite of a good number of water resources, we have shortage of usable water. This is due to increasing population, urbanisation and industrialisation. There is a need to optimize use of water and also conserve surface run off of water by means of rain water harvesting, ground water conservation, making use of recycling methods etc. [19]

II.1.5 Pollutant sources:

"I am, therefore I pollute" is a statement applying to a multitude of processes: ▪ Motor vehicles including cars, buses, airplanes, ships, and off-road vehicles ▪ Chemical and petroleum refineries ▪ Manufacturing facilities ▪ Commercial operations including dry cleaners, bakeries, and garages ▪ Plants generating electric power by burning coal, oil, or natural gas ▪ Agricultural operations growing crops or raising animals ▪ Food processing operations ▪ Mining ▪ Construction and road building ▪ Military operations ▪ Forestry operations ▪ Municipal operations including drinking water and wastewater treatment, and road maintenance ▪ Activities occurring in commercial and municipal buildings, and in private dwellings including, e.g., consumer product use.

As population grows, pollution grows. And in wealthy locales, consumption per individual typically grows over time too, and technologies become larger. Thus, without concerted effort to prevent it, pollution and other forms of environmental degradation will also grow.[20]

a. organic water pollutants:

A whole host of water pollutants are organic compounds, which include virtually all carbon-containing compounds. These may be nontoxic, highly biodegradable materials, such as waste food in sewage, that are nevertheless bad for water because of the dissolved oxygen consumed when they degrade.[21]

b. inorganic water pollutants :

exemple: Cyanide HCn Hydrogen sulfide, H_2SNitrite ion, NO_2 - [21]

II.1.6 Monitoring water quality:

Water is essential to man both directly and indirectly through agriculture and industry in which vast quantities are used for cooling, energy production, irrigation, refrigeration, washing, solvents etc. Risk of contamination can render water dangerous, unpleasant, or unusable. Point sources of water pollution include domestic and industrial waste whilst non-point sources include agricultural and urban run-offs. Analysis of water is important for estimating the nature and concentration of contaminants and hence fitness for use. Artificial contaminants are mainly of domestic and industrial origin, and are increasing in similarity because of the expanding domestic use of chemicals (cosmetics, detergents, paints, garden insecticides and fertilizers). Water quality can be assessed by direct analysis of chemical substances or by indirect effects, e.g. pH, colour, turbidity, odour, impact on dissolved oxygencontent.[22]

II.1.7 Water Pollution – Parameters:

Water may be called polluted when the following parameters stated below reach beyond

a specified concentration in water.

a. **Physical parameters:** Color, odor, turbidity, taste, temperature and electrical conductivity constitute the physical parameters and are good indicators of contamination. For instance, color and turbidity are visible evidences of polluted water while an offensive odor or a bitter and difference than normal taste also makes water unfit for drinking.
b. **Chemical parameters:** These include the amount of carbonates, sulphates, chlorides,

fluorides, nitrates, and metal ions. These chemicals form the total dissolved solids,

Present in water.

c. **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 are duction 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.[19]

II.2 Heavy metals:

II.2.1 Metals:

A metal is an electropositive element. There are over 70 metals in the earth's crust. Examples include copper, gold, iron, platinum, silver and tungsten. Chemically, in solution, a metal atom releases an electron to become a positive ion. In bulk metals are solids and tend to have high melting and boiling points (an exception is mercury). They are lustrous, relatively dense, malleable, ductile, cohesive and highly conductive to both electricity and heat. Metals are crystalline in structure and the individual crystals contain positive metal ions. The outer valency electrons appear to be so loosely held that they are largely interspersed amongst the positive ions forming an electron cloud which holds the positive ions together. The mobility of this electron cloud accounts for the electrical conductivity. The crystal structure also explains the hardness and mechanical strength of metals whereas the elasticity is explained by the ability of the atoms and ions to slide easily over each other. Metals can be blended with other metals to produce alloys with specific properties and applications[22]**.**

II.2.2 General of Heavy metals:

Heavy metals, which have widespread environmental distribution and originate from natural and anthropogenic sources, are common environmental pollutants. In recent decades, their contamination has increased dramatically because of continuous discharge in sewage and untreated industrial effluents. Because they are non-degradable, they persist in the environment; accordingly, they have received a great deal of attention owing to their potential health and environmental risks. Although the toxic effects of metals depend on the forms and routes of exposure, interruptions of intracellular homeostasis include damage to lipids, proteins, enzymes and DNA via the production of free radicals. Following exposure to heavy metals, their metabolism and subsequent excretion from the body depends on the presence of antioxidants (glutathione, _-tocopherol, ascorbate, etc.) associated with the quenching of free radicals by suspending the activity of enzymes (catalase, peroxidase, and superoxide dismutase). Therefore, this review was written to provide a deep understanding of the mechanisms involved in eliciting their toxicity in order to highlight the necessity for development of strategies to decrease exposure to these metals, as well as to identify substances that contribute significantly to overcome their hazardous effects within the body of living organisms.[23]

II.2.3 Heavy metal water pollutants:

The heavy metals are those metals of relatively higher atomic numbers. Some heavy metals are considered among the most troublesome and toxic water pollutants.

Lead, Pb (from its Latin name of plum bum), is arguably the most common heavy metal pollutant because of its widespread use in industry and in the manufacture of lead storage batteries as well as its former uses as a leaded additive to gasoline, as a pigment in white house paint, and as an anticorrosive primer applied prior to painting steel. Exposure to lead causes a number of adverse health effects and is suspected of causing mental retardation in exposed children. Lead was widely used in plumbing, and its use in solder to join together copper water pipe was banned only recently. [21]

II.2.4 Definition of heavy metals:

These metallic elements (mercury, arsenic, and lead) that are able to induce toxicity even at lower levels of exposure are considered systemic toxicants. Occupying the top position on the list of hazardous substances[23], “A metal of relatively high density (Specific gravity greater than about 5) or of high relative atomic weight (especially one i.e poisonous) one mercury or lead.” It has been includes density, atomic weight, atomic number, or periodic table position. Density criteria range from above 3.5 g/cm3 to above 7 g/cm3 . Atomic weight definitions start at greater than sodium (22.98) to greater than 40.[n 1] Atomic numbers of heavy metals are generally given as greater than 20; sometimes this is capped at 92 (uranium). Hawkes suggested referring to heavy metals as "all the metals in Groups 3 to 16 that are in periods 4 and greater. The term "heavy metals" was in use as far back as 1817, when Gmelin divided the elements into nonmetals, light metals and heavy metals.Light metals had densities of 0.860–5.0 gm/cm3 ; heavy metals 5.308–22.000.In 1868, Wanklyn and Chapman speculated on the adverse effects of the heavy metals "arsenic, lead, copper, zinc, iron and manganese" in drinking water.[24]

II.2.5 Trace Metals:

A large number of trace metals are transported to the oceans from natural sources. However, these natural sources are supplemented by releases from anthropogenic processes which, for some metals, can exceed natural inputs. Trace metals are found in the water, biota and sediment compartments of the marine system, but potentially the most hazardous environmental effects to human health arise when they enter the food chain. The relationship between the total concentration of a trace metal in the environment and its ability to cause toxic effects in organisms is complex, and two important constraints must be considered.[25]

II.2.6 Metal toxicity:

Metal toxicity or metal poisoning is the toxic effect of certain metals in certain forms and doses on life. Some metals are toxic when they form poisonous soluble compounds. Certain metals have no biological role, i.e. are not essential minerals, or are toxic when in a certain form In the case of lead, any measurable amount may have negative health effects. Often heavy metals are thought as synonymous, but lighter metals may also be toxic in certain circumstances, such as beryllium and lithium. Toxic metals sometimes imitate the action of an essential element in the body, interfering with the metabolic process to cause illness. Many metals, particularly heavy metals are toxic, but some heavy metals are essential, and some, such as bismuth, have a low toxicity. Most often the definition of toxic metals includes at least cadmium, lead, mercury and the radioactive metals. Metalloids (arsenic, polonium) may be included in the definition. Radioactive metals have both radiological toxicity and chemical toxicity. Metals in an oxidation state abnormal to the body may also become toxic: chromium(III) is an essential trace element, but chromium(VI) is a carcinogen. Toxic metals can bio accumulate in the body and in the food chain. Therefore, a common characteristic of toxic metals is the chronic nature of their toxicity. This is particularly notable with radioactive heavy metals such as radium, which imitates calcium to the point of being incorporated into human bone, although similar health implications are found in lead or mercury poisoning. The exceptions to this are barium and aluminium, which can be removed efficiently by the kidneys.[24]

II.2.7 Toxic heavy metals and healthy problems:

- Long term exposure to cadmium is associated with renal dysfunction. Cadmium is biopersistent and once absorbed remains resident for many years. High exposure can lead to obstructive lung diseases and has been linked to lung cancer. Cadmium may also cause bone defects in humans and animals.

- Low exposure to chromium can irritage the skin and cause ulceration.long term exposure can cause kidney and liver damage. It can also cause damage to circulatory and nerve tissues.

- Aluminium toxicity is associated with the development of bone disorders including fractures,osteopenia and osteomalacia.

- Monomethylmercury causes damage to the brain and the central nervous system while fetal and post-natal exposure have given rise to abortion, congenital malformation and development changes in young children. Exposure to high levels of arsenic can cause death. All types of arsenic exposure can cause kidney and liver damage and in the most severe exposure there is erythrocyte hemolysis.

- High doses of copper can cause anemia, liver and kidney damage, and stomach and intestinal irritation.

- Excessive amounts of nickel can be mildly toxic. Long term exposure can causes decreased body weight, heart and liver damage and skin irritation.

- Manganese is known to block calcium channels and with chronic exposure results in CNS dopamine depletion. This duplicates almost all of the symptomology of parkinson’s Disease.[24]

II.2.8 Nickel:

I.2.8.1 History:

Nickel had been in use centuries before its actual discovery and isolation. As far back as 3500 BC Syrian bronzes contained a small amount of the element. In 235 BC, coins in China were minted from nickel. However there was no real documentation of the element until thousands of years later. In the 17thcentury, German miners discovered a red colored ore they believed to contain copper. They discovered upon analysis that there was no copper but that a useless, smelly material was actually present. Thinking the ore was evil they dubbed it "Kupfernickel" or Old Nick's Copper, which meant false or bad copper. Swedish scientist Baron Axel Frederich Cronstedt in 1751 finally isolated nickel from an ore closely resembling kupfernickel. Hence, he named this new element after the traditional mineral. At the time of its discovery nickel was thought to be useless but as its valuable properties came to light the demand for the metal increased dramatically. The usefulness of nickel as a material in alloys was eventually discovered as the strength, corrosion resistance and hardness it adds to other metals came to be appreciated. In the 1800s, the technique of silver plating was developed with a nickel-copper-zinc alloy being utilized in the process. Today, stainless steel, another nickel containing alloy, is one of the most valuable materials of the 20th century. [26]

II.2.8.2 Characteristics of nickel :

- "Its color is half-way between that of silver and pure tin.
- "It is not affected by air or atmospheric water, that is, it does not rust.
- "It is perfectly ductile; rods can be made from nickel when it has been heated and one can beat them into very thin plates when cold. Because of this property, nickel cannot be considered a semi-metal and takes
- its place amongst 'perfect' metals.
- "Its specific weight or density is 8.279 for molten nickel and 8.666 for wrought nickel.
- "Its strength is considerable.
- "It has a high melting point and so is extremely difficult to melt, at least as difficult as manganese.
- "The metal oxidized very little on being heated until red, when it becomes a little duller than platinum, gold or silver. Thus nickel is not only a perfect metal but also a noble one.
- "The action of magnets on nickel is very great, only slightly less than their action on iron.[27]

II.2.8.3 Uses of Nickel and its Compounds:

The primary use of nickel is in the preparation of alloys such as stainless steel, which accounts for approximately 67% of all nickel used in manufacture. The greatest application of stainless steel is in the manufacturing of kitchen sinks but it has numerous other uses as well. Other nickel alloys also have important applications. An alloy of nickel and copper for example is a component of the tubing used in the desalination of sea water. Nickel steel is used in the manufacture of armor plates and burglar proof vaults. Nickel alloys are especially valued for their strength, resistance to corrosion and in the case of stainless steel for example, aesthetic value. Electroplating is another major use of the metal. Nickel plating is used in protective coating of other metals. In wire form, nickel is used in pins, staples, jewellry and surgical wire. Finely divided nickel catalyses the hydrogenation of vegetable oils. Nickel is also used in the coloring of glass to which it gives a green hue. Other applications of nickel include: -Coinage -Transportation and construction -Petroleum industry -Machinery and household appliances -Chemical industry. Nickel compounds also have useful applications. Ceramics, paints and dyes, electroplating and preparation of other nickel compounds are all applications of these compounds. Nickel oxide for example is used in porcelain painting and in electrodes for fuel cells. Nickel acetate is used as a mordant in the textiles industry. Nickel carbonate finds use in ceramic colours and glazes. [28]

II.2.9 Lead:

II.2.9.1 Definition:

Lead is a gray-white, soft metal with a low melting point, a high resistance to corrosion, and poor electrical conducting capabilities. It is highly toxic. In addition to its highly concentrated ores, lead is naturally available in all environmental media in small concentrations. From the atmosphere, lead is transferred to soil, water, and vegetation by dry and wet deposition. A significant part of lead particles from emissions sources is of submicron size and can be transported over large distances. Larger lead particles settle more rapidly and closer to the source. Lead in soil binds hard, with a half-life of several hundred years. New depositions, primarily atmospheric, therefore contribute to increased concentrations. Atmospheric deposition is the largest source of lead in surface water, as well. Only limited amounts are transported to water from soil. Terrestrial and aquatic plants show a strong capability to bioaccumulate lead from water and soil in industrially contaminated environments (WHO 1989). Lead can also be taken up by grazing animals, thus entering the terrestrial food chain. Natural atmospheric lead concentrations are estimated to be in the range of 0.00005 micrograms per cubic meter (µg/m3). Urban concentrations are around 0.5 µg/m3, and annual average concentrations may reach 3 µg/m3 or more in cities with heavy traffic (WHO 1987).[29]

II.2.9.2 Sources and Uses

Mining, smelting, and processing of lead and lead containing metal ores generate the greatest part of lead emissions from stationary sources. In addition, the combustion of lead-containing wastes and fossil fuels in incinerators, power plants, industries, and households releases lead into the atmosphere. Airborne ambient lead concentrations reaching over 100 µg/m3 have occasionally been reported in the vicinity of uncontrolled stationary sources, decreasing considerably with distance from the source due to the deposition of larger lead particles. As a result of the extensive use of alkyl-lead compounds as fuel additives, vehicular traffic is the largest source of atmospheric lead in many urban areas, accounting for as much as 90% of all lead emissions into the atmosphere (Brunekreef 1986). High concentrations of lead in urban air have been attributed to vehicular emissions in various countries (Lovei and Levy 1997). Traffic-generated lead aerosols are mostly of the submicron size; they can penetrate deeply into the lungs after inhalation, and they are transported and dispersed over large distances (Brunekreef 1986). With the phase out of leaded gasoline, the relative contribution of traffic to environmental lead concentrations is changing.

Due to its special physical characteristics, lead has been used in a variety of products. Water distribution systems frequently contain lead pipes or lead solder, contaminating drinking water. Lead carbonate (“white lead”) was highly popular as a base for oil paints before its use was banned in most countries in the first half of the twentieth century. Lead-based paint and dust contaminated by such paint still represent significant sources of human exposure in several countries. Lead-acid batteries contribute to the contamination of all environmental media during their production, disposal, and incineration. Lead compounds may be also used as stabilizers in plastics. Other lead-based products include food-can solder, ceramic glazes, crystal glassware.

II.2.9.3 Brief explanation about Lead toxicity:

- Lead is a metal, it is present in the 4th group and period 6th of the periodic table.
- Lead atomic number 82, atomic mass 207.2 and density 11.4 gcm^{-3}.
- Lead has a very low melting point 327.40 ^{0}C and boiling point 1725 ^{0}C .
- Sulphur combined with lead to give PbS, $PbS0_4$.
- Oxygen combined with lead to give $PbC0_3$ and ranges from 10 to 30 mg kg-1 in the earth’s crust.
- Lead is used as solders, bearings, cable covers, ammunition, plumbing, pigments and caulking.
- Solders(Sn) and antimony (Sb) sleeve bearings, printing and high detail castings.

- Ionic Lead, Pb(II) , lead oxides and hydroxides and lead-metal oxyanion complexes are the general forms of Pb that are released into the soil, ground water and surface waters.

- The most stable forms of lead are Pb(II) and lead hydroxyl complexes.

- Lead(II) is the most common and reactives form of Pb, forming mononuclear and poly nuclear oxides and hydroxides.

- Lead hydroxides, lead sulphide is the most stable solid form with in the soil matrix and forms under reducing conditions, the concentration of sulphide increased.

- Lead(II) compounds are predominantly ionic forms I.e Pb^{+2}, SO_4 $-^{2}$.

- Another lead (II) compounds such as PbO_2 are strong oxidants.

- Lead forms several basic salts such as $Pb(0H)_2$, $2PbC0_3$ which is most widely used white paints pigment and the source of considerable chronic lead poisoning to children who ate peeling white paint.

- Lead dioxide and lead sulphate are participants in the reversible reaction that occurs during the charge and discharge of lead storage battery.

- The spectrophotometric dithizone method for Pb is subject to much interference. [30]

II.2.9.4 sources of lead:

Lead is used in the building industry for proofing flashing and for sound proofing.

- It is also used in solders, bearings, cable covers, ammunition, plumbing, pigments, paints important candles.

- Lead is used in pipes i.e. PVC.

- Lead is used in cermics and dishware.

- Lead is also used in corrosion-resistant paints. It has a red bright red color.

- Lead is used in batteries and sinkers in fishing.

- Lead enters water bodies from industrial mine and smelt discharges from dissolution of old lead plumbing.

- Jewelly, drinking water, lunch-boxes.[31]

  - **health effects**:
  - Inhalation and ingestion are the two routes of exposures and effects from both are the same.

- Lead affected by the gastrointestinal tract, kidney and central nervous system.

- Lead breaks the blood-brain barrier and interferes with the normal development of brain in infants.

- Lead is exposed from air and food in roughly equal proportions.

- Lead is observed to lower IQ levels in children shorted attention span, hyperactivity and mental deterioration with children under the age of six.

- Lead can cause serious injury to the brain nervous system red blood cells and kidneys.

- Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure.[32]

- Various effects occur over a broad range of doses with the developing young and infants being more sensitive than adults.

- Lead poisoning, which is so severe as to cause evident illness.

- Higher concentrations are more likely to be found in leafy vegetables and fruits like corn, beans, tomatoes, squash, strawberries and apples.

- It is cummulation body poison. Natural waters generally upto 20ppb of Pb, although in some cases 400ppb.[24]

II.2.10 Chemistry of chromium:

II.2.10.1 diffinition:

Chromium, Cr, also loosely called Chrome, is the twenty-first element in relative abundance with respect to the earth's crust, yet is the seventh most abundant element because Cr is concentrated in the earth's core and mantle. It has atomic number 24 and belongs to the group 6(VI B) of the Periodic Table. On a tonnage basis, chromium ranks forth among the metals and thirteenth of all mineral commodities in commercial production. Chronium was discovered by Vauquelin in 1779 in Siberian red lead, the mineral Crocoite, PbCrO, , In 1798 he isolated the new metal by reduction of CrO, with charcoal at high temperature. The name chromium (from Greek chroma, color) was suggested for the new element because of its many colored compounds. Chromium, relatively recently, is recognized as a biologically necessary trace element, The first conclusive evidence demonstrating a metabolic role for chromium was obtained by Mertz and Schwartz' in a series of investigations the first of which appeared

in 1955.[33]

II.2.10.2 general properties of heavy metals[34]:

- They occur near the bottom of the periodic table.
- Have high densities.
- Toxic in nature.
- Non degradable.

III. Adsorption and method analyses

III.1 Adsorption:

III.1.1 Abstract:

Adsorption is considered to be one of the most effective technologies widely used in global environmental protection areas. Modeling of experimental adsorption isotherm data is an essential way for predicting the mechanisms of adsorption, which will lead to an improvement in the area of adsorption science. [35]

The chemical adsorption isotherm reveals information about the active surface of a material and has been employed for many years as a standard analytical tool for the evaluation of catalysts. Temperature-programmed reaction techniques have emerged from the 1950's as an indispensable companion to chemisorption isotherm analyses in many areas of industry and research.[36]

III.1.2 Adsorption phenomena:

The molecules at a surface of a material experience imbalanced forces of intermolecular interaction which contribute to the surface energy. It causes accumulation of molecules of a solute or gas in contact with the substance. This preferential accumulation of substrate molecules at the surface is called adsorption which is purely a surface phenomenon. The surface active material is referred to as the adsorbent and the molecules which are accumulated on the adsorbent called adsorbate molecules. The strength by which adsorbate molecules are attached with the adsorbents determines the nature of adsorption. Normally, release of energy in the range of 8 to 25 kJ/mole due to adsorption is termed as physisorption whereas a much larger energy comparable to chemical bonding energy leads to chemisorption. There are always some exceptions to these values. The prescribed value of energy differentiating physisorption and chemisorption are based on general experience.

When an adsorbed molecule receives energy equal to or greater than the energy of adsorption, it will leave the surface. This phenomenon is the reverse of adsorption and is called as desorption. When the number of molecules striking the surface and staying there is equal to the number of molecules that are leaving(evaporating) the surface the system is said to be in equilibrium. All the atoms or molecules adsorbed on the surface do not have identical environment since distribution of free energy on the surface is not always smooth because of the differences in the energy of the molecular orbital's of the adsorbent and also due to other internal interactions.[19]

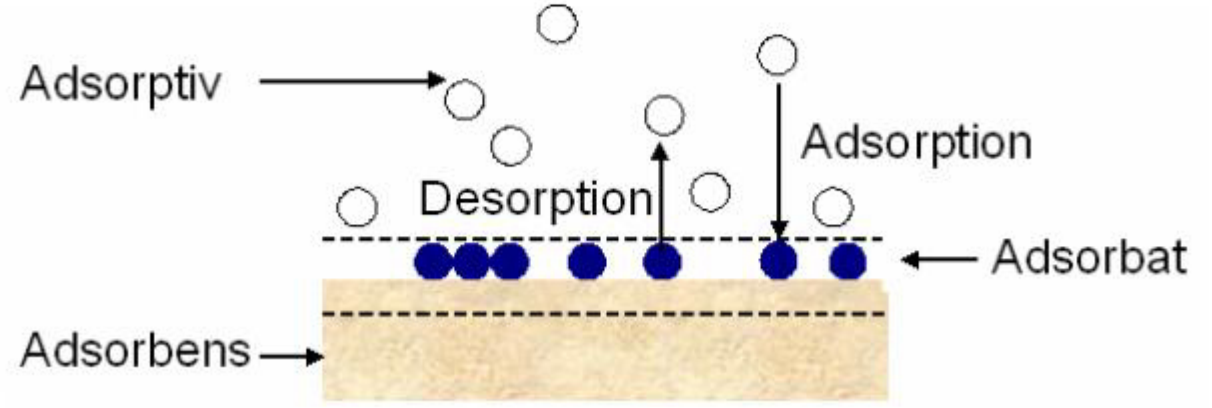
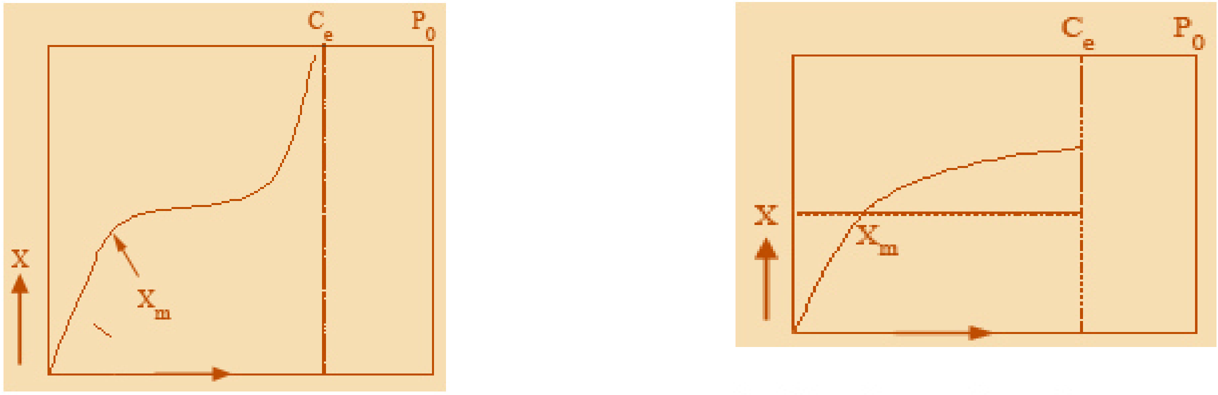


Figure III.1.2: adsorption and desorption phenomena

III.1.3 Adsorption Isotherms:

A relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent is known as Adsorption Isotherm. Two types of typical adsorption isotherms are shown in the following Figures A & B. Figure A shows adsorption with monolayer formation at saturation point. Figure B shows a situation when several layers of adsorbate molecules are formed on the surface of the adsorbent (multilayer adsorption).[37]



B. Multilayer adsorption

A. Monolayer adsorption

Figure III.1.3: mono ad multilayer adsorption isotherm

III.1.4 Differentiating physical and chemical adsorption:

A solid material usually exhibits a heterogeneous distribution of surface energy. Gas, vapor, or liquid molecules may become bound to the surface if they approach sufficiently close to interact. The solid is called the adsorbent; the gas or vapor molecule prior to being adsorbed is called the adsorptive and while bound to the solid surface, the adsorbate.

Physical adsorption is the result of a relatively weak solid-gas interaction. It is a physical attraction resulting from non specific, relatively weak Vander Waal's forces and adsorption energy usually not exceeding 80kJ/mole, with typical energies being considerably less. Physically adsorbed molecules may diffuse along the surface of the adsorbent and typically are not bound to a specific location on the surface. Being only weakly bound, physical adsorption is easily reversed.

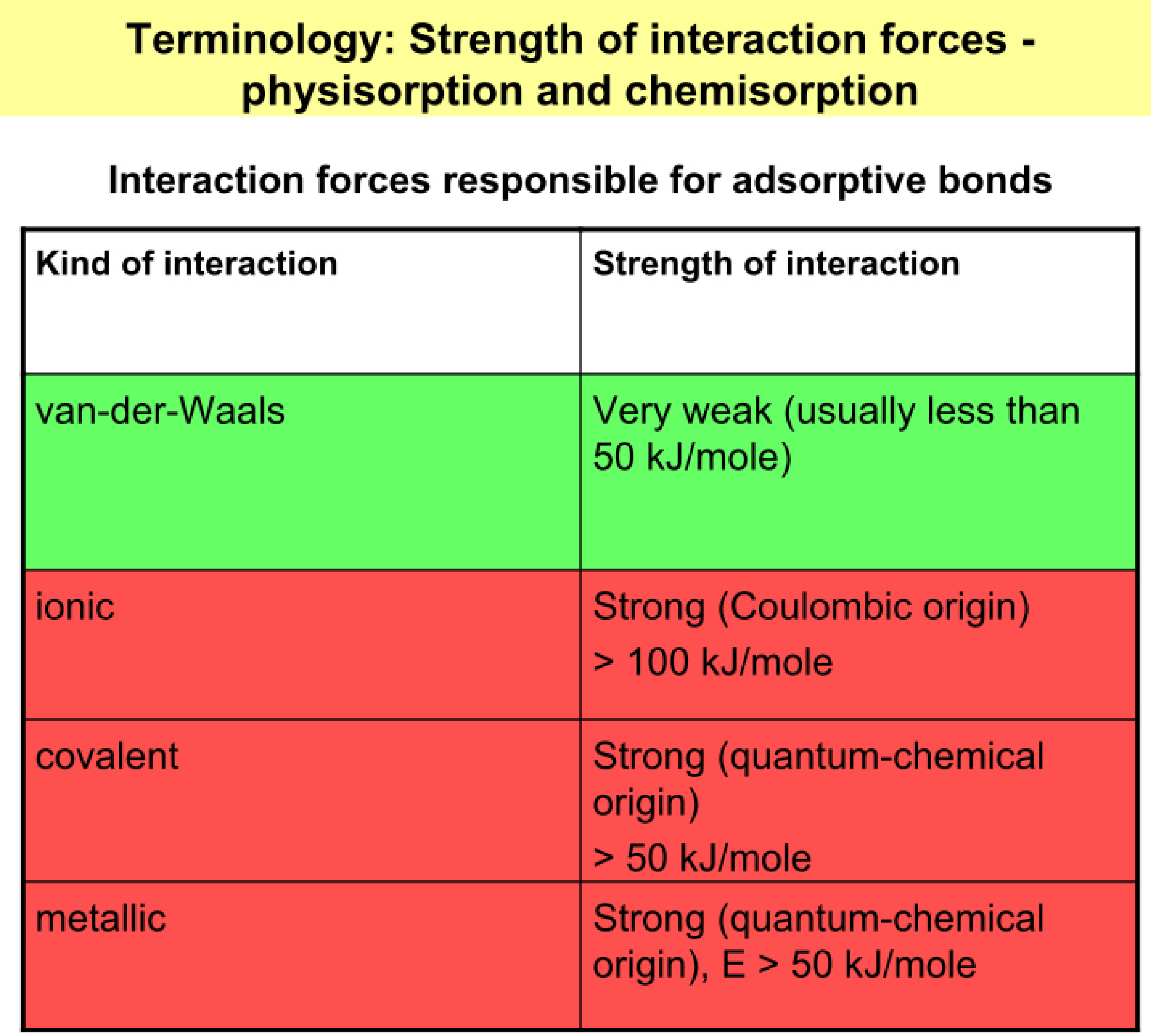
Adsorption also can result in a surface complex, a union much stronger than a physical bond with heats of adsorption up to about 600 kJ/mole for C-N bonds and 800 kJ/mole for chemical bonds. A chemical bond involves sharing of electrons between the adsorbate and the adsorbent and may be regarded as the formation of a surface compound. Due to the bond strength, chemical adsorption is difficult to reverse.

Physical adsorption takes place on all surfaces provided that temperature and pressure conditions are favorable. Chemisorptions', however, is highly selective and occurs only between certain adsorptive and adsorbent species and only if the chemically active surface is cleaned of previously adsorbed molecules.

Under proper conditions, physical adsorption can result in adsorbed molecules forming multiple layers. Chemisorptions, in the typical case, only proceeds as long as the adsorptive can make direct contact with the surface; it is therefore a single-layer process. Exceptions can exist if the adsorptive is highly polar such, NH_3 being an example. Both physical and chemical adsorption may occur on the surface at the same time; a layer of molecules may be physically adsorbed on top of an underlying chemisorbed layer. The same surface can display physisorption at one temperature and chemisorption at a higher temperature. For example, at liquid nitrogen temperature (77 K) nitrogen gas is adsorbed physically on iron but at

800 K, an energy level too high for physical adsorption bonds, nitrogen is adsorbed chemically to form iron nitride.[36]

Table III.1.4 : Terminology: strength of interaction forces-physisorption and chemisorptions.



Terminology: Strength of interaction forces - physisorption and chemisorption

Interaction forces responsible for adsorptive bonds

Kind of interaction	Strength of interaction
van-der-Waals	Very weak (usually less than 50 kJ/mole)
ionic	Strong (Coulombic origin) > 100 kJ/mole
covalent	Strong (quantum-chemical origin) > 50 kJ/mole
metallic	Strong (quantum-chemical origin), E > 50 kJ/mole

III.2 Basic UV-Vis Theory, Concepts and Applications:

III.2.1 Introduction :

The molecular spectroscopy is the study of the interaction of electromagnetic waves and matter. The scattering of sun's rays by raindrops to produce a rainbow and appearance of a colorful spectrum when a narrow beam of sunlight is passed through a triangular glass prism are the simple examples where white light is separated into the visible spectrum of primary colors.

This visible light is merely a part of the whole spectrum of electromagnetic radiation, extending from the radio waves to cosmic rays. All these apparently different forms of electromagnetic radiations travel at the same velocity but characteristically differ from each other in terms of frequencies and wavelength (Table 1).

Table 1: The electromagnetic spectrum

Radiation type	Wave length λ , (Å)	Frequency $\nu = c / \lambda$, (Hz)	Applications
radio	10^{14}	3×10^{4}	Spin orientation
Nuclear magnetic resonance	10^{12}	3×10^{6}	
Television	10^{10}	3×10^{8}	
Radar	10^{8}	3×10^{10}	
Microwave	10^{7}	3×10^{11}	Rotational
Far infrared	10^{6}	3×10^{12}	Vibrational
Near infrared	10^{4}	3×10^{14}	
Visible	$8 \times 10^{3} - 4 \times 10^{3}$	3.7×10^{14} - 7.5×10^{14}	Electronic
Ultraviolet	3×10^{3}	1×10^{15}	
X-rays	1	3×10^{18}	
Gamma rays	10^{-2}	3×10^{20}	Nuclear transitions
Cosmic rays	10^{-4}	3×10^{22}	

The propagation of these radiations involves both electric and magnetic forces which give rise to their common class name electromagnetic radiation. In spectroscopy, only the effects associated with electric component of electromagnetic wave are important. Therefore, the light wave traveling through space is represented by a sinusoidal trace (figure 1). In this diagram λ is the wavelength and distance A is known as the maximum amplitude of the wave. Although a wave is frequently characterized in terms of its wavelength λ, often the terms such as wave number (ν), frequency (ν), cycles per second (cps) or hertz (Hz) are also used.

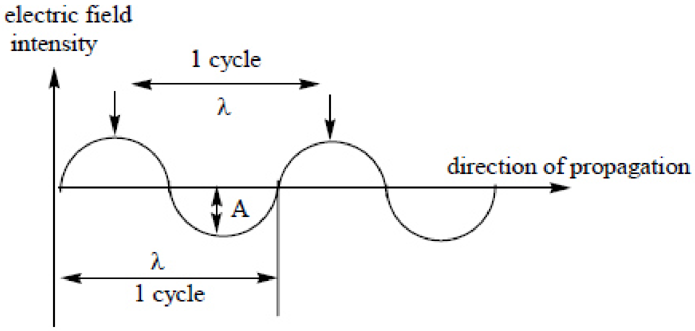


Figure 1: Wave like propagation of light (λ = wavelength , A = amplitude)

The unit commonly used to describe the wavelength is centimeters (cm), the different units are used to express the wavelengths in different parts of the electromagnetic spectrum. For example, in the ultraviolet and visible region, the units use are angstrom (Å) and nanometer (nm). In the infrared region, the commonly used unit is wave number (ν), which gives the number of waves per centimeter. Thus

The four quantities wavelength, wave number, frequency and velocity can be related to each other by following relationships

$$\textbf{Wavelength } (\lambda) = 1 / \nu = c / \nu$$

$$\textbf{Wave-number } (\nu) = 1 / \lambda = \nu / c$$

$$\textbf{Frequency } (\nu) = c / \lambda = c\,\nu$$

$$\textbf{Velocity } (c) = \nu\lambda = \nu / \nu$$

III.2.2 Absorption of Different Electromagnetic radiations by Organic Molecules :

In absorption spectroscopy, though the mechanism of absorption of energy is different in the ultraviolet, infrared and nuclear magnetic resonance regions, the fundamental process is the absorption of a discrete amount of energy. The energy required for the transition from a state of lower energy (E_1) to state of higher energy (E_2) is exactly equivalent to the energy of electromagnetic radiation that causes transition.

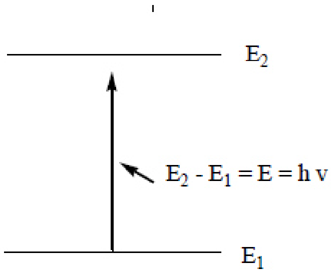


Figure 2: Energy transition for the absorption of any electromagnetic radiation

$E_1 - E_2 = E = h\nu = h\,c / \lambda$

Where E is energy of electromagnetic radiation being absorbed, h is the universal Planck's constant, 6.624×10^{-27} erg sec and ν is the frequency of incident light in cycles per second (cps or hertz, Hz), c is velocity of light 2.998×10^{10} cm s^{-1} and λ = wavelength (cm) .

Therefore, higher is the frequency, higher would be the energy and longer is the wavelength, lower would be the energy. As we move from cosmic radiations to ultraviolet region to infrared region and then radio frequencies, we are gradually moving to regions of lower energies.

A molecule can only absorb a particular frequency, if there exists within the molecule an energy transition of magnitude $E = h\nu$.

a. **Ultraviolet – visible spectroscopy:** (λ 200 - 800 nm) studies the changes in electronic energy levels within the molecule arising due to transfer of electrons from π- or non-bonding orbitals. It commonly provides the knowledge about π-electron systems, conjugated unsaturations, aromatic compounds and conjugated non-bonding electron systems etc.

b. **Infrared spectroscopy:** (ν 400-4000 cm^{-1}) studies the changes in the vibrational and rotation movements of the molecules. It is commonly used to show the presence or absence of functional groups which have specific vibration frequencies viz. C=O, NH_2, OH, CH, C-O etc.

c. **Nuclear magnetic resonance:** (radiofrequency ν 60-600 MHz) provides the information about changes in magnetic properties of certain atomic nuclei. ^{1}H and ^{13}C are the most commonly studied nuclei for their different environments and provide different signals for magnetically non-equivalent nuclei of the same atom present in the same molecule.

d. **Ultraviolet and Visible Spectroscopy:** This absorption spectroscopy uses electromagnetic radiations between 190 nm to 800 nm and is divided into the ultraviolet (UV, 190-400 nm) and visible (VIS, 400-800 nm) regions. Since the absorption of ultraviolet or visible radiation by a molecule leads transition among electronic energy levels of the molecule, it is also often called as electronic spectroscopy. The information provided by this spectroscopy when combined with the information provided by NMR and IR spectral data leads to valuable structural proposals.

III.2.3 Nature of Electronic Transitions:

The total energy of a molecule is the sum of its electronic, its vibration energy and its rotational energy. Energy absorbed in the UV region produces changes in the electronic energy of the molecule. As a molecule absorbs energy, an electron is promoted from an occupied molecular orbital (usually a non-bonding n or bonding π orbital) to an unoccupied molecular orbital (an anti bonding π^* or σ^* orbital) of greater potential energy (figure 3). For most molecules, the lowest-energy occupied molecular orbital's are σ orbital's, which correspond to σ bonds. The π orbital's lie at relatively higher energy levels than σ orbital's and the non-bonding orbital's that hold unshared pairs of electrons lie even at higher energies. The anti bonding orbital's (π^* and σ^*) are orbital's of highest energy. The relative potential energies of these orbital's and various possible transitions have been depicted in figure 3.

The saturated aliphatic hydrocarbons (alkanes) exhibit only σ - σ^* transitions but depending on the functional groups the organic molecules may undergo several possible transitions which can be placed in the increasing order of their energies viz. n to π^* < n to σ^* < π to π^* < σ to π^* < σ to σ^*. Since all these transitions require fixed amount of energy (quantized), an ultraviolet or visible spectrum of a compound would consist of one or more well defined peaks, each corresponding to the transfer of an electron from one electronic level to another. If the differences between electronic energy levels of two electronic states are well defined i.e. if the nuclei of the two atoms of a diatomic molecule are held in fixed position, the peaks accordingly should be sharp. However, vibrations and rotations of nuclei occur constantly and as a result each electronic state in a molecule is associated with a large

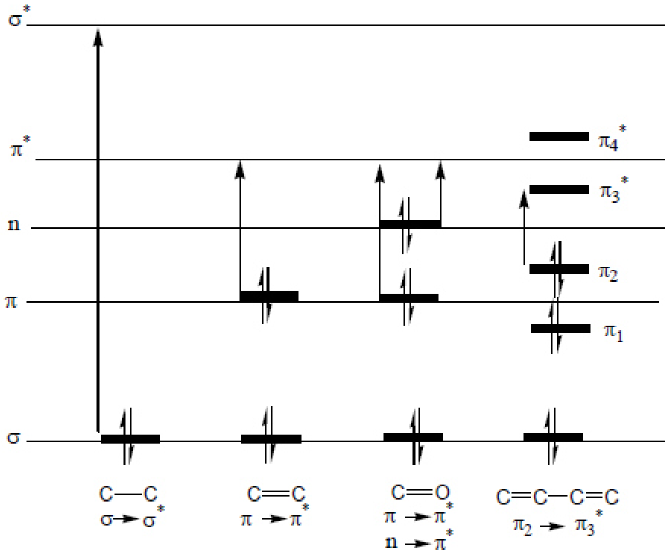


Figure 3 : Relative energies of orbital's most commonly involved in electronic spectroscopy of organic molecules

number of vibrational and rotational states. At room temperature, the molecules in the ground state will be in the zero vibration level ($G\upsilon_o$). This is shown schematically in figure 4. The transition of an electron from one energy level to another is thus accompanied by simultaneous change in vibration and rotational states and causes transitions between various vibration and rotational levels of lower and higher energy electronic states. Therefore many radiations of closely placed frequencies are absorbed and a broad absorption band is obtained. When a molecule absorbs ultraviolet or visible light of a defined energy, an assumption is made that only one electron is excited form bonding orbital or non-bonding orbital to an anti-bonding orbital and all other electrons remain unaffected. The excited state thus produced is formed in a very short time i.e. of the order of 10^{-15} seconds. In accordance with Franck-Condon principle, during electronic excitation the atoms of the molecule do not move.

The most probable transition would appear to involve the promotion of one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), but in many cases several transitions can be observed, giving several absorption bands in the spectrum. We can have a general view of the possible transitions prevailing in organic compounds.

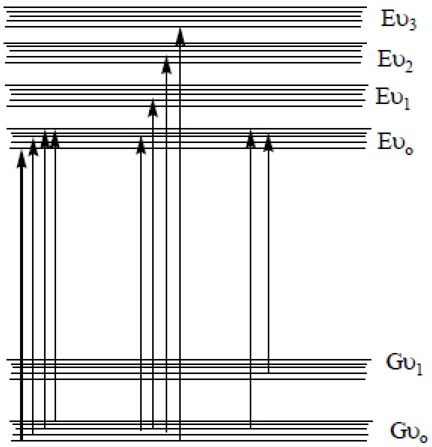


Figure 4 : Energy level diagram showing excitation between different vibrational and rotational levels of two electronic states

Alkanes can only undergo σ to σ* transitions. These are high-energy transitions and involve very short wavelength ultraviolet light (< 150 nm). These transitions usually fall out-side the generally available measurable range of UV-visible spectrophotometers (200-1000 nm). The σ to σ* transitions of methane and ethane are at 122 and 135 nm, respectively. In alkenes amongst the available σ to σ* and π to π* transitions, the π to π* transitions are of lowest energy and absorb radiations between 170-190 nm.

In saturated aliphatic ketones the lowest energy transition involves the transfer of one electron of the nonbonding electrons of oxygen to the relatively low-lying π* anti-bonding orbital. This n to π* transition is of lowest energy (~280 nm) but is of low intensity as it is symmetry forbidden. Two other available transitions are n to π* and π to π*. The most intense band for these compounds is always due to π to π* transition.

In conjugated dienes the π to π* orbital's of the two alkene groups combine to form new orbital's – two bonding orbitals named as π_1 and π_2 and two anti bonding orbital's named as π_3* and π_4*. It is apparent that a new π to π* transition of low energy is available as a result of conjugation. Conjugated dienes as a result absorb at relatively longer wavelength than do isolated alkenes .

III.2.4 Principles of Absorption Spectroscopy : Beer's and Lambert's Law:

The greater the number of molecules that absorb light of a given wavelength, the greater the extent of light absorption and higher the peak intensity in absorption spectrum. If there are only a few molecules that absorb radiation, the total absorption of energy is less and consequently lower intensity peak is observed. This makes the basis of Beer-Lambert Law which states that the fraction of incident radiation absorbed is proportional to the number of absorbing molecules in its path.

When the radiation passes through a solution, the amount of light absorbed or transmitted is an exponential function of the molecular concentration of the solute and also a function of length of the path of radiation through the sample. Therefore,

$$\mathrm{Log}\ I_o / I = \varepsilon\ c\ l$$

Where I_o = Intensity of the incident light (or the light intensity passing through a reference cell)

I = Intensity of light transmitted through the sample solution

c = concentration of the solute in mol l^{-1}

l = path length of the sample in cm

ε = molar absorptivity or the molar extinction coefficient of the substance whose light absorption is under investigation. It is a constant and is a characteristic of a given absorbing species (molecule or ion) in a particular solvent at a particular wavelength. ε is numerically equal to the absorbance of a solution of unit molar concentration (c = 1) in a cell of unit length (l = 1) and its units are $\text{liters.moles}^{-1}.\text{cm}^{-1}$. However, it is customary practice among organic chemists to omit the units.

The ratio I / I_o is known as transmittance T and the logarithm of the inverse ratio I_o / I is known as the absorbance A.

Therefore

$- \text{Log } I / I_o = - \log T = \varepsilon\, c\, l$

and $\text{Log } I_o / I = A = \varepsilon\, c\, l$

or $A = \varepsilon\, c\, l$

For presenting the absorption characteristics of a spectrum, the positions of peaks are reported as λ_{max} (in nm) values and the absorptivity is expressed in parenthesis.

III.2.5 Spectral Measurements :

The UV-Vis spectra are usually measured in very dilute solutions and the most important criterion in the choice of solvent is that the solvent must be transparent within the wavelength range being examined. Table 2 lists some common solvents with their lower wavelength cut off limits. Below these limits, the solvents show excessive absorbance and should not be used to determine UV spectrum of a sample.

Table 2 : Common solvents with their cut-off limits

. S. No.	Solvent	Cut-off wavelength (nm)
1	Acetonitrile	190
2	Water	191
3	Cyclohexane	195
4	Hexane	201
5	Methanol	203
6	95% ethanol	304
7	1,4-dioxane	215
8	Ether	215
9	Dichloromethane	220
10	Chloroform	237
11	Carbon tetrachloride	257
12	Benzene	280

Of the solvents listed in table 2, water, 95% ethanol and hexane are the most commonly used solvents. Each is transparent in the region of UV-Vis spectrum. For preparing stock solutions, the sample is accurately weighed and made up to volume in volumetric flask. Aliquats are removed from this solution and appropriate dilutions are made to make solutions of desired concentration. For recording the spectrum 1 cm square quartz cell is commonly used. These require approx. 3 ml of solution. The quartz cell containing solution is placed in the path of light beam and spectrum is recorded by varying the wavelength of incident light.

III.2.6 Solvent Effects:

Highly pure, non-polar solvents such as saturated hydrocarbons do not interact with solute molecules either in the ground or excited state and the absorption spectrum of a compound in these solvents is similar to the one in a pure gaseous state. However, polar solvents such as water, alcohols etc. may stabilize or destabilize the molecular orbital's of a molecule either in the ground state or in excited state and the spectrum of a compound in these solvents may significantly vary from the one recorded in a hydrocarbon solvent.

(i) π to π* Transitions

In case of π to π* transitions, the excited states are more polar than the ground state and the dipole-dipole interactions with solvent molecules lower the energy of the excited state more than that of the ground state. Therefore a polar solvent decreases the energy of π to π* transition and absorption maximum appears ~10-20 nm red shifted in going from hexane to ethanol solvent.

(ii) n to π* Transitions

In case of n to π* transitions, the polar solvents form hydrogen bonds with the ground state of polar molecules more readily than with their excited states. Therefore, in polar solvents the energies of electronic transitions are increased. For example, the figure 5 shows that the absorption maximum of acetone in hexane appears at 279 nm which in water is shifted to 264 nm, with a blue shift of 15 nm.

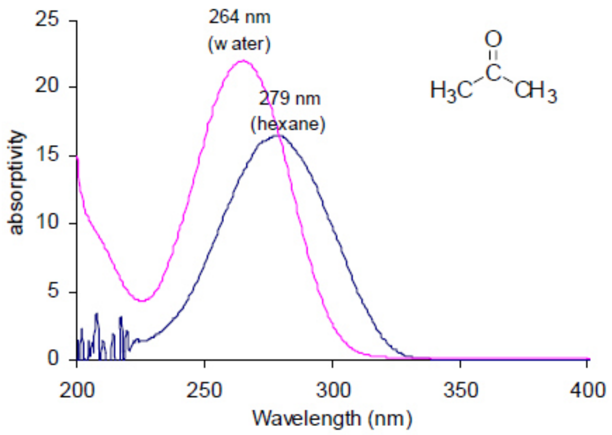


Figure 5 : UV-spectra of acetone in hexane and in water

III.2.7 Some important terms and definitions

(i) **Chromophore:** The energy of radiation being absorbed during excitation of electrons from ground state to excited state primarily depends on the nuclei that hold the electrons together in a bond. The group of atoms containing electrons responsible for the absorption is called chromophore. Most of the simple un-conjugated chromophores give rise to high energy transitions of little use. Some of these transitions have been listed in table 3.

Table 3: Absorption maxima of simple un-conjugated chromophores.

Chromophore	Transition	ε_{max}	λ_{max} (nm)
σ – bonded electrons			
(C-C, C-H etc.)	σ to σ^*		~ 150
Lone pair electrons			
-O-, -N-, -S-	n to σ^*	100-1000	~ 190
C=O, C=N	n to π*	15	~300
	π to π*	500	~190
R-C≡N	n to π*	5	~ 170
R-COOH, $RCONH_2$, RCOOR	n to π*	50	~ 210

For example, alkanes contain only single bonds with only possible σ to σ^* type electronic transitions. These transitions absorb radiations shorter than wavelengths that are experimentally accessible in usually available spectrophotometers. In saturated molecules with heteroatom bearing non-bonding pairs of electrons, n to σ^* transitions become available. These are also high energy transitions. In unsaturated compounds, π to π* transitions become possible. Alkenes and alkynes absorb ~ 170 nm but the presence of substituent's significantly affects their position. The carbonyl compounds and imines can also undergo n to π* transitions in addition to π to π*. Amongst these, the most studied transitions are n to π* as these absorb at relatively longer wavelength 280-300 nm. These are low intensity (ε 10-100) transitions.

(ii) Auxochrome: The substituents that themselves do not absorb ultraviolet radiations but their presence shifts the absorption maximum to longer wavelength are called auxochromes. The substituents like methyl, hydroxyl, alkoxy, halogen, amino group etc. are some examples of auxochromes.

(iii) Bathochromic Shift or Red shift: A shift of an absorption maximum towards longer wavelength or lower energy.

(iv) Hypsochromic Shift or Blue Shift: A shift of an absorption maximum towards shorter wavelength or higher energy.

(v) Hypochromic Effect: An effect that results in decreased absorption intensity.

(vi) Hyperchromic Effect: An effect that results in increased absorption intensity.[35]

III.3 Infrared IR:

III.3.1 Introduction:

The qualitative aspects of infrared spectroscopy are one of the most powerful attributes of this diverse and versatile analytical technique. Over the years, much has been published in terms of the fundamental absorption frequencies (also known as group frequencies) which are the key to unlocking the structure–spectral relationships of the associated molecular vibrations. Applying this knowledge at the practical routine level tends to be a mixture of art and science. While many purists will argue against this statement,[38]

III.3.2 the origins of the infrared spectrum:

In the most basic terms, the infrared spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate to the vibration of specific sets of chemical bonds from within a molecule. First, it is important to reflect on the distribution of energy.

possessed by a molecule at any given moment, defined as the sum of the contributing energy terms (Equation 1):

$$\mathbf{E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational}}$$

The translational energy relates to the displacement of molecules in space as a function of the normal thermal motions of matter. Rotational energy, which gives rise to its own form of spectroscopy, is observed as the tumbling motion of a molecule, which is the result of the absorption of energy within the microwave region. The vibrational energy component is a higher energy term and corresponds to the absorption of energy by a molecule as the component atoms vibrate about the mean center of their chemical bonds. The electronic components linked to the energy transitions of electrons as they are distributed throughout the molecule, either localized within specific bonds, or delocalized over structures, such as an aromatic ring. In order to observe such electronic transitions, it is necessary to apply energy in the form of visible and ultraviolet radiation (Equation 2):[38]

$$\mathbf{E = h\upsilon \quad frequency/energy}$$

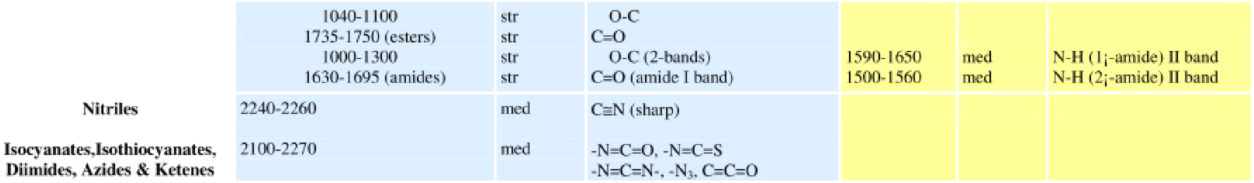
III.3.3 Functional Groups:

In the following table some main functional are mentioned.

Table III.3.3: Typical infrared absorption frequencies

Typical Infrared Absorption Frequencies

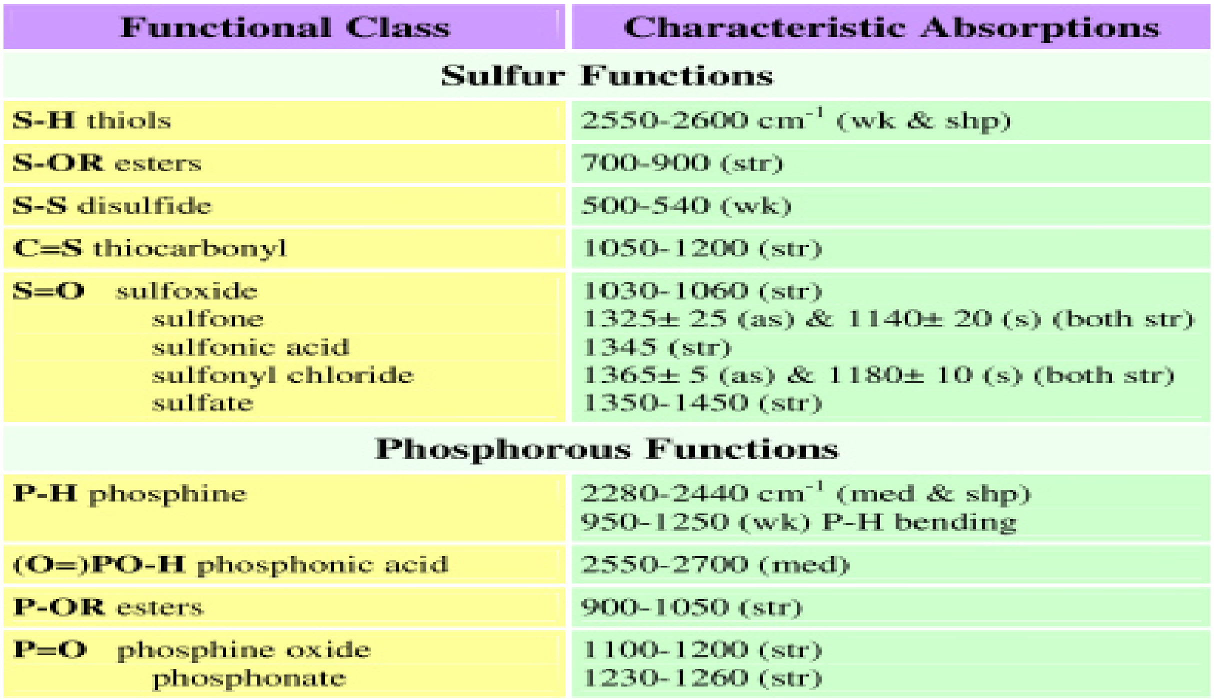
	Stretching Vibrations			Bending Vibrations		
Functional Class	Range (nm)	Intensity	Assignment	Range (nm)	Intensity	Assignment
Alkanes	2850-3000	str	CH$_3$, CH$_2$ & CH 2 or 3 bands	1350-1470 1370-1390 720-725	med med wk	CH$_2$ & CH$_3$ deformation CH$_3$ deformation CH$_2$ rocking
Alkenes	3020-3100 1630-1680 1900-2000	med var str	=C-H & =CH$_2$ (usually sharp) C=C (symmetry reduces intensity) C=C asymmetric stretch	880-995 780-850 675-730	str med med	=C-H & =CH$_2$ (out-of-plane bending) cis-RCH=CHR
Alkynes	3300 2100-2250	str var	C-H (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
Arenes	3030 1600 & 1500	var med-wk	C-H (may be several bands) C=C (in ring) (2 bands) (3 if conjugated)	690-900	str-med	C-H bending & ring puckering
Alcohols & Phenols	3580-3650 3200-3550 970-1250	var str str	O-H (free), usually sharp O-H (H-bonded), usually broad C-O	1330-1430 650-770	med var-wk	O-H bending (in-plane) O-H bend (out-of-plane)
Amines	3400-3500 (dil. soln.) 3300-3400 (dil. soln.) 1000-1250	wk wk med	N-H (1°-amines), 2 bands N-H (2°-amines) C-N	1550-1650 660-900	med-str var	NH$_2$ scissoring (1°-amines) NH$_2$ & N-H wagging (shifts on H-bonding)
Aldehydes & Ketones	2690-2840 (2 bands) 1720-1740 1710-1720 1690 1675 1745 1780	med str str str str str str	C-H (aldehyde C-H) C=O (saturated aldehyde) C=O (saturated ketone) aryl ketone α,β-unsaturation cyclopentanone cyclobutanone	1350-1360 1400-1450 1100	str str med	α-CH$_3$ bending α-CH$_2$ bending C-C-C bending
Carboxylic Acids & Derivatives	2500-3300 (acids) overlap C-H 1705-1720 (acids) 1210-1320 (acids) 1785-1815 (acyl halides) 1750 & 1820 (anhydrides) 1040-1100 1735-1750 (esters) 1000-1300 1630-1695 (amides)	str str med-str str str str str str str	O-H (very broad) C=O (H-bonded) O-C (sometimes 2-peaks) C=O C=O (2-bands) O-C C=O O-C (2-bands) C=O (amide I band)	1395-1440 1590-1650 1500-1560	med med med	C-O-H bending N-H (1¡-amide) II band N-H (2¡-amide) II band
Nitriles	2240-2260	med	C≡N (sharp)			
Isocyanates,Isothiocyanates, Diimides, Azides & Ketenes	2100-2270	med	-N=C=O, -N=C=S -N=C=N-, -N$_3$, C=C=O			



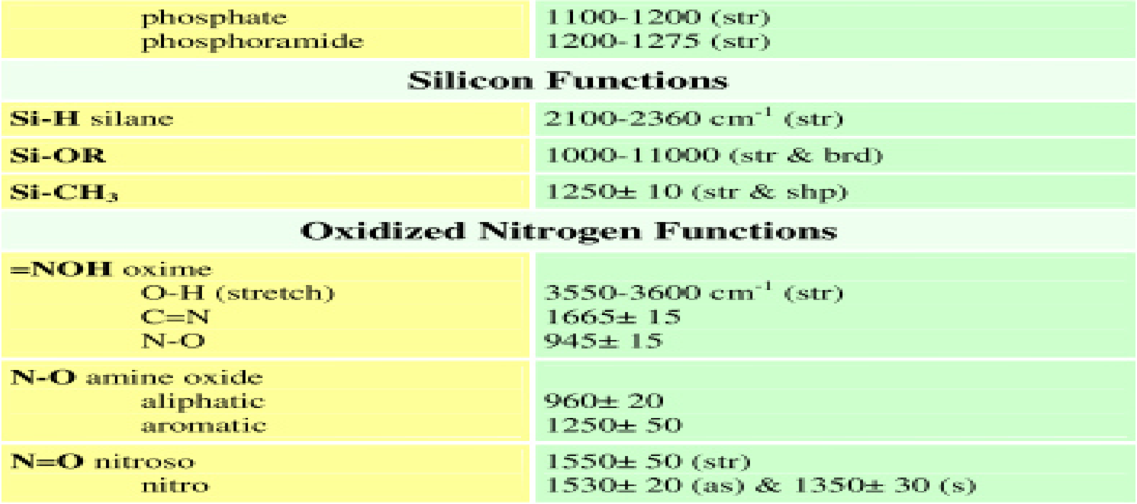
- **Other Functional Groups:**

Infrared absorption data for some functional groups not listed in the preceding table are given below. Most of the absorptions cited are associated with stretching vibrations. Standard abbreviations (str = strong, wk = weak, brd = broad &shp = sharp) are used to describe the absorption bands.

Other Functional Groups

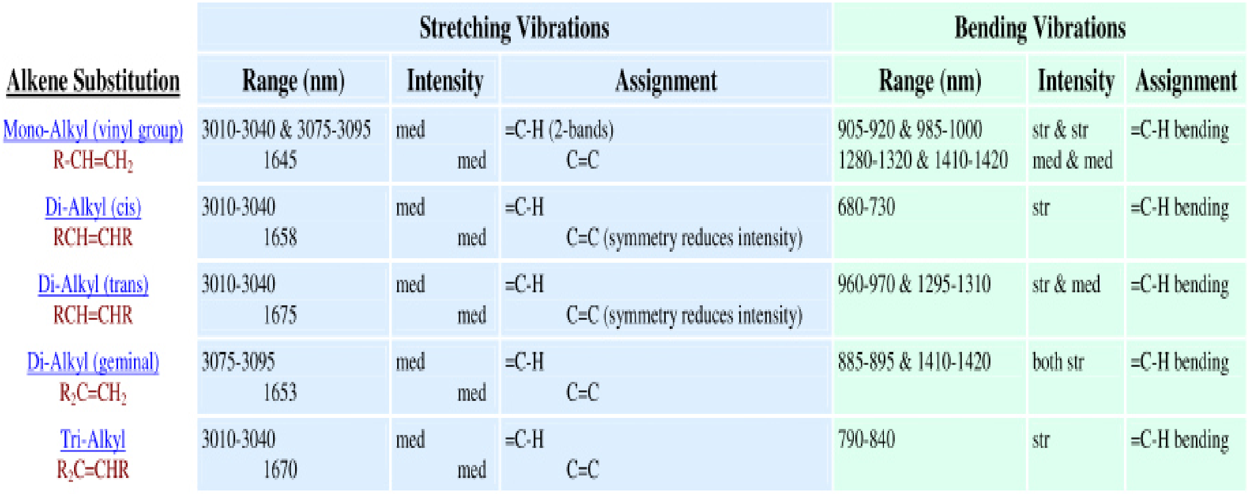


Functional Class	Characteristic Absorptions
Sulfur Functions	
S-H thiols	2550-2600 cm^{-1} (wk & shp)
S-OR esters	700-900 (str)
S-S disulfide	500-540 (wk)
C=S thiocarbonyl	1050-1200 (str)
S=O sulfoxide sulfone sulfonic acid sulfonyl chloride sulfate	1030-1060 (str) 1325± 25 (as) & 1140± 20 (s) (both str) 1345 (str) 1365± 5 (as) & 1180± 10 (s) (both str) 1350-1450 (str)
Phosphorous Functions	
P-H phosphine	2280-2440 cm^{-1} (med & shp) 950-1250 (wk) P-H bending
(O=)PO-H phosphonic acid	2550-2700 (med)
P-OR esters	900-1050 (str)
P=O phosphine oxide phosphonate	1100-1200 (str) 1230-1260 (str)



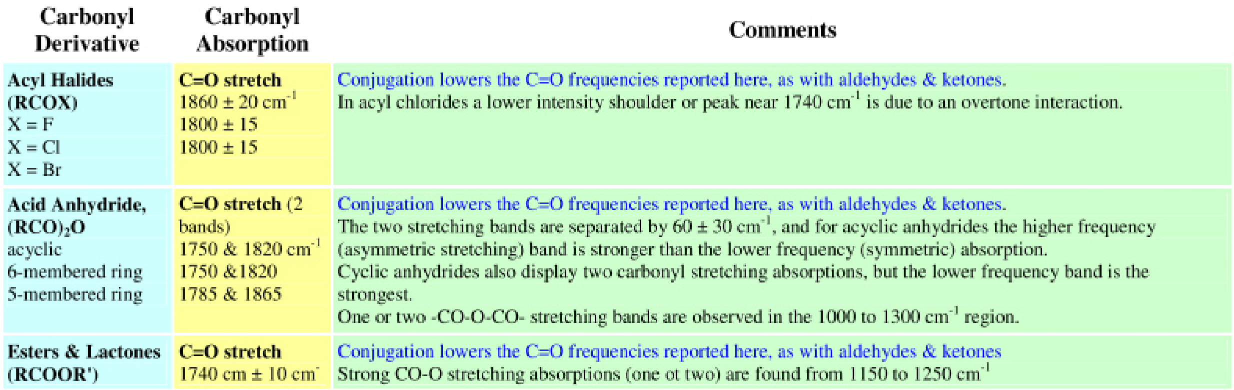
Functional Class	Characteristic Absorptions
phosphate phosphoramide	1100-1200 (str) 1200-1275 (str)
Silicon Functions	
Si-H silane	2100-2360 cm^{-1} (str)
Si-OR	1000-11000 (str & brd)
Si-CH$_3$	1250± 10 (str & shp)
Oxidized Nitrogen Functions	
=NOH oxime O-H (stretch) C=N N-O	 3550-3600 cm^{-1} (str) 1665± 15 945± 15
N-O amine oxide aliphatic aromatic	 960± 20 1250± 50
N=O nitroso nitro	1550± 50 (str) 1530± 20 (as) & 1350± 30 (s)

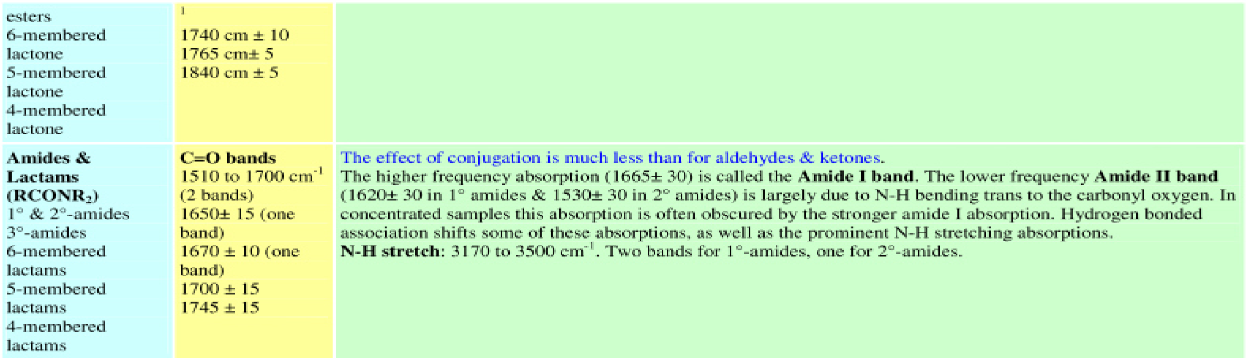
➢ Alkene Absorption Frequencies:



	Stretching Vibrations			Bending Vibrations		
Alkene Substitution	Range (nm)	Intensity	Assignment	Range (nm)	Intensity	Assignment
Mono-Alkyl (vinyl group) R-CH=CH$_2$	3010-3040 & 3075-3095 1645	med med	=C-H (2-bands) C=C	905-920 & 985-1000 1280-1320 & 1410-1420	str & str med & med	=C-H bending
Di-Alkyl (cis) RCH=CHR	3010-3040 1658	med med	=C-H C=C (symmetry reduces intensity)	680-730	str	=C-H bending
Di-Alkyl (trans) RCH=CHR	3010-3040 1675	med med	=C-H C=C (symmetry reduces intensity)	960-970 & 1295-1310	str & med	=C-H bending
Di-Alkyl (geminal) R$_2$C=CH$_2$	3075-3095 1653	med med	=C-H C=C	885-895 & 1410-1420	both str	=C-H bending
Tri-Alkyl R$_2$C=CHR	3010-3040 1670	med med	=C-H C=C	790-840	str	=C-H bending

➢ Carboxylic Acid Derivatives:





Carbonyl Derivative	Carbonyl Absorption	Comments
Acyl Halides (RCOX) X = F X = Cl X = Br	**C=O stretch** 1860 ± 20 cm^{-1} 1800 ± 15 1800 ± 15	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones. In acyl chlorides a lower intensity shoulder or peak near 1740 cm^{-1} is due to an overtone interaction.
Acid Anhydride, (RCO)$_2$O acyclic 6-membered ring 5-membered ring	**C=O stretch** (2 bands) 1750 & 1820 cm^{-1} 1750 &1820 1785 & 1865	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones. The two stretching bands are separated by 60 ± 30 cm^{-1}, and for acyclic anhydrides the higher frequency (asymmetric stretching) band is stronger than the lower frequency (symmetric) absorption. Cyclic anhydrides also display two carbonyl stretching absorptions, but the lower frequency band is the strongest. One or two -CO-O-CO- stretching bands are observed in the 1000 to 1300 cm^{-1} region.
Esters & Lactones (RCOOR')	**C=O stretch** 1740 cm ± 10 cm^{-}	Conjugation lowers the C=O frequencies reported here, as with aldehydes & ketones Strong CO-O stretching absorptions (one ot two) are found from 1150 to 1250 cm^{-1}
esters 6-membered lactone 5-membered lactone 4-membered lactone	^{1} 1740 cm ± 10 1765 cm± 5 1840 cm ± 5	
Amides & Lactams (RCONR$_2$) 1° & 2°-amides 3°-amides 6-membered lactams 5-membered lactams 4-membered lactams	**C=O bands** 1510 to 1700 cm^{-1} (2 bands) 1650± 15 (one band) 1670 ± 10 (one band) 1700 ± 15 1745 ± 15	The effect of conjugation is much less than for aldehydes & ketones. The higher frequency absorption (1665± 30) is called the **Amide I band**. The lower frequency **Amide II band** (1620± 30 in 1° amides & 1530± 30 in 2° amides) is largely due to N-H bending trans to the carbonyl oxygen. In concentrated samples this absorption is often obscured by the stronger amide I absorption. Hydrogen bonded association shifts some of these absorptions, as well as the prominent N-H stretching absorptions. **N-H stretch**: 3170 to 3500 cm^{-1}. Two bands for 1°-amides, one for 2°-amides.

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Experimental part:

I. Extraction of pine tar:

I.1 method:

We take a bit of pine bark and place it in a closed container and put it over the fire, Put a small hole connected to the tube, Keep at the end of the tube another container for collecting the tar this process showing in the following figure:

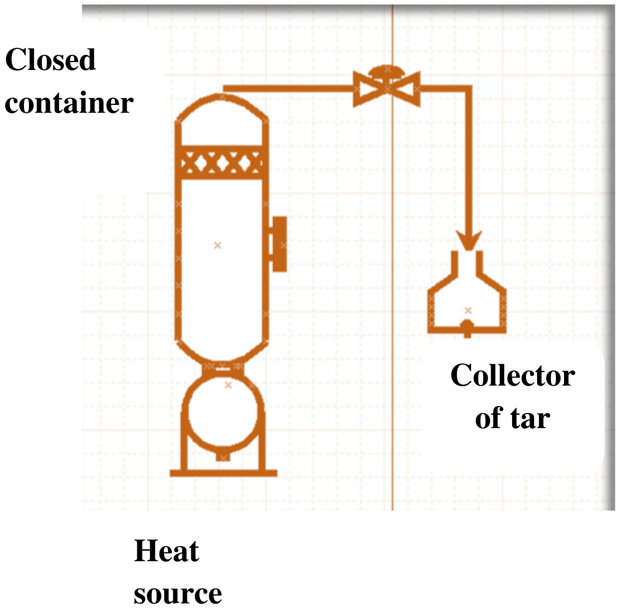


Figure I.1: Scheme for extraction of tar

R.M:

In this studies we use tar coming from the market not tar extracted in the house after confirmation by IR that are same, they have same composition.

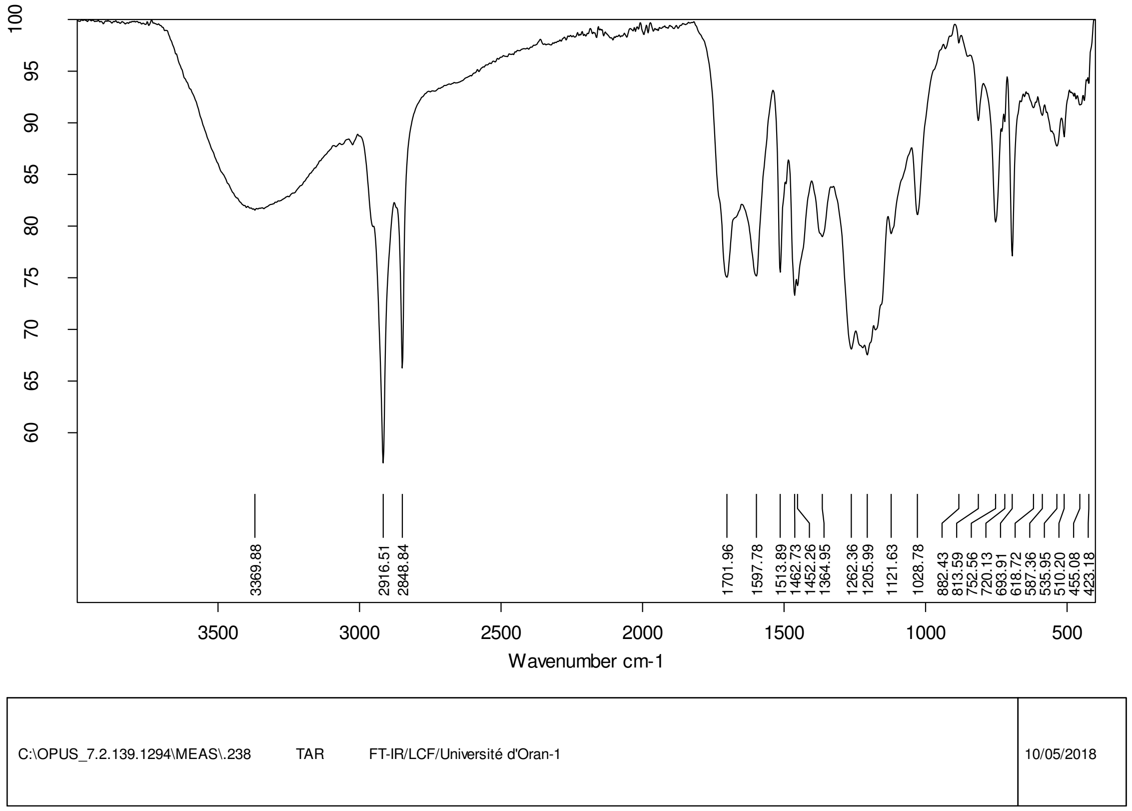
I.2 Calculate the yield:

$$R= m_0\text{-}me/m_0$$

$$R=0.040-0.035/0.040$$

$$\mathbf{R=12.5\%}$$

I.3 infrared spectrum IR for tar:



FigureI.3: The infrared spectrum of tar

The spectrum IR for pine tar are illustrated in figure **I.3**, the main characteristic bands of pine tar are shown in the table I.3

Table I.3: the main characteristic bands of pine tar

Frequency cm^{-}	function
1028	C-H aromatic aliphatic
3369	O-H free
2916	C-H
813	para substitutes
752	ortho substitutes
1701	C=O
1597	C-C benzene cycle

II. Thermodynamic and kinetic study:

II.1 Introduction:

in this chapter all the experimental results obtained are presented and discussed the experimental program carried out has considered the study of the adsorption of heavy metals as pollutant by use pine tar. the heavy metals uses in this experience are nickel, lead and chromium. The collar indicator is Xylenol orange for lead and nickel and carbazone bases for chromium.

II.2.1 Xylenol orange: is an organic reagent.

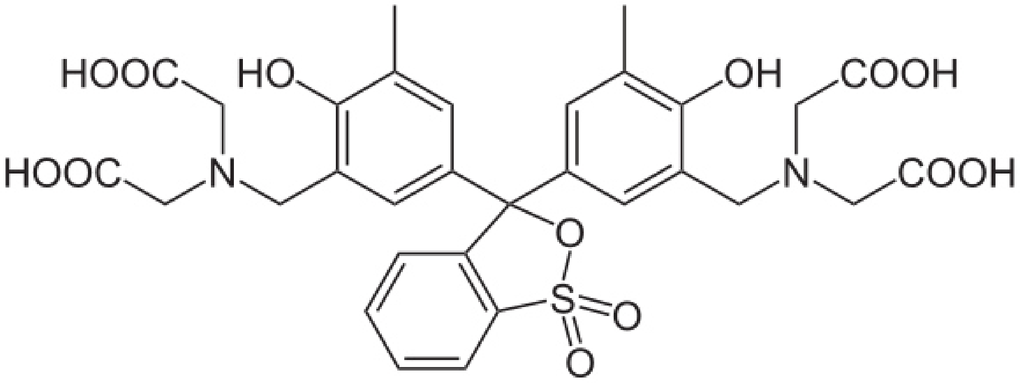


Figure II.2.1: Structure of Xylenol orange

II.2.2 The properties of Xylenol orange are mentioned in this table :

Table II.2.2: the properties of Xylenol orange

Properties	
Chemical formula	$C_{31}H_{32}N_2O_{13}S$
Molar mass	672.66 g·mol^{-1}
Melting point	195 °C (383 °F; 468 K)
Solubility in water	200 mg/mL

II.3.1 Crabazone bases : 1,5 Diphenyl Carbazone

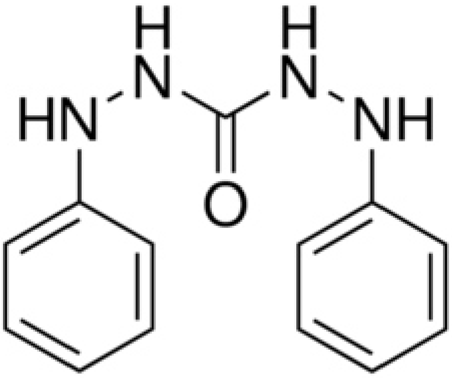


Figure II.3.1: The structure of 1,5 Diphenyl Carbazone

II.3.2 Indicator for chromium: is carbazone bases Consists of:

- 0.05g carbazone
- 50 mil of acetone
- 5 mil of sulphuric acid H_2SO_4

We take 10 mil and add 40 mil of water an add 5 mil of sulphuric acid H_2SO_4 again.

II.4 kinetic study of nickel fixation on tar pine:

II.4.1 Introduction:

Ni^{+2} nickel

the adsorption rate of nickel on the pine tar is determined by addition of 0.025 g of pine tar to 4mil of water contents of nickel with concentration of 10^{-4}g/l for know the best condition for this adsorption we do some experience for that the results obtained in different physicochemical conditions at the bottom.

II.4.2 traces the calibration curve:

For trace the calibration curve take some concentration and measure the absorbance of each point the result showing in the table number II.4.2

Table II.4.2: the experimental value of the concentration according to absorbance

C (g/l)	**10^{-4}**	**7.10^{-5}**	**$4{,}9\ .10^{-5}$**	**$1{,}9\ .10^{-5}$**	**$3{,}8\ .\ 10^{-6}$**	**$1{,}79\ .10^{-6}$**
A	**0.791**	**0.388**	**0.353**	**0.314**	**0.098**	**0.078**

The curved line of the concentration according to the absorbance is showing in figure II.4.2

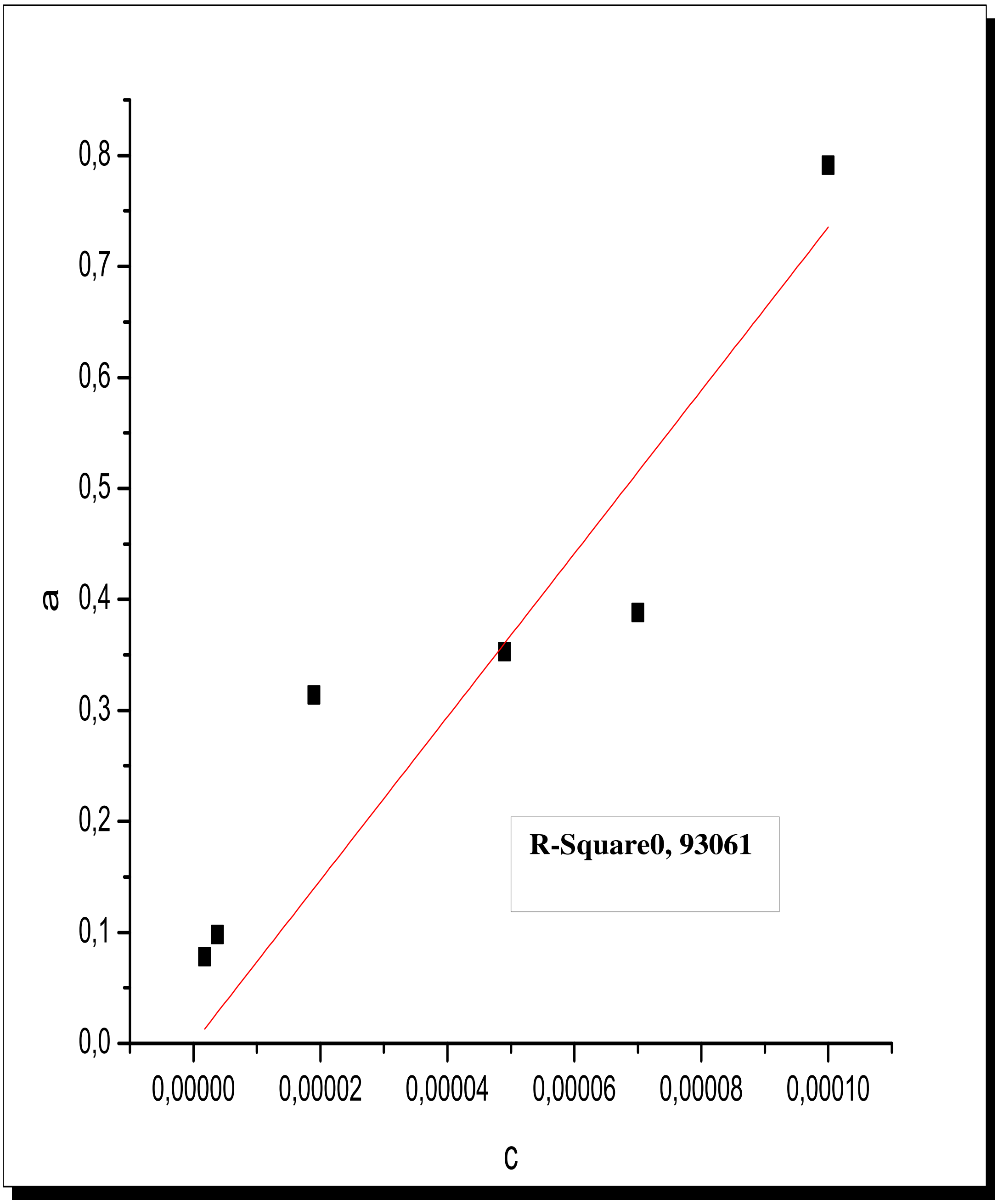


Figure II.4.2: the calibration line of nickel the line pass through the origin which proves that the Beer Lambert law is verified

II.4.3 Turns effect of nickel:

We study this effect by do many test in deference speed and deference time we find the result which appear in the following curves:

The conditions of this experience are:

A_0=0.791 for C_0=10^{-4}g/l t=(18_25) °C and weight=0.025g

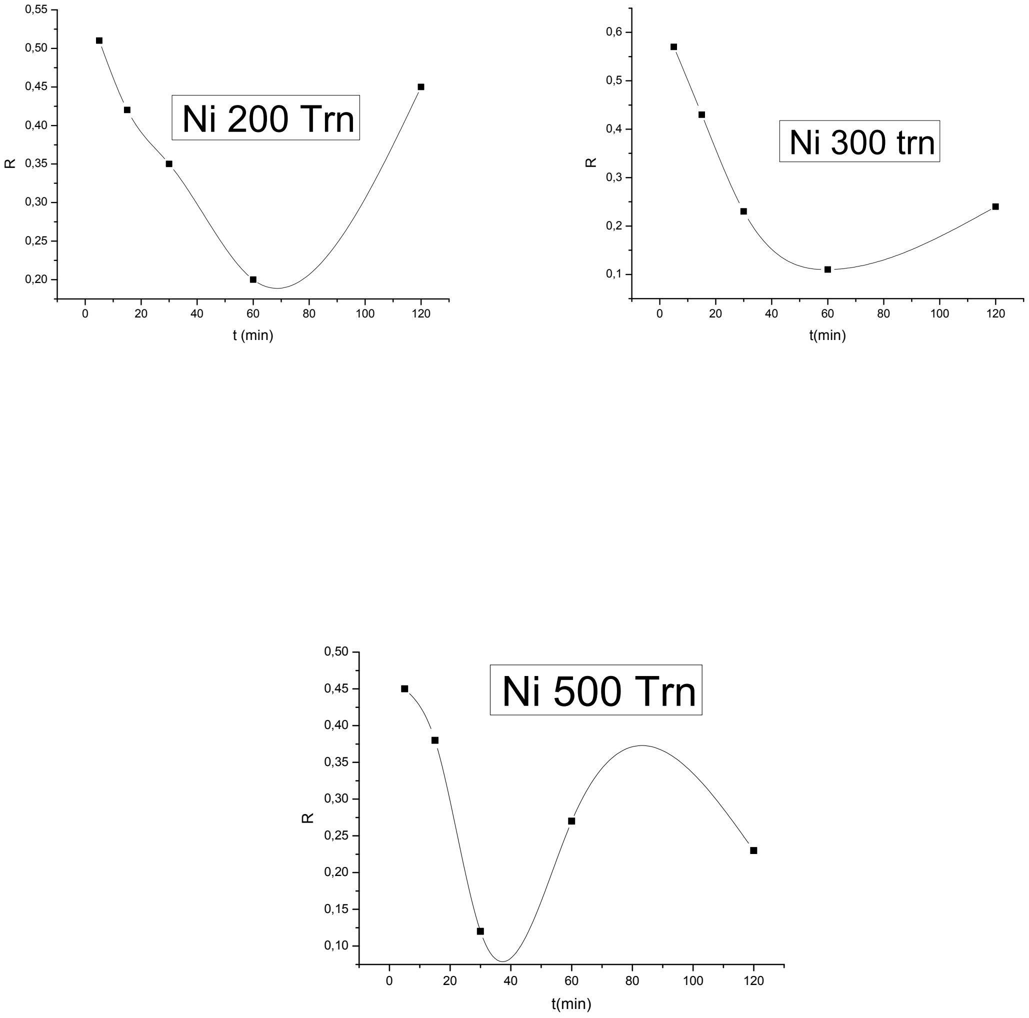


Figure II.4.3: Change in the yield in terms of time at each speed (200.300.500)trn/min

According to this result the best turn numbers corresponds to the high yield of nickel on the tar is at speed of 300 turn/min and time at 5 min.

II.4.4 Temperature effect:

We study this effect by do many test in deference temperature and deference time we find the result which appear in the following curves:

The conditions of this experience are:

A_0=0.791 for $C_0=10^{-4}$g/l and speed = 300trn/min and weight=0.025g

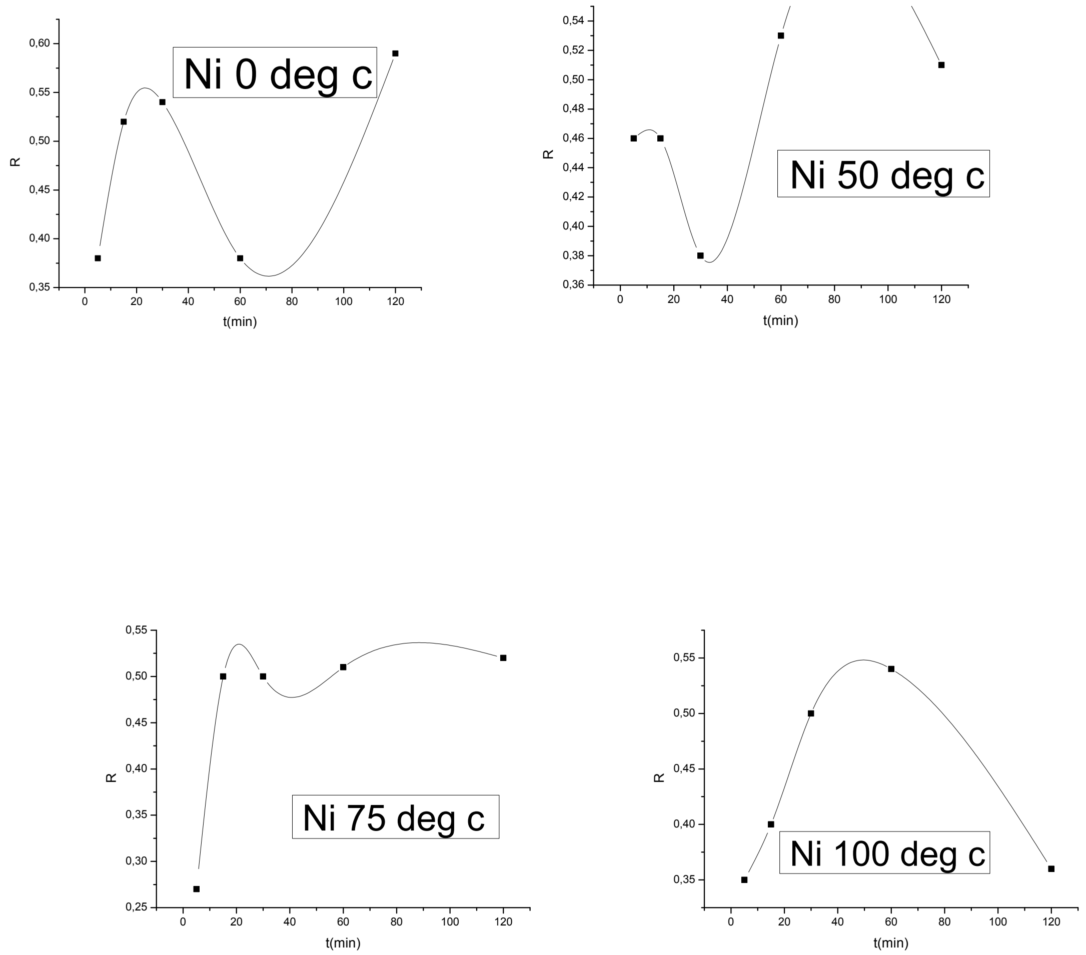


Figure II.4.4: Change in the yield in terms of time at each temperature (0^0C.50^0C.75^0C.100^0C) for nickel

According to this result the best temperature corresponds to the high yield of nickel on the tar it is lab temperature **t=(18_25) °C**.

II.4.5 pH effect:

We study this effect by do many test in deference pH; we find the result which appears in the following curve:

The conditions of this experience are:

A_0=0.791 for C_0=10^{-4}g/l and T=(18_25) °C and contact time=5min ,of weight=0.025g

And Speed=300trn/min

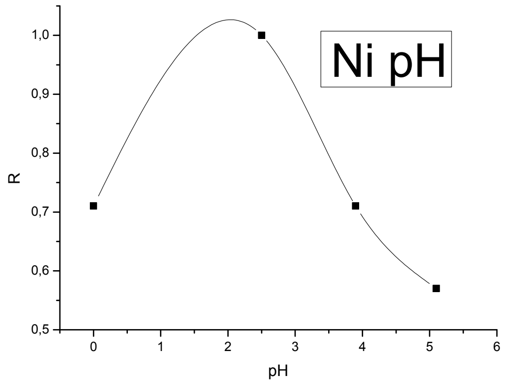


Figure II.4.5 : Change in the yield in terms of pH

According to this result the best pH corresponds to the high yield of nickel on the tar it is at the pH=2, 5.

II.4.6 Weight effect:

We study this effect by do many test in deference weight; we find the result which appears in the following curve:

A_0=0.791 forC_0=10^{-4}g/l and T= (18_25) °C and time=5min and speed=300trn/min

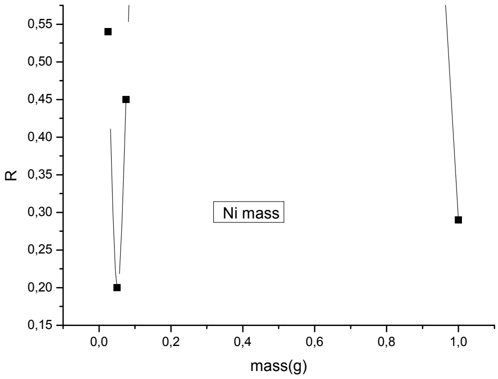


Figure II.4.6 : Change in the yield in terms of mass

According to this result the best weight corresponds to the high yield of nickel on the tar it is at the m=0,025g.

II.4.7 Result:

- According to all this result and when we compare experimental values we can find that the best condition for adsorption of the nickel on pine tar are:
  - Speed:300trn/min
  - Time of contact :5 min
  - Temperature: **t=(18_25) °C**
  - Weight:0.025(g)
  - pH:2,5

II.5 Adsorption phenomena:

II.5.1 Introduction:

The process of Adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate and adsorbent.

II.5.2 what is Adsorption Isotherm?

The process of Adsorption is usually studied through graphs know as adsorption isotherm. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature. Different adsorption isotherms have been Freundlich, Langmuir and BET theory.

II.5.3 Equation describing the adsorption isotherms:

Various equations have been proposed to describe the most representative models of a real model; those of Langmuir and frendlich are the most commonly used.

- **Basic Adsorption Isotherm:**

In the process of adsorption, adsorbate gets adsorbed on adsorbent.

$$\text{Adsorbate} + \text{Adsorbent} \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{Adsorption}$$

$$A + B \rightleftharpoons AB$$

According to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favored.

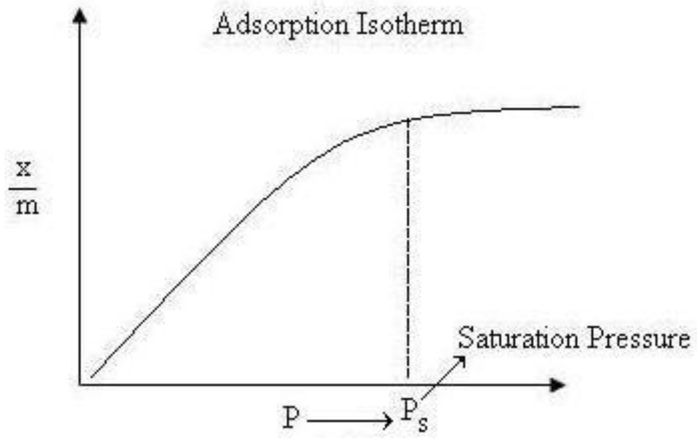


Figure II.5.3:Basic Adsorption Isotherm

From the graph, we can predict that after saturation pressure Ps, adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, Adsorption is independent of pressure.

II.5.4 Freundlich Adsorption Isotherm:

In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm.

$\mathbf{Q_e=K_f\,C_e^N}$ --------------(1)

Where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and gas at particular temperature. Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure

II.5.6 Langmuir Adsorption Isotherm:

In 1916 Langmuir proposed another Adsorption Isotherm known as Langmuir Adsorption isotherm. This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

$$A(g) + B(S) \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AB$$

Where A(g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

- **The Langmuir Isotherm:**

This isotherm described adsorbate-adsorbent systems in which the extent of adsorbate coverage is limited to one molecular layer at or before a relative pressure of unity is reached (i.e. Type I). Although the isotherm is more usually appropriate for the description of chemisorption, the equation is nevertheless obeyed at moderately low coverages by a number of systems, and can be readily extended to describe the behaviour of binary adsorbate systems.

The isotherm was formulated on the basis of a dynamic equilibrium between the adsorbed phase and the gaseous or vapour phase. The implicit assumptions are:

- No lateral interaction between adsorbed molecules, thus the heat of adsorption is constant and independent of coverage

- Each adsorbate molecule occupies only one site
- The adsorbed molecule remained at the site of adsorption until it is desorbed (i.e. the adsorption is localized)

The Langmuir isotherm equation derived on the basis of assumption of uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface is expressed as:

$$Q_e = \frac{Qmax\ Kl\ Ce}{1+Kl\ Ce} \text{ ----------(2)}$$

II.5.7 **Adsorption isotherm study:** The linear equation for Langmuir and Freundlich isotherm models are expressed as follows:

Freundlich isotherm: **$\log Qe = \log K_F + (1 / n) \log Ce$** ----------- (3)

Langmuir isotherme : **$(1 / Qe) = (1 / K_l Q_{max} C_e) + (1 / Q_{max})$** -------- (4)

Q_e : remaining amount of solute at equilibrium.

Q_{max}: maximum amount adsorbed.

K_l: adsorption equilibrium constant for the adsorbate adsorbent couple.

C_e: Residual concentration of solute at equilibrium in mg / **l.**

K_f, N: freundlich constant.

R.M:

This two formula applicated for all three metals

II.6. Isothermal fixing of nickel on the tar:

II.6.1 Langmuir isotherm:

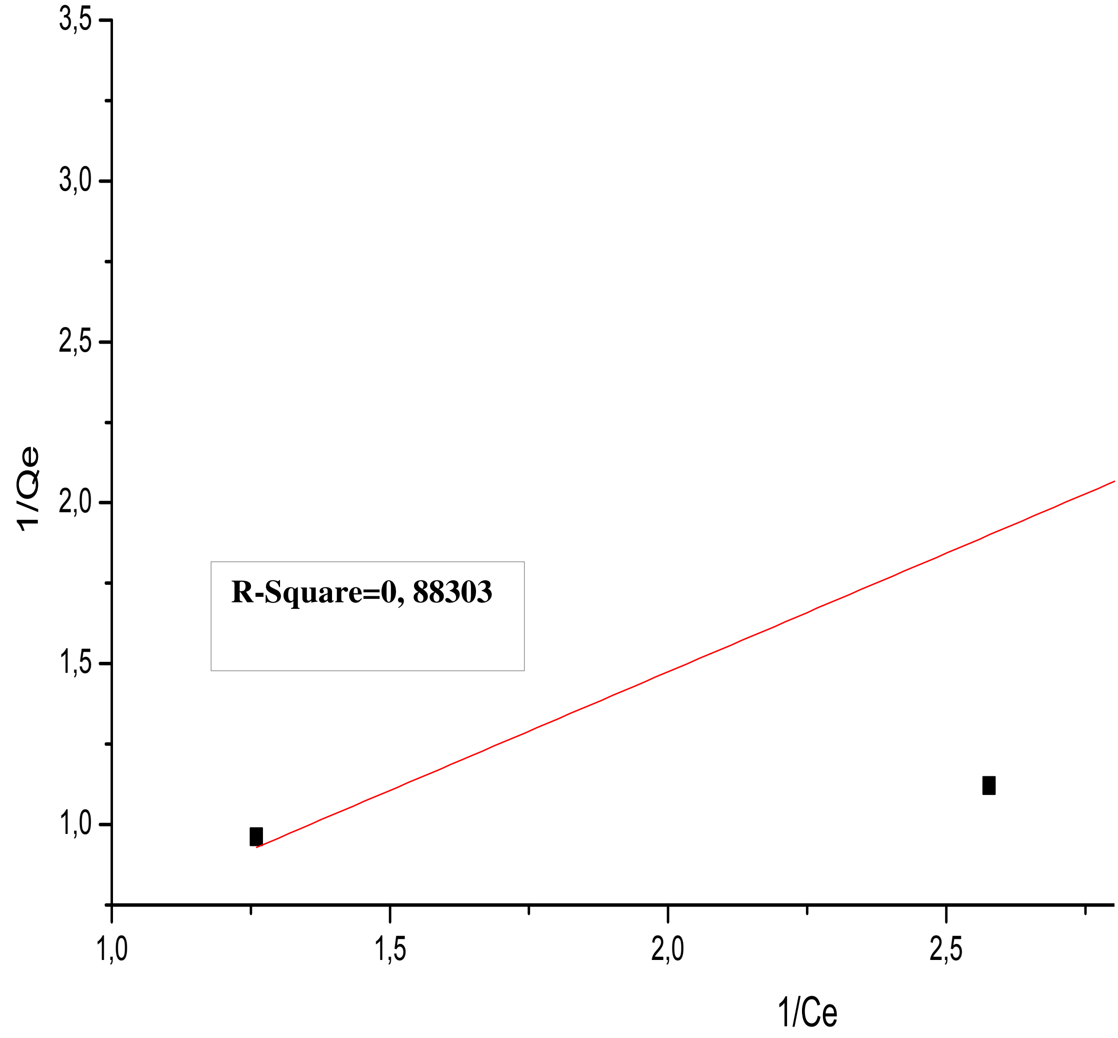


Figure II.6.1: Curved line for Langmuir isotherm for nickel

II.6.2 Freundlich isotherm:

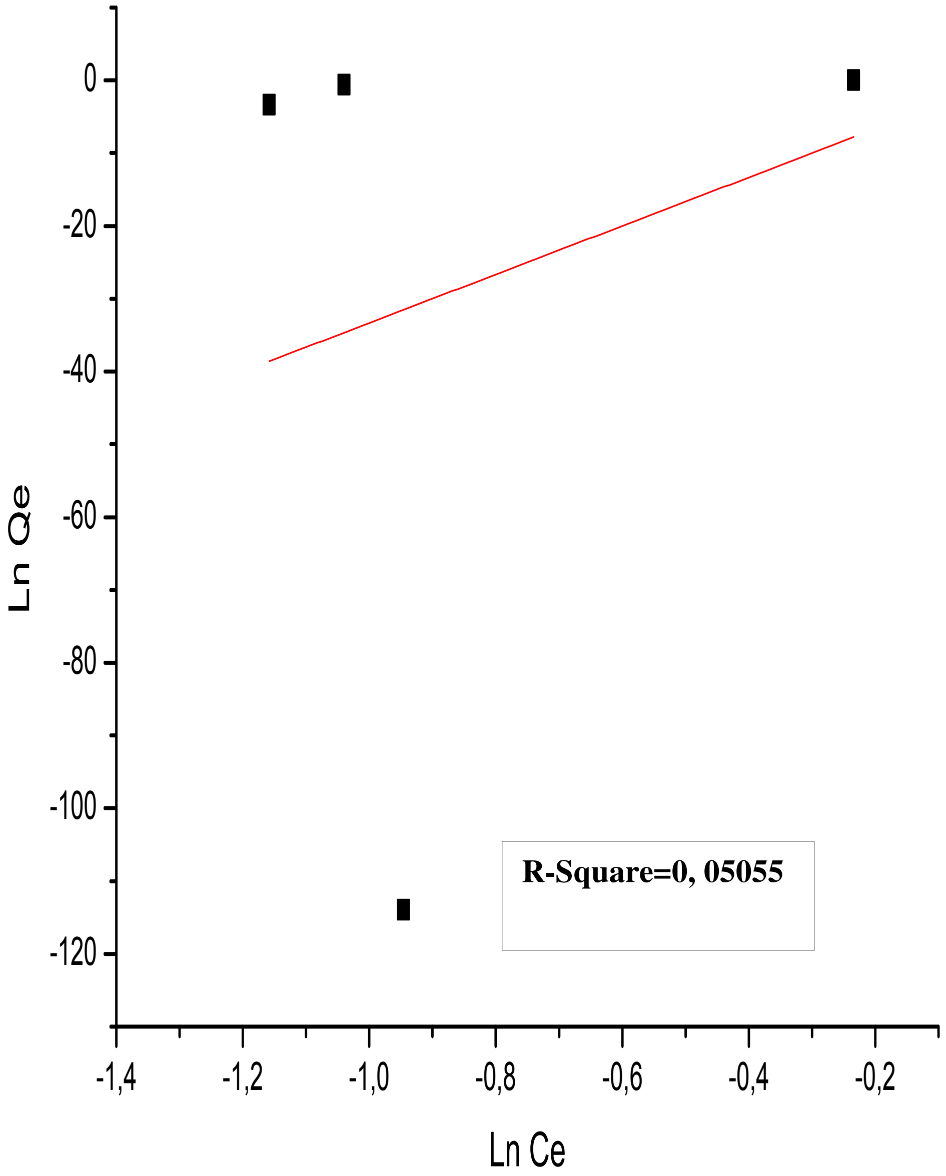


Figure II.6.2 : curved line for freundlich isotherm for nickel

The curves show isothermal l indicating the saturation of the sites of the surface and thus formation of a monolayer a similar behavior was obtained in the case of adsorption of heavy metals on the tar.

From the above figure we deduce that the model of langmuir is adequate for modeling the isothermal adsorption in the field of concentration studied because linear regression coefficient value for langmuir is better than freundlich . the adsorption capacity near 57% at pH equal 5.4 and 100% at pH equal 2.5.

II.7 Thermodynamic study:

The standard thermodynamic parameter heat of adsorption ΔH^0 entropy ΔS^0 and free enthalpyΔG^0 for adsorption of nickel on the tar we use the following equation:

$$\Delta G^0 = -RT \, \mathrm{Ln}\, k_c \text{ ----------------- } (5)$$

$$\Delta G^0 = \Delta H^0 + T\Delta S^0 \text{ ------------------- } (6)$$

$$\mathrm{Ln}\, k_c = \frac{\Delta S0}{T} - \frac{\Delta H0}{RT} \text{ --------------------- } (7)$$

$$k_c = \frac{Ce - C0}{Ce} \text{ --------------------------} (9)$$

the thermodynamic parameters ΔH^0 ,ΔS^0 are determined graphically by carrying ln K according to the temperature inverse of the environments.

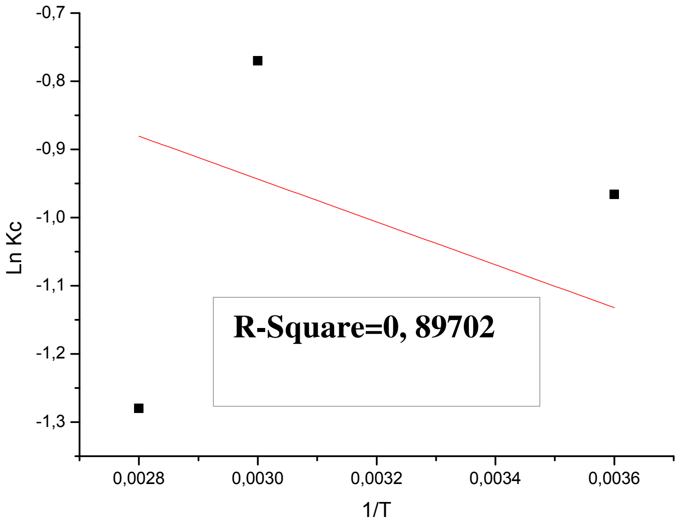


Figure II.7: the curved line of Ln Kc according to 1/T for nickel thermodynamic parameter are in the following table :

Table II.7 thermodynamic parameter for nickel-tar fixation

	ΔH^0 Kj mol^{1-}	**ΔS^0 j mol^{1-} k^{-1}**	**ΔG^0 Kj mol^{1-} A T=273.15 k**
Tar-nickel	**2.71**	**-6.89**	**-2.19**

According to the table II.7 ΔH^0 is positive that mean the reaction between tar and nickel is endothermic, the entropy variation is negative , the entropy decreases means the order increases, and free energy $\Delta \mathbf{G^0}$ is negative means spontaneous reactions.

II.8 Lead Pb: kinetic and thermodynamic study of lead fixation on pine tar.

II.8.1 Introduction:

Pb^{+2} **Lead**

the adsorption rate of lead on the pine tar is determined by addition of 0.025 g of pine tar to 4mil of water contents of lead with concentration of 10^{-4}g/l for know the best condition for this adsorption we do some experience for that the results obtained in different physicochemical conditions at the bottom.

II.8.2 traces the calibration curve:

For trace the calibration curve take some concentration and measure the absorbance of each point the result showing in the table number II.8.2.

Table II.8.2: the experimental value of the concentration according to absorbance

C(g/l)	**10^{-4}**	**$7{,}1\ .10^{-5}$**	**$6{,}17\ .10^{-5}$**	**$5{,}55\ .10^{-5}$**	**$2{,}74\ .10^{-5}$**	**$1{,}37\ .10^{-5}$**
A	**0.587**	**0.451**	**0.351**	**0.321**	**0.222**	**0.213**

The curved line of the concentration according to the absorbance is showing in figure II.8.2

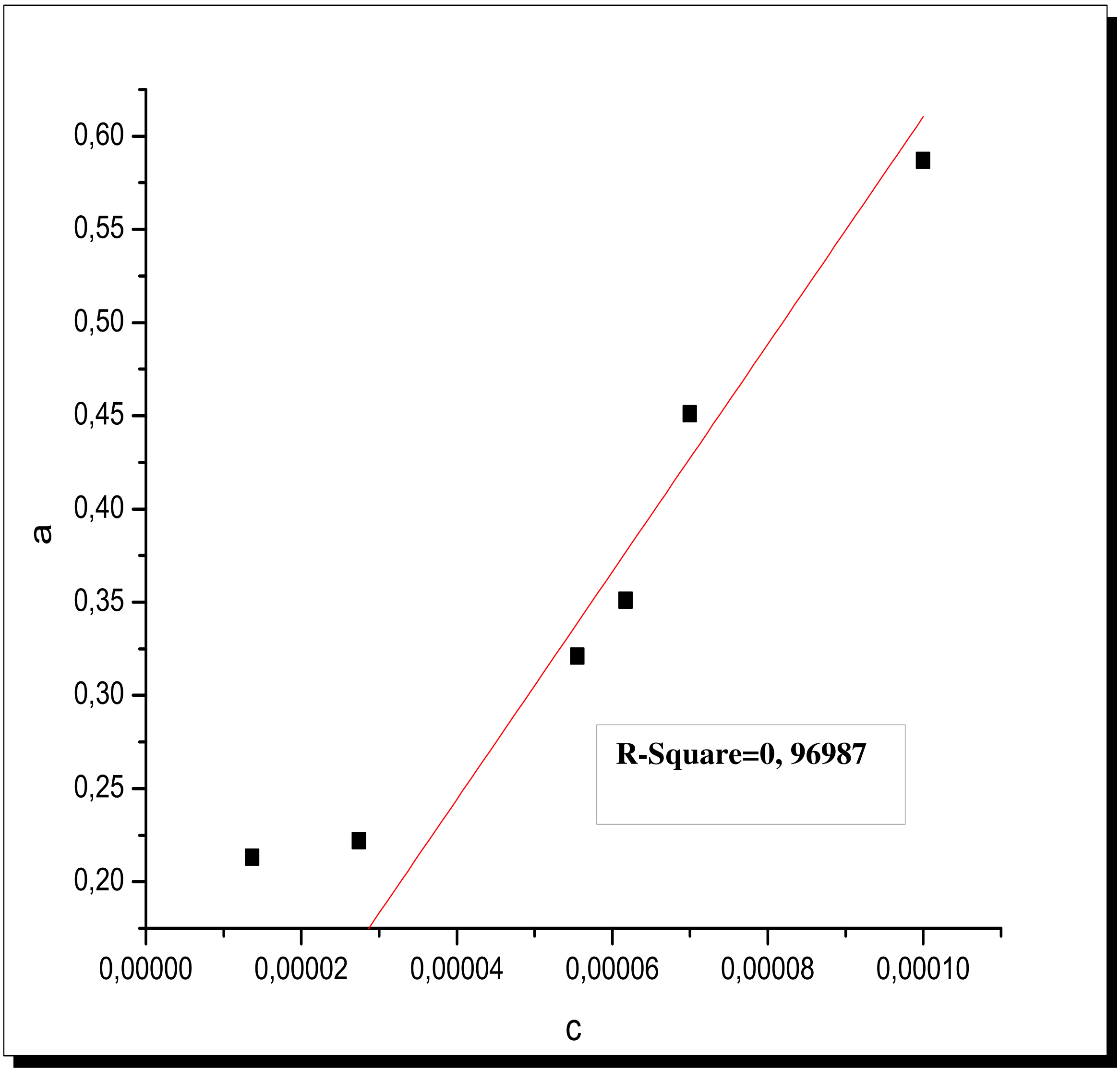


Figure II.8.2: the calibration line of lead

the line pass through the origin which proves that the Beer Lambert law is verified

II.8. 3 Turns effect of lead:

We study this effect by do many test in deference speed and deference time we find the result Which appear in the following curves:

The conditions of this experience are:

A_0=0.587 for C_0=10^{-4}g/l t=(18_25) °C and weight=0.025g

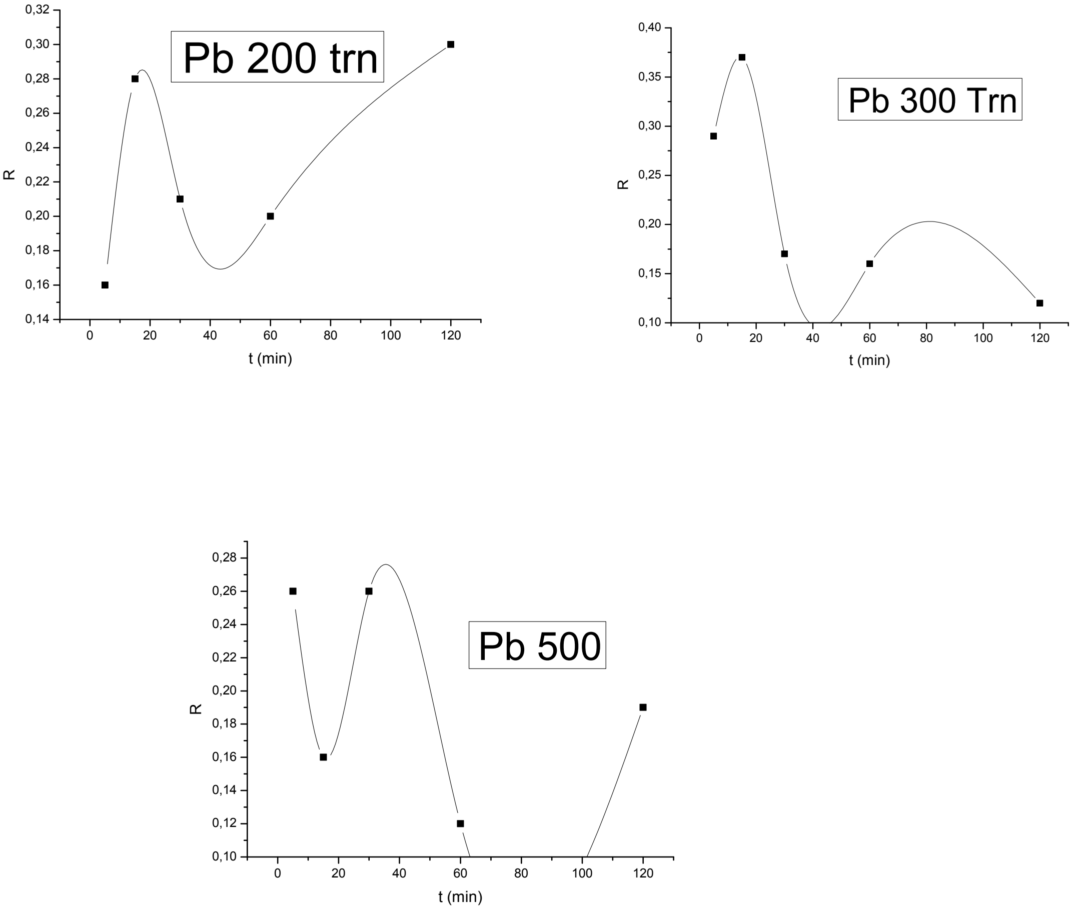


Figure II.8. 3: Change in the yield in terms of time at each speed (200.300.500)

According to this result the best turn numbers corresponds to the high yield of lead on the tar it is at speed of 300 turn/min and contact time at 15 min.

II.8.4 Temperature effect:

We study this effect by do many test in deference speed and deference time we find the result which appear in the following curves:

The conditions of this experience are:

A_0=0.587 for C_0=10^{-4}g/l and speed=300trn/min and weight=0.025g

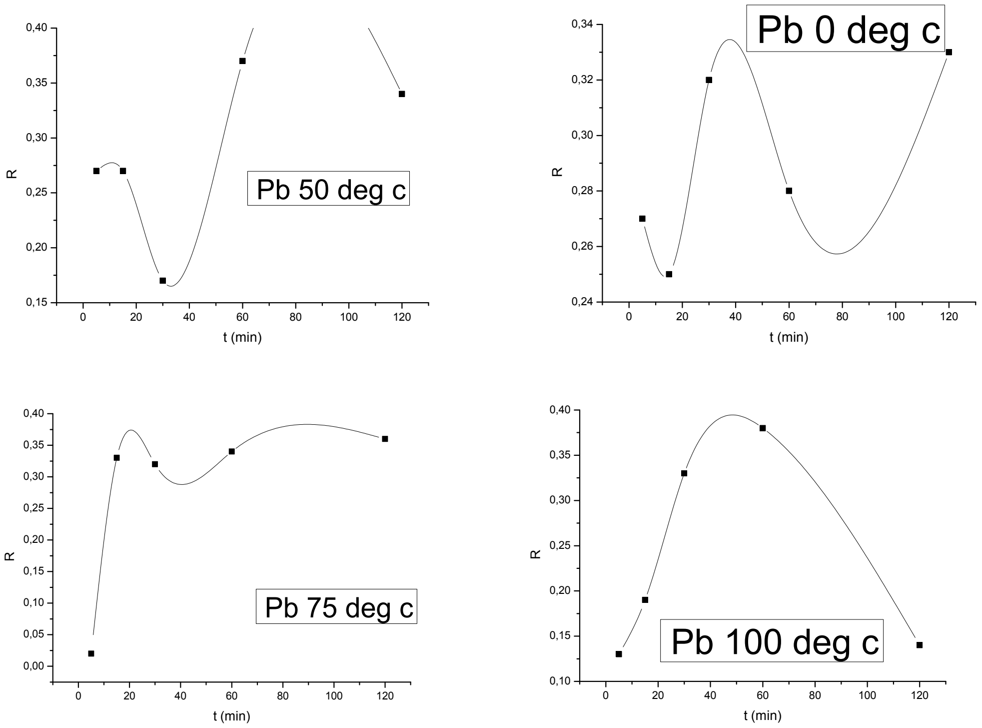


Figure II.8.4: Change in the yield in terms of time at each temperature (0^{0}C.50^{0}C.75^{0}C.100^{0}C)

According to this result the best temperature corresponds to the high yield of lead on the tar it is at lab temperature.

II.8.5 pH effect:

We study this effect by do many test in deference pH we find the result which appear in the following curve:

The conditions of this experience are:

A$_0$=0.587 for C$_0$=10^{-4}g/l and T= (18_25) °C and contact time=15min weight=0.025g

And speed at 300 trn/min

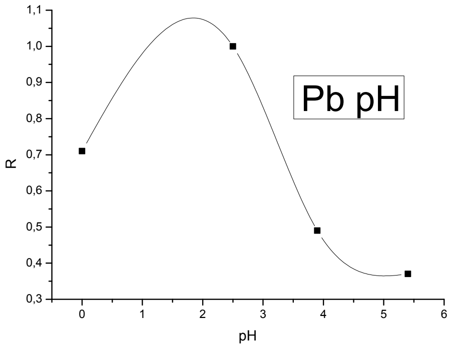


Figure II.8.5 : Change in the yield in terms of pH

According to this result the best pH corresponds to the less absorption of lead on the tar it is at the pH=2.5.

II.8.6 Weight effect:

We study this effect by do many test in deference weight we find the result Which appear in the following curve:

The conditions of this experience are:

A_0=0.587 for C_0=10^{-4}g/l and T= (18_25) °C and contact time=15min and speed=300trn/min

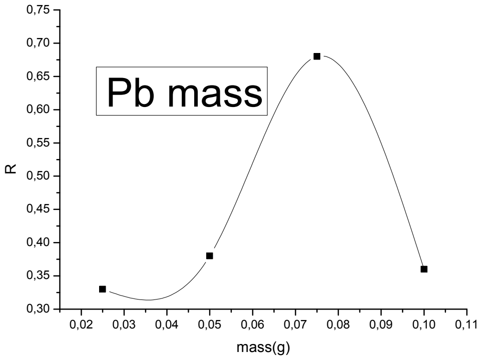


Figure II.8.6: Change in the yield in terms of weight

According to this result the best weight corresponds to the high yield of lead on the tar it is at .7the m=0.025g.

II.8.7 Result

- According to all this result and when we compare experimental values we can find that the best condition for adsorption of the lead on pine tar are:
  - Speed: 300trn/min.
  - Time of contact: 15 min.
  - Temperature: **t=(18_25) °C**
  - Weight: 0.075(g).
  - pH: 2.5.

II.8.8 Isothermal fixing of lead on the tar:

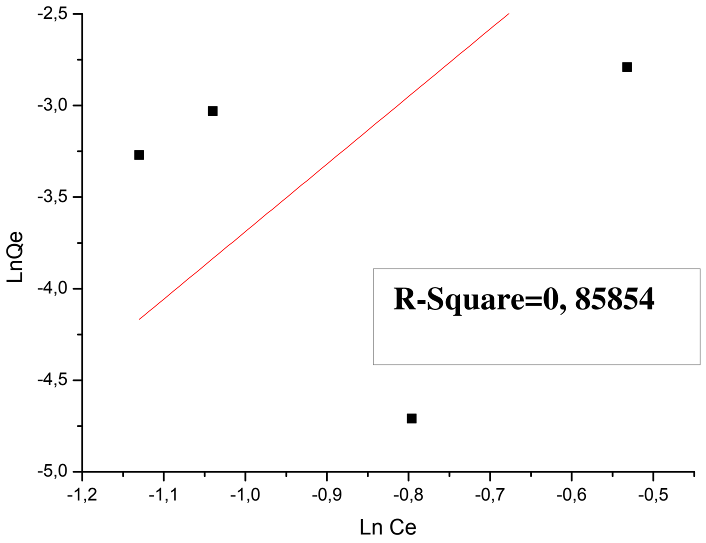


Figure II.8.8.1: curved line for freundlich isotherm for lead

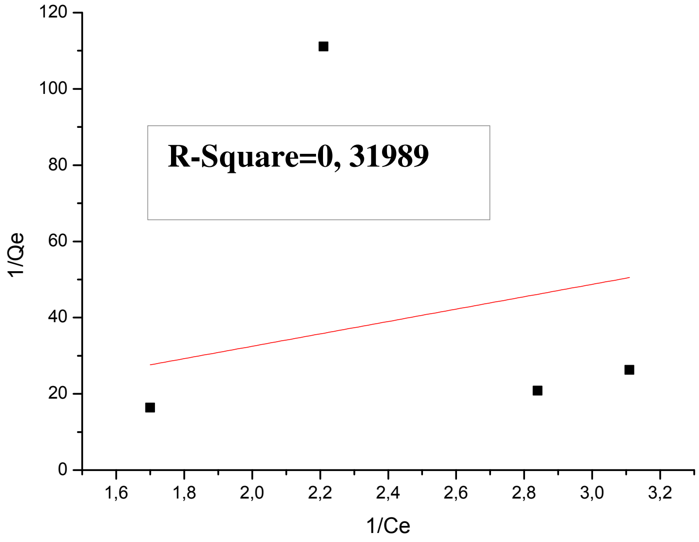


Figure II.8.8.2: curved line for langmuir isotherm for lead

the curves show isothermal l indicating the saturation of the sites of the surface and thus formation of a monolayer a similar behavior was obtained in the case of adsorption of heavy metals on the tar.

From the above figure we deduce that the model of freundlich is adequate for modeling the isothermal adsorption in the field of concentration studied because linear regression coefficient value for freundlich is better than langmuir . the adsorption capacity near 69% at pH solution equal 5.1 and 100% at pH equal 2.5.

II.8.9 thermodynamic study for lead: the equation is for lead like nickel.

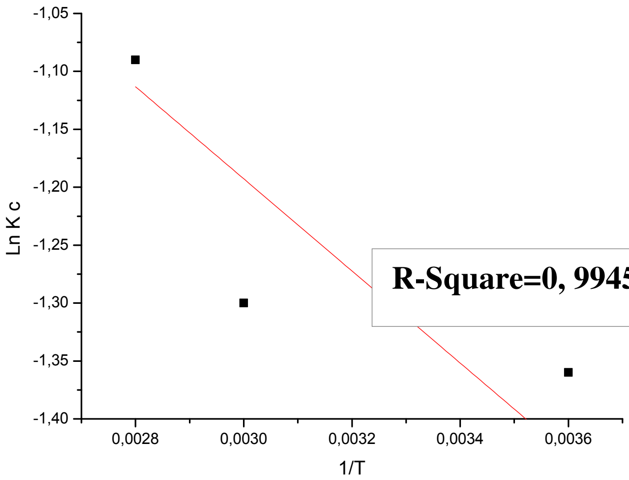


Figure II.8.9: the curved line of Ln Kc according to 1/T for lead

Table II.8.9: thermodynamic parameter for lead-tar fixation

	ΔH^0 Kj mol^{1-}	**ΔS^0 j mol^{1-} k^{-1}**	**ΔG^0 Kj mol^{1-} A T=273.15 k**
Tar-lead	**0.83**	**-8.93**	**-3.08**

According to the table Table II.8.9 ΔH^0 is positive that mean the reaction between tar and lead is endothermic, the entropy variation is negative the entropy decreases means the order increases, free energy $\Delta \mathbf{G^0}$ is negative means spontaneous reactions.

II.9 Chromium: kinetic and thermodynamic study of Chromium fixation on pine tar.

II.9.1 Introduction:

Cr^{+3} **Chromium**

the adsorption rate of chromium on the pine tar is determined by addition of 0.025 g of pine tar to 4mil of water contents of chromium with concentration of 10^{-2}g/l for know the best condition for this adsorption we do some experience for that the results obtained in different physicochemical conditions at the bottom.

II.9.2 traces the calibration curve:

For trace the calibration curve take some concentration and measure the absorbance of each point the result showing in the table number **II.9.2:**

Table II.9.2: the experimental value of the concentration according to absorbance

C(g/l)	$\mathbf{4.10^{-2}}$	$\mathbf{24\ .10^{-3}}$	$\mathbf{1{,}44\ .10^{-2}}$	$\mathbf{8{,}38\ .10^{-3}}$	$\mathbf{4{,}93\ .10^{-3}}$
A	**0.649**	**0.412**	**0.275**	**0.21**	**0.058**

The calibration line of the concentration according to the absorbance is showing in figure II.9.2.

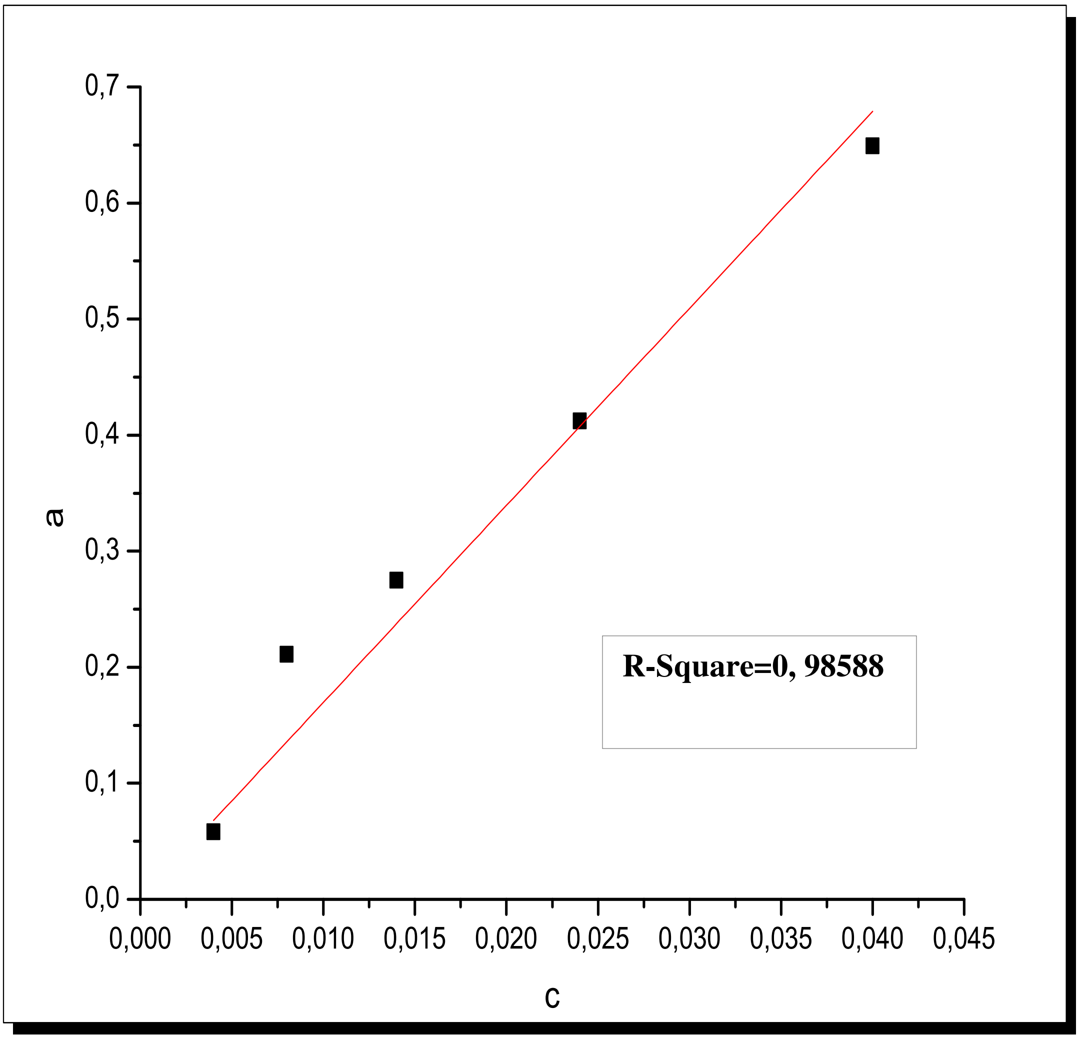


Figure II.9.2: the calibration line of chromium

the line pass through the origin which proves that the Beer Lambert law is verified

II.9.3 Turns effect of chromium:

We study this effect by do many test in deference speed and deference time we find the result which appear in the following curves:

The conditions of this experience are:

A_0=0.235 for C_0=10^{-2}g/l t=(18_25) °C and weight=0.025g

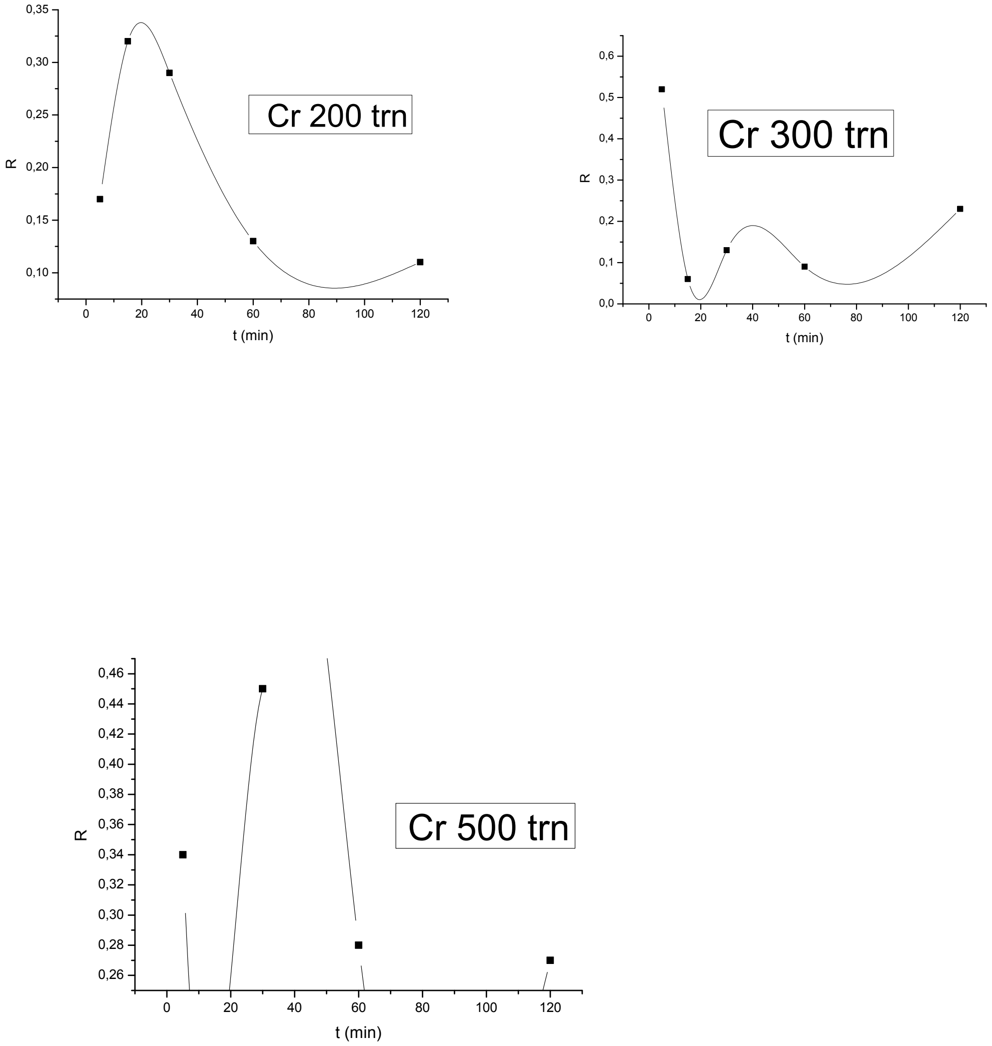


Figure II.9. 3: Change in the yield in terms of time at each speed (200.300.500)trn/min

According to this result the best turn numbers corresponds to the high yield of the fixation of chromium on the tar it is 300 turn/min at contact time of 5 min.

II.9.4 temperature effect:

We study this effect by do many test in deference speed and deference time we find the result which appear in the following curves:

The conditions of this experience are:

A_0=0.235 for C_0=10^{-2}g/l and speed=300trn/min weight=0.025g

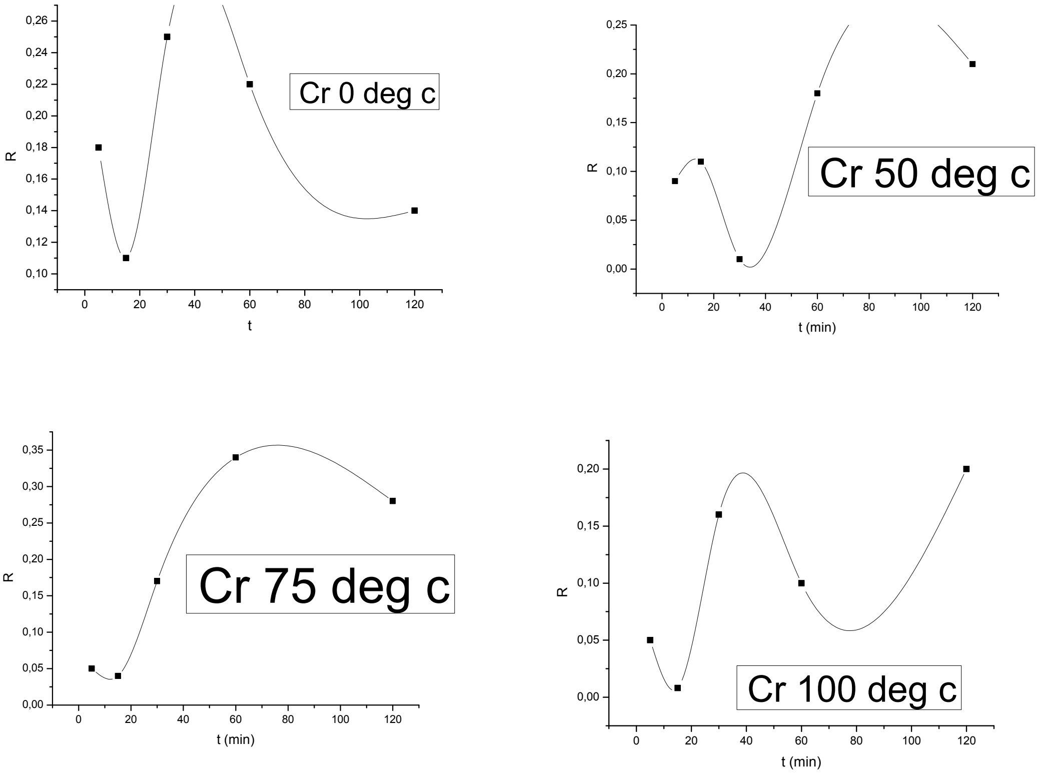


Figure II.9.4 : Change in the yield in terms of time at each temperature (0^0C.50^0C.75^0C.100^0C)

According to this result the best temperature corresponds to the high yield of chromium on the tar it is at lab temperature.

II.9.5 pH effect:

We study this effect by do many test in deference pH we find the result which appear in the following curve:

The conditions of this experience are:

A_0=0.235 for C_0=10^{-2}g/l and T=lab temperature and speed=300trn/min and time=5min weight=0.025g

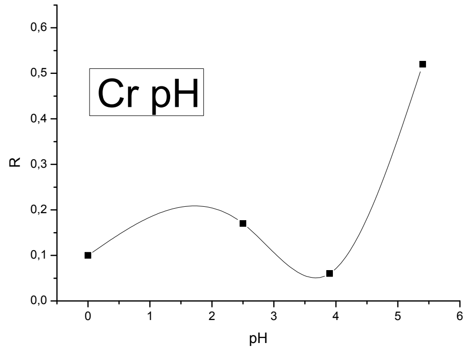


Figure II.9.5: Change in the yield in terms of pH for chromium

According to this result the best pH corresponds to the high yield of chromium on the tar it is at the pH=5,4.

II.9.6 Weight effect:

We study this effect by do many test in deference pH we find the result which appear in the following curve:

The conditions of this experience are

A_0=0.235 for $C_0=10^{-2}$g/l and T= (18_25) °C and speed=300trn/min and contact time=5min

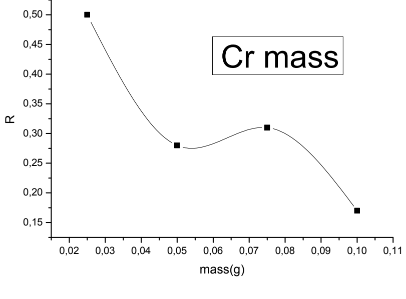


Figure II.9.6: Change in the yield in terms of weight of tar for chromium

According to this result the best weight corresponds to the less absorption of chromium on the tar it is at the m=0.025g.

II.9.7 Result:

- According to all this result and when we compare experimental values we can find that the best condition for adsorption of the nickel on pine tar are:
    - Speed:300trn/min
    - Time of contact :5 min
    - Temperature: **t=(18_25) °C**
    - Weight:0.025(g)
    - pH:5.4

II.9.8 Isothermal fixing of chromium on the tar:

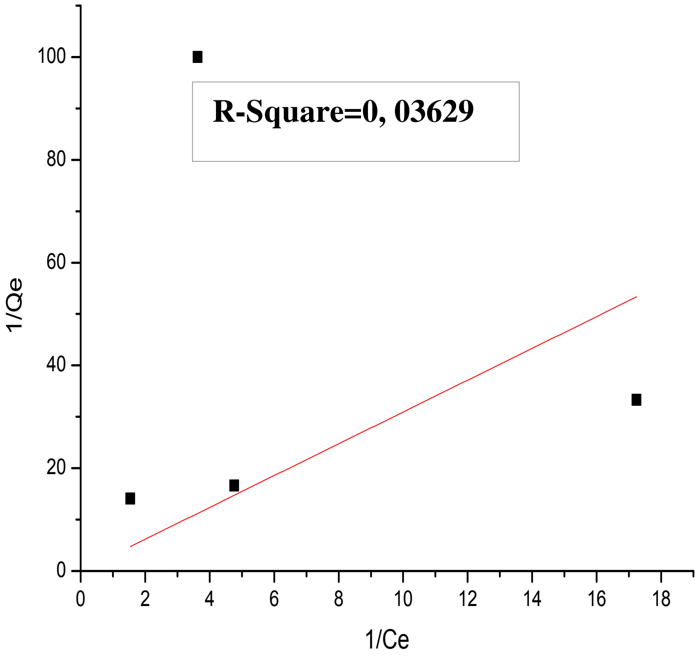


Figure II.9.8.1: curved line for langmuir isotherm for chromium

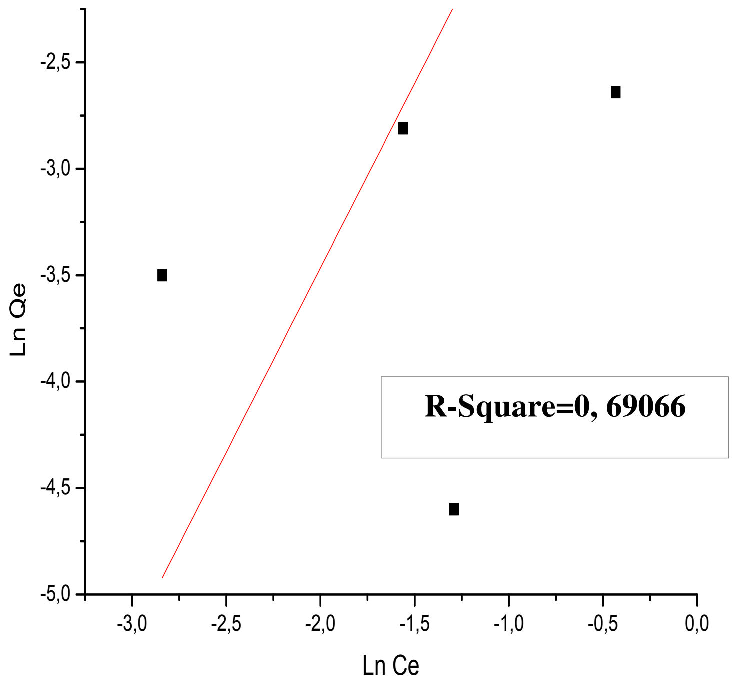


Figure II.9.8.2: curved line for freundlich isotherm for chromium

The curves show isothermal l indicating the saturation of the sites of the surface and thus formation of a monolayer a similar behavior was obtained in the case of adsorption of heavy metals on the tar.

From the above figure we deduce that the model of freundlich is adequate for modeling the isothermal adsorption in the field of concentration studied because linear regression coefficient value for freundlich is better than langmuir . The adsorption capacity of chromium on pine tar near 52% at pH solution equal 5, 4.

II.9.9 thermodynamic study: the equation is same for chromium like lead and nickel.

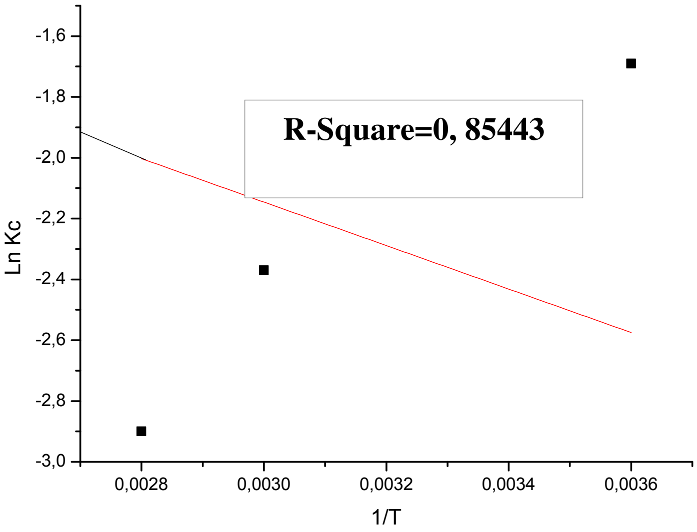


Figure II.9.9 :the curved line of Ln Kc according to 1/T for chromium

Table II.9.9: thermodynamic parameter for chromium-tar fixation

	ΔH^0 Kj mol^{1-}	**ΔS^0 j mol^{1-} k^{-1}**	**ΔG^0 Kj mol^{1-} A T=273.15 k**
Tar-chromium	**9.41**	**-15.87**	**3.83**

According to the table II.9.9 ΔH^0 is positive that mean the reaction between tar and chromium is endothermic, the entropy variation is negative, the entropy decreases means the order increases, free energy **ΔG^0** is positive means Unfavorable, or non-spontaneous reactions.

III. comparison between the spectrum of the tar before and after adsorption for three metals

III.1 comparison between the spectrum of the tar before and after adsorption for nickel

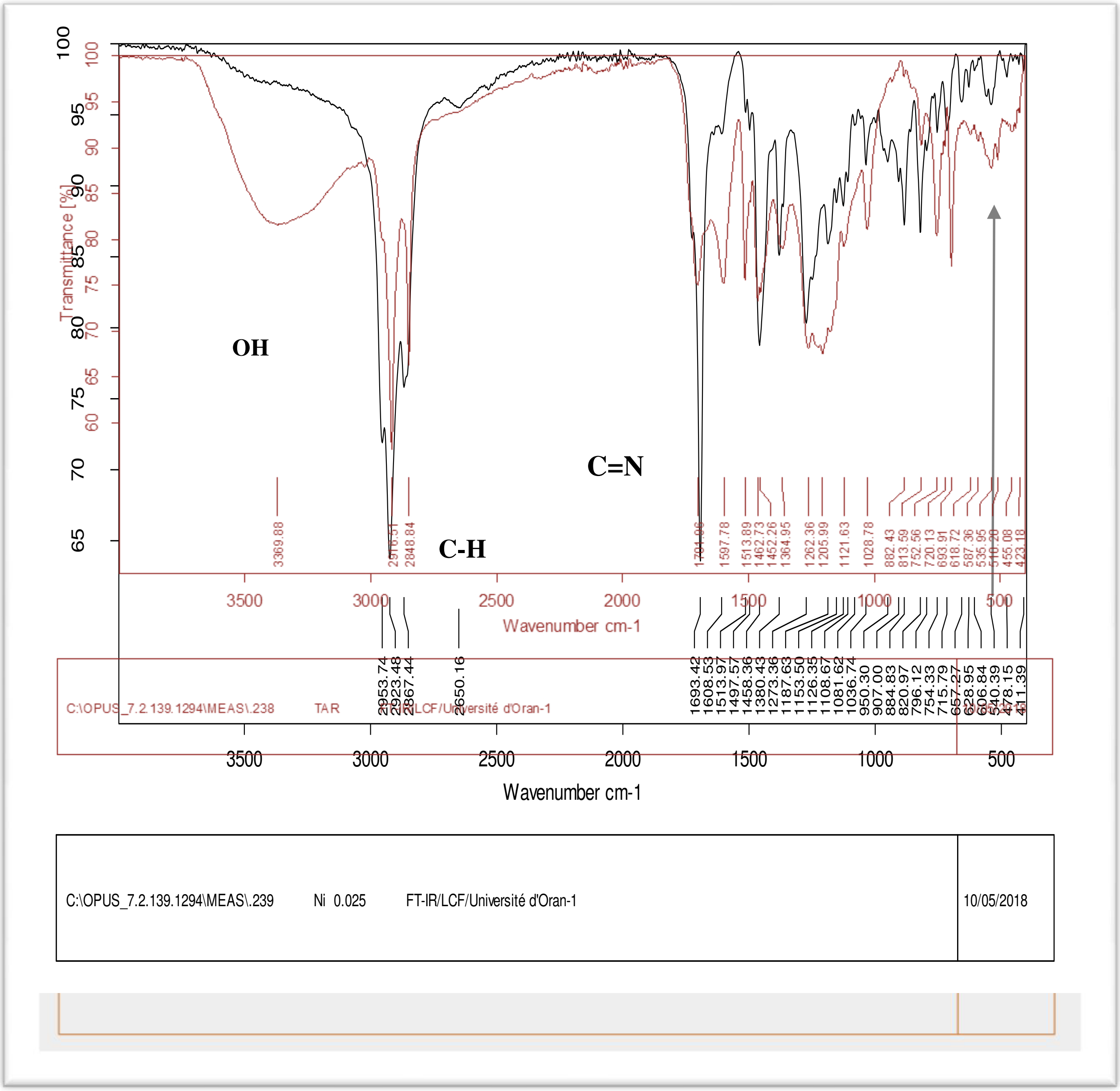


Figure III.1: Infrared Spectrum comparison between of tar-nickel and tar

By comparing the two spectra we find the disappearance of bond OH at 3369 cm^{-} and appearance another two bonds at 907 and 950 cm^{-} showing by Arrow in the graph the disappearance of this bond and appearance of new band for ν (Ni–O) at 520-510 cm-1 [41] region due to fixation of nickel on the tar.

III.2 comparison between the spectrum of the tar before and after adsorption for lead:

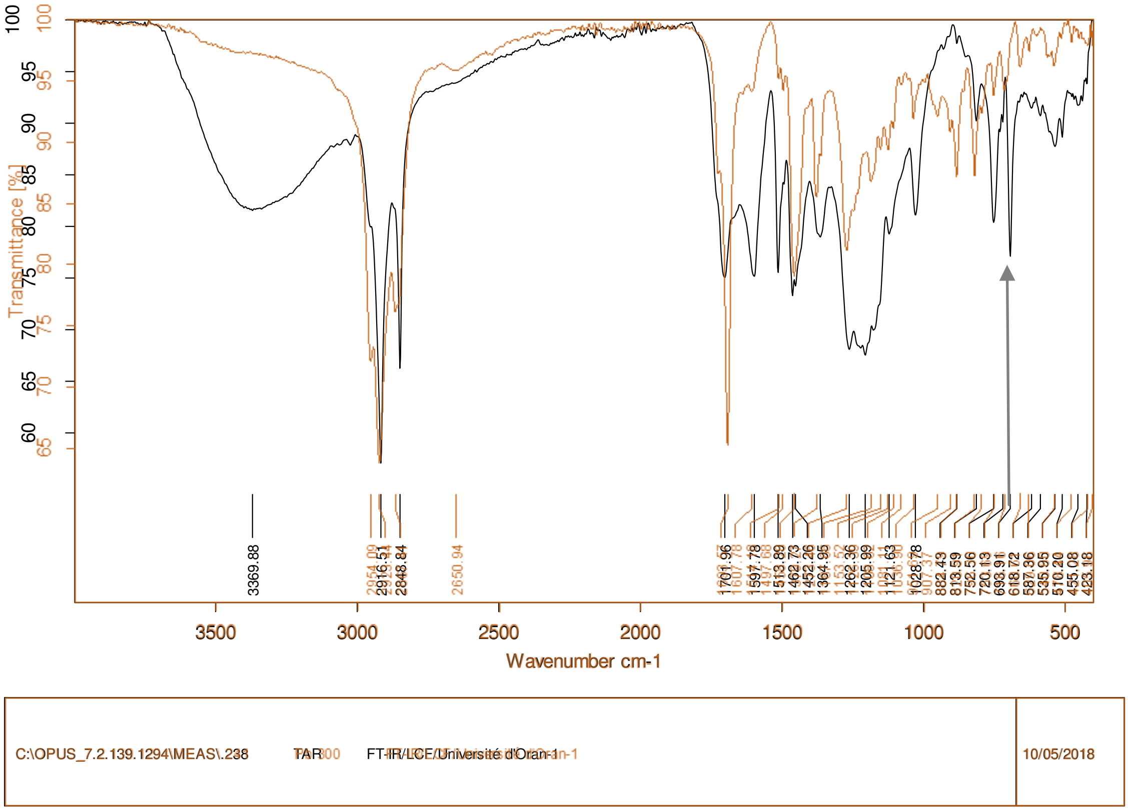


Figure III.2: Infrared Spectrum comparison between of tar-lead and tar

By comparing the two spectra we find the disappearance of bond OH at 3369 cm^{-} and appearance another two bonds at 907 and 950 cm^{-} showing by Arrow in the graph the disappearance of this bond and appearance of new band for ν (Pb–O) at 844 cm-^{1} [42]region due to fixation of lead on the tar.

III.3 Comparison between the spectrum of the tar before and after adsorption for chromium

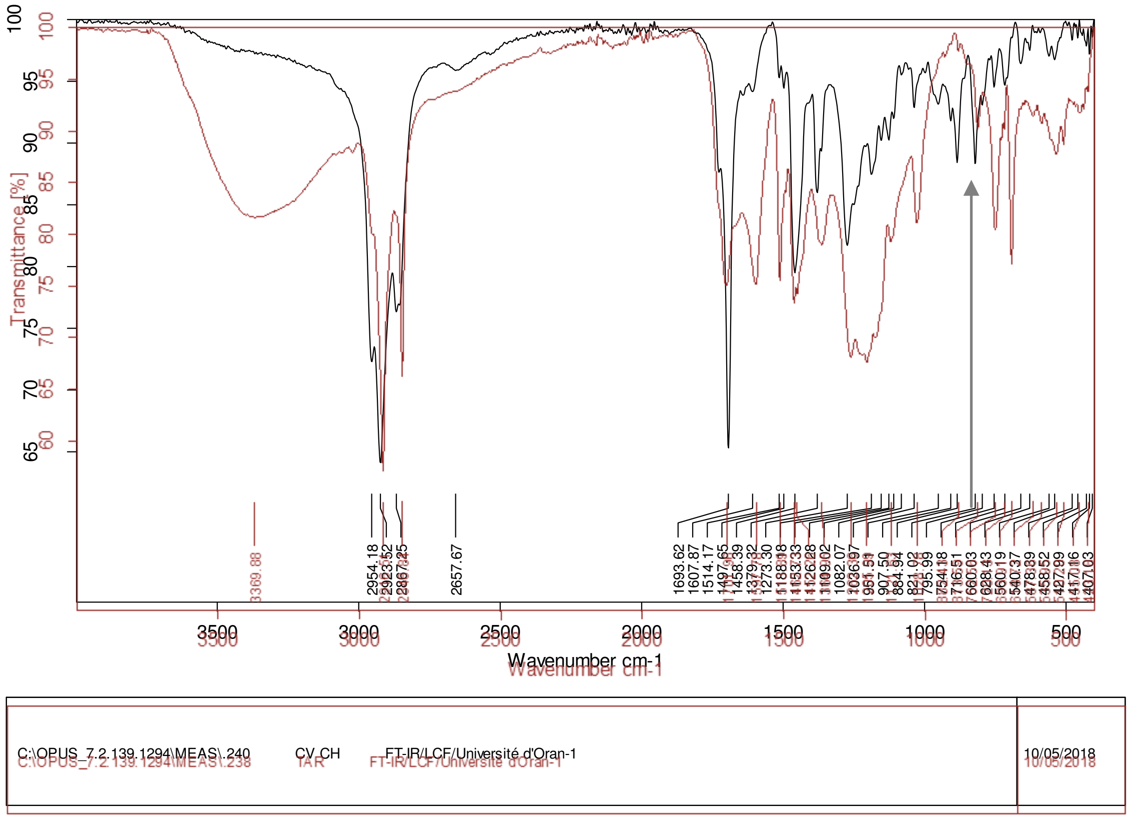


Figure III.3: Infrared Spectrum comparison between of tar-chromium and tar

By comparing the two spectra we find the disappearance of bond OH at 3369 cm^{-} and appearance another two bonds at 907 and 950 cm^{-} showing by Arrow in the graph the disappearance of this bond and appearance of new band for ν (Cr–O) at 885 cm^{-1} νs845 cm^{-1} [43]region due to fixation of chromium on the tar.

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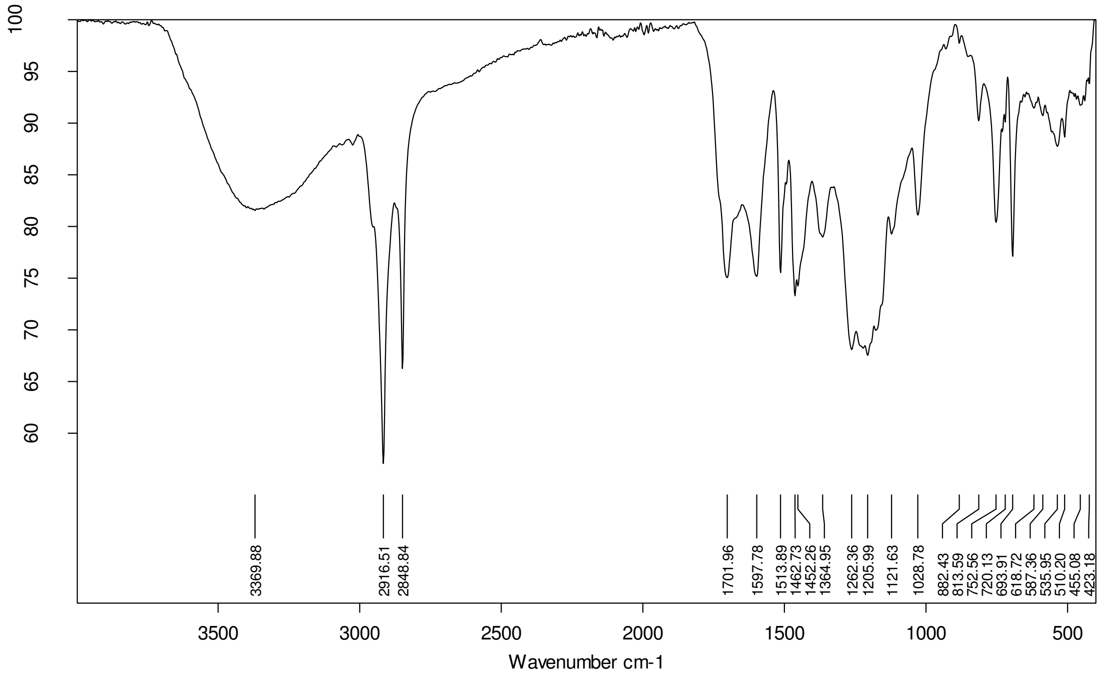

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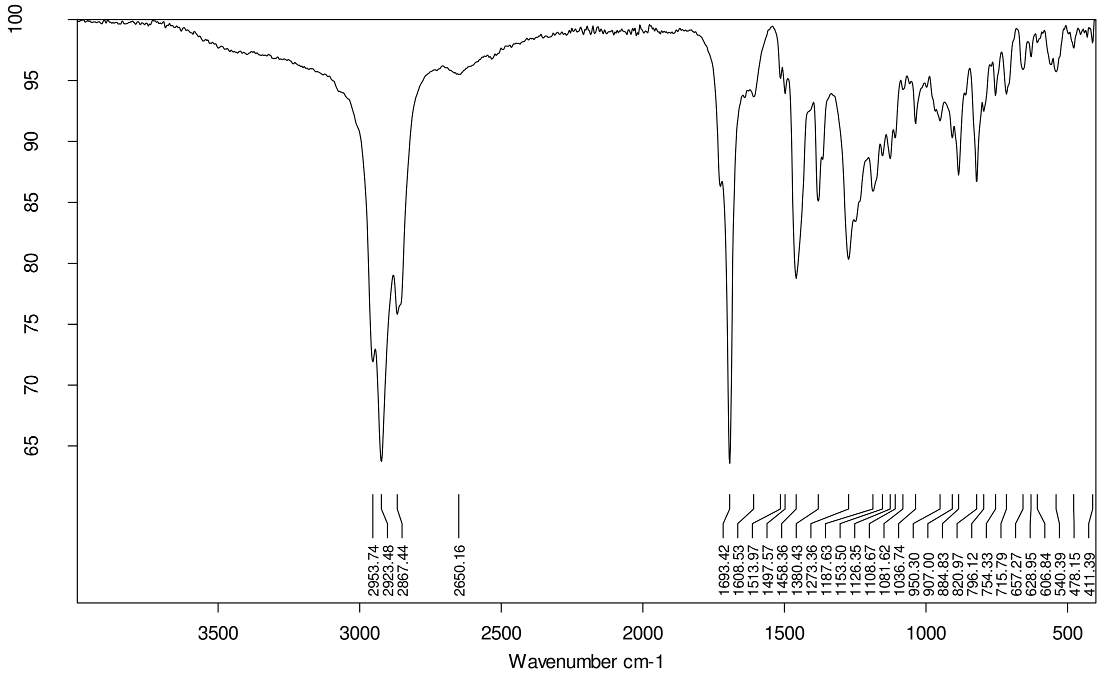

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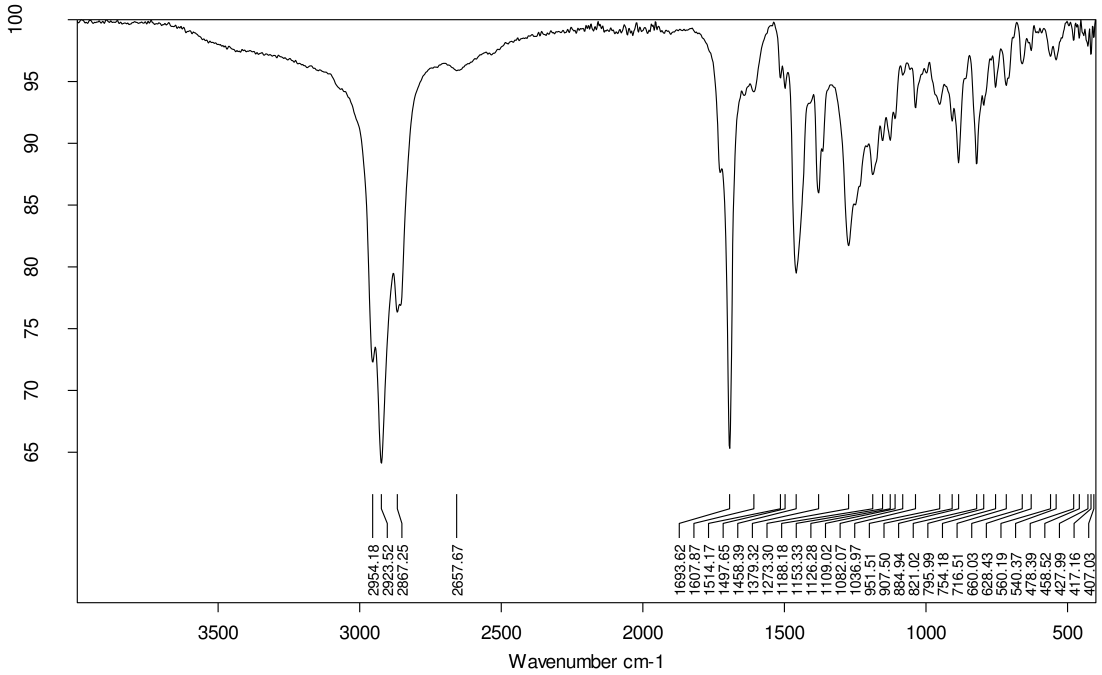

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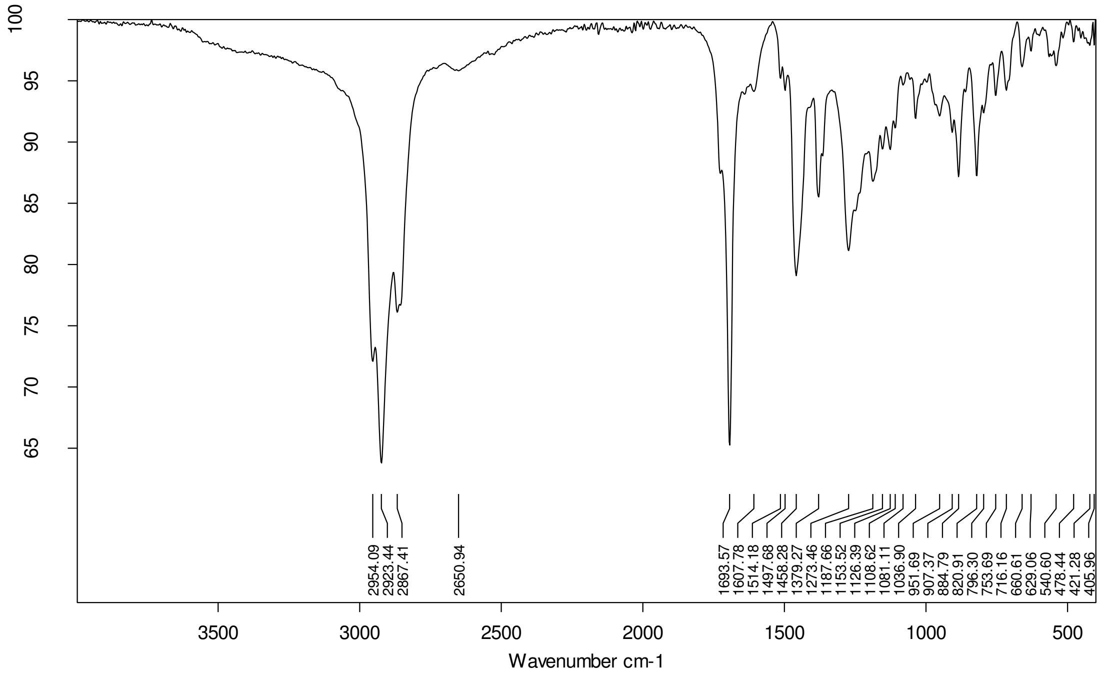

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ملخص

تعتبر المعادن الثقيلة من بين أهم العناصر التي تلوث المياه ومن بين هذه المعادن النيكل والرصاص والكروم إن وجود هذه المعادن بتركيزات عالية داخل الماء يؤثر سلبا على الطبيعة وعلى صحة الإنسان.و لقد استعملت عدة طرق من اجل تخفيض تركيزها داخل المياه ومن بين هذه الطرق استخدام النباتات ومشتقاتها في ذالك لقد حاولنا في هذا الموضوع معالجة تلوث المياه عن طريق استخدام قطران الصنوبر المستخرج من لحاء شجرة الصنوبر وكانت النتائج ممتازة حيث أن كمية من القطران تبلغ 0,025 غ أدت إلى إزالة نسبت 57 % من النيكل في درجة حرارة مابين 18 و25 درجة مئوية ودرجة حموضة المحلول تقدر ب 5,4 وسرعة خلط تقدر ب 300 دورة في الدقيقة في مدة 5 دقائق أما بالنسبة للكروم . ففي نفس الظروف تمت إزالة نسبة 52% أما بالنسبة للرصاص فقد تحققت إزالة نسبة 69% في نفس الظروف مع تغيير كمية القطران إلى 0,075 غ كما إن النسبة وصلت إلى 100% مع النيكل و الرصاص عند درجة حموضة تقدر ب 2,5.

Résumé

Les métaux lourds sont parmi les éléments les plus importants qui polluent l'eau, notamment le nickel, le plomb et le chrome, dont la concentration dans l'eau est préjudiciable à la nature et à la santé humaine. Dans ce cas, nous avons essayé de traiter la pollution de l'eau en utilisant du tar de pin extrait de l'écorce du pin, les résultats sont excellents: une quantité de tar de 0,025 g conduit à l'enlèvement de 57% du nickel entre 18 et 25 ° C. L'acidité de la solution est estimée à 5.4 Dans un même temps, 52% ont été éliminés du chrome a pH=5.4 et 69% ont été éliminés dans les mêmes conditions a pH=5.3, le tar passant à 0,075 g. Le taux atteint 100% pour le nickel et le plomb à un pH de 2,5.

Abstract

Heavy metals are among the most important elements that pollute water. Among these minerals are nickel, lead and chromium. The presence of these minerals at high concentrations in the water adversely affects nature and human health. Several methods have been used to reduce their concentration in the water. In this case, we tried to treat water pollution by using pine tar extracted from the bark of the pine tree. The results were excellent. A quantity of tar of 0.025 g resulted in the removal of 57% of nickel at 18 to 25 ° C. The acidity of the solution is estimated at **5.4** And a mixing speed of 300 rpm for 5 minutes. In the same circonstances, 52% was removed for chromium at pH=5.4. As for the lead, 69% was eliminated in the same conditions, with the tar changing to 0.075 g for pine tar mass and pH=5.3. The rate reached 100% for nickel and lead at a pH of 2.5.