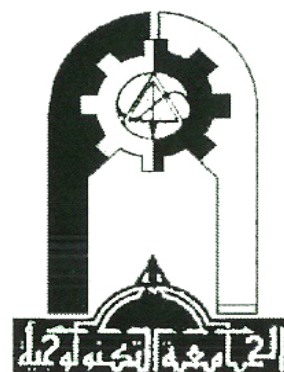


**Ministry of Higher Education
& Scientific Research
University of Technology
Chemical Engineering Department**



Studying The Use Of modified Activated Carbon To Remove Mercury From Natural Gas

A research

**Submitted to the Department of Chemical Engineering of the
University of Technology in Partial Fulfillment of the
Requirements for the Degree of Higher diploma in Chemical
Engineering / Petroleum Refining And Gas Technology .**

By

Ammar H. Abdulrazzaq
(B.Sc. in Chemical Engineering 2005)

Supervised by

Assist. Prof. Dr. Mohammed I. Mohammed

February

2012

Supervision Certification

I certify that this research in titled "Studying The Use Of modified Activated Carbon To Remove Mercury From Natural Gas" was prepared under my supervision at the department of chemical engineering university of technology , in partial fulfillment of higher diploma in chemical engineering .

Supervisor

Assistant Professor Dr. Mohamed Ibrahim

Signature:

Date : / /2012

In view of available recommendation I forward this research for debate by the examination committee .

Assistant professor Dr. Mohamed Ibrahim

Deputy Head Of Department For

Scientific And Post Graduate

Signature :

Date: / / 2012

CERTIFICATE

We certify that we have read this research entitled "Studying The Use Of modified Activated Carbon To Remove Mercury From Natural Gas " by Ammar H. Abdulrazzaq and as an Examining Committee examined the student in its contend and that in our opinion it meets the standard of the degree of Diploma in Chemical Engineering Petroleum and Gas Refining .

Signature :

Assistant professor Dr. Mohamed Ibrahim

Supervisor

Date: / / 2012

Signature: Signature:

Dr . Shahrazad R. Rauof

Dr . Najat j. Saleh

Chairman

Member

Data :- / / 2012

Data :- / / 2012

Approved for the University Of Technology

Signature:

Dr . Prof. Dr. Momtaz A. zablouk

Head of the Chemical Engineering Department

Data :- / / 2012

ABSTRACT

Iraqi North Gas Company is using activated carbon (AC) to remove mercury from natural gas . But the activated carbon partially break into small particles cross through the filters , causing a partial blockage of subsequent parts of purification units such as strainer .Therefore , we find it necessary to look for a substitute material for AC in order to avoid problems resulting from the use in the purification column as a mercury absorbent material .Such material must possess good mechanical properties as well as adsorption characteristics better or equal to the properties of AC

In this work , several types of adsorbed materials have been prepared and examined for the purpose of choosing the optimal specimen of them . The specimens were fabricated as a semi ceramic material (after has been subjected to 700 °C under oxygen free atmosphere) in order to gain good mechanical specifications . The specimens named BC [Bentonite and Clay] were prepared from different composition of bentonite and clay, while BCA [Bentonite ,Clay and Activated Carbon (AC)] was fabricated from bentonite (25%) ,Clay (25%) and AC (50%) .

BCA , BC and AC were employed as adsorbents to study the adsorption characteristics of mercury from water using a UV-spectrometer. In general BCA give a higher adsorption properties than the other adsorbent material as well as has a better mechanical properties than AC reference material (already used as an absorbent for Hg in north gas company) . Different samples with different concentrations of Hg ion were prepared by dissolving mercury nitrate in water .The adsorption capacity of Hg^{+2} on to both AC and BCA increased with the increase of mass quantity as well as the increased in contact time . It was found that the contact time needed to reach equilibrium is 50 min for AC and 40 minutes for modified BCA sample .The surface area of BCA and AC are 440.77 and 554.1832 m^2g^{-1} respectively .The maximum adsorption capacities of Hg ion calculated by the Langmuir model are 441.1 ,439.65 mg g^{-1} with BCA and AC , respectively at $C_0=15 \text{ mg l}^{-1}$.

The compression strength for both (AC and BCA samples) was measured using California Bearing Ratio (CBR) technique .The maximum CBR value for BCA was 850 N/ mm² while AC exhibited a zero resistance towards the compression. Therefore it was concluded that the BCA sample posse's good adsorbent properties for removal of Hg from water as well as mechanical properties as compared with AC and could be possibly used as an adsorbent material for removal Hg from natural gas.

Acknowledgment

- *I must thank God for this mercy and blesses.*
- *I would like to express my sincere thanks, deep gratitude and appreciation to my supervisor Assist. Prof. Dr. Mohammed I. Mohammed for her kind supervision, advice, reading and valuable guidance throughout the work.*
- *My respectful regards to Prof. Dr. Momtaz A. Zablouk head of chemical engineering department for his kind help in providing facilities.*
- *I would like to convey my thanks to all staff of chemical engineering department and the North Gas Company for their assistance and helpful advice during the work.*
- *My grateful thanks to the staff of central library for their help and cooperation throughout the research.*
- *Also I would like to express my thanks and gratitude to my good friends for their support and constant encouragement.*
- *Finally, my sincere thanks my family due to their patience and moral support during my study.*

Ammar H. Abdulrazzaq

ABSTRACT

Iraqi North Gas Company is using activated carbon (AC) to remove mercury from natural gas . But the activated carbon partially break into small particles cross through the filters , causing a partial blockage of subsequent parts of purification units such as strainer .Therefore , we find it necessary to look for a substitute material for AC in order to avoid problems resulting from the use in the purification column as a mercury absorbent material .Such material must possess good mechanical properties as well as adsorption characteristics better or equal to the properties of AC .

In this work , several types of adsorbed materials have been prepared and examined for the purpose of choosing the optimal specimen of them . The specimens were fabricated as a semi ceramic material (after has been subjected to 700 °C under oxygen free atmosphere) in order to gain good mechanical specifications . The specimens named BC [Bentonite and Clay] were prepared from different composition of bentonite and clay, while BCA [Bentonite ,Clay and Activated Carbon (AC)] was fabricated from bentonite (25%) ,Clay (25%) and AC (50%) .

BCA , BC and AC were employed as adsorbents to study the adsorption characteristics of mercury from water using a UV-spectrometer. In general BCA give a higher adsorption properties than the other adsorbent material as well as has a better mechanical properties than AC reference material (already used as an absorbent for Hg in north gas company) . Different samples with different concentrations of Hg ion were prepared by dissolving mercury nitrate in water .The adsorption capacity of Hg^{+2} on to both AC and BCA increased with the increase of mass quantity as well as the increased in contact time . It was found that the contact time needed to reach equilibrium is 50 min for AC and 40 minutes for modified BCA sample .The surface area of BCA and AC are 440.77 and 554.1832 m^2g^{-1} respectively .The maximum adsorption capacities of

Hg ion calculated by the Langmuir model are 441.1 ,439.65 mg g⁻¹ with BCA and AC , respectively at C₀=15 mg l⁻¹.

The compression strength for both (AC and BCA samples) was measured using California Bearing Ratio (CBR) technique .The maximum CBR value for BCA was 850 N/ mm² while AC exhibited a zero resistance towards the compression. Therefore it was concluded that the BCA sample posse's good adsorbent properties for removal of Hg from water as well as mechanical properties as compared with AC and could be possibly used as an adsorbent material for removal Hg from natural gas.

LIST OF CONTENT

	<u>Page</u>
Acknowledgment.....	I
Abstract.....	II
List of contents.....	IV
List of Abbreviations.....	VII
Nomenclature	VIII
Greek Symbols	VIII
List of Tables	IX
List of Figure	X

CHAPTER ONE – INTTODUCTION

1.1- General Introduction	1
1.2- Mercury Levels Detected In Natural Gas.....	3
1.3- The Aim Of Study	4

CHAPTER TWO – LITERATURE SURVEY

2.1- Methods Of Mercury Removal In Gas And Liquid Process....	5
2.1.1- Low Temperature Separation	5
2.1.2- Non Regenerative Method.....	6
2.1.3- Regenerative Method	8
2.1.4- Membrane Method	11
2.1.5- Granular Bentonite	13

2.1.6- Natural Clays	13
2.1.7- Other Methods	13
2.2- The Process Description Of Removal Hg From Iraqi Natural GAS...	14
2.3- Activated Carbon Drum	17
2.4- The Analytical Method Of Mercury	20

CHAPTER THREE – THEORETICAL PART

3.1-Adsorption Kinetic Studies	21
3.1.1-The Fractional Power Model	21
3.5.2- Pseudo-First-Order (Lagergren)	21
3.5.3- Pseudo-Second-Order	22
3.5.4- Intra-Particle Diffusion	22
3.6-Adsorption Isotherm Studies	23
3.6.1-The Langmuir Isothermal Model	23
3.6.2- The Freundlich Isothermal Model	24
3.6.3- The Temkin Isotherm Model	25
3.6.4- The Dubinin - Radushkevich Isotherm Model ...	25

CHAPTER FIVE – EXPERIMENTAL PART

4.1- Materials	26
-----------------------------	-----------

4.2- Preparation Method	27
4.3 -The BCA Treat With Sulfuric Acid	31
4.4- CBR Test To Estimate Of Mechanical Strength	32
4.5- Density Measurement (Hg Displacement Method)...	33
4.6- Determination Of Moisture Content Of Adsorbent Material.....	35
4.7- Surface Area Measurement.....	36
4.8- Preparation Of Mercury Solution.....	36
4.9-Determination Of Lamda Maximum And Calibration Curve.....	37
4.10-Adsorption Experiments Study.....	39
4.10.1-The effect of time on the adsorption capacity.....	39
4.10.2-The effect of quantity or mass of adsorbent on the adsorption capacity ...	39

CHAPTER FIVE – RESULT AND DISCUSSION

5.1- Determination of Lamda maximum (λ_m).....	41
5.2- Calibration Carve.....	42
5.3- The Effect Of Contact Time On Adsorption.....	43
5.4- The Effect Of Quantity On Adsorption.....	44
5.5- Adsorption Behavior of acid activated BCA specimen	45
5.6- The result of physical properties	46

CHAPTER SIX–CONCLUSION & RECOMMENDATIONS

6.1- Conclusions	49
6.2- Recommendation For Further Work	50

REFERENCES

51

LIST OF Abbreviations

Symbol	Definition
AC	Activated Carbon
AGR	Acid Gas Removal
BCA	Bentonite , Clay And Activated Carbon
BET	Brunauer , Emmett and Teller
CBR	California Bearing Ratio
EPA	Environmental Protection Agency
FDA	Food and Drug Administration
HGR Activated Carbon	A sulfur-impregnated granular activated carbon
HgSIV	Mercury Removal and Recovery Molecular Sieve
IGCC	Integrated Gasification Combined Cycle
IGME	Inter Granular Metal Embrittlement
K.O. drum	Knock Out Drum
LLC	Ivy League college in Philadelphia, Pennsylvania
LPG	Liquid Petroleum Gas
LME	Liquid Metal Embrittlement
LTS	Low Temperature Separation
MGA	Membrane Gas Absorption
LNG	Liquid Natural Gas
OSHA	Occupational Safety and Health Administration
oxi-MGA	Oxidative Membrane Gas Absorption
UV -spectrometer	Ultraviolet / Visible Spectrometer
UOP	Universal Oil Products

Nomenclature

Symbol	Definition	Units
C_0	Initial Concentration of solute in solution	mg/L or ppm
C_e	Concentration of solute remaining in solution after adsorption is complete (at equilibrium)	mg/L or ppm
D	The activity coefficient related to mean adsorption energy	(mol ² /J ²)
h	The initial sorption rate	mg/g .hour
K	Adsorption equilibrium constant	1 mg ⁻¹
k_1	Kinetic constant	
k_2	The kinetic constant of the process	
k_p	The Intra-particle constant	
k_T	The Temkin's Constant	Lit / mg
m	Mass of adsorbent (mg or g)	(mg or g)
Q	The quantity of adsorbate required to form a single monolayer on unit mass of adsorbent	mg/g
q_{D-R}	The maximum adsorption capacity	mg/ g
q_e	Adsorption capacity at equilibrium	mg/g
q_t	Adsorption capacity	mg/g
R_L	The separation factor	
t	Time	Minute
V	Constant	
x	Amount of solute adsorbed	(μg, mg, or g)

Greek Symbols

Symbol	Definition	Units
ε	The Polanyi potential	(kJ ² mol ²)
ρ	The density	Kg / m ³
ρ_B	The density of the bed	Kg/ m ³
ρ_p	The density of particle	Kg/ m ³

List of Tables

Table	Page
Table (1.1) :- UOP report	3
Table (2.1) :-The activated carbon chemical list	19
Table (4.1) :- Physical properties of bentonite	27
Table (4.2) :- The compositions of different samples of BC and BCA specimens	28
Table (4.3) :- Surface area and pore volume of activated carbon and BCA	36
Table (4.4) :-Physical and chemical properties of mercury nitrate	37
Table (4.5):- The diluted solution	38
Table(5.1) :- Characterization of BCA and AC	47

List of Figures

Figure	Page
Figure (2.1) :- Low Temperature Mercury Separation Process	6
Figure (2.2) :- HgSIV Mercury Removal and Recovery System	9
Figure (2.3) :- Integrated Carbon/Zeolite Hg-Removal System	10
Figure(2.4) :- Removal of mercury from a gas stream by oxi-MGA	12
Figure (2.5) :- Dehydration Unit	16
Figure (2.6) :- The activated carbon drum	18
Figure (4.1) :- The heat treatment regime	29
Figure (4.2) :- The photograph of muffle furnace	29
Figure (4.3) :- Arrangement of material inside the heating container	30
Figure (4.4) : Optical microscope picture (x100) in the surface of BCA1	31
Figure (4.5) :- Optical microscope picture (x100) in the surface of acid treated BCA	32
Figure(4.6) :-A schematic diagram of apparatus (made of glass)to measure the density	34
Figure (4.7) :- UV – spectrometer device	38
Figure (5.1) :- Lamda maximum (λ_m) curve	41
Figure(5.2) :- The calibration curve	42
Figure (5.3) :- The effect of contact time	43
Figure (5.4) :- The effect of quantity on adsorption	44
Figure (5.5) :- The adsorption % of acid activated BCA specimen	45
Figure (5.6) :- A photograph of BCA and BC samples	48

1.1-GeneralIntroduction:-

Raw natural gas typically consists primarily of methane (CH_4) , the shortest and lightest hydrocarbon molecule. It also contains varying amounts of :-

Heavier gaseous hydrocarbons :- ethane (C_2H_6), propane (C_3H_8), normal butane ($\text{n-C}_4\text{H}_{10}$), isobutene ($\text{i-C}_4\text{H}_{10}$), pentanes and even higher molecular weight hydrocarbons . When processed and purified into finished by-products , all of these are collectively referred to as LNG (Liquid Natural Gas) . LNG is also compose of a trace of other gases such as :-

(CO_2) , (H_2S) , (CH_3SH) , ($\text{C}_2\text{H}_5\text{SH}$) , (N_2) , (He) and water vapor . Very small amounts of mercury primarily in elemental form , but chlorides and other species are possibly present ^[1] .

Mercury in natural gas is present predominantly as elemental mercury. However , in theory , mercury could be present in other forms :- inorganic (such as HgCl_2) , organic (such as CH_3HgCH_3 , $\text{C}_2\text{H}_5\text{HgC}_2\text{H}_5$) and organo-ionic (such as ClHgCH_3) compounds ^[2] . Elemental mercury and organo-mercury compounds are present in natural gas throughout the world . Researches has shown that when mercury comes into contact with an aluminum metal surface (aluminum is a common material used in liquefaction heat exchangers) , aluminum diffuses from the interface into the mercury droplet where it is rapidly converted to aluminum oxide (Al_2O_3) by reaction with air or water . In the Liquid Petroleum Gas (LPG) process , the presence of water can occur if there is water breakthrough from the dehydrators beds in the front end . Presence of air can occur if the heat exchanger or nearby equipment had to be taken out-of-service for entry/maintenance . By this mechanism , metallic mercury actually bores into the aluminum leaving behind “whiskers” of Al_2O_3 ^[3] . Attacks by

mercury will occur only when liquid mercury is present at temperatures above its melting point of (-39°C) and if the protective metal oxide film has been damaged^[4]. However, when equipment is being defrosted temperatures can reach above mercury melting point. Two major types of mercury corrosion can be observed. These are Inter Granular Metal Embrittlement (IGME) and Liquid Metal Embrittlement (LME). Amalgam induced corrosion is shown by any metal capable of forming an amalgam with mercury. The metal can show its full reactivity and attack by air or water is rapid. LME involves the diffusion of mercury into the grain boundaries and results in cracks developing along the grain boundary. This type of attack does not involve air or water and once initiated progresses rapidly. This type of corrosion affects a broad range of materials (aluminum alloys, copper based alloys eg Monel 400 and some types of steel eg 316 L)^[5]. Moreover mercury has long been known to be a toxic, persistent, bio-accumulative pollutant with a wide range of ecosystem and human health effects. Accordingly removal of mercury from LNG is necessary for workers, public and environmental safety and refinery equipment corrosion protection. The Environmental Protection Agency (EPA) has set a limit of 2 parts of mercury per billion parts of drinking water (2 ppb). The Food and Drug Administration (FDA) has set a maximum permissible level of 1 part of methyl mercury in a million parts of seafood (1 ppm). The Occupational Safety and Health Administration (OSHA) has set limits of 0.1 milligram of organic mercury per cubic meter of workplace air (0.1 mg/m³) and 0.05 mg/m³ of metallic mercury vapor for 8-hour shifts and 40-hour work weeks. The Occupational Safety and Health Administration (OSHA) mercury limit in air is 50 µg/Nm³. Activated carbon bed is usually used as an adsorbent material for reduction natural gas mercury content to less than 0.01 µg/Nm³. There are some disadvantages when activated carbon is used as a bed for removal of mercury from the stream of LNG gas, indeed the low resistance

to attrition , low of hardness and frictional force . These leading to form a fine carbon particle causes blockage in strainer and consequently led to increase in differential pressure of the process . In order to overcome the limitation of activated carbon , its necessary therefore to develop a new material which is the main objective of present work .

1.2- Mercury Levels Detected In Natural Gas : -

The detection level of elemental mercury in natural gas in many regions around the world was reported by Universal Oil Products (UOP)^[6].The results are summarized in Table (1.1) below.As it can be gathered from this data that the middle east gas(including Iraq) has a lowest concentration of mercury:-

Region	Mercury concentration in $\mu\text{g}/\text{m}^3$
North Africa	1-100
North America	1-20
South America	1-105
South east Asia	10-2000
Middle East	1-10
Europe	1-50

1.3- The Aim Of Study :-

The main objective of this work is to develop an alternative material has either a similar adsorption properties of Activated Carbon (AC) or better and has a higher physical and mechanical properties in order to avoid the formation of fine particles .

2.1- Methods Of Mercury Removal In Gas And Liquid Process :-

There are several method to remove mercury from gas and liquid stream consisting of :-

2.1.1-Low Temperature Separation :-

The first experience with mercury removal from natural gas , using the Low Temperature Separation (LTS) process , was at the aforementioned Groningen fields in 1972 . The process is shown schematically in Figure (2.1) . Natural gas from the field is precooled and the water is condensed out . Dry glycol is then injected to further dry the gas to prevent water condensation in the pipeline . After heat exchange , for additional precooling , the gas is expanded through a Joule Thomson valve . The wet glycol , now containing the condensed mercury , is then separated from the natural gas . The gas leaves this separation process containing about 1-15 mg/Nm³ of mercury , depending on the temperature of the process . Although this level of mercury may be acceptable in the natural gas , it would be unacceptable in LNG or inIntegrated Gasification Combined Cycle (IGCC) fuel gas in order of magnitude better removal would be required . For example , the two early Indonesian LNG plants , Arun and Badak , use activated carbon adsorption beds to remove mercury from natural gas before the liquefaction cycle . The Eastman coal-to-chemicals plant is also equipped with activated carbon adsorption beds . Operating the LTS process at very low temperatures would improve mercury separation significantly . However , further treatment of the water/mercury condensed phase is required . The LTS process , in applications where virtually total removal of mercury is necessary , is not a very economic nor a practical method and has been superseded by adsorption ^[7] .

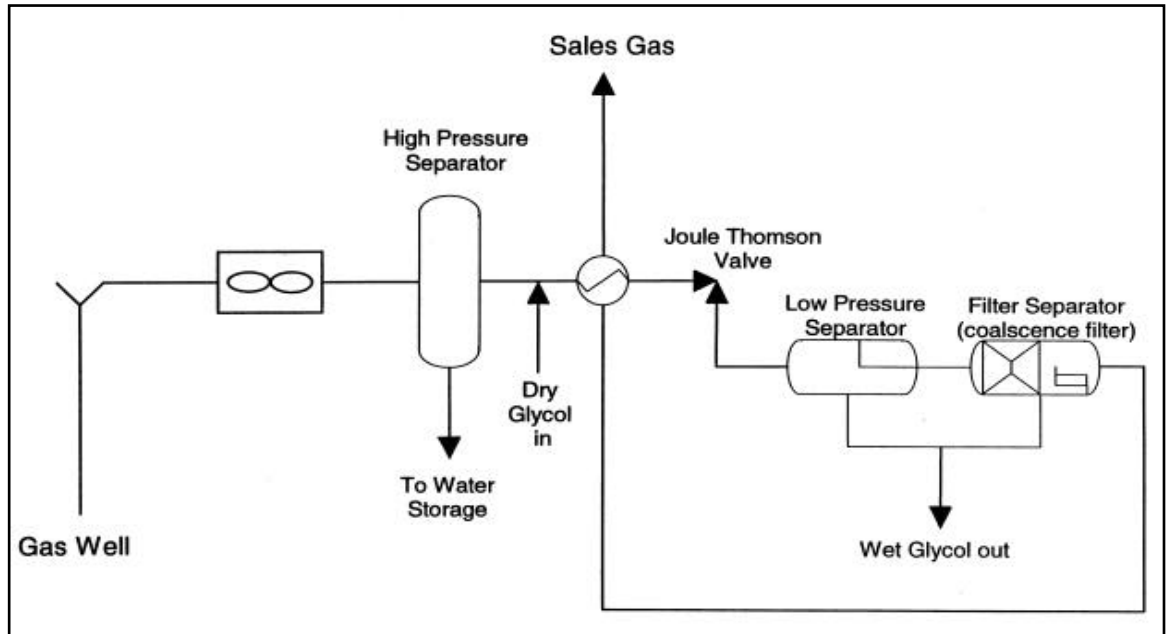


Figure (2.1) :- Low Temperature Mercury Separation Process .

2.1.2- Non Regenerative Method :-

Non-regenerative types of mercury sorbents , the process fluid flows through the sorbent bed for a number of years , after which the sorbent is replaced. The mercury is removed from the process fluid and stays on the sorbent . The plus side of this approach is its simplicity . The down side is the installation cost , the additional pressure drop , and the disposal cost of the used sorbent . Metal sulfide or mixed sulfides dispersed within a solid carrier such as activated carbon or alumina . The mercury reacts with the sulfide and stays on the sorbent . Metal sulfides and polysulfide's were found to be effective in removing elemental mercury . Copper sulfide and zinc sulfide containing solid mass are the predominant metals used to remove mercury from gas and liquid ^[8] . In some cases where trace H₂S removal is required , the metal oxide version is used to remove the H₂S that converts the oxide into the sulfide , which then removes the mercury

.Johnson Matthey^[9] promotes their mixed-oxide H_2S scavenging media as an alternative to carbon , preferably upstream of acid gas removal such that H_2S adsorbed from the raw natural gas reacts quantitatively with the mercury . This minimizes equipment contamination and avoids contamination of ancillary process streams such as acid gas , condensate and mole sieve regeneration gas. A number of different products of sorbents are being offered by various manufacturers . Most are available in the pellet form . The particle sizes of sorbents generally vary from 0.9 to 4 mm pellets . The smaller particles of sorbents offer better mercury removal efficiency , but give a higher pressure drop , while the reverse is true for the larger ones . These products of particle can be used in both gas and liquid hydrocarbon service and they are also not damaged by contact with liquid water ^[10] .

In Halide-impregnated activated carbon particles the mercury reacts with the halide , such as iodide , to form HgI_2 that stays on the sorbent . The product cannot be used where there is the danger of liquid water contacting the sorbent since liquid water will wash off the halide and may cause vessel corrosion . Some other products like (HgSIV , HGR activated carbon ,...etc) are available that contain proprietary ingredients and which are claimed to offer improved performance in treating natural gas liquids and which are not damaged by liquid water ^[10] .

Mercury removal from natural gas is perhaps most commonly achieved with activated carbon impregnated with sulphur to form non-toxic mercury sulfide (HgS) ^[11]. HgS is stable up to 450°C (840°F) , and will not elute from the carbon bed under fluctuating conditions . The carbon is non-regenerable in situ , but a properly designed bed will reportedly last for many years . Due to carbon's affinity for water and heavy hydrocarbons , location is invariably downstream of dehydration and dew point control.

2.1.3- Regenerative Method :-

Zeolite adsorbents (Molecular Sieves) have been used by the natural gas industry primarily for drying ^[12]. In the early 1970s, when the mercury problem surfaced, Universal Oil Products (UOP) began work on a zeolite adsorbent that would remove mercury from natural gas. The result was the development of a type 13X molecular sieve, loaded with about 0.5 wt% sulfur, that would remove mercury to very low levels. This work was followed by the development of a better molecular sieve product in the 1980s dubbed HgSIV. UOP's ^[7]regenerative HgSIV can simultaneously dehydrate and remove mercury. The product is made by coating the outside rim of an appropriate molecular sieve particle with elemental silver to a nominal depth of 1 mm, such that the silver occupies the outside but no more than 35% of the total particle. Mercury is captured by formation of the silver amalgam while water is adsorbed within the interior. Both are periodically regenerated with hot sales gas according to conventional dehydration practice. The HgSIV adsorbent can be employed as a stand-alone unit, or in combination with an upstream bulk, non-regenerative mercury-removal bed such as sulphur-impregnated carbon. In the stand-alone case, mercury and water are condensed from the regeneration gas, with subsequent recovery of salable liquid mercury. HgSIV is capable of removing mercury from natural gas to below detectable level ($<0.01\text{mg/Nm}^3$). Several different process configurations can be used. One of these is shown in Figure (2.2). This Option requires no new vessels or piping and does not add to the pressure drop. The dehydrator is regenerated with a small slip stream of the plant residue gas. The spent regeneration gas is cooled to knock out most of the water and put back into the sales gas line. The dehydrator acts to divert all of the mercury and some of the water around the cold box. The recovered hydrocarbons will be mercury-free.

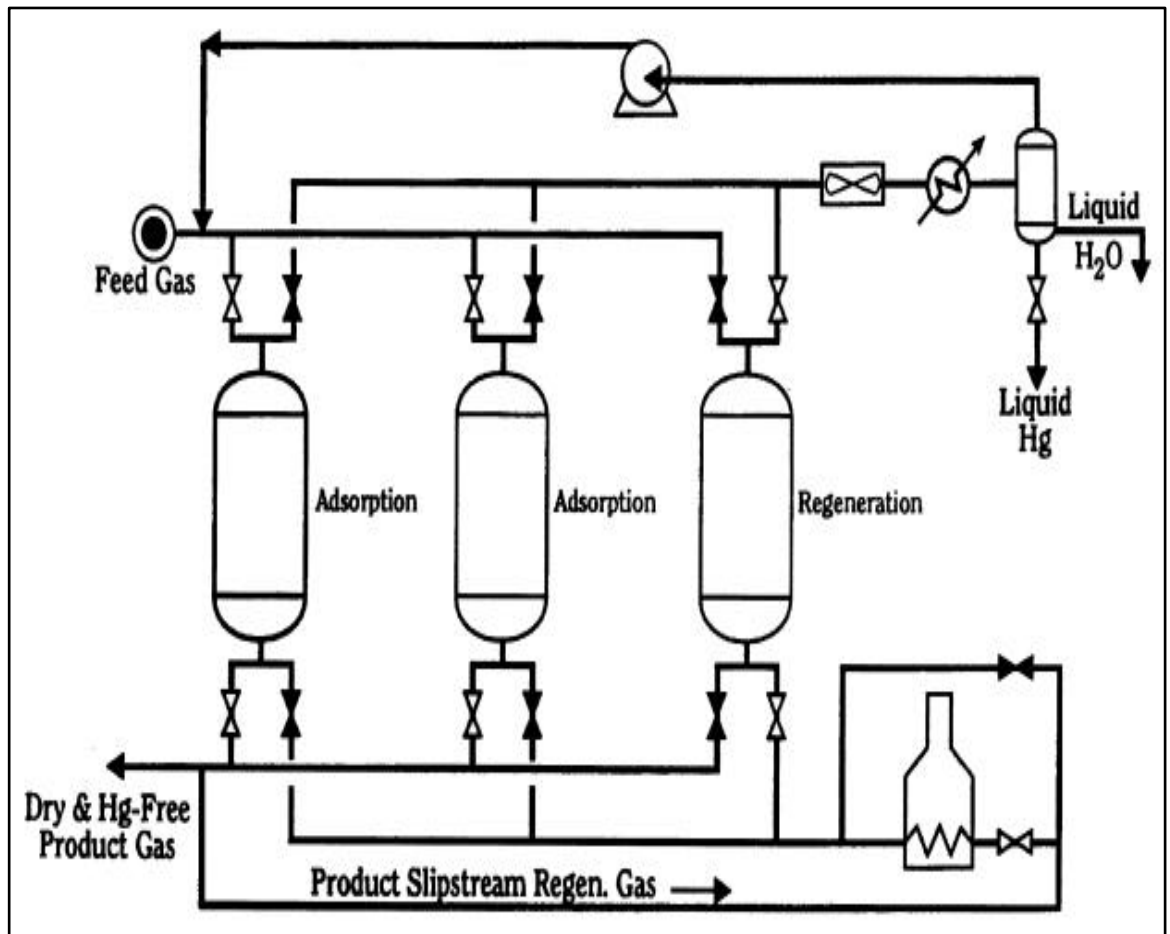


Figure (2.2) :- HgSIV Mercury Removal and Recovery System .

Other process schemes are possible . A bulk non- regenerable mercury removal unit could be used upstream of the acid gas removal unit . In this case , a carbon bed could be used to remove the bulk of the mercury , while a regenerable zeolite trim bed is downstream of the Acid Gas Removal (AGR) unit to remove the balance of the mercury . The regeneration gas from the zeolite unit could then be recycled back to the bulk mercury removal unit . Such a scheme is depicted in Figure(2.3) ^[7] .

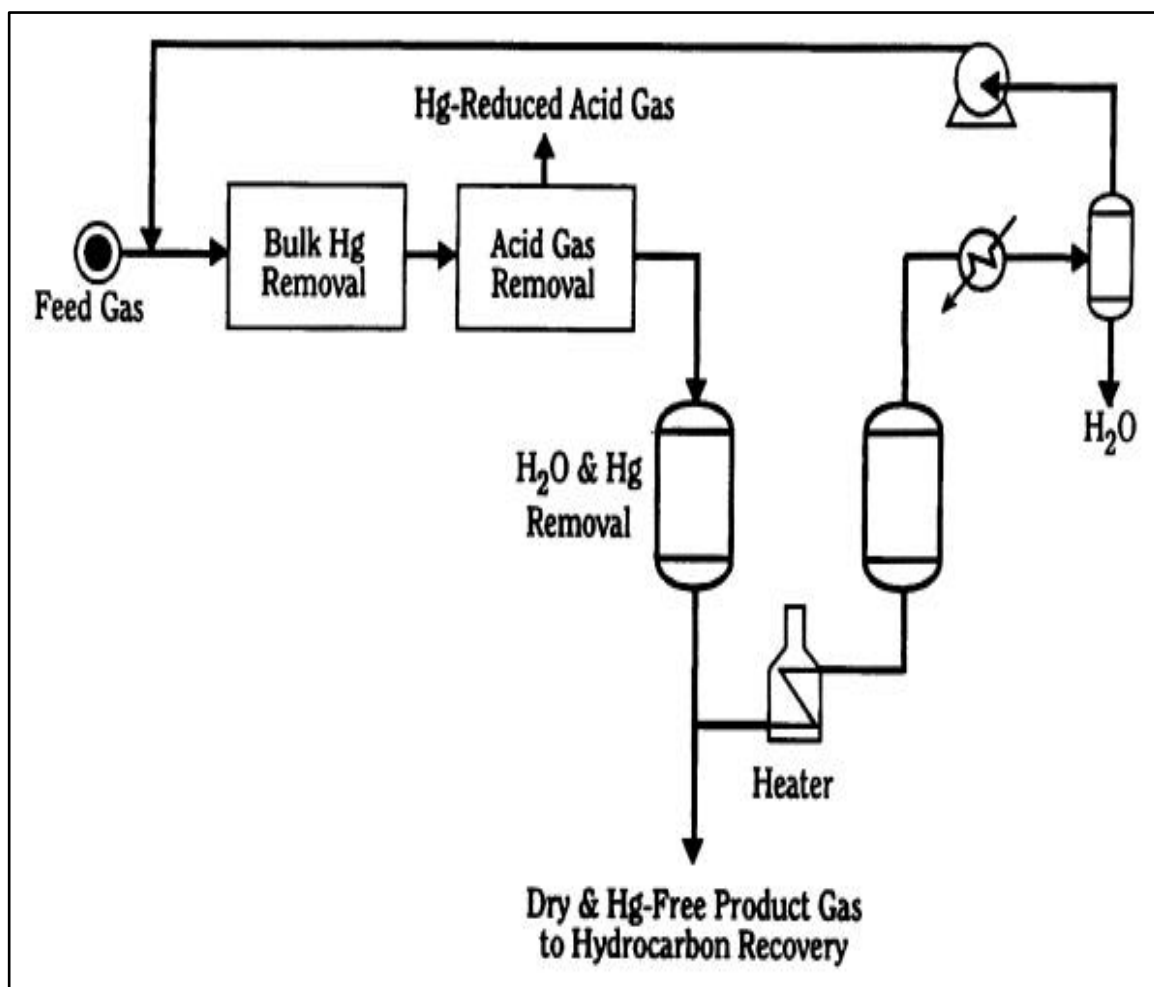


Figure (2.3) :- Integrated Carbon/Zelite Hg-Removal System .

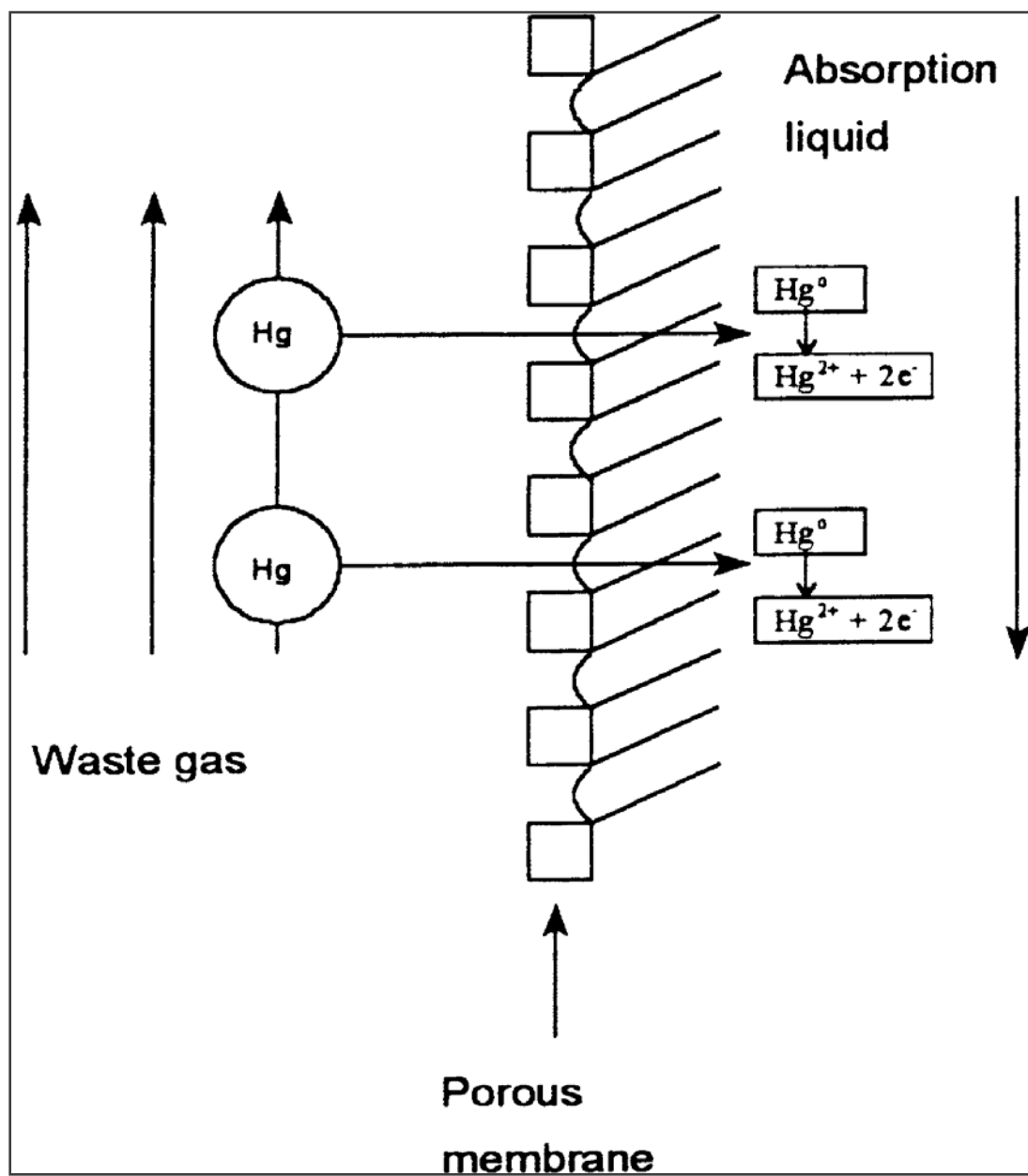
Regenerative mercury removal is usually practiced simultaneously with another regenerative adsorption application such as drying . By replacing some of the drying adsorbent with a dual function water and mercury removal adsorbent , both water and mercury are removed in the dehydrator . The mercury , like the water , is regenerated off the adsorbent leaving with the spent regeneration gas . The plus side of this approach is no additional equipment cost , no additional pressure drop , and the possibility of recovering most of the mercury as a separate mercury stream .The mercury is not permanently held on the adsorbent and the spent regeneration gas may require some secondary mercury removal treatment .

2.1.4- Membrane Method:-

Mercury from waste-incineration and soil thermal treatment off-gas , natural gas and the glycol-overhead in a natural gas dryer are removed by oxidative Membrane Gas Absorption (oxi-MGA) . In membrane gas absorption (oxi-MGA) a liquid absorption phase and the gas phase to be treated are contacted via a membrane . For the removal of mercury , an oxidizing absorption solution is used , as indicated in Figure (2.4) some general advantages of MGA . Over conventional methods are ^[13] :-

- Possibility of extreme liquid to gas flow ratio without channeling or flooding.
- Modular design giving flexible operation.
- Skid-mounted.
- Predictable scale-up .
- Very high contact-surface area to volume ratio .

The application of a membrane absorber for the removal of mercury vapor at low concentrations is especially advantageous over the use of a conventional absorber since only limited amounts of absorption liquid are required . The oxidizing liquids (absorption liquid) that were used in this process were aqueous solutions of H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$ because these solution were strong oxidizer , friendly and ecologically sound removal of mercury , a high mercury load and prevent precipitation on the membrane. The mercury in the gas stream was passed through the membrane and oxidized by absorbent liquid from Hg^0 to Hg^{+2} , as shown in figure (2.4) .



Figure(2.4) :- Removal of mercury from a gas stream by oxi-MGA

2.1.5- Granular Bentonite :-

Granular bentonite has been assessed regarding its capacity to remove Hg(II) from aqueous solutions^[14]. The granular bentonite has selectivity toward Hg. The adsorption capacities of granular bentonite towards the metals expressed in milligrams metal per gram granular bentonite is 1.7 for Hg.

2.1.6- Natural Clays :-

The impregnated sulfur containing compounds on natural clays (bentonite, china clay and ball clay) are used them in the removal of Hg(II). The treated clays used as adsorbents for removing mercury from water and drilling mud samples obtained from oil platforms^[15].

2.1.7- Other Methods :-

Several other methods to remove mercury have been investigated over the years. Among these was the use of selenium on activated carbon. However, selenium's high toxicity causes potential disposal problems for the spent carbon. Sorption by chromic acid on silica gel has also been tried, but found to result in very low mercury loadings^[7].

Carbon molecular sieve is also directed to a process for removing mercury vapor from gas stream^[16]. Carbon molecular sieve (CMS, or Molecular Sieving Carbon, MSC) is an interesting material as a model of activated carbons since it has a uniform and narrow micropore size distribution.

Other investigation found that used manganese oxides to removal of elemental mercury from dry methane gas^[17].

2.2- The Process Description of Removal Hg From Iraqi Natural Gas :-

The treated gas stream from the sweetening unit is cooled to approximated 38 °C through cooler to condense out excess water . This cooling reduces significantly the required amount of molecular sieve dryer . The water condensate , after separation from the gas stream in the Knock Out drum , was returned to the sweetening unit for reuse . The gas is normally not cooled enough to condensate hydrocarbons . Any condensate hydrocarbon , if present in the K.O. drum are sent to the burning pit . The gas from the K. O. drum flows to the charge – gas dryer before proceeding to the downstream , low-temperature separation section . The gas is dried to prevent plugging due to freeze – ups and hydrate formation at low temperature . Two vessels containing molecular sieve desiccant are provided; these alternate between on- stream drying service and regeneration, on an 8 hour cycle (cycle length will be longer with new desiccant and progressively decline with time) . An inter bed moisture probe monitors operation and detects water break through from the bed . The dried gas is sent to the activated carbon bed , where any trace amount of mercury in the gas stream are removed . The gas flow through the filter consist of three layers of mesh [the inner layer (mesh 20), the middle layer (mesh 60) and the outer layer (mesh 325)] , to remove desiccant dust and other solids which may cause plugging in the down – stream equipment . The gas is then compressed to approximately 46 kg/cm² with a side stream draw off at about 32.6 kg/cm² G , for dryer regeneration gas .Before entering the chilling section , the compressor discharge is cooled to 40 °C with cooling water . The vapor , separation in the compressor discharge drum is sent to the chilling section , while the hydrocarbon condensate is directed to the Deethanizer . The side stream from the charge- gas compressor , is first

heated in the fired heater to 343 °C and then used as the regeneration gas for all the dryers in the plant . The regeneration gas , after dryer regeneration , is cooled with cooling water to 38 °C. The regeneration gas is then sent to the regeneration gas K. O. Drum where water is removed . The water separated from the K.O. drum is degassed in the degassing drum before being discharge to the waste water treatment . The regeneration gas from the K.O.Drum is recycled back to the absorber in the sweetening unit , for acid gas removal . During cool-drum period , the regeneration gas is cooled approximately 40 °C being sent to the dryers ^[18].

K.O.DrumDryerSection Drum

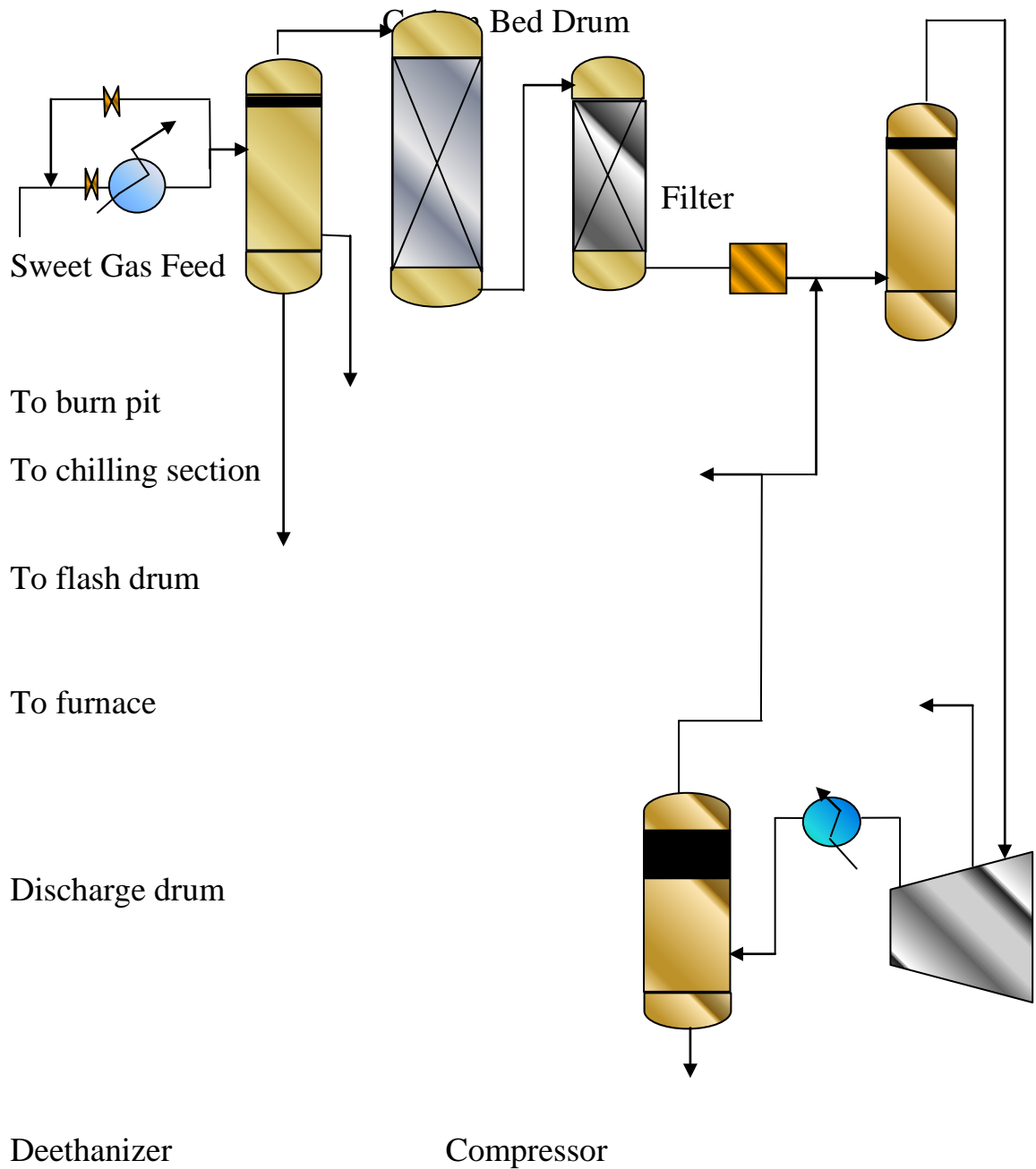


Figure (2.5):-The Dehydration Unit.

2.3- Activated Carbon Drum :-

The activated carbon drum location is after dryer . It is content 31000 Kg of activated carbon no regenerative fixed bed .The fixed bed putting on Tyler 10 mesh s.s.screen with bottom support grid . Design support grit to carry (3300 mm) bed of activated carbon 580 Kg/ m³ and 1 Kg/cm² pressure drop across bed . The dried gas inter the drum from the top and exit from the bottom . The exiting stream filtrated by filter type (cartridge 10~25 micron) to remove activated carbon , fine powder , desiccant dust and other solids which may cause plugging in the down – stream equipment . Flow rate of gas pass through the drum is 325,188 Kg/hr . The drum pressure and temperature is 26.4 Kg/cm² and 38 °C. The drum is with dimension shown in Figure (2.6) below ^[18] . The activated carbon chemical list give characterization of carbon bad in Table (2.1) .There are some disadvantages when activated carbon is used as a bed for removal of mercury from the stream of LNG gas, indeed the low resistance to attrition ,low of hardness and frictional force . These leading to form a fine carbon particle causes blockage in strainer and consequently led to increase in differential pressure process . In order to overcome the limitation of activated carbon, its necessary therefore to develop a new material used as a bed instead of carbon bed in order to avoid the drawback of activated carbon.

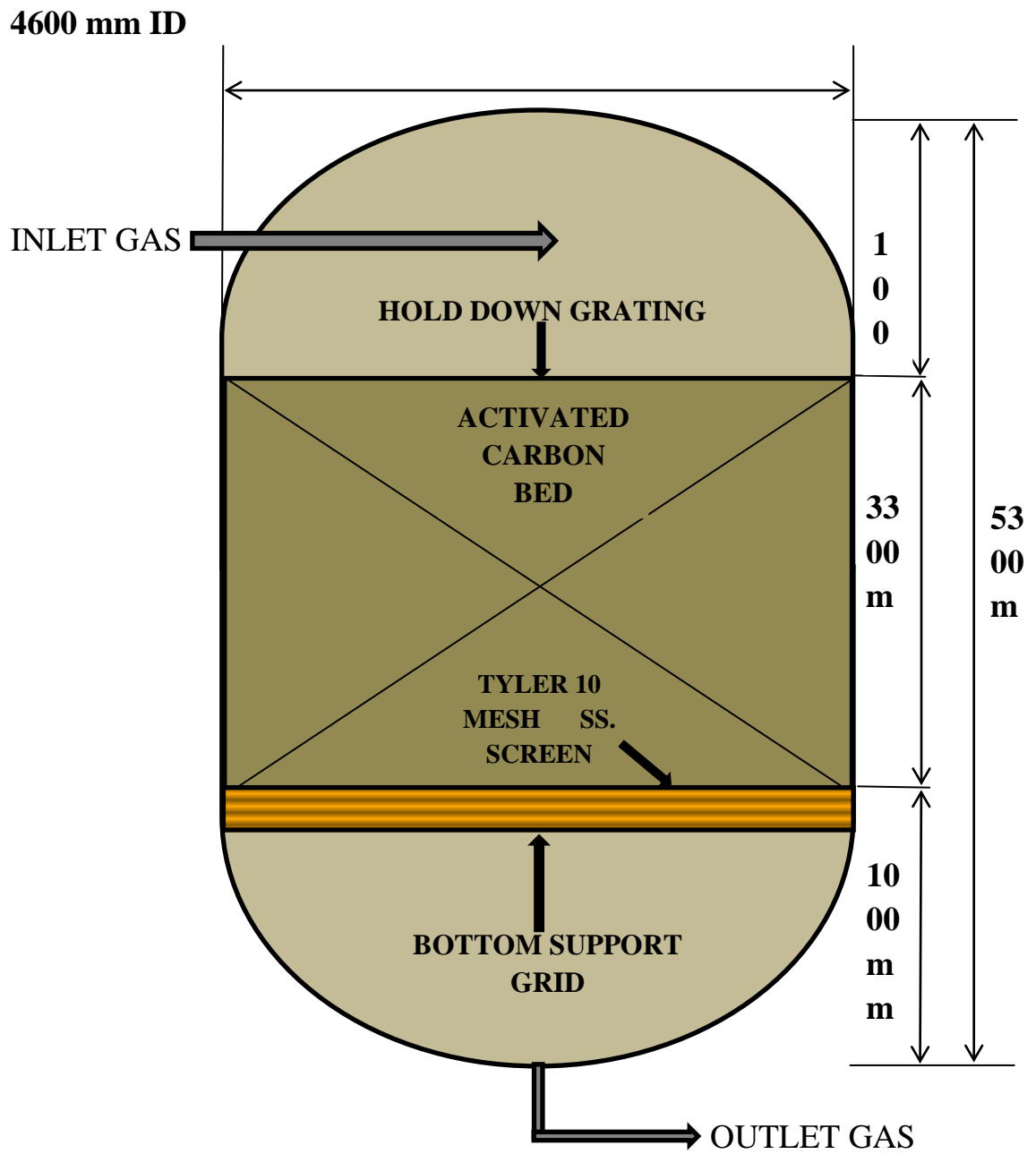


Figure (2.6) :- The Activated Carbon Drum .

Table (1.2) :-The activated carbon chemical list ^[18] :-

- Service	activated carbon that used to remove mercury from gas stream
- Band name	Pittsburgh type HGR (4*10)
- Manufacturer	Cargon Corporation
- Initial charge	62000 Kg 31000 Kg for each unit
- Remaks	<p>expected life : 10 years</p> <p>Sulfur content . min : 10 %</p> <p>Moisture . max : 3 % as packed</p> <p>Mesh size . u. s. sieve : (4*10)</p> <p>Bulk density : 0.58 g/cc</p> <p>Volume : 53.4 m³</p> <p>Surface area 1100 m²/gm.</p>
- Package	200 L steel drum

2.4- The Analytical Method Of Mercury :-

The mercury is present at low level in natural gas . A number of analyzers are available that claim capability at the level of parts per trillion by volume :-

- 1- Electron fluorescence ^[19].
- 2- Cold vapor atomic absorbance ^[20].
- 3- Atomic emissions spectra or electrical resistance^[21] .

All of them rely on the principle of passing a sample stream through a trap and then desorbing the mercury from the trap as a concentrated pulse into the detector . Some of these traps may consist of silver or gold gauze or gold-coated inert particles such as silica or sand . The desorption is accomplished by applying external heat .

Laboratory studies found that an atomic emissions spectrometer (such as Hewlett Packard Model 5921A) coupled with a good quality gas chromatograph (such as Hewlett Packard Model 58900) ^[22] provide an accurate way to measure mercury in both gas and liquid samples , as long as proper column technology is used . The electrical resistance type mercury analyzer manufactured by Arizona Instrument Co. works well for both laboratory studies and field analyses . In this analyzer , one leg of a Wheat stone bridge arrangement is made of gold film . As mercury passes over the film , mercury amalgamates with the gold , changing its resistance .

3.1-Adsorption Kinetic Studies^[23],^[14]:-

There are several model to estimate adsorption kinetic based on the experimental results obtained .

3.1.1-The Fractional Power Model :-

In the fractional power model, k and v are constants, v being a positive number less than (1) . The product k · v is known as the “specific biosorption rate at unit time”

$$q_t = k \cdot t^v \quad \dots\dots\dots(3-1)$$

Linear expression of equation

$$\ln q_t = \ln k + v \cdot \ln t \quad \dots\dots\dots(3-2)$$

where

q_t = Adsorption capacity (mg/g)

t = Time (minute or hour)

3.5.2- Pseudo-First-Order (Lagergren) :-

This equation was used for the sorption of liquid / solid system and is one of the most widely used sorption rate equations for the sorption of a solute from a liquid solution .

$$q_t = q_e [1 - \exp(-k_1 \cdot t)] \quad \dots\dots\dots(3-3)$$

Linear expression of equation

$$\log (q_e - q_t) = \log q_e - \frac{k}{2.303} \cdot t \quad \dots\dots\dots(3-4)$$

3.5.3- Pseudo-Second-Order :-

In this model assumes that two reactions are occurring :- the first one is fast and reaches equilibrium quickly , while the second one is a slower reaction that can continue for long time periods . k_2 represents the kinetic constant of the process . equilibrium constant , k_2 , and the square of the adsorption capacity in equilibrium , q_e :-

$$q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + q_e \cdot k_2 \cdot t} \dots\dots\dots(3-5)$$

Linear expression of equation

$$\frac{t}{q_t} = \frac{1}{q_e^2 \cdot k_2} + \frac{t}{q_e} \dots\dots\dots(3-6)$$

k_2 = The kinetic constant of the process $= \frac{h}{q_e^2}$

h = The initial sorption rate (mg/g .hour)

3.5.4- Intra-Particle Diffusion :-

Intra-Particle diffusion has been allowed to test the transport of the adsorbate from the solution towards the pores of the adsorbent is the limiting stage of the adsorption process . this equation should be a straight line .

$$q_t = k_p \cdot t^{0.5} \dots\dots\dots(3-7)$$

3.6-Adsorption Isotherm Studies^[23],^[14]:-

The Langmuir, Freundlich, Temkin and Dubinin– Radushkevich (D-R) isotherm models were used to quantify the adsorption capacity of BCA for the removal of Hg(II) ions from aqueous solutions .

3.6.1-The Langmuir Isothermal Model :-

The Langmuir isotherm equation assumes that fixed individual sites exist on the surface of the adsorbent , each of these sites being capable of adsorbing one molecule , resulting in a layer one molecule thick over the entire carbon surface . The Langmuir model also assumes that all sites adsorb the adsorbate equally .

$$q_e = \frac{Q \cdot k \cdot C_e}{1 + k \cdot C_e} \dots\dots\dots(3-8)$$

linear expression is

$$\frac{1}{q_e} = \frac{1}{k \cdot Q} \cdot \frac{1}{C_e} + \frac{1}{Q} \dots\dots\dots(3-9)$$

Where

K= Adsorption equilibrium constant (1 mg⁻¹) .

Q = The quantity of adsorbate required to form a single monolayer on unit mass of adsorbent (mg/g) .

A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter R_L , known as the separation factor given by equation :-

$$R_L = \frac{1}{1 + K C_e} \dots\dots\dots(3-10)$$

The value of R_L lies between 0 and 1 for a favorable adsorption, while ($R_L > 1$) represents an unfavorable adsorption, and ($R_L = 1$) represents the linear adsorption, while the adsorption operation is irreversible if ($R_L = 0$).

3.6.2- The Freundlich Isothermal Model :-

The Freundlich isotherm equation assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. This equation assumes that each class of adsorption site adsorbs molecules, as in the Langmuir Equation. The Freundlich Isotherm Equation is the most widely used and will be discussed further.

$$\frac{x}{m} = k \cdot C^{1/n} \quad \dots\dots\dots(3-11)$$

Linear expression is

$$\ln \frac{x}{m} = \ln k + \frac{1}{n} \ln C \quad \dots\dots\dots(3-12)$$

where

x = Amount of solute adsorbed (μg , mg , or g)

m = Mass of adsorbent (mg or g)

C = Concentration of solute remaining in solution after adsorption is complete (at equilibrium) (mg/L)

K, n = Constants that must be determined for each solute, carbon type, and temperature.

3.6.3- The Temkin Isotherm Model :-

The Temkin model isotherm assumes that (1) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent – adsorbate interactions, and (2) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (mg per g) and K_T (lit per mg) are Temkin's constants.

$$q_e = q_T \ln(k_T \cdot C_e) \dots\dots\dots(3-13)$$

linear expression is

$$q_e = q_T \cdot \ln(k_T) + q_T \cdot \ln(C_e) \dots\dots\dots(3-14)$$

3.6.4- The Dubinin - Radushkevich Isotherm Model :-

The D-R equation assumes that the amount adsorbed corresponding to any adsorbate concentration is a Gaussian function of the Polanyi potential. In the D-R equation, q_{D-R} is the maximum adsorption capacity (mg per g), D is the activity coefficient related to mean adsorption energy (mol^2/J^2) and ε is the Polanyi potential (kJ^2/mol^2).

$$q_e = q_{D-R} \cdot \exp(-D \cdot \varepsilon^2) \dots\dots\dots(3-15)$$

linear expression is

$$\ln q_e = \ln q_{D-R} - D \cdot \varepsilon^2 \dots\dots\dots(3-16)$$

Where

$$\varepsilon = RT \ln(1 + C_e^{-1})$$

4.1- Materials :-

Material which has been suggested as mercury adsorbent should have the following properties:

- 1- Hard to resist the erosion caused by a stream of natural gas in adsorbent bed in order to avoid the formation of fine powder .
- 2- Has either a similar adsorbent properties of AC or better.
- 3- Should be inert and not react with natural gas.

For these purposes a semi ceramic material was prepared consisting of:-a clay,bentoniteand ACas an adsorbent materials.Then after mixing with water were dried and treated at high temperature in order to convert into ceramic material. The prepared samples were tested as adsorbent for removing mercury from aqueous solution.TheAC was also tested under similar conditionfor comparison. The Bentonite -Clay-Activated carbon (BCA) sample was the best than other samples because the BCA was exhibited better adsorption toward solution than other samples and it has the best hardness .

The Granular Activated Carbon(AC) used in this work was obtained from the North Company for gas production and then used as a reference for comparison . Bentonite powder is supplied by State company of Surveying and Mining .Some characteristics of this bentonite are presented in Table (4.1) . Bentonite powder was granulated and activated by H_2SO_4 before used, followed the procedure done byMohamed et al^[24].

Table (4.1) :- Physical properties of bentonite ^[24] .

Density (kg/m ³)	740
Specific surface area (m ² /g)	240.03
Water absorption% by wt.	115
Acidity	0.16
PH	3

4.2- Preparation Method :-

Different samples with different concentration of adsorbent material have been prepared throughout the course of this research as listed in Table(4.2) .BC samples consisted different amounts of bentonite(B) and clay(C), while (BCA) sampleconsisted of two kind of adsorbent[activated bentonite(B) and activated carbon(AC)]and natural clay(C) used as a binder. In each case the materials were crushed, grounded and sieved through 200 sieve meshes . Materials after sieved were mixed carefully with water and the paste obtained were form into smalls rectangular imparts with a dimension (3x5x3mm) . The specimens then dried in oven(supplied by Nabertherm Lilienthal ,Germany) at 60°C for 24 hours .

Table (4.2) :- The compositions of BC and BCA specimens.

Sample	Clay	Bentonite	Activated carbon
BC1	20%	80%	-----
BC2	30%	70%	-----
BC3	40%	60%	-----
BC4	50%	50%	-----
BC5	60%	40%	-----
BCA	25%	25%	50%

Heat treatment follows the heat treatment regime shown in Figure (4.1) . The resulting dried specimens of BCA were heated up to 700 °C at a rate of 10 °C / min and then soaked for 2 h in oxygen free atmosphere using muffle furnace .The photograph of furnace is shown in Figure (4.2) . This was achieved by placing the specimens in a rectangular St. steel container (10x20x10cm) dimensions , covered with a mixture of coal and silica as shown in Figure (4.3) . Standard control specimens of AC without any additive supplied by North gas company to be used as a reference . Figure (4.4) shows photomicrograph(x100) of the specimen after heat treatment , its clearly shows the homogeneity of distribution of all components within the specimen . Photomicrograph was obtained using optical microscope [Supplied by Leitz company] . All of the photomicrographs presented in this work obtained by the same instrument.

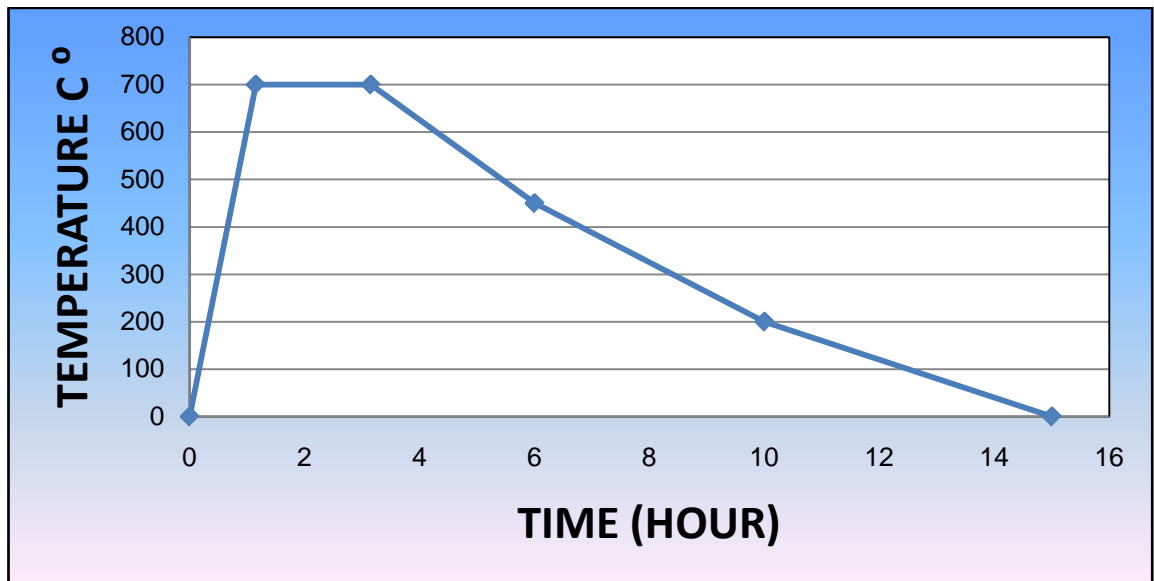
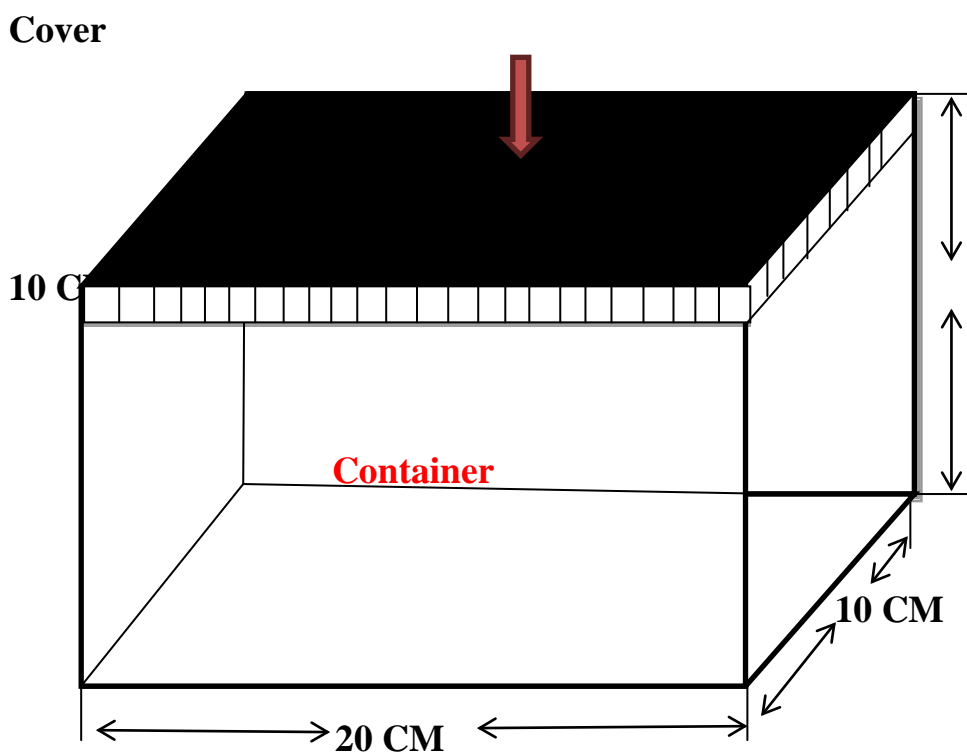
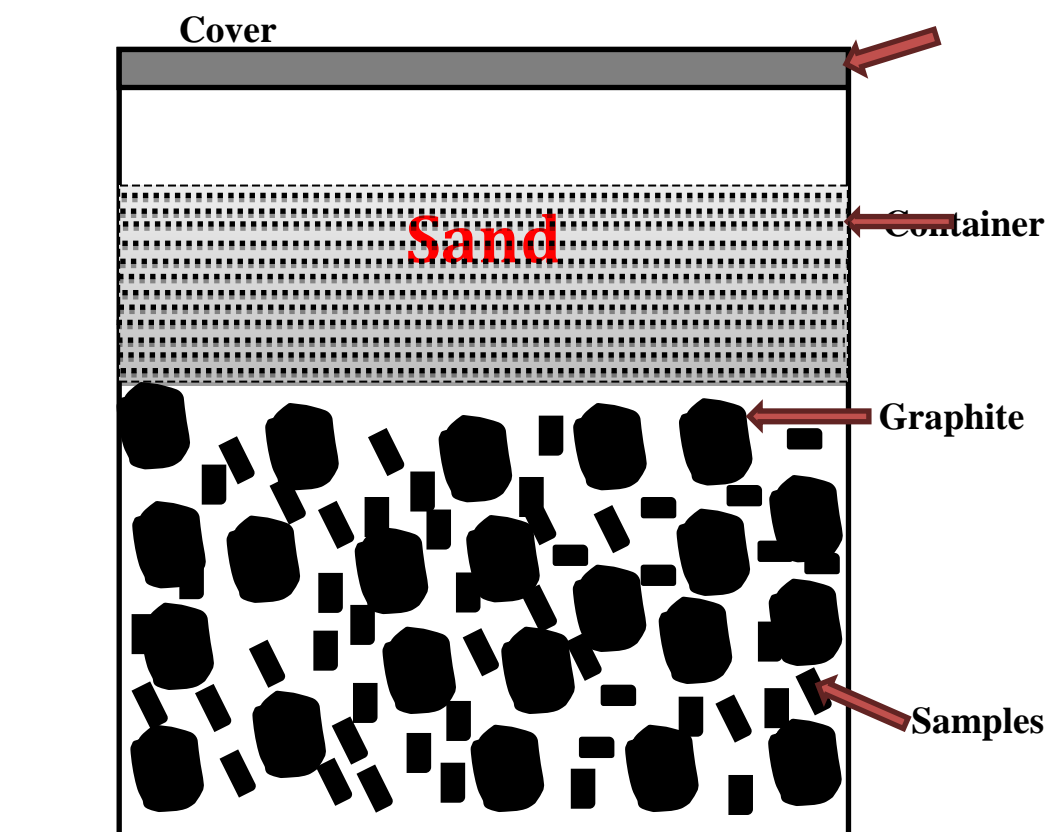


Figure (4.1) :- The heat treatment regime .



Figure (4.2) :- The photograph of muffle furnace.



Figure(4.3) :-Arrangement of material inside the heating container .

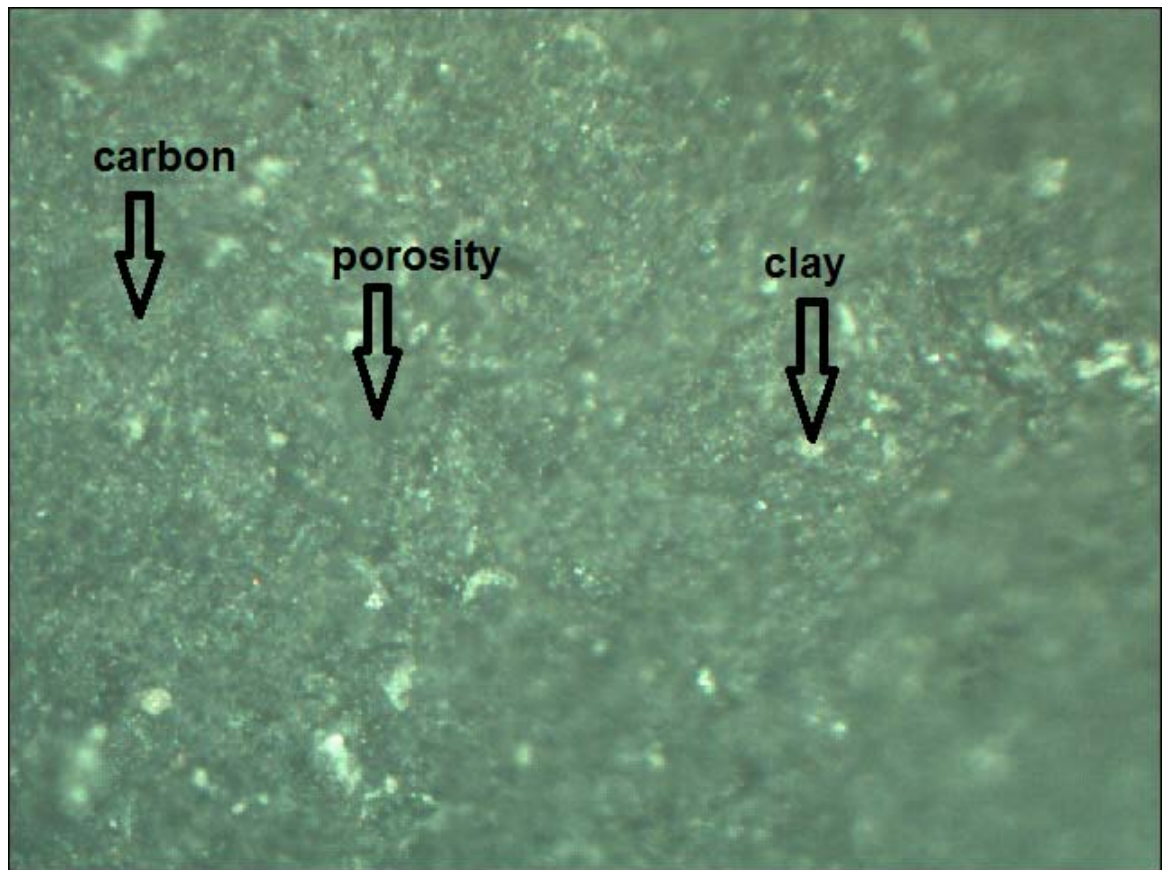
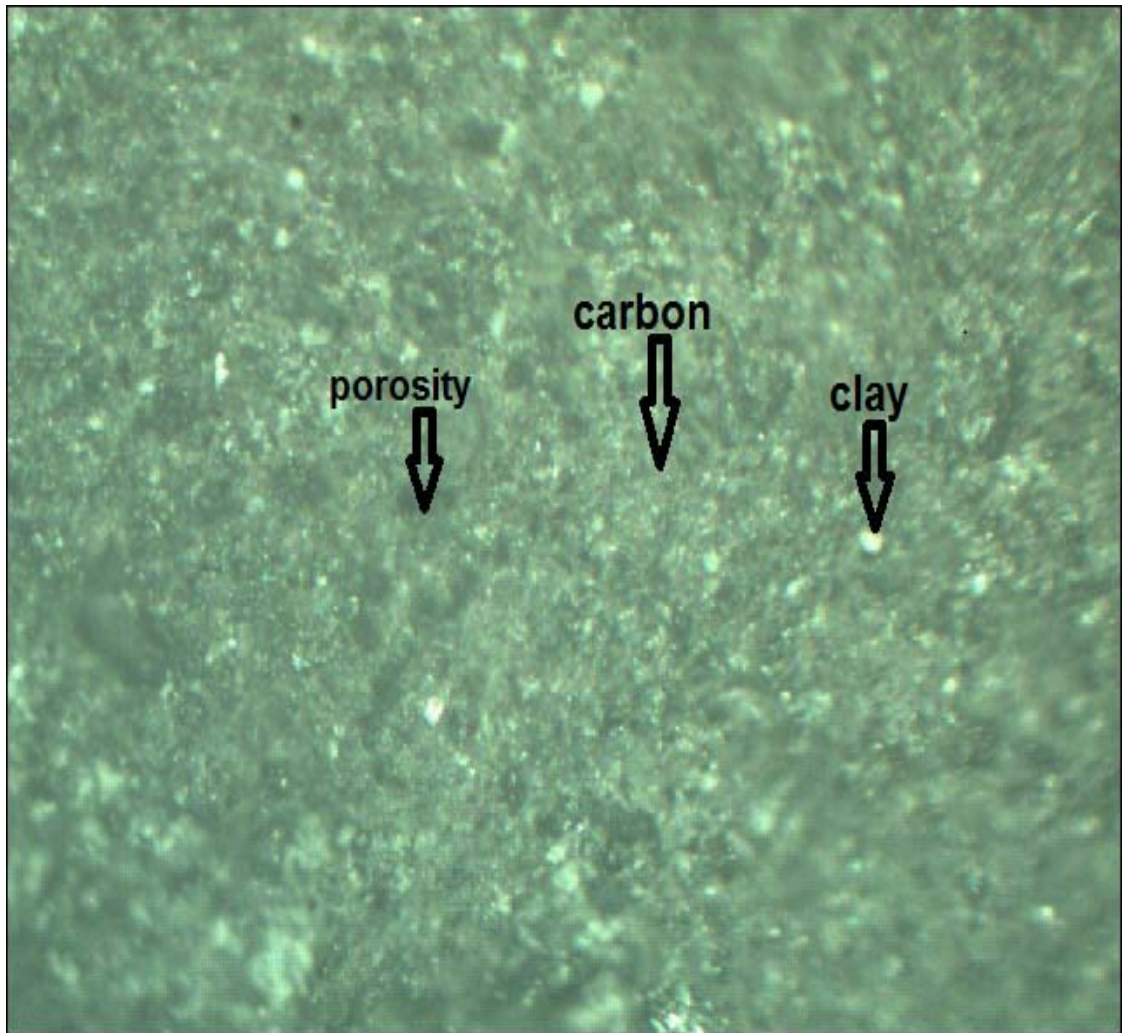


Figure (4.4) : Optical microscope picture (x100) in the surface of BCA .

4.3 -The BCA Treat With Sulfuric Acid:-

Some of the specimens is more activated by treating with 2% solution of sulfuric acid . The mixture (BCA with acid) was stirred for 2 hour, and then filtrated, wished with distilled water to remove adsorbed acid until the water PH is equal to 5. Then the specimen was dried at 100 °C . Optical photograph picture of the surface is shown in Figure (4.5) .



Figure(4.5) :- Optical microscope picture (x100) in the surface of acid treated BCA .

4.4- CBR Test To Estimate Of Mechanical Strength :-

California Bearing Ratio (CBR) test method is usually used to evaluating the strength of cohesive materials having maximum particle sizes less than 3/4 in(19 mm).CBR instrument type electric (ELE)was used to measure the strength of BCA and AC samples. Test were performed by applying a break load on a specific layer of the sample placed in closed cylinder.

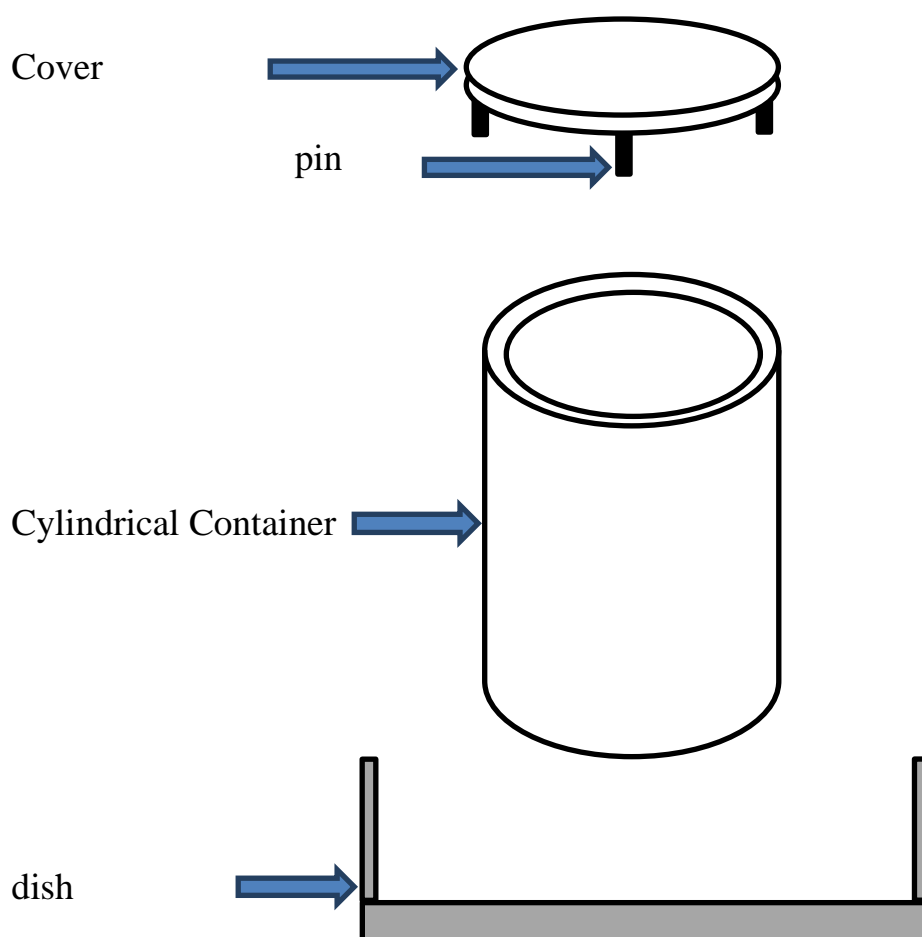
4.5- Density Measurement (Hg Displacement Method) :-

Mercury displacement method was used to measure the density in this work[ASTM -method D2854- 83].A schematic diagram of apparatus (made of glass) is shown in Figure(4.6) . It consisted of :-

- a) Cover in which three pins were embedded in the bottom face.
- b) Cylindrical container (2.5 cm diameter x 5 cm height).
- c) Dish .

The measurement was performed as follows:-

- 1- Container was filled up with mercury.
- 2- Then the cover was placed so as to remove the amount of mercury which was equivalent to pins volume and the cover was replaced.
- 3- The sample was immersed completely in mercury , pressed by cover the some of the mercury was dispersed out of the container. Its volume was equal to the volume of the sample . Mercury was collected on a dish and weighed by 4 digits electronic balance , then the density was calculated by calculating the volume from the mass and density of mercury (13.55 g/cm^3) .The average of several measurements was taken in each case to minimize the error. From this method , the density of BCA was calculated and its equal to 522.05 Kg / m^3 .



Figure(4.6) :-A schematic diagram of apparatus (made of glass)to measure the density .

4.6- Determination Of Moisture Content Of Adsorbent Material:-

This test was carried out according to [ASTM- method D2867– 83].
The test was carried out as follows :-

- 1- The weight of dry closed capsule was determined.
- 2- Ten grams of BCA were transferred to the capsule. The weight of capsule with sample was determined accurately.
- 3- The capsule was opened and placed with its lid in a preheated oven (145 to 155 °C) for 3 hours.
- 4- The sample was dried to constant weight then it was removed from the oven with the capsule closed , cooled to ambient temperature, the capsule was weighed again accurately.
- 5- Moisture contents was calculated as follows :-

$$\text{Moisture content} = \left[\frac{(C-D)}{(C-B)} \right] \times 100 \quad \text{.....(2-3)}$$

$$\text{Moisture content} = 3.8 \%$$

Where

B = weight of capsule + cover (**gm**)

C = weight of capsule + cover + original sample (**gm**)

D = weight of capsule + cover + dried sample (**gm**)

4.7- Surface Area Measurement :-

Total surface area and pore volume for adsorbent material were measured by Republic of Iraq Petroleum R & D Center using (BET-Method of N₂ adsorption) .The result are listed in Table(4.3) below :-

Table (4.3) :-Surface area and pore volume of Activated Carbon and BCA .

SAMPLE	SURFACE AREA (m² / gm)	PORE VOLUME (cm³ / gm)
ACTIVATED CARBON	554.18	0.4065
BCA	440.77	0.2717

4.8- Preparation Of Mercury Solution :-

Aqueous solutions containing mercury were prepared using analytical reagents and distilled water. Stock solutions containing (225 mg metal/ L or 225 ppm) were prepared using “analytic grade” nitrates of mercury. All working solutions were prepared by diluting the stock solution with distilled water . PH adjustments were performed using nitric acid or sodium hydroxide 0.1 N aqueous solutions .The physical and chemical properties of mercury nitrate that was used in preparation of stock solution was summarized in Table (4.4) below .

Table (4.4) :-Physical and chemical properties of mercury nitrate ^[25] :-

Molecular formula	Hg₂(NO₃)₂·2H₂O.
Molecular weight	561.22.
Specific Gravity	4.78 g/ml @ 4°C.
Melting Point	70°C decomposes.
Appearance	Slight yellow crystalline powder.
Solubility	Soluble in water and alcohol .

4.9-Determination Of Lamda Maximum And Calibration Curve:-

Lamda maximum (λ_m) was measured for stock solution by using a UV-spectrometer (Shimadzu model 160A , Japan) and found to be 225 nm. The concentration of Hg in the filtrate was determine by measuring the absorption of UV – Spectrum at 225 nm Lamda maximum (λ_m) using UV – Spectrometer . λ_m was determined at maximum absorption of UV-light. The calibration curve of mercury nitrate in water samples were found by diluting stock solution with different amount in distilled water ranged from 225 - 0.0675 ppm as shown in Table (4.5). Figure (4.7) is show photograph of UV – spectrometer type Shimadzu model 160A , Japan .

Table (4.5):- The diluted solution.

sample	mL of stock solution	mL of water	Concentration (ppm)
1	66.67	33.33	150
2	44.44	55.56	100
3	22.22	77.78	50
4	4.44	95.56	10
5	0.44	99.56	1
6	0.9	99.1	2.025
7	0.7	99.3	1.575
8	0.5	99.5	1.125
9	0.3	99.7	0.675
10	0.1	99.9	0.225
11	0.05	99.95	0.113
12	0.03	99.97	0.0675



Figure (4.7) :- UV – spectrometer device .

4.10-Adsorption Experiments Study :-

4.10.1-The effect of time on the adsorption capacity :-

The effect of time on the adsorption capacity was investigated in the time range (10 – 60 min) . A blank experiment (without adsorbent) was performed to check that no Hg consumption occurred other than by adsorption on adsorbent .Experiments on the adsorption of mercury nitrate on adsorbents were carried out under batch conditions. One gram of adsorbent material was mixed with aqueous mercury nitrate solutions (30 ml) in the measuring cylinders (100 ml) and it was sealed and then was agitated at 180 rpm using magnetic stirrer for a specified period of contact time one hour. The mercury nitrate concentrations in solution was 15ppm for all of the samples. The conditions of the tests were at atmospheric pressure and room temperature (25 ± 1 °C) .The PH of the solution was kept at 7 adjusted by 0.1M of NaOH. At the end of every adsorption test, the samples were filtrated by filter paper ,and analyzed for the mercury nitrate concentration by UV- spectroscopy .

4.10.2- The effect of quantity or mass of adsorbent on the adsorption capacity :-

The effect of quantity or mass of adsorbent on adsorption of mercury ions was investigated by varying the mass of adsorbent from 0.4 g to 2g. In each case the adsorbent material (either BCA or AC) were mixed with 100 ml of mercury nitrate solution in a glass beaker . The mercury nitrate concentration in all of the samples were (20 ppm) .The samples in beakers were mixed carefully by stirrer for one hour and the concentration of mercury nitrate remaining in the solutions (after filtration) were determined by using UV- spectroscopy .

The adsorbed Hg was calculated as follows :-

$$q = \frac{(C_o - C_t) \cdot V}{M} \dots\dots\dots(4-1)$$

Where

q =The amount of Hg adsorbed by adsorbent material (mg g⁻¹) .

C₀=The initial Hg concentration (mg L⁻¹) .

C_t= The final Hg concentration after a certain period of time (mg L⁻¹) .

V =The initial solution volume (L) .

M=The adsorbent dosage (g) .

The percentage of mercury nitrate adsorption by adsorbent was calculated by using the equation below :-

$$q\% = \frac{(C_o - C_t)}{C_o} \cdot 100 \dots\dots\dots(4-2)$$

5.1-Determination of Lamda maximum (λ_m) :-

The concentration of Hg in the filtrate was determine by measuring the absorption of UV – Spectrum at 225 nm Lamda maximum(λ_m) using UV –Spectrometer . λ_m was determined at maximum absorption of UV-light by mercury nitrate in the solution , the spectrum shown in Figure (5.1) .

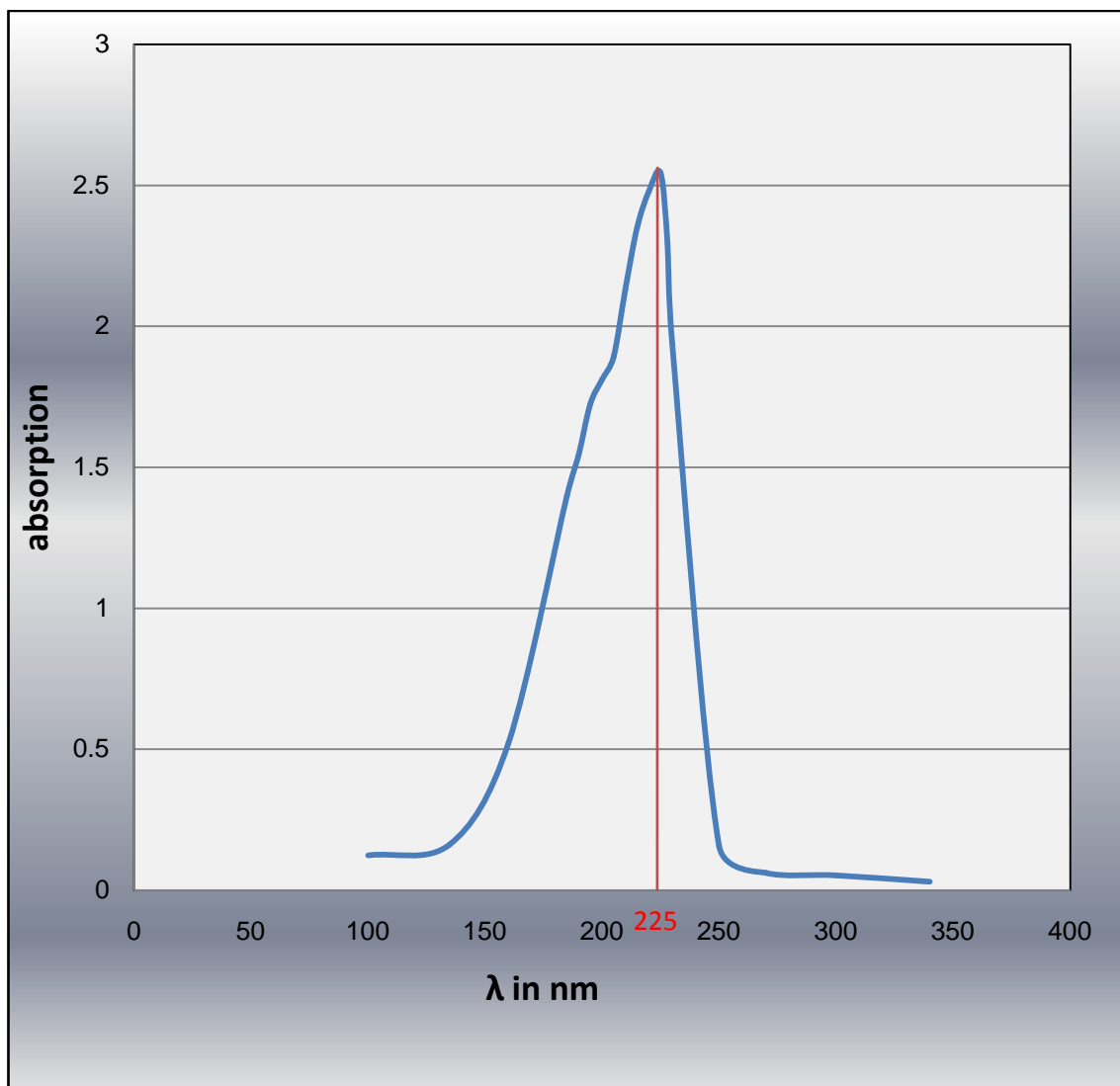
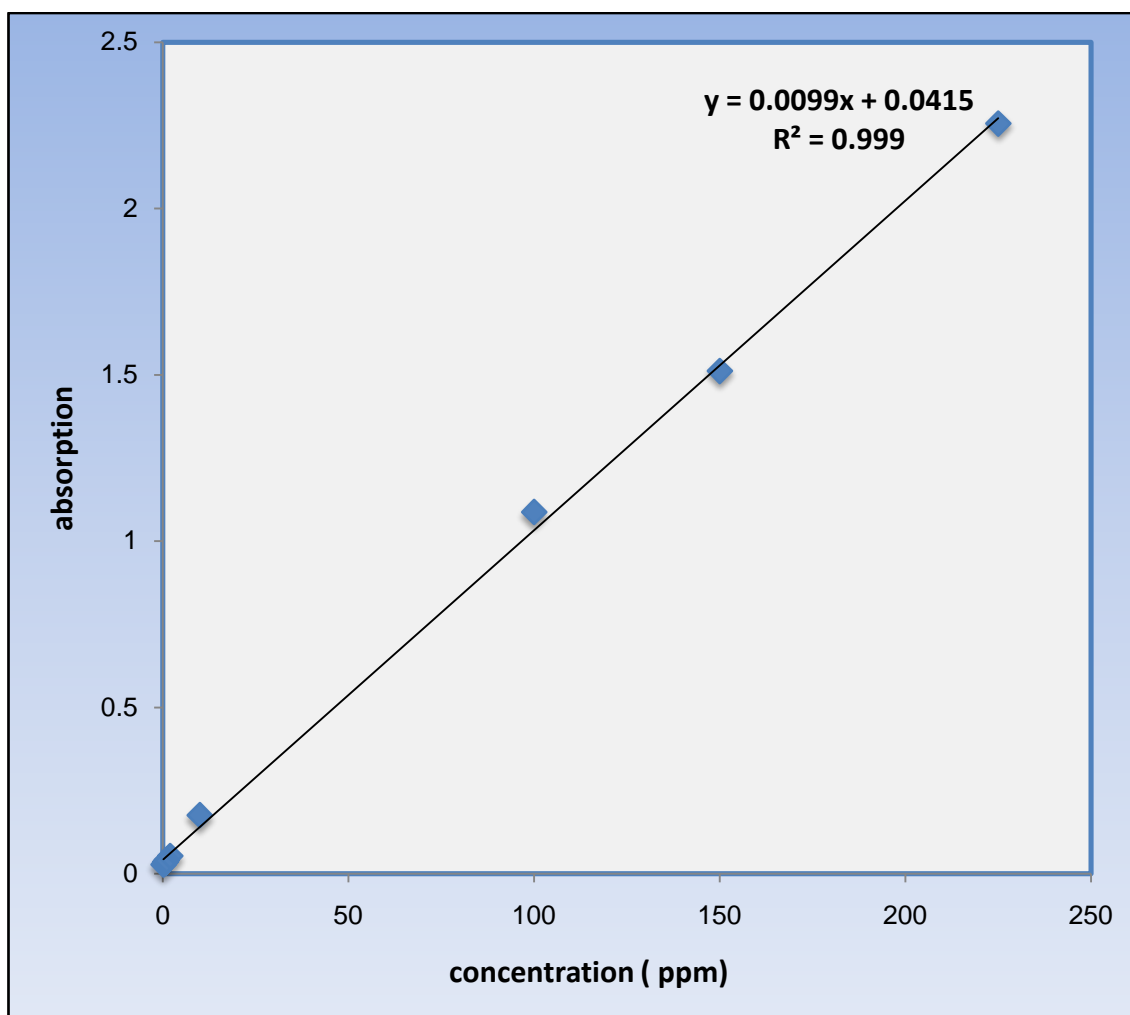


Figure (5.1) :-Lamda maximum (λ_m) curve

5.2- Calibration Curve :-

Figure (5.2) was plotted between different concentration of mercury nitrate in the solution in ppm and absorption of UV– Spectrometer at $\lambda_m = 225$ nm . The absorption of UV – Spectrometer is increases until a maximum value is reached .



Figure(5.2) :-The calibration curve .

5.3- The Effect Of Contact Time On Adsorption :-

The adsorption behavior of Hg by Bentonite , Clay and Activated Carbon (BCA) in relation to the effect of contact time was carried out by varying the contact time from 10 minutes to 1 hours at a Hg concentration of $C_0 = 15$ (ppm or mg/lit), a dose of adsorbent of 1g/30mLit , and pH of 7. The results presented in Figure (5.3) show the adsorption rate reach to the equilibrium after 40 minutes. Similar behavior was achieved when Activated Carbon (AC) is used as shown in Figure (5.3). The contact time is about 50 minute to reach equilibrium. Accordingly results of contact time showed that the BCA give a shorter time in comparison with AC type .It is indicating that by using BCA ,the reaction is fast and the adsorption site are well exposed as compared to AC which has closer capacity for adsorption.

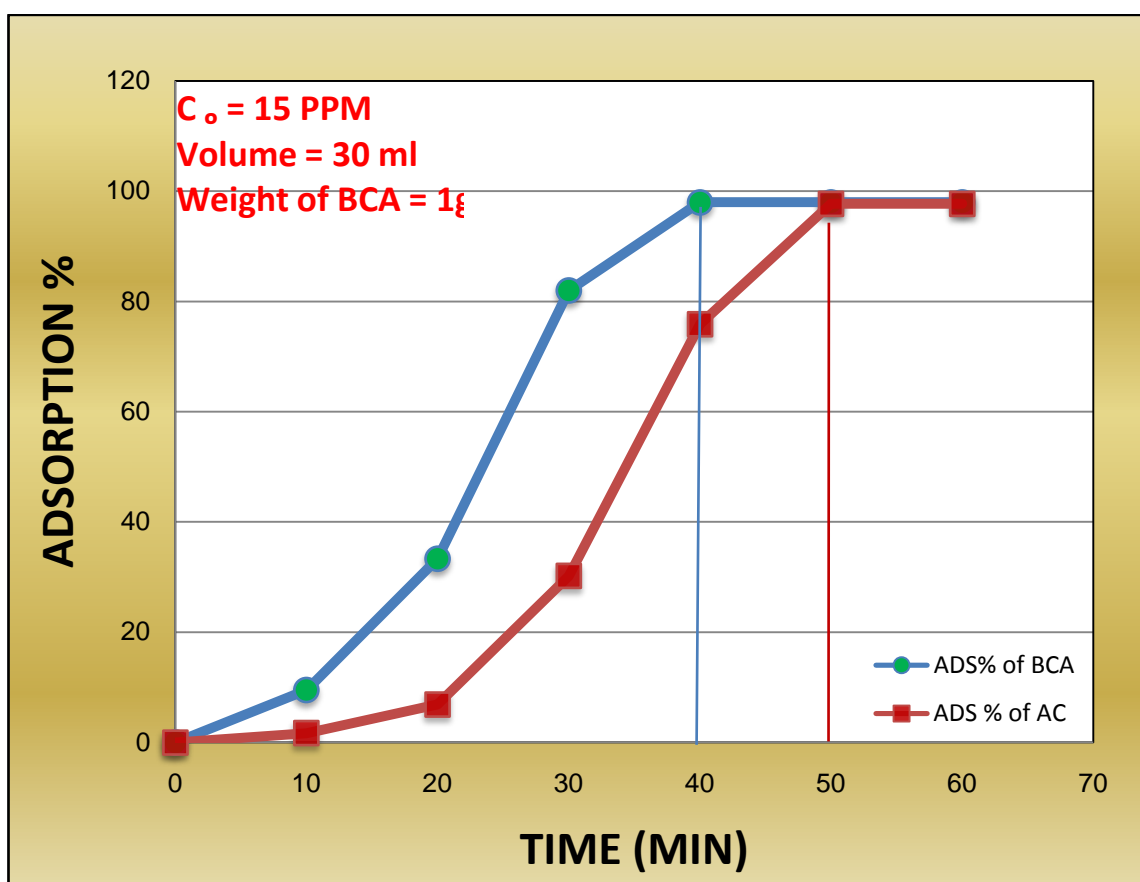


Figure (5.3) :- The effect of contact time .

5.4- The Effect Of Quantity On Adsorption :-

The adsorption isotherm of Hg on BCA is shown in Figure (5.4). The result showed that adsorption % of Hg as a function of quantity of BCA in the solution. The observed line obeys the Langmuir and Freundlich isotherm. Result obtained shows that 2 g of BCA is required to remove all of mercury in the solution. Similar result was obtained when AC is used as shown in the same figure.

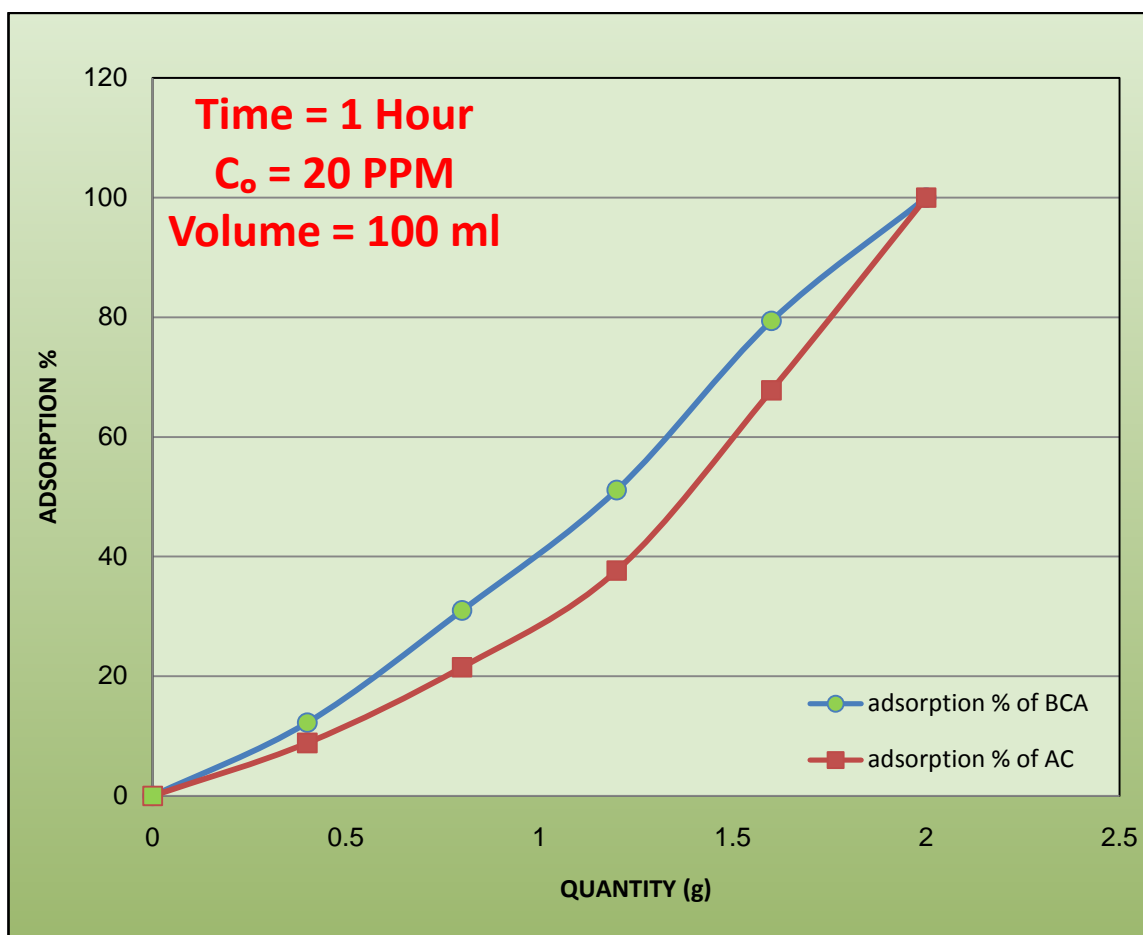


Figure (5.4) :- The effect of quantity on adsorption .

5.5- Adsorption Behavior of acid activated BCA specimen:-

The acid activated BCA specimen exhibited a different behavior, as shown in Figure (5.5). It can be identify two regions , the region one start 0.4g to 1.2 g which represent the portion belong to adsorption mechanism while the portion of the curve beyond 1.2mg exhibited adsorption behavior . This behavior can be attributed in part to the limited in adsorption capacity of material. In such case, accumulation of Hg particle is increased over the equilibrium point leading to decrease in the force of attraction between the activated site of adsorbent and Hg particles .

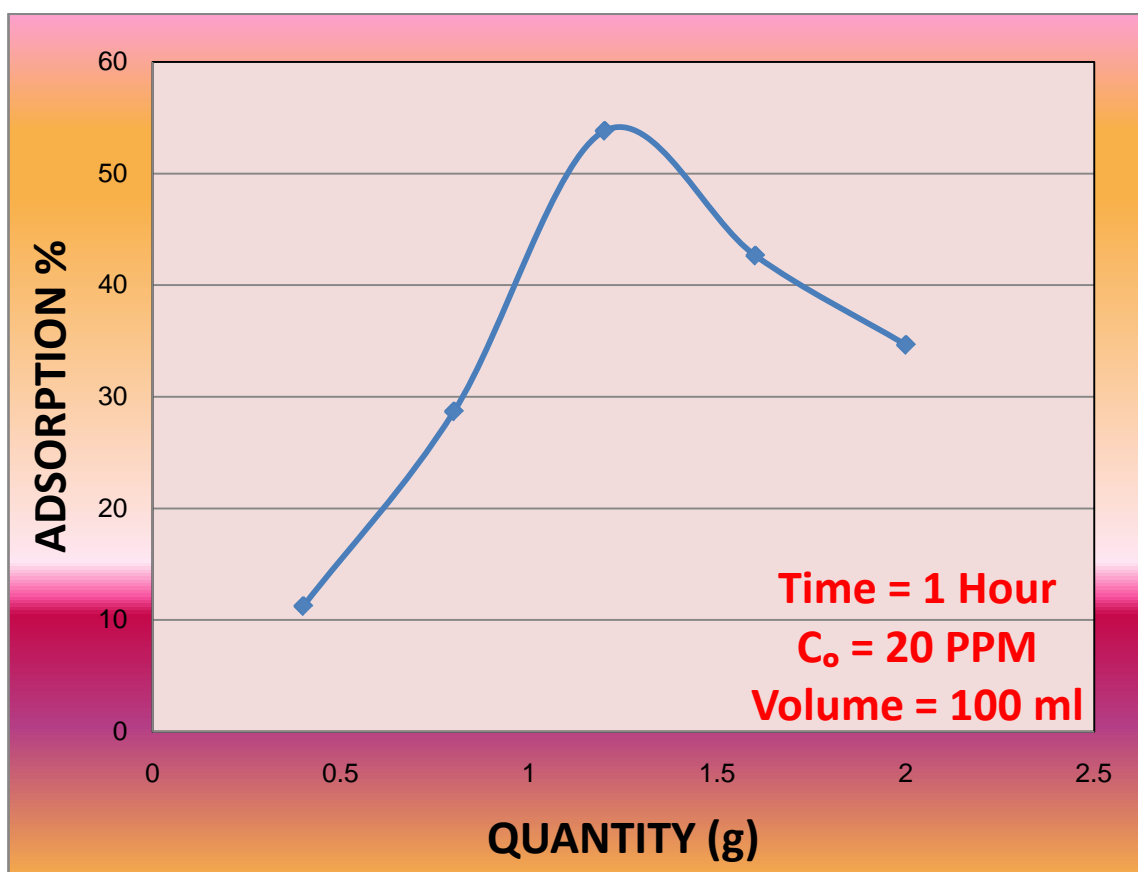


Figure (5.5) :-The adsorption % of acid activated BCA specimen .

5.6- The result of physical properties:-

The apparent densities of AC and BCA were calculated according to the ASTM-D2854 – 83 are 522.05kg/m^3 and 580kg/m^3 with AC and BCA respectively. The decreasing in the value of density of BCA is probably due to the use of 50% of bentonite - clay in the initial composition of BCA specimen and also due to the treatment of material in high temperature (700°C). This leading to produce a material with high porosity as clearly shown in Figure (5.6).

The result of measuring surface area of BCA ($440.77\text{m}^2/\text{g}$) is reduced by about 20% of AC ($554.1832\text{m}^2/\text{g}$) and this is mainly due to the use of clay as a binding agent which already have low surface area.

The compression strength for both (AC and BCA samples) was measured using California Bearing Ratio (CBR) technique .The maximum CBR value for BCA was 850N/mm^2 while AC exhibited a zero resistance towards the compression. Accordingly the new material has gained a higher mechanical strength than AC and hence the resistance to erosion during use as absorbent material in the mercury purified bed will be high also and better than AC .

A summary of all of characterization for both BCA and AC are shown in Table (5.1) .

Table(5.1) :-Characterization of BCA and AC .

Sample	BCA	AC
Density (ρ) Kg / m ³	522.05	580
Density of particle (ρ_p)Kg / m ³	870.08	960.67
Adsorption Capacity (µg/g)	441.1	439.65
Adsorption %	98% in 40 min	97.7% in 50 min
Porosity (ϵ) of bed	0.6	0.4
Surface area (m ² /g)	440.77	554.1832
Pore volume (cm ³ /g)	0.2717	0.4065
Fine powder released	Less	more



Figure (5.6) :-A photograph of BCA and BC samples .

6.1-Conclusions:-

The following conclusions could be drawn from this study:-

- 1- The BCA material which was prepared in this work as an alternative material to AC for mercury removal from aqueous solution was simple in preparation and not expensive, particularly compared with other adsorbent material discussed in chapter two included AC. Nevertheless many parameters of importance for mercury removal technique have been studied successfully ,and it might be very useful in the development of mercury removal column bed of natural gas refinery plant.
- 2- Many samples with different amount of adsorbent materials(i.e. Clay , bentonite , Activated carbon) have been prepared and the results show that the sample with 25% clay,25% bentonite and 50% activated carbon and named BCA has a much higher adsorption than the other samples.BCA sample is a refractory material after has been Subjected to 700 °C under oxygen free atmosphere .Accordingly the material possess a higher mechanical properties than AC a lone and then the formation of dust causes blockage in strainer might be either eliminated or reduced into lower rate.
- 3- In general ,the contact time to reach equilibrium are 50min for BCA as compared with 60min for AC suggests that BCA posses highly potential applications for removal of Hg^{2+} from its solution.
- 4- The surface area of BCA is $440.77\text{m}^2\text{g}^{-1}$ proximately close to AC surface area .

- 5- The maximum adsorption capacities of Hg^{2+} calculated by the Langmuir model are 441.1 , $439.65 \mu\text{g g}^{-1}$ with BCA and AC ,respectively at $C_0=15 \text{ mg l}^{-1}$.
- 6- The density of BCA is approximately lower than that of activated carbon.

6.2-Recommendation For Further Work :-

- 1- Further work is needed on application the same material but in removal of mercury from natural gas .
- 2- Further work is necessary to design a column bed under the condition of new material .
- 3- Further measurement is needed to investigate the mechanical properties of new material .

Reference

References :-

- [1] Dave , K. , "Natural gas processing" , the free encyclopedia,(2011) .
- [2] Corvini ,G., Stiltner, J. , and Clark, K., "Mercury Removal From Natural Gas And Liquid Streams", UOP LLC, Houston , (2006) .
- [3] Hudson, C. , "Implications Of Mercury Removal Bed Material Change Out : Brownfield Versus Greenfield ", Atlantic LNG Company of Trinidad and Tobago ,Aug.(2010).
- [4] Carnell, P. , Row, V., and McKenna, R. , "Minimizing Mercury Emissions from Gas Processing and Liquefied Natural Gas Plants", Johnson Matthey Catalysts (2007) .
- [5] Carnell, P. , Row, V. & McKenna, R. , “ A re-think of the Mercury Removal problem for LNG plants”, Johnson Matthey Catalysts (2007) .
- [6] Eckersley , N. " Advanced mercury removal technologies ", UOP , A Honeywell company , January , (2010) .
- [7] Korens , N. , Simbeck, D. R. and Wilhelm, D. , "Process Screening Analysis Of Alternative Gas Treating And Sulfur Removal For Gasification" , SFA Pacific, Inc. ,Pennsylvania (2002) .
- [8] Sugier, A. , Malmaison, R. , "Process for removing mercury from a gas or a liquid by adsorption on a copper sulfide containing solid mass", Patent, NO. 4,094,777(1976) .

Reference

- [9] Mahin Rameshni , P.E. , " Impurities Removal Options in Sour Gas Field Developments " , Rameshni & Associates Technology & Engineering LLC(2010).
- [10] Markovs, J. , " Optimized Mercury Removal In Gas Plants ",UOP, Houston, March,(2005).
- [11] Mahin Rameshni, P.E. "DEALINGWITH IMPURITIESIN SOUR GAS FIELD DEVELOPMENTS",
<http://www.scribd.com/doc/50644846/Worley-Parson-Dealing-with-Impurities-in-Sour-Fields> ,March(2011).
- [12] Suzuki , M. , " Adsorption Engineering ",Printed in Japan , University of Tokyo (1990).
- [13] van der Vaart, R. , Akkerhuis, J. , Feron, P. , Jansen, B. , "Removal of mercury from gas streams by oxidative membrane gas absorption" , The Netherlands Organization for Applied Scientific Research , Journal of Membrane Science , 187,151,(2000) .
- [14] Fernández-Nava, Y. , Ulmanu, M. , Anger, I. , Marañón, E. , Castrillón, L. , "Use of Granular Bentonite in the Removal of Mercury (II), Cadmium (II) and Lead (II) from Aqueous Solutions" Water Air Soil Pollute, J. of Springer Science,Vol.215,P.239 ,(2011).
- [15] Trakarnpruk, W. , and Chirandorn, N. , " Treated Clay for Adsorption of Mercury(II) Ions", J. Sci. Res., Chulalongkorn University, Bangkok , PP.137-151, Vol. 30, No. 2, (2005) .

Reference

- [16] Matviya, T. M ., Gebhard, R. S. , " Mercury adsorption carbon molecular sieves and process for removing mercury vapor from gas stream " USA , Patent, NO. 4,708,853 , (1985) .
- [17] Takenami, J. ,Uddin, M. A. , Sasaoka, E. , Shioya, Y. , and Takase, T. , " Removal of Elemental Mercury from Dry Methane Gas with Manganese Oxides " , World Academy of Science, Engineering and Technology, Vol.56 ,P. 26, (2009) .
- [18] Iraq North Gas Project , "Process Plant Operating Manual" , Mitsubishi Heavy Industries Company. Volume1.
- [19] Mohamed, A.K. , Bonnet , J. , Larigaldie, S. , Pot , T. , Soutadé, J. and Diop , B. "Electron Beam Fluorescence in Hypersonic Facilities" , The Onera Journal Aerospace Lab , Vol. 33,P.1, (2009) .
- [20] Tavallali, H. and NoroziKhah, H."Design of cold vapor system and assembled on Atomic Absorption Spectrometer for Mercury determination in several waste water samples" ,International Journal of ChemTech Research , Vol.1, No.2,P.390, April-June (2009) .
- [21] THOMAS J. M. AND WILLIAM R. G. "Inductively Coupled Plasma - Atomic Emission Spectrometry", Journal of Springer , VOL . 2 , N O . 1, PP. 1-19(1997).
- [22] Markovs , J. , and Corvini , J. , "MERCURY REMOVAL FROM NATURAL GAS & LIQUID STREAMS " , UOP , Texas , adsorptionsolutions.com/gascondconf.pdf , (2008) .

Reference

[23] Saravanan¹, A., Brindha, V., Manivannan, E. and Krishnan, S., " Kinetics And Isotherm Studies Of Mercury And Iron Biosorption Using Sargassum SP." , International Journal of Chemical Sciences and Applications ISSN 0976-2590 , , Vol. 1, Issue 2, pp. 50-60 , Dec.(2010) .

[24] Mohamed , M . I ., Najat, S.j., Rahek, A.I., " Activation of Iraqi Bentonite Powder with H_2SO_4 and its Application in Oils Bleaching", First conference on modern technologies in oil and gas refining, Department of Chemical Engineering, University of technology, Baghdad, (2011).

[25] www.Scholarchemistry.com , Material Safety Data Sheet , Mercury (I) Nitrate Dihydrate, (2009).

الخلاصة

شركة غاز الشمال تستخدم الكربون الفعال لإزالة الزئبق من الغاز الطبيعي . لكن الكربون الفعال يتكسر جزئياً الى جزيئات صغيرة تمر من خلال المرشحات , مما يسبب انسداد جزئي في الاجزاء اللاحقة من وحدات التصفية مثل الفلاتر . ولذلك، فإننا نجد أنه من الضروري أن نبحث عن بديل لمادة الكربون المنشط من أجل تجنب المشاكل الناتجة عن استخدام هـ في عمود التنقية كمادة ممتزة للزئبق. أن مثل هذه المواد يجب ان تكون ذات خصائص ميكانيكية جيدة ,بالإضافة الى انها تمتلك خصائص امتزاز افضل او مساو لخصائص الكربون المنشط .

في هذا البحث، تم تحضير عدة أنواع من المواد الممتزة وفحصها لغرض اختيار افضل عينة منها. النماذج صُنِعَتْ كمادّة شبه خزفية (بعد أن تعرضت الى 700 درجة مئوية تحت جو خالي من الأوكسجين) من أجل الحصول على مواصفات ميكانيكية جيدة. وقد تم اعداد العينات المسماة BC (Bentonite ,Clay) من نسب مختلفة من (البنتونايت و الطين) , بينما ال BCA [Bentonite ,Clay and Activated Carbon (AC)] صنعت من [البنتونايت (25%) والطين (25%) والكربون المنشط (50%)].

BCA و BC و AC استخدمت كمواد ممتزة لدراسة خصائص امتزاز الزئبق من المياه باستخدام مطياف الاشعة فوق البنفسجية . عموماً ال BCA يعطي افضل خصائص امتزاز من المواد الممتزة الاخرى , و كذلك لديه خواص ميكانيكية افضل من الكربون المنشط (المستخدم كمادة ممتزة للزئبق في شركة غاز الشمال) . واعدت عينات مختلفة بتركيز مختلفة من ايون الزئبق بواسطة اذابة نترات الزئبق في الماء . جُيِّدَ امتزاز Hg^{+2} لكل من BCA و AC مع زيادة كمية الكتلة وكذلك زيادة وقت التلامس . وجد ان وقت التلامس الذي يحتاجه النموذج للوصول الى التوازن هو 50 دقيقة للكربون المنشط و 40 دقيقة للنموذج المعدل (BCA) . المساحة السطحية للنماذج (BCA و AC) هي 440,77 و 554,1832 م² غم على التوالي . الحد الاقصى لسعة الامتزاز يحسب على اساس معادلة (Langmuir model) لكل من (BCA و AC) هي 441,1 و 439,65 ملغم \غم على التوالي عند $C_0 = 15$ ملغم \ لتر .

وقد تم قياس قوة الانضغاط لكل من (BC و BCA) باستخدام تقنية California Bearing Ratio (CBR) . اعلى قيمة California Bearing Ratio (CBR) كانت للنموذج BCA وهي 850 نبوتن \متر مربع بينما ال AC اظهر مقاومة تساوي صفر عند الانضغاط . عليه استنتج بان نموذج ال BCA يمتلك خصائص امتزاز جيدة لأزاله الزئبق من المياه , وكذلك يمتلك خواص ميكانيكية افضل بالمقارنة مع الكربون المنشط , ويمكن استخدامه كمادة ممتزة لأزاله الزئبق من الغاز الطبيعي .



وزارة التعليم العالي والبحث العلمي

الجامعة التكنولوجية

قسم الهندسة الكيميائية

دراسة استخدام الكاريون المنشط المعدل لإزالة الزئبق من الغاز الطبيعي

بحرث مقدم الى

قسم الهندسة الكيميائية في جامعة التكنولوجيا كجزء من متطلبات نيل شهادة الدبلوم

العالي في علوم الهندسة الكيميائية/ تصفية النفط وتكنولوجيا الغاز

إعداد

عمار حسام الدين عبد الرزاق

(بكالوريوس هندسة كيميائية 2005)

بإشراف

أ.م.د. محمد إبراهيم محمد

شباط 2012 م

صفر 1433 هـ