

School of Basic Science

Chemistry Department

Separation and Determination of Inorganic mercury in Enviromental Samples Using polyaniline

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بسم الله الرحمن الرحيم

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صدق الله العظيم

سورة الرحمن الآيات (1 و 2 و 3 و 4)

Dedication

I would like to present this work to my parents who support me during my study also I dedicate it to all my sister and brother who encouraged me to finish this work.

Also I would like to give to whom like knowledge and seek to get it.

Finally, I also present this work to all rebels and martyrs of the seventeen of February who sacrifice for the sake of Libya.

Acknoledgement

First of all I would like to thank Allah who helped me to complete this thesis as a part f or the fulfillment of an MsC course. This work would not have been finished without the support of many people.

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LIST OF TARMS

Term	Name of term
CPs	Conductive polymers
PAN	Polyaniline
LE	Leucoemeraldine
PN	Pernigranilne
EB	Emeraldine base
ES	Emeraldine salt
SPCE	Screen Printed Carbon Electrode
POPD	Poly (O-Phenylenediamine)
ICP	Inductively coupled plasma
LSV	Linear Sweep Vltammetry
CV	Cyclic Vltammetry
ASV	Anodic Stripping Voltammetry
PANMB	Polyaniline methylene blue
SEM	Scanning Electron Microscopy
RS	Raman Spectroscopy
EIS	Electrochemical Impedance spectroscopy
XPS	X- Ray Photon electron spectroscopy
XRD	X - Ray
FTIR	Fourier-Transform Infrared
HNMR	Proton – Nuclear Mystic Resistance
TGA	Thermogravimetric gravimetric analysis

UV	Ultraviolet
PNAANI	Poly(N-AcetylAniline)
PPm	Part per million
PAN/Pt	Polyaniline /platinum
PANOA	Poly(Aniline-Co-O-Aminophenol)
GCE	Glassy Carbon Electrode
ESR	Electron Spain Resonance
SD/PAN	Saoudst/PAN
NMP	Nuclear Magnetic Partners
RGAC	Raw Granular Activated Carbon
GFAAC	Graphite Furnace Atomic Adsorption Spectrometry
US,EPA	USA, Environmental Protection Agency
GPE	Graphite past Electrode
DPASV	Differential pulse anodic stripping voltammetry
ATR	Attenuated Aotal Reflection

Abstract (in English)

The synthesis of Conductive polymers from monomers containing conjugated double bonds such as aniline, pyrole, and thiophene, and their derivatives has become the subject of many recent studies. A plyaniline (PAN) prepared by chemical method using different oxidation reagents, was studied for Hg(II) removal from aqueous solutions. From the results, it was found that, PAN prepared by chemical method using $K_2Cr_2O_7$, and HCl gave the best results for % removal, and emeraldine salts. Batch adsorption results showed solution pH values had a major impact on mercury adsorption by this sorbent with optimal removal observed around (pH 4 to 5). At both acidic and alkaline solutions beyond this optimal pH window, sorption capacity of PAN was substantially lowered, with the impact less pronounced at pH above 6. In the range of 0.02M – 0.2M, and 1M, the effect of ionic strength on adsorption of Hg(II) 0n PAN surface was also studied. The adsorption mechanism was proposed by analyzing the XRD, FTIR, SEM, and XPS spectra data before and after adsorption of mercury on (PAN) surface. The results show that all the nitrogen matrix including imine, protonated imine and amine could be responsible for mercury adsorption.

Abstract (in Arabic)

للبوليمرات أهمية كبيرة في مجالات الأبحاث العلمية ،البيئية ،الصناعية والطبية ولذلك تحظى باهتمام كبير وعدد وافر من الدراسات والبحوث والأوراق العلمية والمناقشات تم نشرها مما يجعلها أحد أهم عناوين البحث العلمي في العصر الحديث

تنقسم البوليمرات إلى أربعة أنواع :

-البوليمرات (الشائعة؛ شديدة الصلابة؛ الأكسدة والاختزال؛ المتعاقبة)

والنوع الأخير هو الأهم بالنسبة لعملي لأن البوليمر المستخدم في العمل (البولي أنيلين) أحد البوليمرات التي تنتمي للنوع الرابع (البوليمرات المتعاقبة)

تم تحضر البوليمر بطريقة الأكسدة الكيميائية باستعمال عدة أحماض ومواد مؤكسدة ومن خلال النظر إلى البولي أنيلين الناتج باستعمال تلك الأحماض والمواد المؤكسدة وجد أن البولي أنيلين الناتج باستعمال حمض الهيدروكلوريك وثيوكرومات البوتاسيوم (كمادة مؤكسدة) هو الأفضل لذلك تم استخدامه في هده الدراسة.

فكرة العمل تتلخص في عملية نزع وتقدير الزئبق الغير العضوي من محاليله المائية عن طريق إمتزاز ايونات الزئبق على سطح البولي أنيلين في صورته المفضلة في العمل وهي ملح الإميرالدين.

الدراسة تضمنت المتغيرات التالية:

(الزمن؛ التركيز؛ نوع الوسط؛ القوة الأيونية)

عدة أجهزة تم استخدامها لمعرفة ما إذا كان ايونات الزئبق قد تم امتزازها على سطح البولي أنيلين باستخدام الطرق التحليلية الآلية الآتية:

(Mercury analyzer ,FTIR ,SEM ,XPS ,XRD)

أوضحت النتائج التي أظهرتها هذه الدراسة ان أيونات الزئبق غير العضوي تمتزعلي سطح البولي أنيلين ومن خلال هذه النتائج لوحظ إن أفضل زمن للامتزاز كان6 ساعات وأفضل درجة حموضة كانت pH 4 وثبت إن تأثير التركيزكان طردى طردي بينما كان تأثير القوة الأيونية عكسيا علي كلا من النسبة المئوية للنزع(R %) ومعدل الادمصاص(Qe)

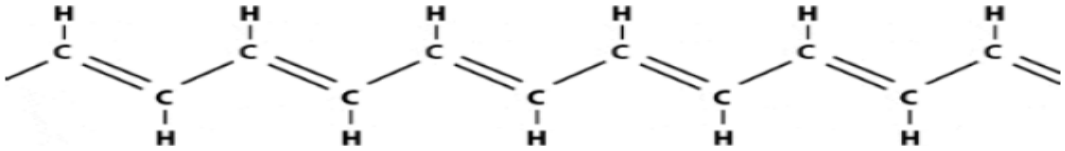
1.1.1-THE CONDUCTING POLYMERS

Conducting polymers (CPs) can be defined as large cyclically conjugated electroactive polymers, that is, they are capable of undergoing oxidation/reduction themselves [1].

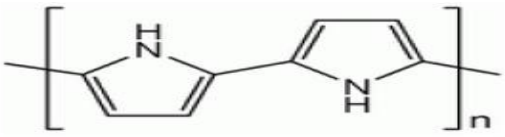
Generally there are considered to be four primary types of conducting polymers [2]. The first and most widely used commercial conducting polymers are composites in which an originally non-conducting polymer matrix is filled with a powdered conductive medium such as carbon or metal to give rise to its conductivity. Applications for such composites are varied and could be used for solder substitutes and antiseptic. The second group of polymers is called ironically conducting polymers. Here electrical conductivity is as result of movement of ions. An example of such a polymer is polyethylene oxide, in which lithium ions are mobile. These kinds of polymers find application in the battery industry. The third group of polymers is called redox polymers. These contain immobilized redox centers (electroactive centers). These centers are not necessarily in contact with one another, but can conduct charge by electron transfer from one center to another by what is known as a “hopping” mechanism, In this mechanism, electrons tunnel from one redox center to another through an insulating barrier. There must be a large number of redox centers so as to ancrease the probability of such tunneling . The fourth group is conjugated polymers . these polymers consist of alternating single and double bonds, creating an extended

π-network. Electron movement within this π-framework is the source of conductive. Polyaniline (PAN), an example of such a polymer. Other common examples of conjugated polymers are shown in figure (1.1).

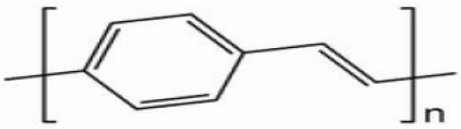
The difference between redox polymers and conjugated polymers may be subtle. However, in conjugated polymers, conduction within one polymer chain is based on the conjugated nature of the polymer molecules and the resulting mobility of π-electrons and not on immobilized redox centers.



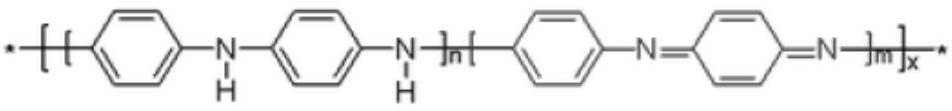
Polyacetylene (PA)



Polypyrole (PPY)



Poly (p-phenylene vinylene)



Polyaniline (PAN)

Fig(1.1): Structure of some Common Conjugated Polymers

1.1.2-SYNTHESIS OF CONDUCTING POLYMERS

There are two main methods of synthesizing CPs, namely [3]; chemical synthesis and electropolymerization. The electro chemical synthesis, which I used for my work, is amore preferred method due to its reproducibility and simplicity. The synthesis is carried out at room temperature, and the desired polymer film thickness can be achieved by simply varying the potential or current with time. Most electrochemical synthesis proceeds through radical coupling polymerization, while chemical syntheses are condensation polymerization. Condensation polymerization generally involves loss or elimination of a chemical species resulting from the reaction of end groups on monomer molecules

1.1.3-Chemical preparation of polymers

1.1.4-ELECTROCHEMICAL METHODS

Constant potential (or potentiostatic), constant current or (galvanostatic) and potential sweep methods are usually used for electropolymerization of PAN and its derivatives. These procedures are advantageous for controlling the amount of product because the polymerization can proceed only when the monomer is oxidized at the electrode. Standard electrochemical techniques, which employ a divided cell containing a working, a counter electrode and a reference electrode generally, produce the required films. The commonly used working

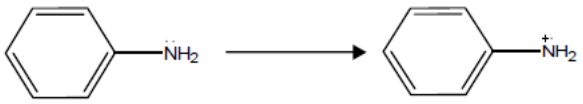
electrodes are conducting substrates such as gold, carbon, platinum, and indium-tin oxide coated glass plates. Semi-conducting materials including n-doped silicon, gallium arsenide, and cadmium sulfide and semi-metal graphite are also employed for the growth of polymer films. It is important to remember that many CPs synthesized by electrochemical methods are oligomers, with chain lengths ranging from about 8 monomer units, which is much less than the typically portrayed 100,000 units of some aniline [3]. Even for the best CPs, morphology is poor nowhere approaching the morphology routinely obtained in common organic polymers such as polyethylene.

1.2-Polyaniline(PAN)

1.2.1-Mechanism of polymerization

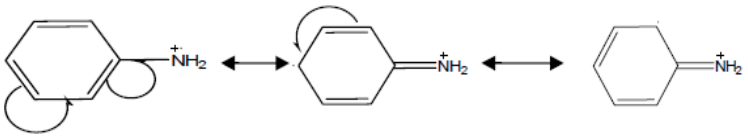
1.2.2-Chemical and Electrochemical polymerization

As early as 1962, Mohilner et al.[4] investigated the kinetics of the electrochemical oxidation of aniline in sulfuric acid and deduced that the initial oxidation requires the formation of aniline radical. Since then the nature of the intermediates of PAN synthesis have been proposed based on cyclic voltammograms. The first stage of the PAN synthesis was found to be the formation of $C_6H_5NH_2$ cation radical through the transfer of electron from an SP^3 orbital of nitrogen atom to the electrode during electrochemical oxidation.



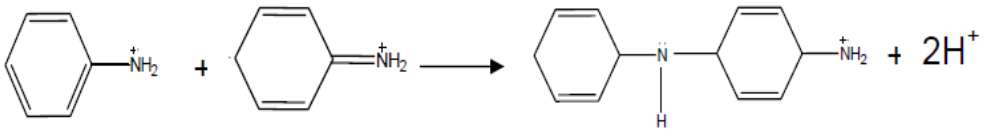
1.1

The aniline radical is resonance stabilized as shown



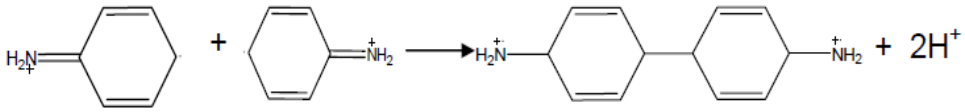
1.2

These radicals may then combine in different way to form poly aniline. Head to tail coupling or 1,4-substiteution is believed to predominate and produce p-aminodiphenyl amine.



1.3

A competing reaction involves tail-tail coupling of aniline, which forms benzidine.



1.4

Kinetics studies led Mohilner et al.[4] To the conclusion that the oxidation of aniline occurs via a free radical mechanism that produces the emeraldine octamer as the primary product. Amore detailed mechanism as proposed by Wei and Coworkers [5]. Is presented below in figure (1.2).

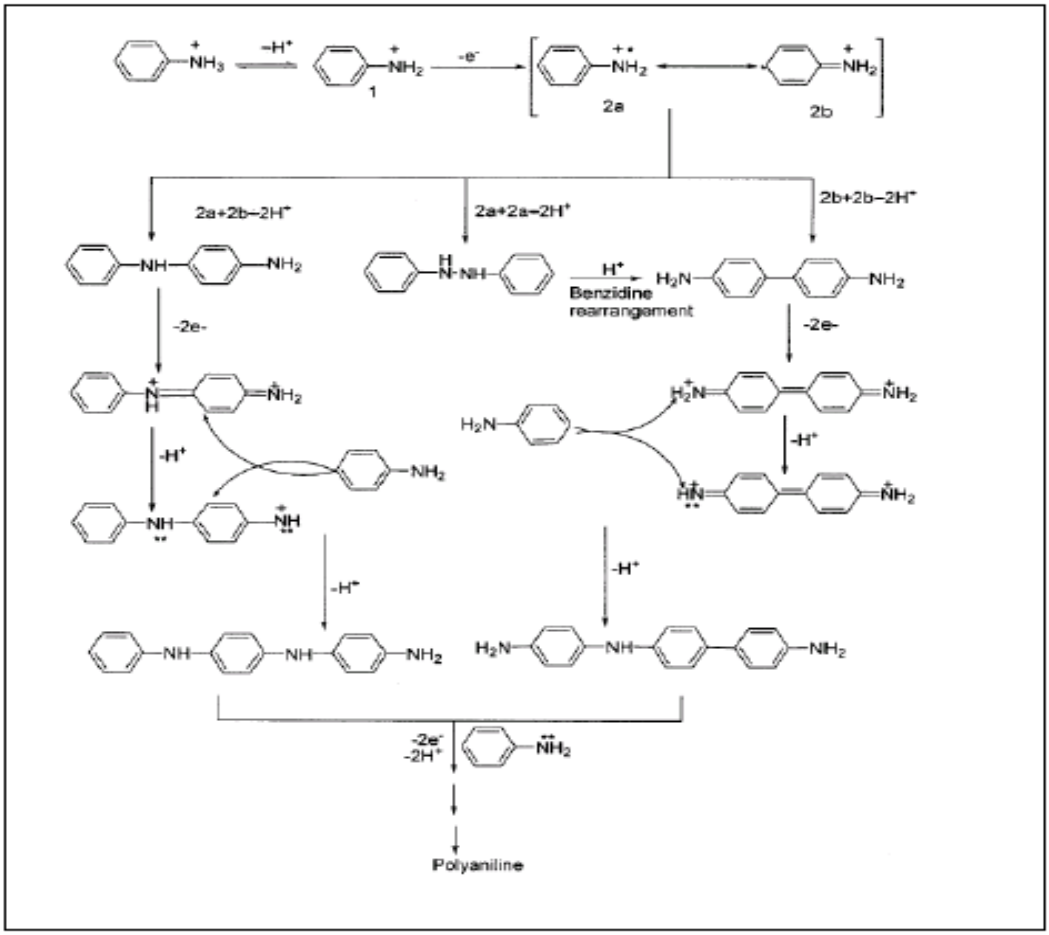
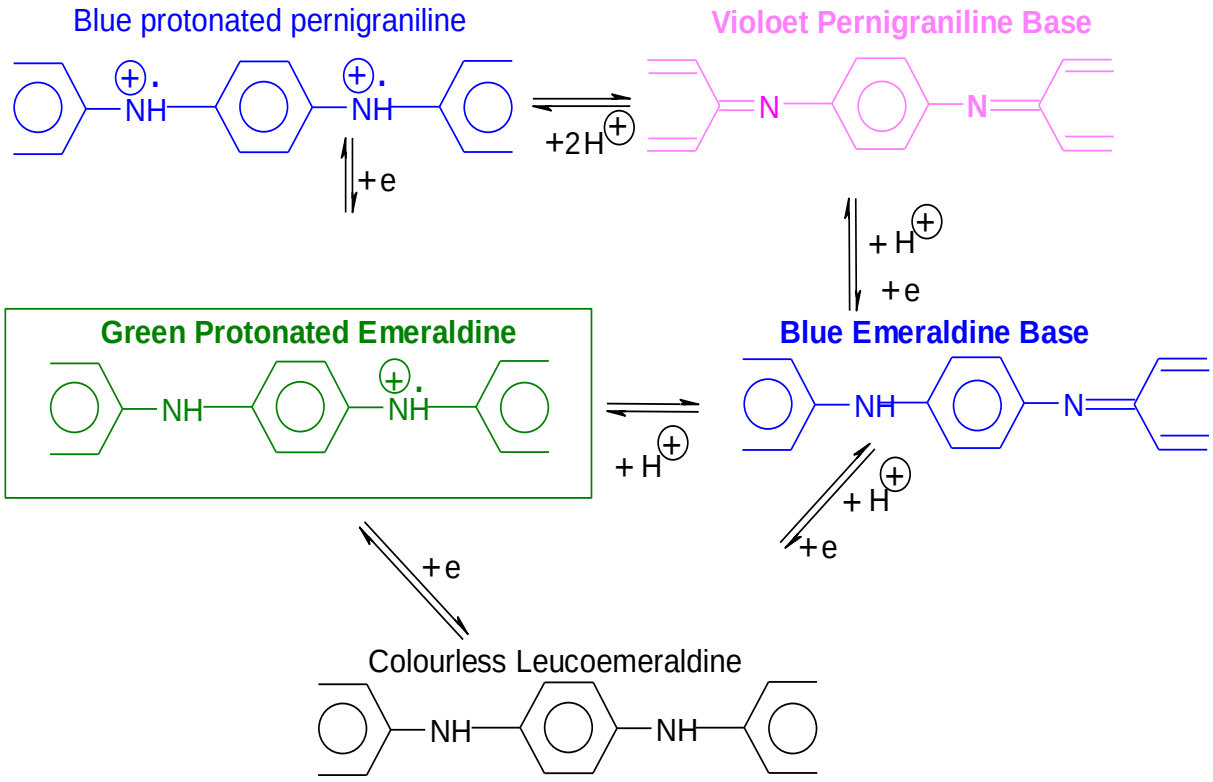


Fig (1.2): Mechanism of Electropolymerization of Aniline.[4].

It well known that PAN has a variety of oxidation states that are both pH and potential dependent. It is generally agreed that PAN has three different fundamental forms: leucoemeraldine (LE: fully reduced), emeraldine base (EB: half oxidized), and pernigraniline (PN: fully

oxidized). The only electrically conducting one is, however, the emeraldine salt form (ES: half oxidized), which is the protonated form of EB.

The four forms are as follow in figure (1.3).



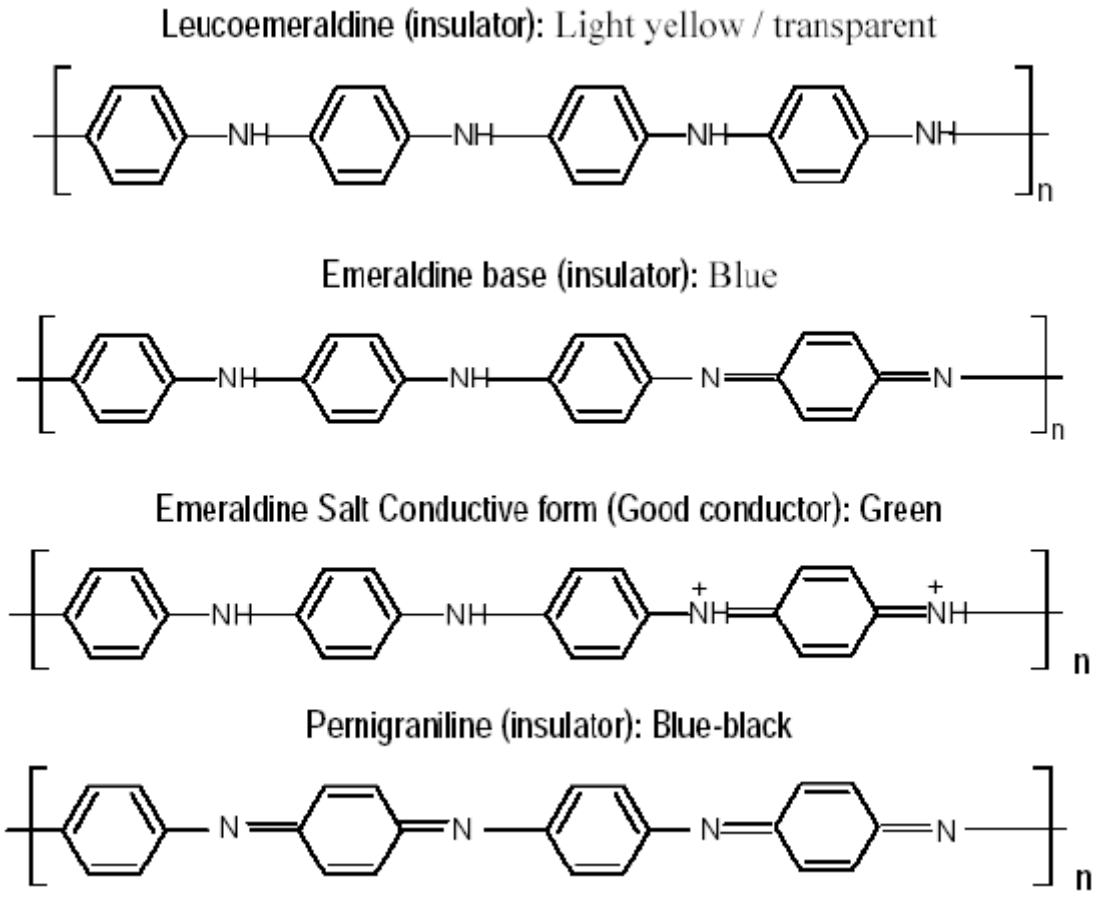


Fig (1.3): The four forms of polaniline

1.2.3-Other properties of polyaniline

Polymerization yield

Based on the stiochiometry of the oxidation reaction Fig(1.4), the polymerization of 1.0 g aniline hydrochloride yields theoretically 0.840 g of PANI hydrochloride. The apparent yield of PANI hydrochloride under the standard polymerization condition approaches 100 % within the experimental error Table (1.5). The elemental analysis indicates Table (1.1) that more bulky counterions, like sulfate or hydrogensulfate anions,

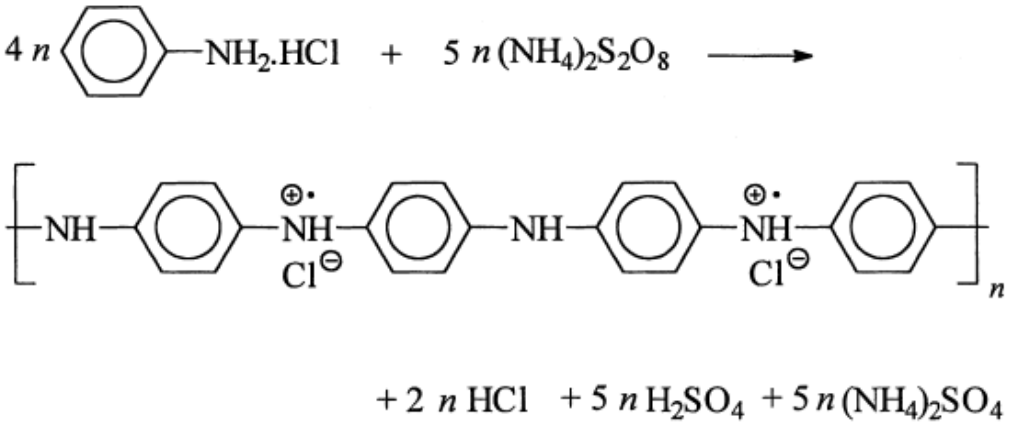


Fig. (1.4) Oxidation of aniline hydrochloride with ammonium peroxydisulfate yields polyaniline (emeraldine) hydrochloride.

Table(1.1): Elemental composition

Reaction conditions[a]	% C	% H	% N	% Cl	% S
Polyaniline hydrochloride					
Standard	59.7	4.9	10.6	11.1	1.0
+ 1 M HCl	59.6	4.8	10.6	12.1	0.5
Expected [b]	*66.2*	*4.6*	*12.9*	*16.3*	–
Polyaniline base (obtained after deprotonation of polyaniline hydrochloride)					
Standard	75.0	5.0	13.9	0.6	0.3
+ 1 M HCl	74.0	4.8	13.6	2.3	0.3
Expected [b]	*79.5*	*5.0*	*15.5*	–	–

[a]0.2 M aniline hydrochloride oxidized with 0.25 M ammonium peroxydisulfate at room temperature and in the presence of excess HCl as specified.
[b]Based on formulae shown in Fig. 1.

My participate in the protonation of PAN along with the chloride anions. This would lead to an apparent increase in the yield. The yield is higher when the polymerization are carried out at the reduced temperature. Increased acidity of the reaction medium leads, on the other hand, to its reduction [6].

1.2.4-Elemental composition

The differences in elemental composition of PAN prepared under standard conditions and in an excess of 1 M HCl are small Table (1.1). The results of elemental analysis clearly indicate the presence of oxygen in PAN (12.5 % hydrochloride and 5.1% in the base). This may be due to bound water molecules or, more likely, to partial oxidation of the PAN chains. The structure depicted in Fig(1.5) is thus idealized. The presence of sulfur in hydrochlorides is partly due to the residual sulfate counterions produced by the reduction of peroxydisulfate during polymerization Fig(1.4).

Hydrochloride acid is removed from the aniline hydrochloride after deprotonation with ammonium hydroxide Fig (1.5). The relative participation of carbon and nitrogen in PAN base is thus increased, at the expense of the lower content of chlorine. We can see that some chlorine remains in PAN base even after deprotonation, indicating a partial benzene-ring substitution with chlorine [7]. The content of covalently bound chlorine is higher when the oxidation of aniline hydrochloride takes place in excess HCl (Table 1.2). Partial sulfonation of benzene rings is responsible for the presence of sulfur in the PAN base (Table 1.2).

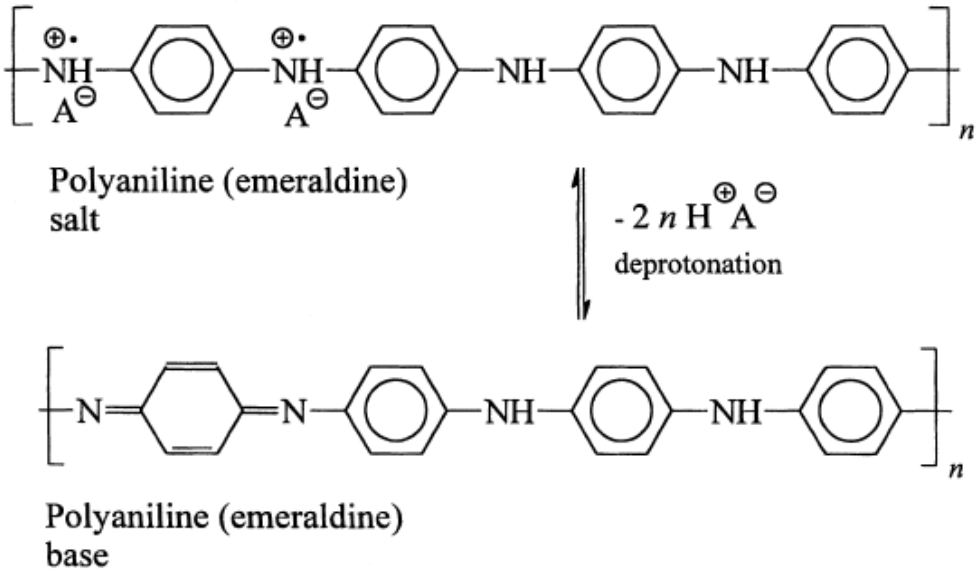


Fig (1.5) polyaniline (emeraldine) salt is deprotonated in alkaline medium to polyaniline (emeraldine) base A^- is an arbitrary anion, e.g., chloride.

1.2.5-Density

The average value of PAN hydrochloride density found on all 94 pellets prepared from various samples was 1.329 ±0.027 g cm^{-3} at 20 ^{0}C. the method of preparation had no significant effect on the density of PAN Table (1.2). The density determined on 27 and 19 pellets compressed from two single PAN powders yielded the standard deviation of 0.008 g cm^{-3} (0.6 %) in both cases. Polyaniline sulfate has a density of 1.43 g cm^{-3} [8]. An inconclusively higher density of samples prepared in the absence of excess HCl may thus be assigned to partial protonation with sulfate counterions. The average density of 16 PANI bases was 1.245± 0.006 g cm^{-3}.

Table (1.2): Density of PAN hydrochloride and PAN base at 20 ^{0}C (number of prepared sample is given in parentheses.

Reaction conditions[a]	Density (g cm^{-3})	
	PANI hydrochloride	PANI base
~20 °C	1.333 ± 0.016 (54)	1.244 ± 0.008 (4)
~0 °C	1.323 ± 0.046 (24)	1.242 ± 0.007 (4)
+ 1 M HCl, ~20 °C	1.326 ± 0.014 (13)	1.250 ± 0.002 (4)
+ 1 M HCl, ~0 °C	1.322 ± 0.007 (3)	1.243 ± 0.007 (4)

[a]0.2 M aniline hydrochloride oxidized with 0.25 M ammonium peroxydisulfate at given temperature and in the presence of excess HCl as specified.

1.2.6-Preparation of polyaniline(PAN)polymer film.

Polyaniline (PAN) polymer films were prepared using a 10 mL solution polyaniline consisting of 0.2M aniline in aqueous 1M HCl polyaniline (PAN) films were grown electrochemically on the surface of the screen-printed carbon electrode (SPCE) by repetitive cyclic voltammetry scanning at 100mv/s from-200 to +1100mv. For 10 cycles at 25c^o [9].

1.2.7-MATRERIALS AND METHODS

Preparation of polymer: polyaniline was prepared adopting the method of Stijskal and Gilbert [10]. One hundred ml(100) of 0.25 M of aqueous solution of ammonium per sulfate $(NH4)_2S_2O_8$ and 0.20 M solution of aniline was dissolved in 100 ml of 1 M aqueous hydrochloric acid (HCl) at 5 ^{0}C.

Polymerization was allowed to proceed overnight in a refrigerator. The green precipitate that formed was removed by filtration, washed with 1 M HCl followed by acetone until clear filtrate was obtained. The obtained polymer was dried in a vacium oven at room temperature (30 ^{0}C) for 6 hours. The green material obtained was identified as the emeraldine hydrochloride.

The emeraldine hydrochloride was converted into the emeraldine base by mixing 1 gram with 10 ml of 3 % solution of ammonium hydroxide (NH_4OH). The mixture was allowed to settle for sevral hours. The resulting blue material was filtered and washed with distilled water and vacuum dried at room temperature for 6 hrs.

Aside from hydrochloric acid, other acids like sulfuric acid (H_2SO_4), nitric acid(HNO_3) and perchloric acid ($HClO_4$) were used in order to obtain doped polyaniline with corresponding counter-ion.

1.3-Fabrication of electrode

The polymer obtained was used as modifier by mixing with graphite powder and mineral oil to form a paste. The prepared polymer (200mg) was mixed with graphite powder (800mg) and oil to form a paste. Electrode assembly was done by filling the open tip of the copper wire inserted with plastic straw with the polymer-graphite paste until thoroughly packed the

paste was compacted around copper wire and smoothened with a glass spatula.[10].

1.3.1-Polyaniline Derivatives

Whereas many papers have been devoted to the electropolymerization and the characterization of the polyaniline-modified electrodes, not a lot of information is available about the properties of the polymeric films formed by the electrooxidation of the aniline derivatives [11]. Among those derivatives, Ortho-phenylenediamine and its polymer poly (O-phenylenediamine) (POPD) have shown interesting properties and thus promising application in various aspects [12]. POPD can be obtained as a thin layer of self-limiting thickness on different conducting substrates via anodic electropolymerization processes [13].

1.3.2-Properties of poly-Ortho-phenylenediamine (POPD)

POPD is a solid. In the reduced form, the film is colorless, and its oxidized form is red. This is contrary to the usual green-blue color of other polyaniline films [11]. Two interesting properties of POPD, different from those that are characteristic for usual conducting polymers like polyaniline makes it promising for applications in electrochemical and bioelectrochemical sensors:

1) As opposed to PAN, the conducting form of POPD is its reduced state, whereas its oxidized state is insulating.
2) POPD film is permselective. Permselective is a term used to define the preferential permeation of certain ionic species through ion-exchange membranes. This Permselectivity of POPD is different from other PAN polymers. When deposited onto an electrode, POPD permits the diffusion of some redox active species to the electrode surface, whereas other species with are retarded at the polymer/solution interface. This useful property of POPD has been widely exploited for the development of sensors [12].

1.3.3-Mechanism of polymerization of POPD

POPD can be prepared electrochemically in acidic, neutral, and alkaline solution. It is very stable in both aqueous solutions and air [14]. POPD easily dissolves in organic solvents such as dimethyl sulfoxide. This ease of dissolution makes it one of the so-called soluble electroactive polymers and provides more flexibility in its ex-situ structural studies in the first step of the polymerization process, oligomers are formed, and in acidic medium, only a small portion of oligomers are polymerized and deposited on the electrode surface [14,15]. The polymerization process is not an autocatalytic one. The electrochemical polymerization of o-phenylenediamine is a self-limiting process because poly (o-phenylenediamine) is an insulating polymer [16]. Barbero et al. [16] have studied the structure and the mechanism of the

electropolymerization of o-phenylenediamine and have proposed the following scheme as shown in figure (1.5).

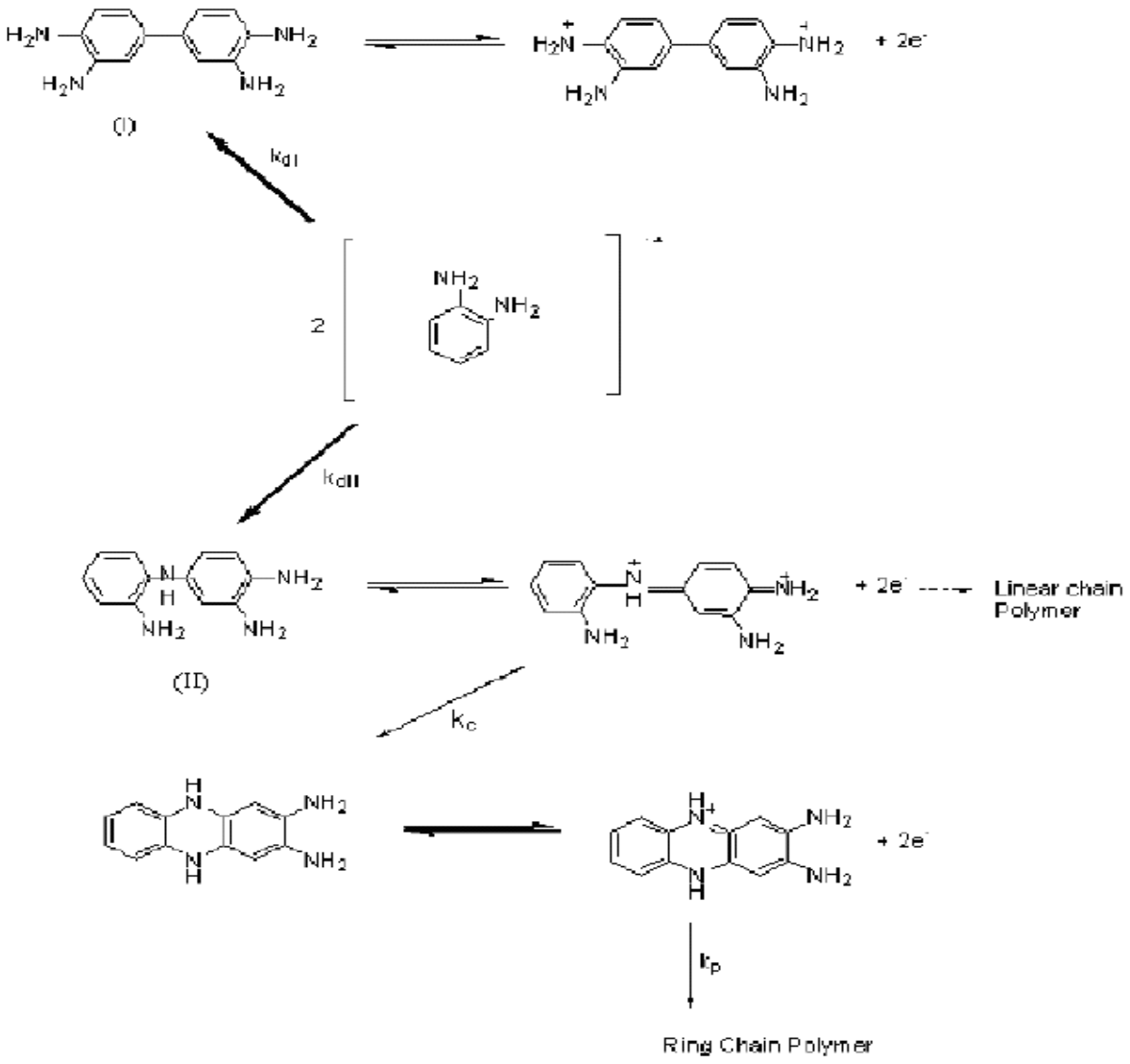
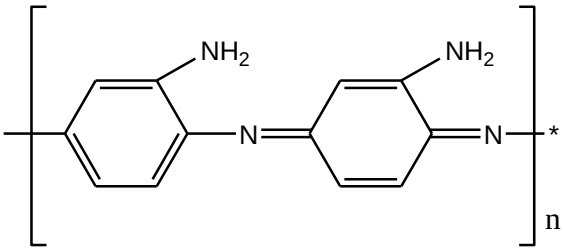


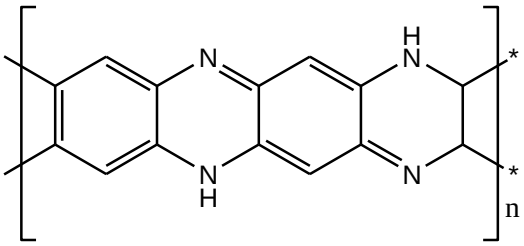
Fig (1.6): Mechanism of polymerization of POPD

Based on the above scheme, the monomer, o-phenylenediamine, is initially oxidized anodically to give the mono-cationic radicals may dimerize by either C-C coupling to give the dimmer 1, or by C-N and coupling and they give the dimmer II. These dimmers are then oxidized to

their respective diction, with the formation of two products. One of the products can undergo a linear polymerization to form a linear chain polymer as below [11]:



The other product can undergo a cyclization reaction to give a ladder structure [17]:



It was found that the rate of cyclization is greater than that of the linear polymerization [16].Thus at the outset, the polymer is composed of linear. Conducting chain; however, it is later dominated by the insulating laddered structure [14,17].

A similar mechanism of polymerization is observed for meta-phenylenediamine. However, only linear polymer chains are formed for para-phenylenediamine, because coupling of monomers can only be either head-to-head or tail-to-tail.

1.3.4-CHEMICAL PREPARATION

1.3.4.1- Standard of polyanilne

project participants followed the same instruction to oxidize 0.2 M aniline hydrochloride with 0.25 M ammonium peroxydisulfate in aqueous medium. Aniline hydrochloride (purum; 2.59 g, 20mmol) was dissolved in distilled water in a volumetric flask to 50 ml of solution. Ammonuim peroxydisulfate (purum; 5.71 g, 25 mmol) was disoloved in water also to 50 ml of solution. Both solution were kept for 1 h at room temperature (~18-24 ^{0}C), thin mixed in a beaker, briefly stirred, and left at rest to polymerize. Next day, the PAN precipitate was collected on a filter, washed with three 100-mL portions of 0.2 M HCl, and similarly with acetone. Polyaniline (emeraldine) hydrochloride powder was dried in air and thin in vacuo at 60 ^{0}C. polyaniline prepared under these reaction and processing conditions are further referred to as “standard” samples. Additional polymerization were carried out in an ice bath at 0-2 ^{0}C. The acidity of reaction mixture was increased by replacing 10 mL of water with 10 ml of 10 M HCl in several experiments [6].

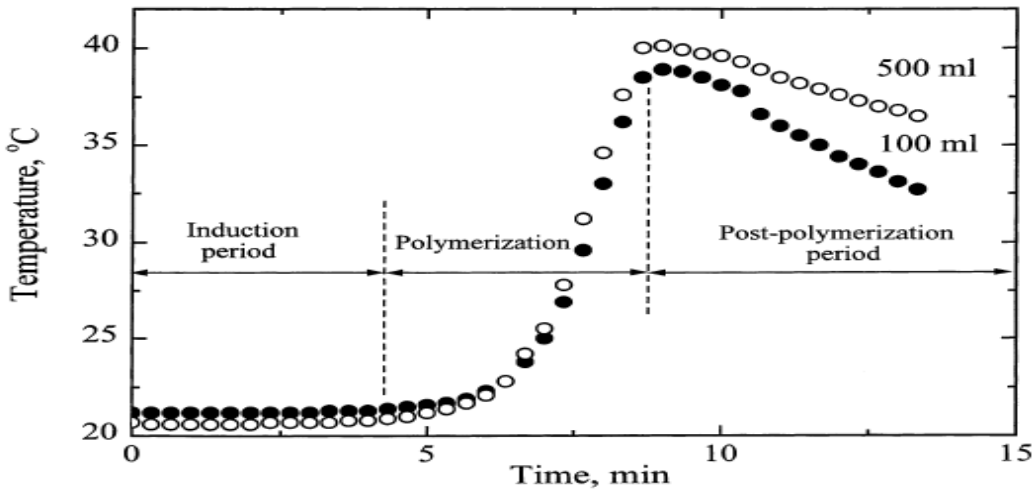
1.3.4.2-Characterization of polyaniline

Conductivity of all samples was measured at room temperature by a four-probe method on pellets compressed at 700 Mpa, 13mm in diameter and 1-1.5 mm thick, using a Keithley 237 high-voltage current source and Keithley 2010 low-noise multimeter [18]. The Archimedes methode was used to determine the polymer density by weighing the pellets in air and in decane at 20 ^{0}C with a Sartorus Research R160P balance.

1.3.4.3-Preparation conditions

Polyaniline of higher molar mass is produced at lower reaction temperature [20-21], but electrical properties of the polmer are not greatly influenced by molar mass. We have selected ambient temperature for the present study while being aware of the ambiguous definition of such condition. As temperature increases during the reaction, this increase being depends on the surface-to-volume ratio of the experimental set-up fig (1.7), the precise control of temperature was not attempted. The effect of reaction temperature on the conductivity of PAN was assessed and is discussed. Polymerization in the presence of excess 1 M HCl, i.e., at higher acidity, proceeds faster than in its absence and yields a product of enhanced conductivity. A still higher concentration of HCL above 2 M concentration leads to the reduction of conductivity [22].The rate of aniline oxidation depends on the presence of various impurities and additives that may

promote the progress of oxidation [19,22]. Distilled water was used; the potential presence of iron (III)ions in tap water may accelerate the aniline oxidation. Washing the PAN precipitate with 0.2 M HCl removes residual monomer, oxidant, and its decomposition product. The treatment with hydrochloride acid solution provides a more uniform protonation of PAN with chloride counterions, although some of the sulfate or hydrogen sulfate anions from the decomposition of peroxydisulfate also participate as counterions. A final washing with acetone removes low-molecular-weight organic inter- mediates and oligomers. It also prevents the aggregation of PAN precipitate during drying. And the product is obtained as a fine powder. The greenish PAN (emeraldine) hydrochloride was stored in polyethylene containers.



Fig(1.7): Temperature profile in the polymerization of aniline 0.2 M aniline hydrochloride oxidized with 0.25 M ammonium peroxydisulfate in 100 ml or 500 ml of aqueous medium. The oxidation was started at room temperature.

1.4-Conductivity of polyaniline

1.4.1-Synthesis of polyaniline in various laboratories

Standard polymerization of aniline have been made by eight individuals from five institution in five different countries (Table 3). The project participants followed written instruction given in the experimental part. The PAN powders were collected from all participant at the institute of Macromolecular chemistry in Prague compressed into pellets, and, subjected to the determination of conductivity at Charles University of 59 Prague within three weeks of preparation.

Table(1.3): Conductivity of PAN hydrochloride prepared according to the same "standard" recip at different institution (A-E) and by various persons

Institution –person	Number of samples	Conductivity[b] (S cm^{-1})	Standard deviation (S cm^{-1})
A–1	5	5.10	1.16
A–2	4	3.82	0.25
A	**9**	**4.53**	**1.08**
B–1	35	4.50	1.56
B–2	3	6.98	0.59
B	**38**	**4.70**	**1.64**
C–1	2	2.37	1.01
C–2	1	2.07	0
C	**3**	**2.27**	**0.35**
D	**6**	**2.08**	**0.37**
E	**3**	**6.41**	**0.66**

[a]0.2 M aniline hydrochloride, 0.25 M ammonium peroxydisulfate, room temperature (~20 °C), 100 ml reaction volume. Cf. Experimental Part.
[b]The average conductivity of all samples prepared by an experimentalist. A similar average of samples prepared within an institution is given in bold.

The average conductivity of 59 samples prepared by all participating laboratories (Table 3) was 4.37 S m^{-1} (standard deviation 40%). This is comparable with the average obtained by a single person who prepared 35 samples of average conductivity 4.50 SCm^{-1}(standard deviation 39%). This means that it was not significant whether experiments were by one person or by more individuals. Virtually the same results were achieved by expermentalists highly experienced in the preparation of PAN and by those who prepared PAN for the first time. The result slightly differed within each institution, even if the same batch of the chemicals was used for the preparation, but a low number of samples does not allow one to make statistically significant conclusions [6].

1.4.2-Effect of reaction conditions

A series of polymerizations was made at altered conditionsTable (1.4), and the results are summarized in Table 5. The reduction of starting reaction temperature to 0-2 ^{0}C nearly doubled the conductivity of the resulting PAN to a value of 7.58 S cm^{-1} (standard deviation 35%) Table (1.5). Higher acidity of the reaction medium also led to the increase in the conductivity to 11.9 S Cm^{-1} (standard deviation 43%)(Table(1.5). Higher acidity of the reaction medium also led to the increase in the conductivity to 11.9cm^{-1} (standard deviation 43 %) Table(1.5). Both trends are in accordance with data reported in the literature,[20,21]. The reduction of

temperature in the acidic media had, however, no marked effect on PAN conductivity Table (1.5). The standard deviation of about 40 % is accepted as being typical for the products of aniline polymerization made under simple experimental conditions.

Polymerization carried out in a five-fold reaction volume yielded product of relatively low conductivity Table(1.4).But still within the experimental error associated with the standard polymerization Table(1.5). This decrease in conductivity could be explained e.g., by the elevation of reaction temperature. The lower surface-to-volume ratio in 500mL batches and consequent reduced heat loss lead to a slightly increased temperature at the end of the reaction and to a slower cooling during the post-polymerization period compared with the standard polymerization Fig.(1.7) but the differences in temperature profile are small. The reduced conductivity of the product is more likely to be attributed to less efficient washing of the larger quantities of PAN processed after polymerization.

Table (1.4): Effect of reaction conditions on the conductivity of PAN hydrochloride

Institution –person	Number of samples	Conductivity (S cm^{-1})	Standard deviation (S cm^{-1})
Polymerization at ~0 °C (instead of room temperature)			
A–1	3	6.58	0.71
B–2	3	8.40	0.38
D	3	4.33	1.77
E	3	11.0	0.31
Polymerization in the presence of excess 1 M HCl			
A–1	7	8.98	2.63
A–2	3	9.04	6.08
B–2	3	17.0	2.52
E	3	16.5	5.17
Polymerization in 500 ml reaction volume (instead of 100 ml)			
A–1	3	3.29	0.19

[a]0.2 M aniline hydrochloride oxidized with 0.25 M ammonium peroxydisulfate.

Table (1.5): Average conductivity of PAN hydrochlorides and PAN bases at 20 ^{0}C and the polymerization yield (number of samples are given parentheses).

Reaction conditions[a]	Conductivity (S cm^{-1})		Yield (%)
	PANI hydrochloride	PANI base	
~20 °C	4.37 ± 1.74 (59)	$(6.0 \pm 1.8) \times 10^{-11}$ (4)	97.9 ± 3.4 (12)
~0 °C	7.58 ± 2.63 (12)	$(8.3 \pm 0.3) \times 10^{-8}$ (4)	102.1 ± 2.5 (10)
+ 1 M HCl, ~20 °C	11.90 ± 5.17 (16)	$(3.9 \pm 1.4) \times 10^{-9}$ (4)	90.7 ± 0.8 (9)
+ 1 M HCl, ~0 °C	9.83 ± 0.51 (4)	$(2.5 \pm 1.9) \times 10^{-8}$ (4)	95.0 ± 1.8 (4)

[a]0.2 M aniline hydrochloride oxidized with 0.25 M ammonium peroxydisulfate at given temperature and in the presence of excess HCl when specified.

1.4.3-Polyaniline base

The conductivity of PAN bases is many orders of magnitude lower compared to that of PAN "salts" Table (1.5) and ranks them among nonconducting materials. The average conductivity of 16 samples was 1.4×10^{-8} S cm^{-1}. Moreover, there are variations in the conductivity of PAN bases, depending on the method of preparation. The lowest conductivities of the order of 10^{-11} S cm^{-1} have been obtained by the deprotonation of standard PAN hydrochloride. Systematic research on the preparation of PAN bases is required, and it would be premature to draw any conclusion on the basis of the present results [6].

1.5-Mercury:

Mercury is the most powerful neurotoxin on the planet [23]. Mercury (Hg) is a shiny liquid metal that is a widespread enve4ronmental contaminant [23].Especially a problem is methyl or ethyl mercury, or mercuric chloride, which is very poisonous. Modern humans have much higher body levels of mercury than did our ancestors because of its greater use in recent times. It has been used for more than 2,000 years. Nowadays, mercury is employed daily by medical and dental practices in thermometers, drugs (more so in the past), and amalgam for fillings; by agriculture in fungicides and pesticides; and by the cosmetics industry.

Mercury in industrial waste has polluted our waters and contaminated our fresh-and salt-water plants and fish.

Inorganic mercury toxicity occurs in several forms: metallic mercury (Hg), mercurous mercury (Hg_2^{2+}), or mercuric mercury (Hg^{2+}). Toxicity from inorganic mercury can result from direct contact through the skin or gastrointestinal tract or from inhalation of mercury vapors. Detection and quantification of inorganic mercury has been the focus of many papers. Common techniques currently used for such assay are stripping voltammetry (where anodic stripping is correlated to metal concentration) and inductively coupled plasma (ICP). An important aspect of my work is the development and use of thin film POPD for quantitative analysis of Hg^{2+}through cathodic peak enhancement.

1.6-Voltammetry

A general definition for the term voltammetry is an electrochemical technique that involves controlling the potential of an electrode while at the same time measuring the current flowing at that electrode. The graph generated from such measurements is called a voltammogram. The electrode in question is referred to as the working electrode so it can be distinguished from other electrodes that are present in the electrochemical cell [24].

Voltammetry is usually performed by connecting an electrochemical potentiostat to an electrochemical cell. The cell contains a test solution and three electrodes: the working, reference, and auxiliary electrodes. Special electronic circuitry in the potentiostat permits the working electrode potential to be controlled with respect to the reference electrode that has no any appreciable current flowing through it. Rather, the current is forced to flow between the working electrode and the auxiliary electrode. This unusual arrangement has two principle benefits. First the reference electrode is protected from internal electrochemical changes caused by current flow. Second, measurement errors related to the resistance of the test solution are kept to a minimum.

1.6.1-Linear Sweep Voltammetry

In linear sweep voltammetry (LSV), a fixed potential range is employed and voltage is scanned from a lower to an upper limit, as shown below in figure (1.8).

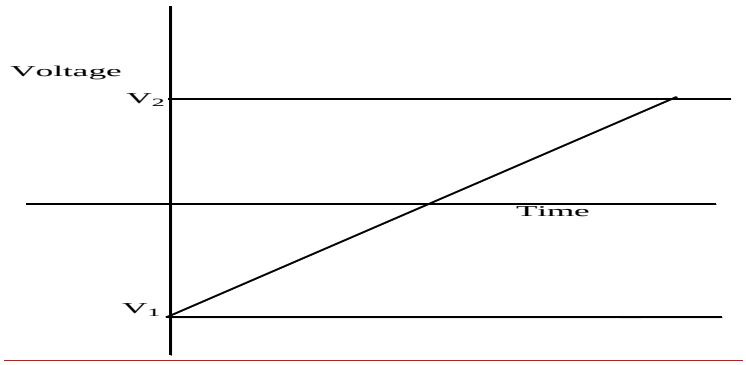


Figure (1.8): potential Wave Generation form in linear sweep voltammetry

The voltage scan rate (v) is calculated from the slope of the line. Besides the voltage scan rate, other characteristics of the linear sweep voltammogram recorded depend on a number of factors including the rate of the electron transfer reaction, and the chemical reactivity of the electroactive species. In LSV measurements, the current response is plotted as a function of voltage rather than time. For example, in the system Fe^{3+}/Fe^{2+} the following graph, figure (1.9), (called a voltammogram) would be seen for a single voltage scan:

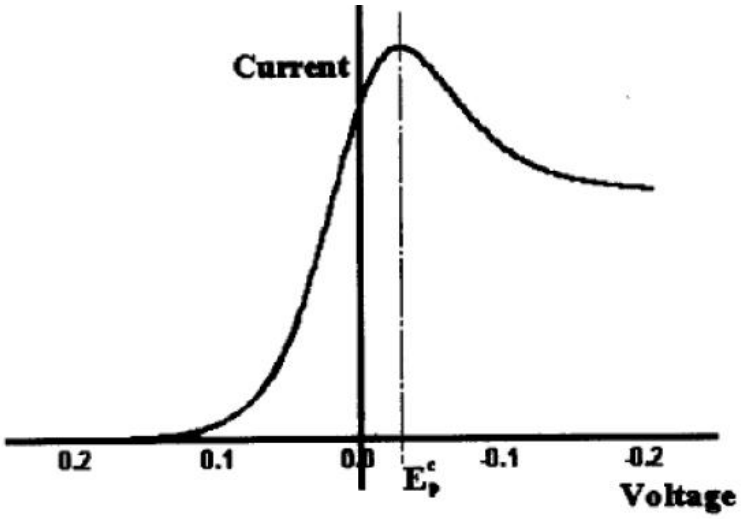


Fig (1.9): Single Voltage Scan

The scan begins from the left hand side of the current voltage plot where no current flows. As the voltage is swept further to the right (to more reductive values) a current begins to flow and eventually reaches a peak before dropping. To rationalize such behavior it is necessary to consider the influence of voltage on the equilibrium established at the electrode surface.

Considering the electrochemical reduction of Fe^{3+} to Fe^{2+} , the rate of electron transfer is fast in comparison to the voltage sweep rate. Therefore, at the electrode surface equilibrium is established identical to that predicted by thermodynamics. The relationship between concentration and voltage is given the Nernst equation [25-26] shown below:

$$E = E^{o} + (RT/nF)(ln[(Fe^{3+})/(Fe^{3+})] \quad \ldots\ldots\ldots\ldots\ldots 1.1$$

Here, E is the applied potential difference and E^0 is the standard electrode potential. So, as the voltage is swept from V_1 to V2 the equilibrium position shifts from no conversion at V_1 to full conversion at V_2 of the reactant at the electrode surface.

1.6.2-Cyclic Voltammetry

A related technique, cyclic voltammetry, consists of measuring the current resulting from an applied potential waveform [26]. The potential is cycled within a given potential range at constant rate and the current is measured as a function of potential. The rate can vary from less than 1MV/S to several hundred V/S. When a high enough potential is applied at an electrode surface to cause oxidation or reduction of species in solution, a current arises due to the detection of the species in the vicinity of the electrode surface. As a consequence, a concentration gradient appears in the solution. The current I is proportional to the gradient slope imposed, in the case of cyclic of voltammetry, however, the potential does not stay

constant. It rises at a constant rate until it reaches a chosen maximum and then decrease again at the same rate. The current does not reach a maximum immediately after imposition of the potential, as the potential is not immediately great enough to give rise to any reaction. The current starts to rise as the potential inters the area when oxidation or reduction can occur. It then continues to rise rapidly at the surface concentration of the species becomes smaller and smaller (the concentration gradient increase). The peak current consists of two components. In addition to the diffusion – controlled current, there is also a contraction from the initial current surge required to adjust the surface concentration of the reactant to its equilibrium concentration as given by the Nernst equation. The current then decays rapidly as the diffusion layers begins to extend further and further away from the electrode surface (gradient slope decrease and, therefore, so does the current). The same progression is seen on the negative scan as well, but in the opposite direction. As shown in figure (1.10), when scanning towards positive potential (Ep^A), the current is donated “anodic” (with corresponding peaks ‘anodic peaks’ Ip^A), and when towards negative potential (Ep^C), the current “cathodic” (Ip^C).

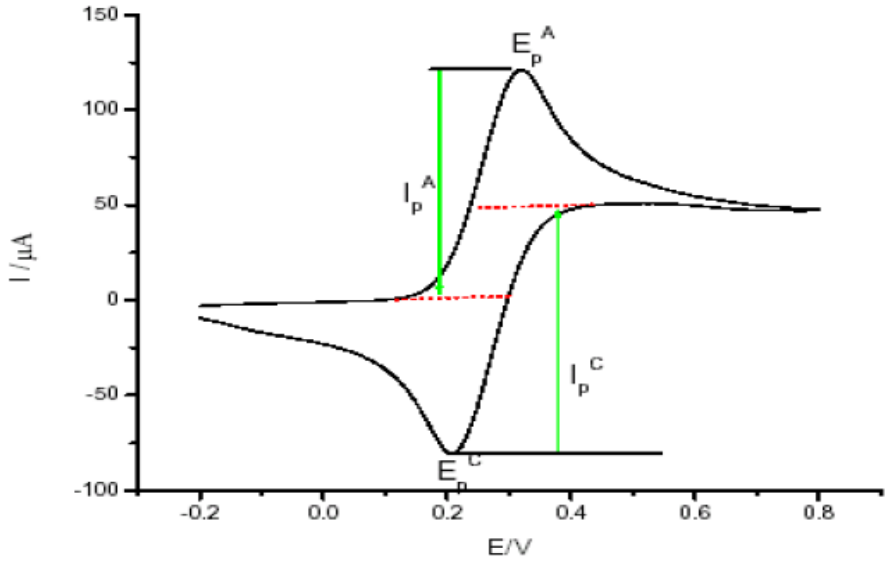


Figure (1.10): CV for a Reversible Reaction

From the anodic and cathodic peak currents and potentials, important parameters characterizing cmemical materials can be calculated, such as rate constants for oxidation/reduction processes and the doping/dedoping within a polymer film.

1.6.3-Anodic Stripping Voltammetry

Anodic Stripping Voltammetry (ASV) is an electrolytic method in which a mercury (Hg) electrode is held at negative potential to reduce metal ions in solution and form an amalgam with the electrode. The solution is stirred to carry as much of the analyte metal(s) to the electrode as possible for concentration into the amalgam. After reducing and accumulating the analyte for some period of time, the potential on the electrode is increased to reoxidize the analyte and generate a current signal. The concentration of the analyte in the Hg electrode, $C_{Hg,}$ is given by:

$$C_{Hg} = \frac{i_1 t_d}{n F V_{Hg}} \quad \text{……..1.2}$$

Where i_1 is the limiting current during reduction of the metal,

t_d is the duration of accumulation,

n is number of moles of electrons transferred in the half reaction,

F is the faraday constant (96,487coulombs/mole of e^-),and

V_{Hg} is the volume of the electrode.

The expression for current produced by anodic stripping depends on the particular type of Hg electrode but is directly proportional to the concentration of analyte concentrated into the electrode. The main advantage of stripping analysis is the preconcentration of the analyte into the electrode before making the actual current measurement. Anodic stripping can achieve detection of concentration as low as 10^{-10} M.

However, it should be noted that while the signal (cathodic peak) for metal reduction is less sensitive than the corresponding anodic stripping (anodic peak), the former can still be correlated to the analyte concentration through calibration. In this work, we seek to detect and quantify some heavy metal ions by eliminating the anodic stripping while at the same time enhancing the cathodic peak. This was achieved using thin polymer film of ortho-phenylenediamine .

2.1-Previous studies

– Vernon Somerset**,** et al explained that: inorganic mercury ions (Hg^{2+}) in laboratory prepared solutions were determined with a screen-printed carbon electrode (SPCE) coated with a polyaniline methylene blue (PAN-MB) polymer layer. The structure and properties of the PAN-MB polymer layer were compared to that of normal polyaniline (PAN) in order to elucidate the structure of the PAN-MB layer. The electricall conducting polymers were prepared by electrochemical polymerization of monomer solutions of aniline, and mixed solutions of aniline with methylene blue onto respective screen-printed carbon electrodes (SPCEs). Scanning Electron Microscopy (SEM) analyses of the SPCE polymer coated electrodes have shown that nanostructured materials have formed with diameters of the PAN nanoclusters and PAN-MB nanorods at approximately 200 nm. Anodic stripping volammetry (ASV) was used to evaluate a solution composed of 1×10^{-6} M Hg^{-2+}, in the presence of the SPCE/PAN-MB polymer sensor electrode. The Hg^{2+} ions were determined as follows: (i) pre-concentration and reduction on the modified electrode surface and (ii) subsequent stripping from the electrode surface during the positive potential sweep. The experimental conditions optimised for Hg^{2+} determination included the supporting electrolyte concentration and the accumulation time. The results obtained

have shown that the SPCE/PAN-MB polymer sensor electrode operates optimally at a p^H 2 with the supporting electrolyte concentration at 0.5 M HCl. A linear calibration curve was found to be in the range of 1×10^{-8} M to 1×10^{-5} M Hg^{2+} after 120s of pre-concentration. The detection limit was calculated and found to be 54.27± 3.28 μGL^{-1} of Hg^{2+}. The results have also shown that a conducting polymer modified SPCE sensor electrode can be used as an alternative transducer for the voltammetric stripping and analyses of inorganic Hg^{2+} ions[24].

– Chun Li; et al reported that conducting polymers (CPs) have been extensively studied and widely applied in various organic devices. To improve the performances or extended the functions of the devices, CPs usually have to be monostuctured. Electrosynthesis provides an effective and convenient one-step approach to CP nanomaterrials. The resulting materials are usually oriented on the electrode surfaces and their properties are easy to be controlled. This critical review focuses on the syntheses of CP nanostructures and nanocomposites by electrochemical polymerization. The applications of the nonmaterial.

  in organic devices such as sensors, actuators and memory devices also will be discussed (III references)[25].

– M.C. Bernard, et al explained that: polyaniline is generally depicted using five schematic structures: leucoemraldine, emeraldine and pernigraniline bases, and then emeraldine salt polaronlatice or bi polaron forms. Films obtained by electropolymerization in acidic solution present all the intermediate organizations between these structures. The paper aims to point out the potentiality of the Raman spectroscopy (RS), only technique able to describe the anal poly aniline because it gives a molecular nomenclature of the polymer. This potentiality is generally undervalued, in reason of the spectra complexity here, a very simple Raman spectra treatment is used to obtain a quantitative characterization of polyaniline films. One can follow the progressive passage between the different polarons organization displayed in function of the polarization potential: polaron lattice, then byipolaronic species are successively formed in the conductive range, and the passage from one to another from corresponds to the maximum of conductivity.Rs is associated here to optical spectroscopy[26].

– R. ANSARI 1**,** et al explained that: this paper deals with anew application of polyaniline synthesized chemically, coated on sawdust via cast method in the form of emeraldine base of mercuric ion on other heavy metals from aqueous solution. Among the different parameters investigated, the effect of pH was found to be the most prominent. It was found that metal

uptake is occurred under neutral or slightly alkaline conditions, while under relatively strong media, the sorption of the investigated metal ions was negligible and desorption is apredominant process.[27]

– Carlos M.G. S.Cruz, et al explained that: the results of systematic electrochemical and ellipsometric study of polyaniline films grown in aqueous solutions under several potentiodynamic conditions on platinum electrodes. The aim of the work was to characterize the mechanism of the growth and the structural properties of polymer in several stages of growth in sulfate and chloride acid solutions. It was observed that under all conditions the electrochemical cycling growth of the polyaniline films starts with a nucleation process during which a hydrous structure is formed. After the nucleation step, the continuation of growth proceeds with an increase of the polymer chain length and an increase in the number of sites in the oxidized state. Finally, after a critical thickness, there is a significant change in the growth mechanism, and the formation of a completely open structure takes place. It was also observed that the degree of the optical and oxi-reduction activities and thus the structure of the films are functions of the upper limit potential and the nature of the electrolyte employed in the synthesis [28].

– Bobby Pejcic, et al reported that: there is considerable interest in the development of electroanalytical sensors (i.e., potentiometric, amperametric, electrochemical biosensors) for the detection of wide range of analytes. The success of many of these sensors is governed by the condition and stability of the membrane /electrode surface. In fact, the response mechanism is dictated primarily by the surface structure and a considerable amount of the work has been undertaken to characterize the interfacial region. Consequently, electrochemical impedance spectroscopy (EIS) has played a pivotal role in the characterization of many types of sensors. EIS has been used to provide information on various fundamental processes (i. e., adsorption/film formation, rate of charge transfer, ion exchange, diffusion, etc.) that occur at the electrode-electrolyte interface. Understanding and manipulating these interfacial processes has assisted in the development of membranes/electrodes with new and improved response characteristics. This paper reviews some of work that has been undertaken using EIS over the past 35 years. More importantly, it evaluates the power of EIS in characterizing a wide range of electrochemical sensors systems [29].

– Longzhen Zheng, et al explained a anovel N-substituted aniline, N-(4-sulfonic butyryl aniline). X.ray photoelectron spectrum (XPS) of the polymer film was examined to propose the polymer molecular structure.

The sulfonated polyaniline was also characterized by ^{1}HNMR, TGA, DTA FTIR, and UV- vis spectra. The sulfonated polyaniline showed high conductivity in neutral aqueous solution which is two orders of magnitude higher than that of poly (N-acetylaniline) (PNAANI).[30]

- Dipak Dutta, et al reported that: a new idea for synthesizing polyaniline in an ordinary filter paper. The synthesis was carried out by a process in which aqueous acidic aniline solution and the oxidizing agent H_2O_2 was added to the paper drop by drop and in sequence. Uniform polymerization could be obtained with addition of reagents in either sequence. The polymer formation led to a green coloration of the paper. Formation of the emeraldine salt of polyaniline was confirmed by UV-vis and FTIR spectroscopy. Scanning electron microscopic measurements were made for surface characterized of the polymer formed in the paper. The same was used as a sensor for ammonia in vapor and in solution, for acid and base as well as end point indication, and also to filter acids and bases. We found that, using the polymer-containing paper, ammonia concentration in a solution as low as 14 PPM could be measured.[31]

- John M.Kinyanjui, et al explained that: the synthesis of polyaniline/platinum composites (PAN/Pt) has been achieved using both chemical and electrochemical methods. The direct chemical synthesis of PANI/Pt proceeds through the oxidation of aniline by $PtCl_6^{2-}$in the

absence of a secondary oxidant. SEM images of these samples indicate that the Pt particles are on the order of~1Um for the chemically prepared composite. Electrochemical PANI/Pt synthesis in initiated by the uptake and the reduction of $PtCl_6^{2-}$in to on a prior electrochemically deposited PANI film. This method produce a uniform dispersion of Pt partials with diameters ranging between 200nm and 1 µm. the results indicates that electrochemical methods may be more suitable for controlling particle dimension. Both materials show reduced proton doping relative to PANI without Pt, indicating the metal particles directly influence proton doping and the oxidation state of the polymer. The electrochemical data indicate that the conductivity in solution is sufficient such that the normal acid doping attainable for PANI/Pt produced using either synthetic method.[32]

- Mark Trojanowicz**,** reported that: a new chievements in the field of analytical application of conducting polymers, most of which were published in the last five years. Based on 171 references mainly to original papers in international scientific journals, the applications of conducting polymers in the design of electrochemical and optical sensors, enzymatic biosensors and immunosensors are reviewed together with application in analytical preconcentration.Procedures and high performance separation techniques.[33]

- Svetlozar Ivanove, et al explained that: conductometric transducing is suggested for electrocatalytic chemical sensors based on conductive polymers. Lateral conductivity of the polymer layers was measured by two- and four- point techniques. The approach was applied for electroanalytical detection of ascorbic acid on the electrocatalytically active polyaniline and poly orthometoxyaniline electrodes. Both polymers displayed a monotonous concentration dependence of their conductance in the analytically important sub-millimolar concentration range of ascorbic acid. The approach was tested in model solutions of ascorbic acid in buffer and applied for detection of ascorbic acid in orange juice.[34]

- Ezzat M. Soliman**,** et al reported that: a new metal chelate Schiff's bases was synthesized .Silica gel chemically bonded diethylenetriamine mono-naphtaldyhyde and mono-salicyaldehyde Schiff's bases (phases I and III) were produced via the interaction of silica gel-modiefied diethylenetriamine with naphtaldehyde and salicyldehyde, respectively. However, phases II and IV arose through the interaction of bis-naphtaldehyde and bis-salicyldehyde Schiff's bases of diethylenetriamine with 3-choropropyltrimethoxysilane modified silica gel. The characterization of such new phases their capabilities towards selective extraction or separation of Fe (III), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) ions were studied and evaluated by both batch and column

techniques as a function of ph and time of contact. Phases III and I showed high performance towards Cu(II) extraction, where their Cu(II) sorption determined to be 0.957 and 0.940 mmol g^{-1}, receptivity of metal ion sorption was discussed in the light of effects of bulkiness as well as orientation of immobilized chelate on sorbent reactivity. Donor sites of phases III and I (di ethylenetrianiline and azomethane nitrogens along with phenolic hydroxyl group oxygen) are fully active, where as phases IV and II are partially active with only participation of oxygen and azomethane nitrogen. The order of increasing thermal stability (IV < II < I < III) and fastness of metal uptacke equilibration process coincides satisfactorily with decreasing bulkiness of the chelate. Results of separation under dynamic conditions of binary mixtures containing Cu (II) with Ni(II), Zn(II), Cd(II) and Pb(II) using phase III are in accordance with its selectivity towards Cu(II) retention relative to the other coexisting ions.[35]

– S.Ashok Kumar, et al explained that: conducting redox active polymers play a critical role in the development of transducers for biosensing. It has been evidenced by increasing numerous reports on conducting and redox active polymers incorporated electrodes for assay of biomolcules. This review highlights the potential uses of electrogenerated polymer modified electrodes and polymer/ carbon nanotubes composite modifier have been

discussed in detail for the quantification of NADH based on mediator or mediatoless methods.[36]

– Pavel Ryant, et al reported that: potato plants were cultivated in the presence of ammonium sulphate or elemental sulphate supplementation into the soil to reveal the effects of different sulphur forms on content of nitrogen, phosphorus, potassium, calcium, magnesium and sulphur, and yield of tubers. During the investigation of the influence of different sulphur forms on yield of potato tubers we did not observe significant changes. Average weight of tubers of control plants per one experimental pot was 335g. application of sulphur in both forms resulted in moderate potato tubers weight reduction per one experimental pot. Further we treated the plants with two different supplements of sulphur with cadmium(II) ions (4mg of cadmium(II) acetate per kilogram of the soil). The significantly lowest cadmium content ($P < 0.05$). was determined in tissues of plants treated with the highest dosage of elemental sulphur(0.64mg Cd/kg) compared to control plants (0.82mg Cd/kg). we also aimed our attention on the cadmium content in proteins, lipids or soluble carbohydrates and ash. Application of sulphate as well as elemental sulphur resulted in significant cadmium content reduction in lipid fraction compared to control plants. In addition to this we quantified content of low molecular mass thiols in potatoes tissues. To determine the

thiols content we employed differential pulse voltammetry Brdicka reaction. After twelve days of the treatment enhancing of thiols levels was observed in all experimental groups regardless to applied sulphur form and its concentration. Finally we evaluated the effect of sulphur supplementation on phytophora infestans infection of potato plants.[37]

– Yucel Sahin, et al reported that: electrochemical preparation of poly(2-bromo aniline) (PBrANI) and poly(aniline-co-2-bromo aniline) [P(An-2-Br An)] was carried out in an acetonitrile solution containing tetrabutyl ammonium perchorate (TBAP) and perchloric acid ($HClO_4$). The cyclic voltammograme during the copolymerization had many features similar to those for the usual polymerization of aniline. The copolymer exhibits a higher dry electrical conductivity value than that of PBr ANI a lower one than that of PANI. The observed decrease in the conductivity of the copolymer relative to PANI is attributed to incorporation of bromine moieties into the polyaniline chain. The structure and properties of the polymer and copolymer were elucidated using cyclic voltammetry (CV), FTIR, and UV-vis spectroscopy.[38]

– Jing Zhang, et al explained that: a copolymer, poly(aniline-Co-m-amino phenol), has been synthesized using repeated potential cyclic. The optimum conditions for the polymerization are that the scan potential rang is controlled between -0.10 and 0.95V (Vs.SCE), and a solution consists

of 0.34M aniline, 0.012 M m-amino phenal and 2M H_2SO_4. The IR spectra of the copolymers demonstrate that the m-amino phenal units are included in the copolymer chains. the cyclic voltammograms of the copolymers in 0.3 Na_2SO_4 solution with various PH values were performed at the potential ranges from -0.20 to 0.80V and at a scan rate of 60m V S^{-1}. The results indicate that the copolymer still hold 41.7% of the electrochemical activity when the copolymer electrode reaction of the copolymer at PH 12.0 is also under mass transfer control. The conductivity of the copolymer prepared under the optimum condition is 1.42 S cm^{-1}, and slightly depends on the PH value. Thus, the PH dependence of the electrical properties of the copolymer is improved compared with poly(aniline-Co-o- amino phenal), and is much better than that of the patent polyaniline.[39]

- Ya Zhang, et al reported that: poly(aniline-Co-o-amino phenol)(PANOA)-modified glassy carbon electrode (GCE) was first used to investigate the electrocatalytic reduction of dichromate in a NaCl solution of P^H Cr(VI) occurred at PANOA-modified GCE. The FT-IR, ESR and XPS results showed that the Cr(VI) can be doped in the PANON films and can convert to less-toxic Cr(III). The doping level Cr/N was 78.2% and trace amount of Cl (0.42%) was detected in the doped PANOA, which indicated that the doping process[40].

– Bakir SARI**,** et al explained that: in this study, conductive homopolymers of o-chloroaniline, P-bromoaniline and N-methylaniline were synthesized electrochemically in perchloric acidic solution and their properties were analyzed. Initially, the maximum oxidation potential values of these monomer solutions were determined by cyclic voltammetry (CV) their conductive polymers were then synthesized under a nitrogen atmosphere using a potentiostate. FTIR spectra were taken in order to analyze the structural properties of the resulting polymers. Thermogravimetric analysis (TGA) was conducted and surface micrographs were taken by Scanning Electron Microscope (SEM). The conductivity levels of the polymers were determined by the four prope techniques. Magnetic properties of the samples were analyzed and the conductions mechanisms were examined. Based on the resulting conductivity data. It was concluded that poly (P-bromoaniline) was of polaron structure, where as poly(O-chloroaniline) and poly(N-methyl aniline) were of bi polaron structure.

Thermogravimetric analysis results indicated that poly (N-methyl aniline) has the highest maximum decomposition temperature, and conductivity measurements revealed poly (O-chloroaniline) has highest conductivity level.[41]

- Resa Ansari 2**,** et al reported that: the adsorption of Cr(VI) from aqueous solutions using sawdust coated by polyaniline (SD/PAN) and polyaniline composites with nylon 66 and polyurethane. Nylon and polyurethane are available common polymers that can be easily dissolved in the solvents of PAN (formic acid and NMP). So, the PAN composites with these polymers can be readily prepared via solvent cast method. Polyaniline (PAN) was synthesized chemically and coated on the surface of sawdust (SD) from formic acid via cast method. It was found that polyaniline in the acid doped from (e.g.HCl). can be used for Cr(VI) ion removal in acidic aqueous solution (PH≤ 2). Adsorption occurs only under acidic conditions and it decreases with increasing the PH of solution significantly. The proposed mechanism for adsorption of Cr(VI) with our currently developed adsorbent seems to be mostly occurring via an anion exchange process. Adsorption of Cr(VI) from water using SD/PAN column is both a simple and efficient method compared to the other adsorbents reported by previous investigators.[42]

- L.Yang, et al explained that: A raw granular activated carbon (RGAC) is modified by polyaniline to improve arsenate adsorption. it is found that the modification does not change The specific surface areas. The content of aromatic ring structures and nitrogen containing functional groups on the modified GAC (MGAC) is increased. The surface positive charge

density is dramatically increased in acidic solutions. The adsorption of As(V) on to both sorbents is highly p^H dependent [43].

– Vojtech Adam, et al reported that: electrochemically biosensors have superior properties over other existing measurements systems because they can provide rapid, simple and low-cost on-field determination of many biological active species and a number of dangerous pollutants. In our work, we suggested a new heavy metal biosensor based on interaction of heavy metal-ions (Cd^{2+} and Zn^{2+}) with phytochelatin, which was adsorbed on the surface of the hanging mercury drop electrode, using adsorptive transfer stripping differential pulls voltammetry. In addition, we applied the suggested technique for the determination of heavy metals in a biological samples-human urine and platinum in a pharmacy Utica drug. The detection limits (3S/N) of Cd(II), Zn(II) and Cis-platin were about 1.0, 13.3 and 1.9 p mole in 5 µL, respectively. On the basis of the obtained results, we propose that the suggested technique offers simple, rapid, and low cost detection of heavy metals in environmental, biological and medical samples.[44]

– Elmer-Rico E. Mojica, et al explained that: polyaniline (emeraldine salt) samples prepared with different acid dopants namely hydrochloric acid (HCl), nitric acid (HNO_3), perchloric acid ($HClO_4$) and sulphuric acid (H_2SO_4) were used as modifier by mixing it with graphite powder and

Nujol oil to form a past. The fabricated Graphite Past Electrodes (GPE) were characterized by Cyclic Voltammetry (CV) and differential pulse anodic stripping voltammetry (DPASV). Voltammetric analysis using different heavy metal ions (mercury, lead, cadmium, copper, zinc, nickel and cobalt) in aqueous solution was performed using the prepared electrodes. All polymer graphite past electrodes detected the presence of mercury (II) ions. In addition to mercury ions, the modified electrodes containing polyaniline prepared with dopants (HNO_3 and HCl) also detected the presence of cadmium(II) ions.[45]

– D.R.Paul[a,1]**,** et al reported that: in the large field of nanotechnology, polymer matrix based nanocomposities have become a prominent area of current research and development. Exfoliated clay-based nanocomposities have dominated the polymer literature but there a large number of other significant areas of current and emerging in-tersest. This review will detail the technology involved with exfoliated clay-based nanocomposities and also include other important areas including barrier properties, flammability,resistance,biomedical,application

electrical/electronic/optoelectronic applications and fuel cell interests. The important question of the “nano-effect”of nanoparticle or fiber inclusion relative to their larger scale counterparts is addressed relative to crystallization and glass transition behavior. Of course other polymer (and

composite)-based properties derive benefits from nanoscale filter or fiber addition and these are addressed.[46]

- Peng Liu, explained that: series of polyaniline/silica nanocheet composites (PANI/SNS) with different contents of the silica nanosheets derived from vermiculite via acid-leaching were prepared via the in site chemical oxidation polymerization. The PANI/SNS composites were characterized with Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), X-ray diffraction (XRD), thermo gravimetric analysis (TGA), and electrical conductivity measurements, it is interesting that the electrical conductivities of the PANI/SNS composites increased with the increasing of the contents of the silica nanosheets added because of the moisture. It was confirmed by the TGA analysis.[47].

- Hossein Eisazadeh, reported that various adsorbents such as bentonite, activated carbon, conductive electroactive polypyrrole composites were employed. The conductive polypyrrole composites were prepared using different surfactants such as sodium dodecylbenzenz sulfonate, hydroxyl propylcellulose, poly(vinyl alcohol) and poly (ethylene glycol) in the presence of $FeCl_3$ as an oxidant respectively. The results indicate that the type of adsorbents and surfactants have a great effect on the removal of arsenic.[48]

– R. ANSARI 3 , et al explained that: polyaniline was synthesized chemically, coated on sawdust via cast method in the form of emeraldine base (EB) from formic acid as solvent, and used as an adsorbent for removal of lead ion or from aqueous solution. The effects of some important chemical and physical factors in removal efficiency have also been investigated. Among the different parameters, the effect of PH was the most prominent. It was found that metal uptake is occurred under neutral or slightly alkaline conditions, while under relatively strong acidic media, the sorption of the investigated metal ions was negligible and desorption is a predominant process. It was found that undoped PANI (EB form) coated on polar substrates such as sawdust (SD) can be used as an effective adsorbent for removal of heavy metal ions in water and waste water treatments. All the previous investigations and applications take advantage of the electrical conductivity (metallic), electrochemical (redox activity) and electrochromic properties of the polyaniline.While, in this research, we have taken advantage of the chelating properties of PANI for metal sorption.[49].

– Paul D. Selid, et al reported that: mercury is a very toxic element that is widely spread in the atmosphere, lithosphere, and surface water. Concentrated mercury poses serious problems to human health, as bioaccumulation of mercury within the brain and kidneys ultimately leads

to neurological diseases. To control mercury pollution and reduce mercury damage to human health, sensitive determination of mercury is important. This article summarizes some current sensors for the determination of both a biotic and biotic mercury. A wide array of sensors for monitoring are described, including biosensors and chemical sensors, while piezoelectric microeantilever sensors, are also described. Additionally, newly developed nanomaterial's offer great potential for fabricating novel mercury sensors. Some of the functional fluorescent nanosensors for the determination of mercury are covered afterwards, the in vivo determination of mercury and the characterization of different forms of mercury are discussed. Finally, the future direction for mercury detection is outlined, suggesting that nanomaterials may provide revolutionary tools in biomedical and environmental monitoring of mercury.[50]

- Nabutaka Endo**,** et al reported that: The hydrophilic conducting polymer colloids consisting of conducting polymer (polyaniline), surfactant stabilizer(poly(vinyl alcohol)) and suitable dopant anion. The colloids incorporated anions in the protonated form and released them in deprotonated form. In addition, incorporated anion can exchange with other anions in immersed solution based on ion exchange equilibrium. The ion exchange properties of this colloidal particle fixed on silica gel

powder was studied. The exchange have been increased in sequence of Cl^- < NO_3^-< Br^-< ClO_4^- < SCN^- on the colloid doping chloride or nitrate. The exchange selectivity is attributed to the hydrophobic interaction between colloid and exchangeable anion and template formed by the incorporated dopant anion.[51]

– Manickam Sivakumar**,** et al explained that: simple and novel sonochemical method for the preparation of polyaniline (PANI), as well as its composite, with Aunanoparticles. This technique utilizes ultrasound radiation as an energy source to facilitate the reaction by reducing the reaction time, as well as significantly increasing the yield. The tremendous increase in the reaction rates is explained on the bases of the intensive bubble collapse conditions, which rapidly generate the oxidative radicals necessary for polymerization.[52]

– R. Ansari 4**,** et al reported that: in this research polypyrrole (PPy) and polyaniline (PANI) conducting polymers which were synthesized chemically on the surface of wood sawdust (SD). These electroactive polymers as coated form on sawdust then were used for sorption or removal of silver ion from aqueous solutions under simple open circuit conditions. The effects of some important parameters such as PH, initial concentration, sorbent dosage, and contact time on uptake of silver ion were also investigated in this research. The experiments were carried out

using both batch and column systems at room temperature. The treatments of the data were carried out using both Freundlich and Langmuir adsorption isotherms. In order to find out the possibility of the regeneration and reuse of the exhausted adsorbent, desorption studies were also performed. It was found that conducting electroactive polymers such as PPy or PANI are efficient sorbents for removal of the silver ions from aqueous solutions. Sorption / desorption processes can be simply carried out with PH control with satisfactory performance. Recovery percentage observed for PANI/SD in column study was more than PPy/SD and SD, under the same operational conditions.[53]

- Medhat Ibrahim, et al explained that: the polymerization of aniline by Cu(II) montmorillonite was studied using attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy[54].

- Douglas Chinn**,** et al explained that: thin films (<200 nm) of chemically prepared polyaniline cast from solutions of formic acid and electrochemically prepared polyaniline films grown on top of the chemical films are characterized electrochemically, by work function changes and conductivity measurements. The oxidized and reduced films exhibit complex relaxation phenomena over time periods ranging from 1 to 900 h. water is seen to play a key role in relaxation phenomenon is suggested as being a change in the ratio of fully doped conducting

material to nonconducting material based on granular morphology it is shown that the two polymers are nearly identical chemically and in their behavior with differences being mainly morphology.[56]

2-2 Aim of this work.

1- prepare poly aniline by chemical method using different oxidants.

2- characterization of poly aniline using XRD, FTIK, SEM, DC, measurement.

3- study the adsorption of Hg(II) on poly aniline.

4- Fit the experiment data of adsorption to mathematical adsorption isotherm such as Langmuir isotherm.

5- Application of this method to real environmental.

EXPERIMENTAL

This chapter describes the experimental aspects of preparation of polyaniline (PAN) and gives the General methodology of the experiments undertaken. It describes the preparation of different kinds of polyaniline also this chapter describes the experimental part of adsorption of Hg(II) on polyaniline (PAN) – dopped with HCl.

3.1-List of chemical used

Table.(3.1): List of Chemistry used

No	Name of materials	The formula	Name of Company
1	Aniline	$C_6H_5NH_2$	WINLAB LABORATORY CHEMICALS
2	Mercury nitrate monohydrate	$Hg(NO_3)_2.H_2O$	WINLAB LABORATORY Reagent
3	Ammonium per sulfate	$(NH_4)_2S_2O_8$	Fluka-Chemica
4	Sodium nitrate	$NaNO_3$	Fluka-Chemica
5	Hydrochloride acid	HCl	Riedel-dehaen
6	Phosphoric acid	H_3PO_4	LABORATORY Reagent
7	Acetic acid	CH_3COOH	LABORATORY Chemicals
8	Nitric acid	HNO_3	Fluka- Chemica
9	Sodium hydroxide	NaOH	LABORATORY Reagent
10	Potassium Iodate	KIO_3	General purpose reagent
11	Potassium dichromate	$K_2Cr_2O_7$	CODEX FARMA COPEA

3.2-Instrumentation

Table. (3.2): Instrumentation

No	Name of instrument	Model	Country
1	Digtal pH meter	WTW 525, pH meter	Germany
2	Stirring Magnitude	Ruhromag	Germany
3	XPS	Scienta ESCA 300	Sweden
4	FTIR	Bruker S100	Germany
5	SEM	AJeal. JEM 100CX II Model	Germany
6	XRD	PW 1800 X-ray diffractometer	Germany
7	Shaker	Edmund Bühllr, KI-2	Germany
8	Electroanalytical balance	Mettler AB104	Germany
9	Mercury analyzer system	Lab Analyzer – 254	Germany

3.3-List of glassware used

Table. (3.3): The glassware used in this study

No	Name of glassware	Volume of glassware(ml)	Company
1	Beakers	50, 100, 250, 500, 600, 800, 1800	Germany
2	Erlenmeyer flask	200,200. 300	Germany
3	Flask	250, 500, 1000	Germany
4	Conical flask	50, 100, 250, 500, 1000, 2000	Germany

3.3.1-Preparation of standard solutions

3.3.1.1-Mercury Nitrate Hg (NO_3).H_2o

-Preparation of 1000 ppm

360 gr/mol of $Hg(N0_3)_2 \rightarrow$ 200.5 gr of Hg

X gr of $Hg(NO_3)_2 \rightarrow$ 1.0 gr of Hg

X = 1.795 gr

Dissolve this weight with distilled water, and put it in a standard volumetric flask(500 ml) there a few drops of nitric acid (HNO_3) were added, and complete it with distilled water to the market.

-Preparation of 100 ppm of $Hg(NO_3)_2.H_2O$

$M_1 \times V_1 = M_2 \times V_2$ ……3.1

$1000ppm \times V_1 = 100ppm \times 250$ ml

$V_1 =$ 25 ml.

Using a pipette 25 ml from the stock solution of 1000ppm was transferred in to 250 ml volumetric flask, and then distilled H_2O added to the mark.

-Preparation of 10ppm of $Hg(NO_3)_2$

$M_1 \times V_1 = M_2 \times V_2$

$100\ PPM \times V_1 = 10\ PPM \times 100$

$V_1 = 10$ ml

10 ml was taken from 100 ppm and putted in 100 ml content and I putted some drops of nitric acid and complete it to the market.

-Preparation of 8 ppm $Hg(NO_3)_2$

$M_1 \times V_1 = M_2 \times V_2$

100 PPM × V_1 = 8 ppm × 100ml

V_1 = 8 ml.

-Preparation of 6 PPM $Hg(NO_3)_2$

$M_1 \times V_1 = M_2 \times V_2$

100 PPM × V_1 = 6 ppm × 100 ml

V_1 = 6 ml.

-preparation of 4 ppm $Hg(NO_3)_2$

$M_1 \times V_1 = M_2 \times V_2$

1000 ppm ×V_1 = 4 ppm × 100 ml

V_1 = 4 ml.

-preparation of 2 ppm $Hg(NO_3)_2$

$M_1 \times V_1 = M_1 \times V_1$

100 ppm × V_1 = 2 ppm × 100 ml

V_1 = 2 ml.

And by using 10 ppm concentration we were prepared (0.2, 0.4, 0.6, 0.8, and 1.0) ppm.

-preparation of 1.0 ppm $Hg(NO_3)_2$

$M_1 \times V_1 = M_2 \times V_1$

10 ppm × V_1 = 1.0 × 50 ml

V_1 = 0.50 ml.

-preparation of 0.8 ppm $Hg(NO_3)_2$

$M_1 \times V_1 = M_1 \times V_1$

10 PPM × V_1 = 0.8 ppm × 50 ml

V_1 = 0.4 ml.

-preparation of 0.6 ppm $Hg(NO_3)_2$

$M_1 \times V_1 = M_2 \times V_2$

10 ppm × V_1 = 0.6 ppm × 50 ml

V_1 = 0.3 ml

-preparation of 0.4 ppm $Hg(NO_3)_2$

$M_1 \times V_1 = M_2 \times V_2$

10 ppm × V_1 = 0.4 ppm × 50 ml

V_1 = 0.2 ml.

-preparation of 0.2 ppm $Hg(NO_3)_2$

$M_1 \times V_1 = M_2 \times V_2$

10 PPM × V_1 = 0.2 PPM × 50 ml

V_1 = 0.1 ml.

3.3.2- Aniline (ANI)

The preparation of molar concentrations of liquid material performed as following:

$$M_C = \frac{Density \times \% \times 1000}{M.Wt \times 100} \quad \text{.....3.2}$$

$$M_C = \frac{1.022 \times 99 \times 1000}{93.13 \times 100}$$

$$M_{C} = 10.9\ M.$$

And then 0.05M of aniline was prepared and there is used to polyaniline as describes below.

$M_1 \times V_1 = M_2 \times V_2$

$10.9\ M \times V_1 = 0.05\ M \times 250\ ml$

$V_1 = 1.2\ M$

3.3.3- Ammonium peroxydisulfate $(NH_4)_2\ S_2O_4$

$$M = \frac{Wt}{M.Wt \times V} \quad \text{.....3.3}$$

$$Wt = M \times M.Wt \times V \quad \text{.....3.4}$$

$$\text{Wt} = 0.03\text{M} \times 228 \frac{\text{gr}}{\text{mol}} \times 0.25$$

Wt = 1.8 gr.

3.3.4-Sulfuric Acid (H_2SO_4)

The preparation of polyaniline was done according to:

$$M_C = \frac{density \times \% \times 1000}{M.Wt \times 100}$$

$$M = \frac{1.835 \times 96\ 1000}{98.078 \times 100}$$

$$M = 17.9\ M$$

And then we prepared 1M of H_2SO_4 from 17.9 M as following:

$M_1 \times V_1 = M_2 \times V_2$

$17.9\text{M} \times V_1 = 1\text{M} \times 1000$

$$\mathbf{V_1} = \frac{1M \times 1000ml}{17.9M}$$

V_1 = 55.9 ml.

3.3.5- hydrochloric Acid (HCl)

The preparation of polaniline was prepared in one molar hydrochloride acide

$$M_C = \frac{Density \times \% \, 1000}{M.Wt \times 100}$$

$$M = \frac{1.186 \times 37 \, 1000}{100 \times 36.46}$$

$$M = 12.035M.$$

$M_1 \times V_1 = M_1 \times V_1$

12.035 × V_1 = 1M × 1000 ml

V_1 = 83.1 ml

3.3.6- Perchloric acid

The same method was used for preparation polyaniline in one molar perchloric acid:

$$M_C = \frac{Density \times \% \times 1000}{M.Wt \times 100}$$

$$\boldsymbol{M_{C} = \frac{1.664 \times 60 \times 1000}{100.46 \times 100}}$$

$$\boldsymbol{M_{C} = 9.93\, M.}$$

$M_1 \times V_1 = M_2 \times V_2$

9.93 M × V_1 = 1M × 1000 ml

V_1 = 100.7 ml.

3.3.7- Acetic Acid

$$M_{C=}\frac{Density \times \% \times 1000}{M.Wt \times 100}$$

$$M_{C=}\frac{1.051 \times 99.5 \times 1000}{60.050 \times 100}$$

$M_1 \times V_1 = M_1 \times V_1$

$17.4\ M \times V_1 = 1M \times 1000\ V$

V_1=57.5ml.

3.3.8- (0.02, 0.2, 2) M Sodium Nitrate

Sodium Nitrate is the salt was used of the ionic strength test, so its necessary know how prepared it.

$$1) Wt_1 = M \times M.Wt \times V_L$$

$$Wt_1 = 0.02 \times 85 \times 0.5$$

$$Wt_1 = 0.85\ gr.$$

$$2) Wt_2 = 0.2 \times 85 \times 0.5$$

$$Wt_2 = 8.5 gr.$$

$$3) Wt_3 = 1.0 \times 85 \times 0.5$$

$$Wt_3 = 42.5 gr.$$

The three weights was dissolved in three volumetric flask 500ml content, and completed to the market with double distilled water, and use them for ionic strength experiments.

3.4-Preparation of polymer

The polymer (PAN) was prepared by chemical method.

3.4.1-Chemical method

The synthesis of conducting polymers containing conjugated double bonds such as pyrrol, thiophene, furan, and their derivatives has become the subject of many recent studies. Furthermore some researchers have synthesized conducting aniline blends and composites. The polyaniline was synthesized by the method of oxidative polymerization of monomeric aniline with potassium per sulfate, potassium iodate, ammonium per sulfate, and potassium dichromate in aqueous acidic media [6].

Polyaniline (emeraldine base)(PAN-EB) was prepared by the chemical oxidation method as following:

1.7 gr of ammonium peroxydisulfate 0.03M $(NH_4)_2S_2O_8$ (oxidation mater) was dissolved in 200 ml of 1.5M HCl (37%).

In another flask 2ml of 0.25 aniline was added to 200 ml of the same acid (HCl).

Both mixtures were kept separately for 1hr time, and then both of them were mixed together, and was butted on magnetic starrier for 6hrs. After 6hrs the mixture was lifted to another day to complete the precipitate of the polymer. The solution was filtrated, and then the precipitate was washed with 300ml 0.2 M HCl for three times, after that the polymer was washed with deionized water until water became colorless, and the process

were repeated with acetone, and then the resultant material (PAN) was dried in air for enough time, and then it was kept in a desecrator.

3.4.1-Preparation of Polyaniline (PAN)/HCl

Polyaniline (PAN)/HCl was prepared as following:

1.7 gr of ammonium peroxydisulfate 0.03 $(NH_4)_2S_2O_8$ (oxidation mater) was dissolved in 200 ml of 1.5M HCl (37%).

In another flask 2ml of 0.25 aniline was added to 200 ml of the same acid (HCl).

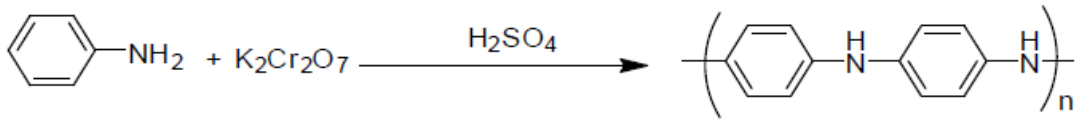
Both mixtures were kept separately for 1hr , and then were mixed togather, stirred by magnetic starrier for 6hrs. After 6hr the mixture was kept for another day to complete the precipitate of the polymer, after that the solution was filtrated, and then the precipitate washed with 0.2M of 300 ml of 0.2 M HCl for three times, after that the polymer was washed with deionized water until water became colorless, and the process were repeated with acetone. And the resultant material (PAN) was dried in air for enough time, and then it was kept in a desecrator. Finally the polymer (PAN) was collected in a specific Erlenmeyer flask for use.

3.4.1.1-preparation of polyaniline(PAN)/HCl with potassium dichromate

2.2gr of potassium dichromate ($K_2Cr_2O_7$) (oxidation mater) was dissolved in 500 ml of 1.5M HCl .

In another flask 2ml of aniline was added to 500 ml of 1.5 M HCl .

Both mixtures were kept separately for 1hr time, and then both of them were mixed togather, and was butted on magnetic starrier for 6hrs. After 6hrs the mixture was lifted to another day to complete the precipitate of the polymer, after that the solution was filtrated, and then the precipitate was washed with 0.2M of with 300 ml of 0.2 M HCl for three times, after that the polymer was washed with deionized water until water became colorless, and the process were repeated with acetone. And the resultant material (PAN) was dried in air for enough time, and then it was kept in a desecrator. Finally the polymer (PAN) was collected in a specific Erlenmeyer flask to use.



3.4.2-Preparation of polyaniline(PAN)/H_2SO_4 `

1.7 gr of ammonium peroxydisulfate 0.03 $(NH_4)_2S_2O_8$ (oxidation mater) was dissolved in 200 ml of 1M H_2SO_4 (37%).

In another flask 2ml of 0.25 aniline was added to 200 ml of the same acid (H_2SO_4).

Both mixtures were kept separately for 1hr time, and then both of them were mixed together, and was butted on magnetic starrier for 6hrs. After 6hrs the mixture was lifted to another day to complete the precipitate of the polymer, after that the solution was filtrated, and then the precipitate was washed with 0.2M of with 300 ml of 0.2 M HCl for three times, after that the polymer was washed with deionized water until water, and with enough amount of acetone, and the process were repeated with acetone. The resultant material (PAN) was dried in air for enough time, and then it was kept in a desecrator. Finally the polymer (PAN) was collected in a specific Erlenmeyer flask to use.

3.4.3-Preparation of polyaniline(PAN)/H_3PO_4

1.6 gr of potassium iodide KIO_3 0.03 (oxidation mater) was dissolved in 200 ml of 1.5M H_3PO_4 (37%).

In another flask 2ml of 0.25 aniline was added to 200 ml of the same acid (H_3PO_4).

Both mixtures were kept separately for 1hr time, and then both of them were mixed to gather, and was butted on magnetic starrier for 6hrs. After 6hrs the mixture was lifted to another day to complete the precipitate of the polymer, after that the solution was filtrated, and then the precipitate

was washed with 0,2M of with 300 ml of 0.2 M HCl for three times, after that the polymer was washed with enough deionized water , and the process were repeated with acetone. The resultant material (PAN) was dried in air for enough time, and then it was kept in a desecrator. Finally the polymer (PAN) was collected in a specific Erlenmeyer flask to use.

3.4.4-Preparation of polyaniline(PAN)/CH_3COOH

1.2 gr of potassium permanganate (oxidation mater) was dissolved in 200 ml of 1M CH_3COOH (37%).

In another flask 2ml of 0.25 aniline was added to 200 ml of the same acid (CH_3COOH).

Both mixtures were kept separately for 1hr time, and then both of them were mixed to gather, and was butted on magnetic starrier for 6hrs. After 6hrs the mixture was lifted to another day to complete the precipitate of the polymer, after that the solution was filtrated, and then the precipitate was washed with 0,2M of with 300 ml of 0.2 M HCl for three times, after that the polymer was washed with deionized water until water became colorless, and the process were repeated with acetone. The resultant material (PAN) was dried in air for enough time, and then it was kept in a desecrator. Finally the polymer (PAN) was collected in a specific Erlenmeyer flask to use.

3.5- Adsorption Experiments

3.5.1- The effect of contact time

In the effect of contact time experiments the pH(4.0), Temperature (the room temperature 18-24 ^{o}C), and concentration (100ppm,200ppm) were fixed and the time was varied by measuring the amount of Hg^{+2} adsorbed on polyaniline(PAN) surface by using the following times (1hr, 3hrs, 6hrs, 12hrs, and 24 hrs)

0.1 gr of the polymer(PAN) was added to 50ml of $Hg(NO_3)_2$ solution in five Erlenmeyer flasks with 200ppm, and then the five Erlenmeyer flasks was putted on centrifuge for 1hr (Erlenmeyer flask 1), for 3hrs (Erlenmeyer flask 2), for 6hrs (Erlenmeyer flask 3), for12 h (Erlenmeyer flask 4), and finally for 24hrs (Erlenmeyer flask 5). Finally the polyaniline was filtrated, and dried in air and in vacuum. Polyaniline (PAN) solid samples were collected in a special Erlenmeyer flasks for measuring (FTIR, XRD, SEM, XPS) spectrum. The supernatant was putted in a special tubes to measuring the residual amount of Hg^{+2} by the analyzer system, removal, and the range of Hg^{+2} adsorption on polyaniline (PAN) surface depending on the contact time.

Table (3.4). The effect of contact time on mercury adsorption on PAN surface using 200 ppm of $Hg(NO_3)_2$ (aq). n =3

NU	Weight. (gr)	Volume. (ml)	Time. (h)	pH	Conc. (ppm)
1	0.1	50	1	4	200
2	0.1	50	3	4	200
3	0.1	50	6	4	200
4	0.1	50	12	4	200
5	0.1	50	24	4	200

The same procedure was repeated with other concentration (100ppm).

Table (3.5). The effect of contact time of mercury adsorption on PAN surface using 100 ppm $Hg(NO_3)_2$ (aq). n=3

Nu	Weight .gr	Volume.ml	Time .h	pH	Conc.ppm
1	0.1	50	1.00	4	100
2	0.1	50	3.00	4	100
3	0.1	50	6.00	4	100
4	0.1	50	12.00	4	100
5	0.1	50	24.00	4	100

3.5.2-The effect of concentration of Hg (II)

In this experiment the equilibration time was fixed at (6hrs), temperature (at room temperature 18±3^{O}C), and the pH at (4.0) , and the concentration was varied as following:

0.1 gr of polyaniline (PAN) was added to several concentrations of Hg(II) solutions (0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0,8.0,and 10.0)ppm in 10 Erlenmeyer flasks after that the ten flasks were centrifuged for 6hrs, and then the polyaniline (PAN) was filtrated and dried on air and under vacuum.

All of the polyaniline (PAN) solid samples were collected in a special containers for measuring (FTIR, XRD, SEM, XPS) spectrum, and the supernatant was collected in a special tubes for measuring the residual amount of Hg^{+2} by mercury analyzer system, to calculate the % removal, and range of adsorption depending on concentration of mercury(Hg^{+2}). The results are shown in table (3.6).

Table (3.6).The effect of concentration on mercury adsorption on PAN surface.n=3

Nu	Wt. (gr)	Vol. (ml)	Time. (h)	Conc. (ppm)	Ph
1	0.1	50	6	0.2	4
2	0.1	50	6	0.4	4
3	0.1	50	6	0.6	4
4	0.1	50	6	0.8	4
5	0.1	50	6	1.0	4
6	0.1	50	6	2.0	4
7	0.1	50	6	4.0	4
8	0.1	50	6	6.0	4
9	0.1	50	6	8.0	4
10	0.1	50	6	10.0	4

3.5.3- The effect of pH

In this experiment the concentration (1.0, 10.0)ppm, the temperature (room temperature)(18±4°C), the time (6hrs) were fixed, and the pH effect was varied for Hg^{+2} solutions as the following:

0.1 g of polyaniline (PAN) was added to 50 ml of (1.0 ppm,10.0 ppm) $Hg(NO_3)_2$ solution. The pH values was varied (2, 4, 5, 6, 7,and 8) in 6 Erlenmeyer flasks with 1.0 ppm Hg(II) ions, and then the 6 Erlenmeyer flasks were centrifuged for 6 hr. After 6hrs the polyaniline

powder was filtrated and dried on air and on vacuum. All of the polyanilne (PAN) solid samples were collected in a special test tubes for measuring (FTIR, XRD, SEM, XPS) spectrum, and the supernatant was collected in other small tubes for measuring the residual amount of Hg^{+2} using mercury analyzer system, and the range of adsorption data is depending on the pH values, as shown in tables (3.7, 3.8, 3.9).

3.5.3.1 -for 1.00ppm Hg (II)

Table (3.7). The effect of pH on mercury adsorption on PAN surface at 1 ppm con, of $Hg(NO_3)_2$ (aq). n=3

Nu	**Wt. (gr)**	**Vol. (ml)**	**T. (h)**	**pH**
1	0.1	50	6	2
2	0.1	50	6	4
3	0.1	50	6	5
4	0.1	50	6	6
5	0.1	50	6	7
6	0.1	50	6	8

Same procedures were repeated with other concentration (10.0 ppm).

3.5.3.2 -for 10 ppm Hg (II).

Table (3.8).The effect of pH on mercury adsorption on PAN surface at 1 ppm con, of $Hg(NO_3)_2$ (aq).

Nu	Wt. (gr)	Vol. (ml)	T. (h)	pH
1	0.1	50	6	2
2	0.1	50	6	4
3	0.1	50	6	5
4	0.1	50	6	6
5	0.1	50	6	7
6	0.1	50	6	8

3.5.4-The effect of Ionic Strength

In this experiment the temperature (room temperature 18-24), pH value (4.2), and the contact time (6hrs) were fixed, and the ionic strength was varied. (0.02, 0.2,1.0) M of $NaNO_3$ solution were added as individual for three times as following:

0.1 gr of polyaniline (PAN) was added to 50 ml of (0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0)ppm $Hg(NO_3)_2$ in 10 Erlenmeyer flasks with 10 ml 0.02 $NaNO_3$, and the 10 Erlenmeyer flasks were putted on centrifuge for 6 hrs, and then the polymer(PAN) was dried after filtration, and it was collected in a special test tubes for measuring (FTIR, XRD, SEM, XPS) spectrum, and the supernatant was collected in a special tubes to measuring

the residual amount of mercury Hg^{+2} by the mercury analyzer system, and then the % removal was calculated, and the adsorption data results is depended on the ionic strength as shown in tables (3.9, 3.10, 3.11).

Table (3.9). The effect of ionic strength on mercury adsorption at 0.02 M N_aNO_3. n=3

Nu	**Wt**	**Vol. ml**	**T. h**	**pH**	**Conc. $Hg(NO_3)_2$. (ppm)**	**Conc. of N_aNO_3.M**
1	0.1	50	6	4	0.2	0.02
2	0.1	50	6	4	0.4	0.02
3	0.1	50	6	4	0.6	0.02
4	0.1	50	6	4	0.8	0.02
5	0.1	50	6	4	1.0	0.02
6	0.1	50	6	4	2.0	0.02
7	0.1	50	6	4	4.0	0.02
8	0.1	50	6	4	6.0	0.02
9	0.1	50	6	4	8.0	0.02
10	0.1	50	6	4	10	0.02

Same procedures were repeated with other concentration (0.2) M.

Table (3.10) The effect of ionic strength on mercury adsorption at 0.2 M N_aNO_3. n=3

Nu. of sample	Wt. of polymer.gr	V. of $Mg(NO_3)_2$ Ml	T. of shaking.h	PH values	Conc. of $Mg(NO_3)_2$ PPM	Conc. $NaNO_3$ M
1	0.1	50	6	4	0.2	0.2
2	0.1	50	6	4	0.4	0.2
3	0.1	50	6	4	0.6	0.2
4	0.1	50	6	4	0.8	0.2
5	0.1	50	6	4	1.0	0.2
6	0.1	50	6	4	2.0	0.2
7	0.1	50	6	4	4.0	0.2
8	0.1	50	6	4	6.0	0.2
9	0.1	50	6	4	8.0	0.2
10	0.1	50	6	4	10	0.2

Same procedures were repeated with other concentration (1.0) M.

Table (3.11). The effect of ionic strength onmercury adsorption at1.0 M N_aNO3

Nu.	Wt. of polymer.(g)r	V. of $Mg(NO_3)_2$.(ml	T. of shaking.(h)	pH values	Conc. of $Mg(NO_3)_2$ (ppm)	Conc. $NaNO_3$. M
1	0.1	50	6	4	0.2	1
2	0.1	50	6	4	0.4	1
3	o.1	50	6	4	0.6	1
4	0.1	50	6	4	0.8	1
5	0.1	50	6	4	1.0	1
6	o.1	50	6	4	2.0	1
7	0.1	50	6	4	4.0	1
8	0.1	50	6	4	6.0	1
9	0.1	50	6	4	8.0	1
10	0.1	50	6	4	10	1

3.5.5-Conductivity measurements

the test samples were prepared in the form of disks 10 mm diameter and 1 mm thickness. The DC electrical conductivity was measured by applying 200 volt upon the sample and a standard resistance connected in series. The potential on the standard resistance was measured using a Kiethly 750 multimeter (USA). Heating was conducted using a tubular furnace with a variac transformer. The temperature was measured by using a Chromel Alumel thermocouple. The measuring cell consisted of spring loaded electrodes enclosed in a glass cell. Ohmic behavior was shown to be valid during the experiment.

4.1-Results and Discussions

4.1.1-The Effect of Contact Time

After examining Hg^{+2} adsorption the equilibration time on polyaniline (PAN) surface using mercury analyzer system, the equilibrium concentration (C_e) was calculated, the effect of contact time on the removal concentration was calculated by the following equation:

Removal $Hg^{+2} = C_0 - C_e$ ……4.1

C_0 : Initial concentration

C_e : Equilibrium concentration

After that the removal percent was calculated by the following equation:

$$\% \, Removal = \frac{(Co - Ce)\times}{Co} \times 100 \ldots\ldots\ldots\ldots 4.2$$

$$\% \, Removal = \frac{100 - 47.73}{100} \times 100$$

$$= 52.27 \ \%$$

The results are presented in table 4.1

4.1.1.1-With 100 ppm

Table (4.1): The relation between % removal and contact time (pH = 4, T = 20 ^{0}C, C_0 =100ppm,)

Nu	Equilibrium concentration Ce (ppm)	Removal concentration (ppm)	% Removal	Time (h)
1	47.73	52.27	52.27	1
2	37.85	62.15	62.15	3
3	24.54	75.46	**75.46**	**6**
4	31.33	68.67	68.67	12
5	30.87	69.63	69,63	24

The adsorption time (% removal) was shown in Fig(4.1)

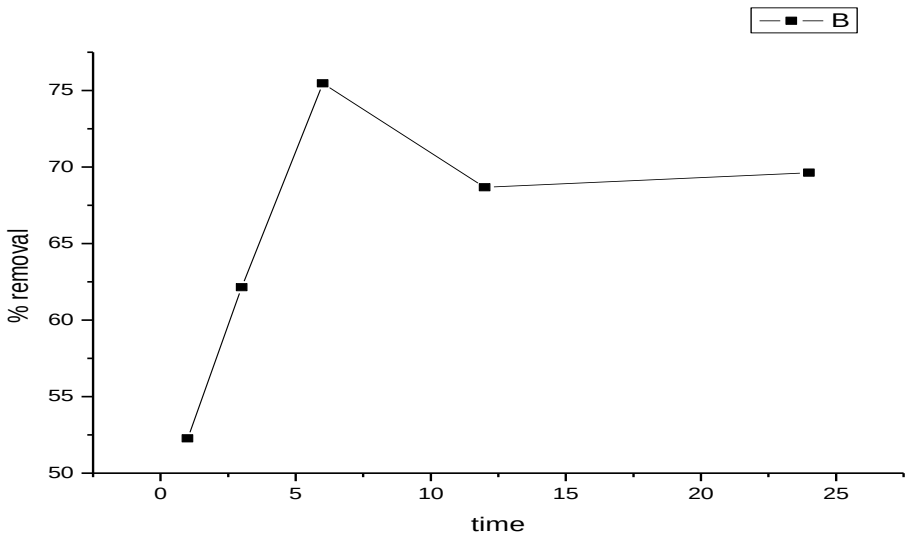


Fig (4.1): The effect of contact time on removal of Hg^{+2} from aqueous solutions for Hg^{+2} percent removal on PAN surface at the initial concentration (100ppm)

From Fig (4.1) it can be seen the optinume Hg^{2+} adsorption equilibration time on polyaniline (PAN) surface was 6hours.

From the initial concentration(C_o), equilibrium concentration (C_e), $Hg(NO_3)_2$ solution volume (V_l), and polyaniline (PAN) weight (Wt.gr) the adsorption capacity at equilibrium (Qe) was calculated by the following equition:

$$\text{Adsorption capacity at equilibrium (Qe)} = \frac{Co-Ce}{Wt.gr} \times Vl \text{.....4.3}$$

$$Qe = \frac{100 - 47.73}{0.1}\ 0.05$$

= 26.135 mg/gr

The results are presented in the table(4.2).

Table (4.2): The relation between adsorption capacity, and contact time.(C = 100ppm, pH = 4, T = 25 ^{0}C)

Time of test (h)	**Adsorption capacity (Qe)**
1	26.135
3	31.075
6	**37.580**
12	34.335
24	34.815

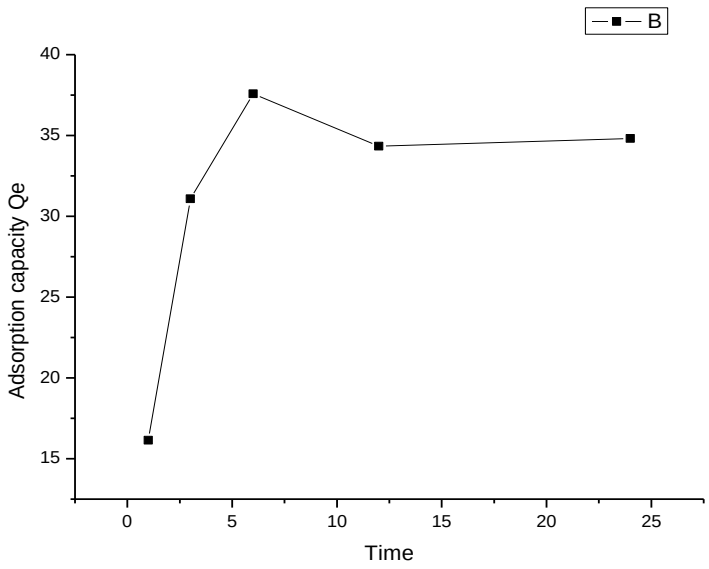


Fig (4.2): The effect of the contact time on Hg^{+2} adsorption capacity at PAN surface (100ppm concentrate on, pH 4, temperature 25)

From the curve (Fig 4.2) was knew that: the best adsorption capacity for the Hg^{2+} on polyaniline (PAN) surface at equilibrium is **37.580**(mg/g).

Same procedures were repeated with other concentration 200 ppm of Hg(II).

4.1.1.2-With 200 ppm

Table(4.3): The relation between % removal, and contact time (200 ppm**,** pH 4, temperature 25)

No of sample	Equilibrium concentration (Ce) ppm	Removal concentration ppm	% Removal	Time h
1	92.68	107.32	53.66	1
2	83.72	116.28	58.14	3
3	80.62	119.38	**59.70**	**6**
4	82.52	117.48	58.74	12
5	82.10	117.90	58.95	24

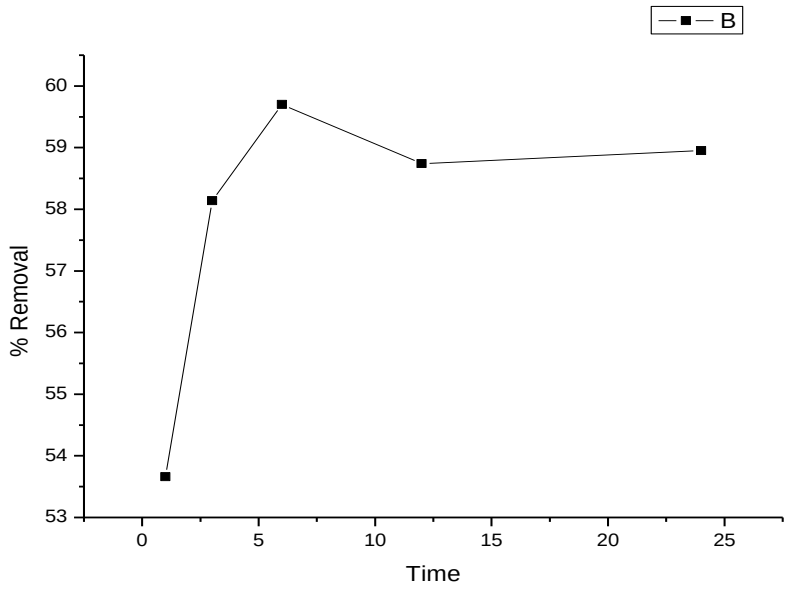


Figure (4.3): The effect of the contact time on % Hg^{+2} removal at PAN surface (200ppm, pH 4, temperature 25)

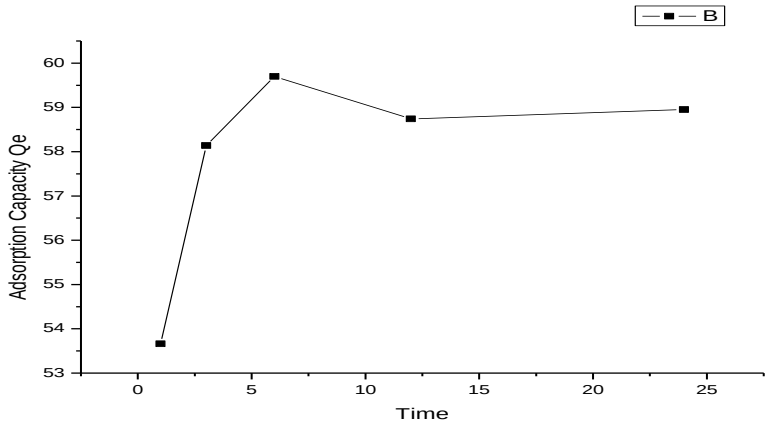
From the results of Fig(4.3), the best adsorption time for Hg^{+2} on (PAN) surface was **6hours.**

After calculation the adsorption capacity at equilibrium (Qe) the results was shown in table (4.4).

Table (4.4): The relation between contact time and adsorption capacity(C = 200ppm, pH = 4, T = 25 ^{0}C)

Time of test (h)	**Adsorption capacity (Qe)(mg/g)**
1	53.66
3	58.14
6	**59.70**
12	58.74
24	58.95

Table (4.4), the best adsorption time for Hg^{+2} on (PAN) surface was **6hours.**



Fig(4.4): The effect contact for Hg^{+2} adsorption capacity on PAN surface at 200ppm of Hg^{+2}

From the results from Fig (4.4), the best adsorption time for Hg^{+2} on PAN surface was **6hrs.**

4.1.2- Results of the effect of concentration of Hg^{+2} ions.

The concentration effect was studied on teu different concentrations of Hg^{+2} (0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0, and 10.0) ppm, the pH, contact time, and temperature were fixed. The percent of removel of Hg(II), and adsorption capacity were calculated by equations (4.1, 4.2, and 4.3) respectively as following:

removal concentration = $C_0 - C_e$

$= 0.2 - 0.0146$

$= (0.1854 \text{ ppm}).$

After that the removal percent (% Removal) was calculated by the following equition:

$$\% \, Removal = \frac{Co - Ce}{Co} \times 100$$

$$= \frac{0.2 - 0.0146}{0.2} \times 100$$

$$= 92.595 \%$$

The result are shown in table (4.5).

Table (4.5).: The relation between % R, and C_0 (pH 4, temperature 25, Time 6hrs)

Nu	Initial concentration (C_0)(ppm)	Equilibrium concentration (C_e) (ppm)	Removal concentration (ppm)	% Removal
1	0.2	0.0146	0.1854	92.595
2	0.4	0.0156	0.3844	93.059
3	0.6	0.0408	0.5592	93.198
4	0.8	0.0490	0.5510	93.867
5	1.0	0.0493	0.9507	95.065
6	2.0	0.0192	1.9808	99.039
7	4.0	0.0232	3.9768	99.418
8	6.0	0.0268	5.9732	99.553
9	8.0	0.0290	7.9710	99.637
10	**10**	0.0342	9.9658	**99.657**

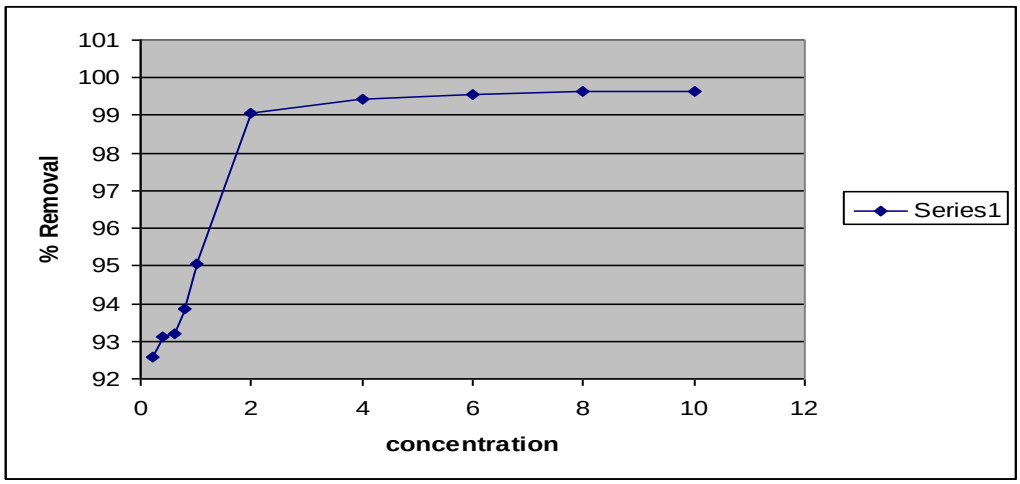


Fig (4.5): The effect of concentration on %Hg^{+2} removal at PAN surface

From the results from Figure (4.5), the best adsorption concentration for Hg^{+2} on (PAN) surface **10** ppm.

The Adsorption Capacity at equilibrium was calculated as following:

$$Qe = \frac{(Co - Ce) \times Vl}{Wt.gr}$$

Qe: Adsorption Capacity at Equilibrium (mg/g).

Co: Initial Concentration (ppm).

Ce: Equilibrium Concentration (ppm).

$$Qe = \frac{(Co - Ce) \times Vl}{Wt.gr}$$

$$Qe = \frac{(0.2 - 0.01465)ppm}{0.1gr} \times 0.05$$

$$Qe = 0.0927 \text{ mg/gr}$$

The result are shown in table(4.6).

Table (4.6): The relation between the adsorption capacity and initial concentrations of Hg^{+2} (pH = 4, T = 25 ^{0}C, Time = 6hrs)

Initial Concentration (Ce) ppm	Adsorption Capacity at Constant (Qe) mg/g
0.2	0.0927
0.4	0.1922
0.6	0.2796
0.8	0.2755
1.0	0.4754
2.0	0.9904
4.0	1.9884
6.0	2.9866
8.0	3.9855
10.0	**4.9829**

Table (4.6) shown in figure(4.6):

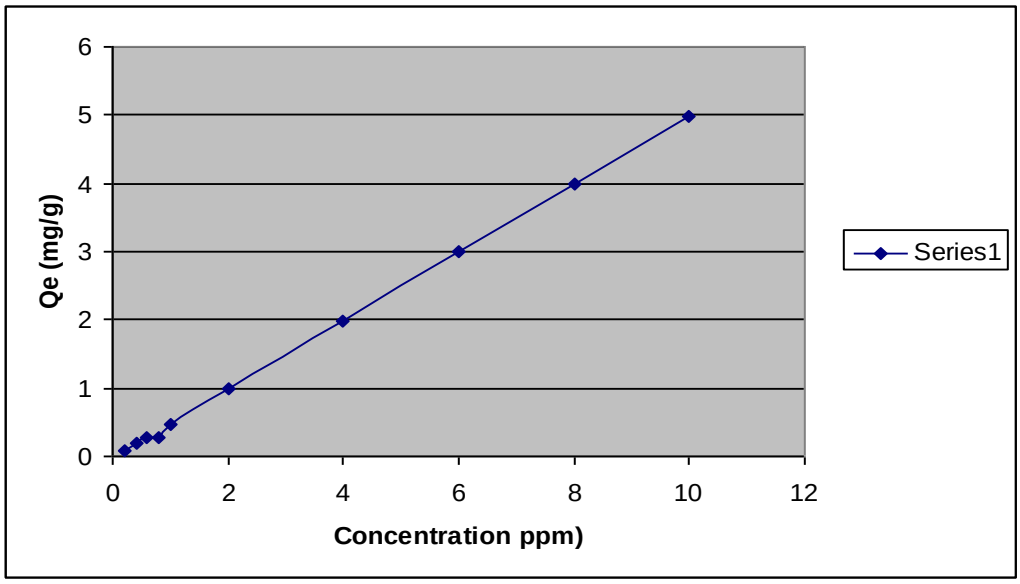


Figure (4.6): The effect of concentration for Hg^{+2} adsorption capacity on PAN surface

From this curve (fig 4.6) was knew that: the best adsorption capacity was at concentration **(10)** ppm

4.1.3- The effect of pH

After examined the Hg^{2+} adsorption pH on polyaniline (PAN) surface, and the equilibrium concentration (Ce) was obtained, %removal of Hg^{+2} was calculated by the following equation:

Removal concentration $= C_o - C_e$

$= 1.0 - 0.00762$

$= 0.99238$ ppm.

After the removal percent was calculated by the following equation:

$$\%\ Removal = \frac{Co - Ce}{Co} \times 100$$

$$= \frac{1.0 - 0.00762}{1.0} \times 100$$

= 99.238 ppm.

Same procedure was repeated and the result are shown in table(4.7).

4.1..3.1 - with 1 ppm Hg^{+2} concentration

The effect of pH was studied on two different concentration of Hg^{+2} (1ppm, and 10ppm). With 1ppm concentration of Hg^{+2}, the results are shown in table (4.7).

Table (4.7): The relation between % removal and different pH values (C_0 = 1ppm, Time = 6hrs, T = 20 ^{0}C,)

Nu	Equilibrium **concentration (ppm)**	**Removal concentration (ppm)**	**% removal**	**PH value**
1	0.00762	0.99238	99.238	2
2	0.00401	0.99599	**99.599**	**4**
3	0.01550	0.98450	98.445	5
4	0.05030	0.94970	94.970	6
5	0.02312	0.97679	97.688	7
6	0.01310	0.98689	98.688	8

From table (4.7) the % removal of Hg^{+2} was calculated at different pH values (2, 4, 5, 6, and 7). The % removal is increased with increase the pH , it reached the optimum value at pH= 4. After that it decreased. This happened because for other ions presens in water.

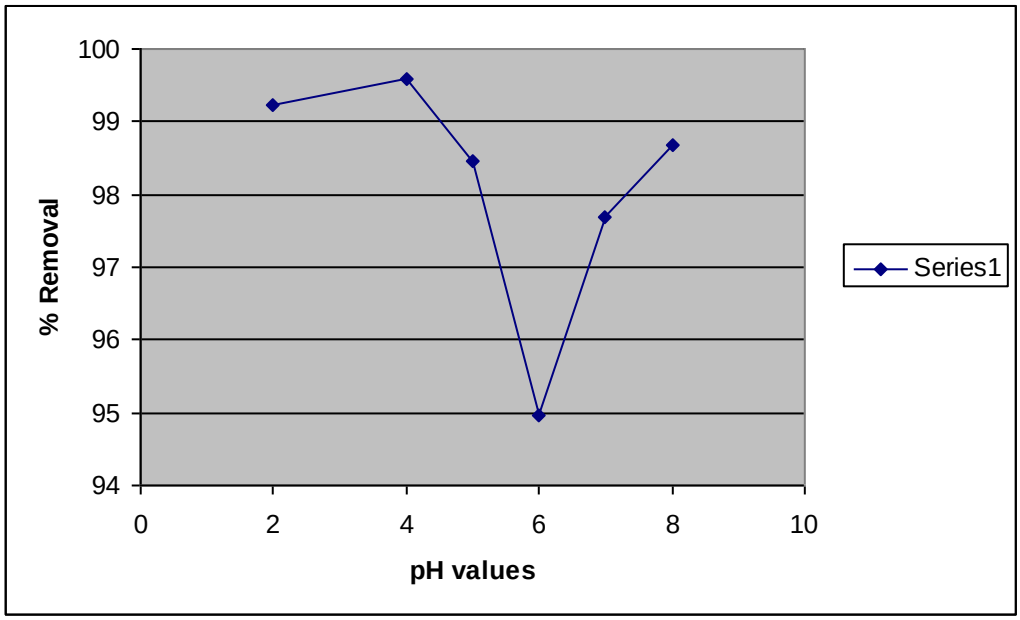


Fig (4.7): The effect of pH value on Hg^{+2} % removal by PAN surface at 1ppm

From this curve fig (4.7) was knew that: the best Hg^{2+} adsorption pH on the polyaniline (PAN) surface was at pH = **4.0**

and from the initial concentration (C_o), equilibrium concentration (C_e), $Hg(NO3)_2$ solution volume (V_l), and polyaniline (PAN) weight (W_t . gr), the adsorption capacity at equilibrium was calculated by the following equation:

$$Adsorption\ capacity\ (Qe) = \frac{Co - Ce}{Wt.gr} \times Vl$$

$$\boldsymbol{Qe} = \frac{(2 - 0.00762)(50)}{0.1(1000)}$$

$$\boldsymbol{Qe} = 0.49619$$

Other results was calculated and shown in table(4.8).

Table (4.8): The relation between Adsorption Capacity and pH values (1 ppm concentration, T = 25 ^{0}C, Time = 6hrs)

pH values	Adsorption Capacity at Constant (Qe) mg/g
2	0.49619
4	**0.49799**
5	0.49225
6	0.47485
7	0.48839
8	0.49344

From the table(4.3.1), the relation between pH and Qe is shown in fig (4.8)

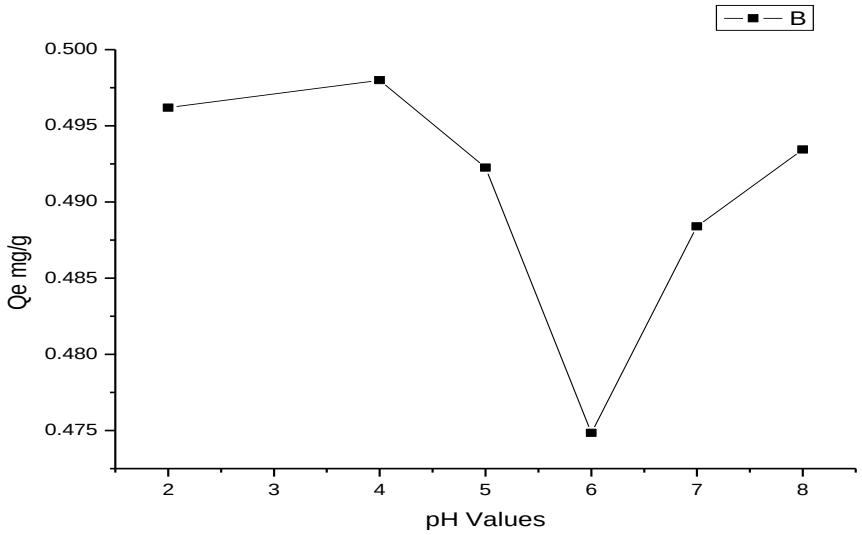


Fig (4.8): The effect of pH value on Hg^{+2} adsorption capacity by PAN

And from this table (4.8), and from fig (4.8) the adsorption capacity at different pH values (2, 4, 5, 6, 7, and 8). The adsorption capacity is increased with increase the pH , after that it reached to optimum value at pH = 4. After that it decreased. This happened because for the other ions presens in water.

4.1.3.2 - 10 ppm Hg^{+2} concentration

With 10ppm concentration of Hg^{+2}, the results are shown in table(4.9)

Table (4.9): the relation between % removal and pH value(C_0 =10ppm, time = 6hrs, T = 20 ^{0}C,)

Nu	Equilibrium concentration (ppm)	Removal concentration (ppm)	% Removal	pH value
1	0.00762	9.9923	98.8522	2
2	0.00401	9.9959	**99.3017**	**4**
3	0.01550	9.9845	98.9347	5
4	0.05030	9.9497	98.8451	6
5	0.02312	9.9768	98.9922	7
6	0.01310	9.9869	99.1398	8

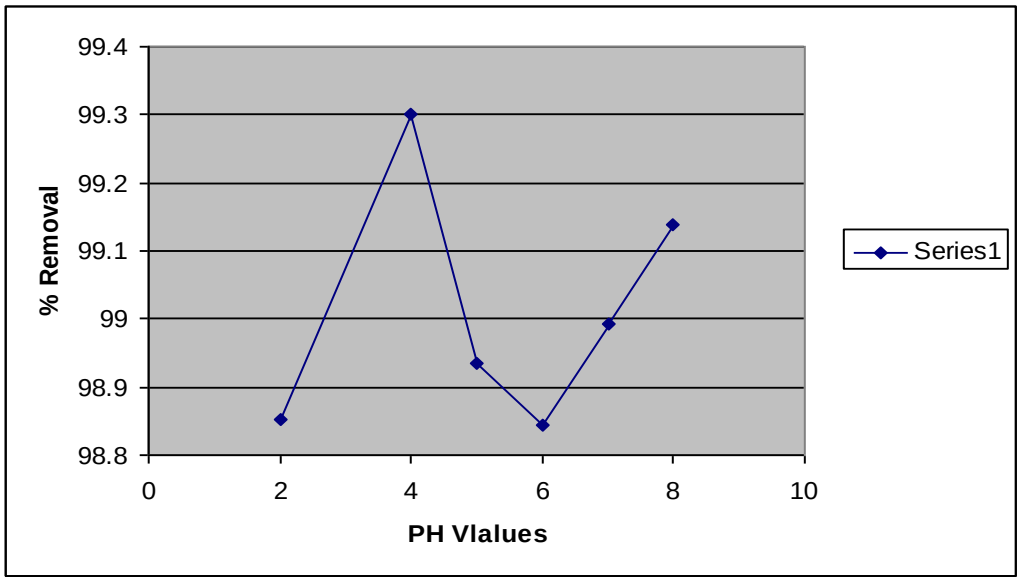


Fig (4.9): The effect of pH value on Hg^{+2} percent removal by PAN surface at 10ppm

From table (4.9) and Fig (4.9) the % removal of Hg^{+2} was calculated at different pH values (2, 4, 5, 6, 7, and 8). The % removal was increased with increase the pH, it reached optimum value at pH = 4. After that it decreased. This happened because for the other ions presens in water.

4.1.3.3 Qe measurements

(Qe) was calculated from the equation 4.2. the relation between pH value and (Qe) was shown in table (4.10), and figure (4.10). From these results the (Qe) (mg/g) is increased to optimum value at pH = 4 after that is decreased.

Table (4.10): The relation between Adsorption Capacity, and pH value.

pH values	Adsorption Capacity at Constant (Qe) mg/g
2	4.9962
4	**4.9979**
5	4.9923
6	4.9748
7	4.9884
8	4.9935

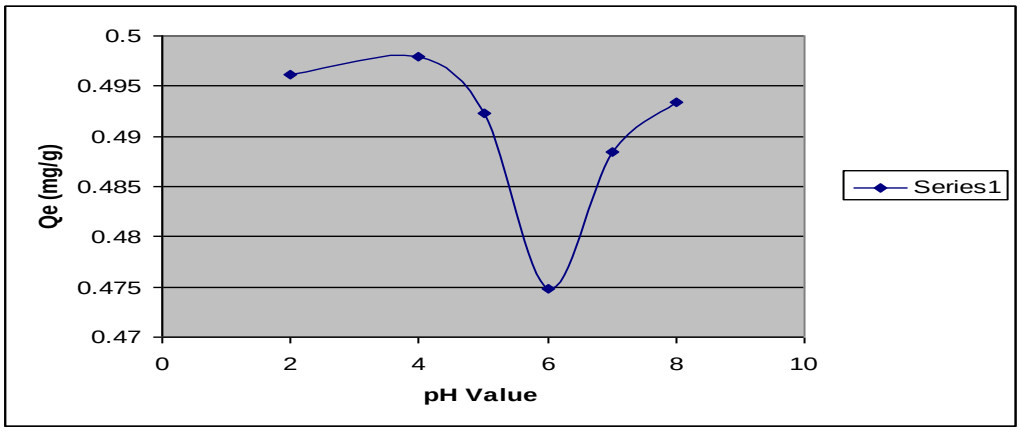


Fig (4.10): The effect of pH value on Hg^{+2} adsorption capacity by PAN surface at 10ppm

From table (4.10), and the Figure (4.10) the Qe (adsorption capacity) of Hg^{+2} was calculated at different pH values (2, 4, 5, 6, 7, and 8). The adsorption capacity (Qe) is increased with increase the pH it reached the optimum value at pH = 4.

4.1.4- Results of effect ionic strength experiment

The effect of the ionic strength on adsorption of Hg^{+2} on (PAN) surface was studied using different concentration of $NaNO_3$ (0.02, 0.20, and 1.00)M.

4.1.4.1 - with 10ml 0.02M N_aNO_3

Table (4.11): the relation between % removal and concentration of Hg^{+2} with 0.02M of $NaNO_3$ as ionic strength(Time = 6hrs, T = 20 ^{0}C, pH = 4)

Nu	Initial concentration (ppm)	Equilibrium concentration (ppm)	Removal concentration (ppm)	% Removal
1	0.2	0.0633	0.1367	68.350
2	0.4	0.0638	0.3362	84.047
3	0.6	0.0642	0.5362	89.299
4	0.8	0.0657	0.7343	91.781
5	1.0	0.0667	0.9333	93.333
6	2.0	0.0670	1.9330	96.650
7	4.0	0.0674	3.9362	98.313
8	6.0	0.0675	5.9325	98.882
9	8.0	0.0678	7.9322	99.152
10	**10**	0.0690	9.9310	**99.310**

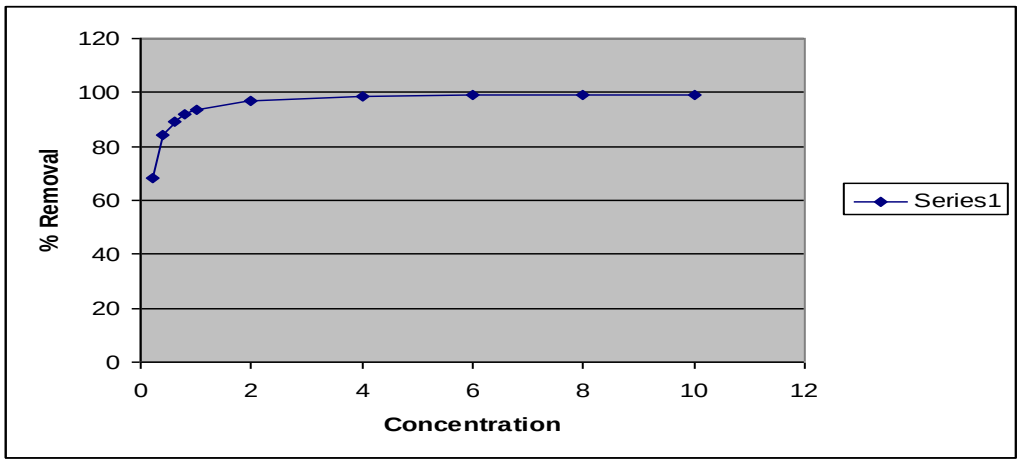


Fig (4.11):The effect of ionic strength on Hg^{+2} % removal by PAN surface at 0.02M of $NaNO_3$

The relation between ionic strength of solution, and % Hg removal are shown in table (4.11), and(4.12), and Figure (4.11), and Figure(4.12), from these results, the % removal, and adsorption capacity is decreased with increase the ionic strength of solution.

Table (4.12): The relation between Adsorption Capacity concentration at Ionic Strength experiment at 0.02 M N_aNO_3

Initial Concentration Co ppm	Adsorption Capacity at Concentration (Qe) mg/g
0.2	0.0684
0.4	0.1681
0.6	0.2681
0.8	0.3672
1.0	0.4667
2.0	0.9665
4.0	1.9681
6.0	1.9681
8.0	3.9661
10.0	**4.9655**

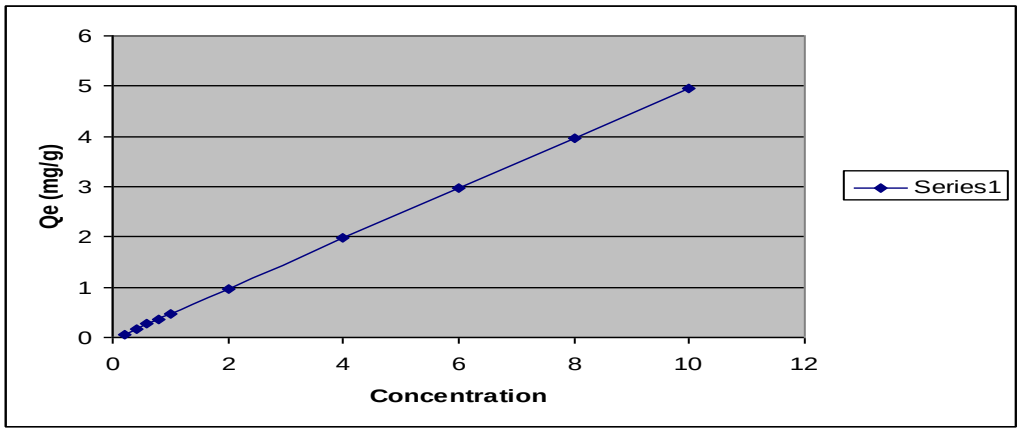


Fig (4.12): the effect of ionic strength on Hg^{+2} adsorption capacity

by PAN surface at 0.02M

Same procedure was done with 0.2 M of $NaNO_3$ as following:

4.1.4.2 - with 10ml 0.2M N_aNO_3

Table (4.14): The results are shown in table(4.14)and Figure(4.13)

Nu	Initial concentration (ppm)	Equilibrium concentration (ppm)	Removal concentration (ppm)	% Removal
1	0.2	0.0731	0.1269	63.440
2	0.4	0.0782	0.3210	80.447
3	0.6	0.1272	0.4728	78.786
4	0.8	0.1098	0.6902	86.274
5	1.0	0.1273	0.8726	87.269
6	2.0	0.1112	1.8888	94.936
7	4.0	0.1151	3.8849	97.122
8	6.0	0.0911	5.9089	98.482
9	8.0	0.1115	7.8885	98.605
10	**10 .0**	0.1335	9.8665	**98.664**

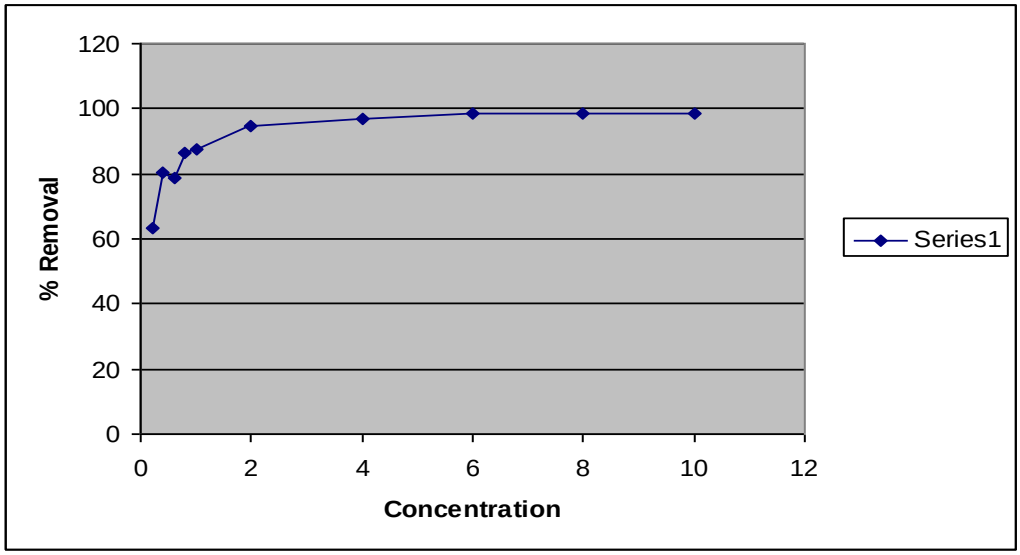


Fig (4.13): The effect of ionic strength on Hg^{+2} % removal by PAN surface at 0.2ppm

Table (4.14): the relation between Adsorption Capacity and Ionic Strength at 0.2 M N_aNO_3

Initial Concentration Co ppm	**Adsorption Capacity at Concentration (Qe) mg/g**
0.2	0.0635
0.4	0.1603
0.6	0.2364
0.8	0.3451
1.0	0.4363
2.0	0.9444
4.0	1.9425
6.0	2.9545
8.0	3.9443
10.0	**4.9333**

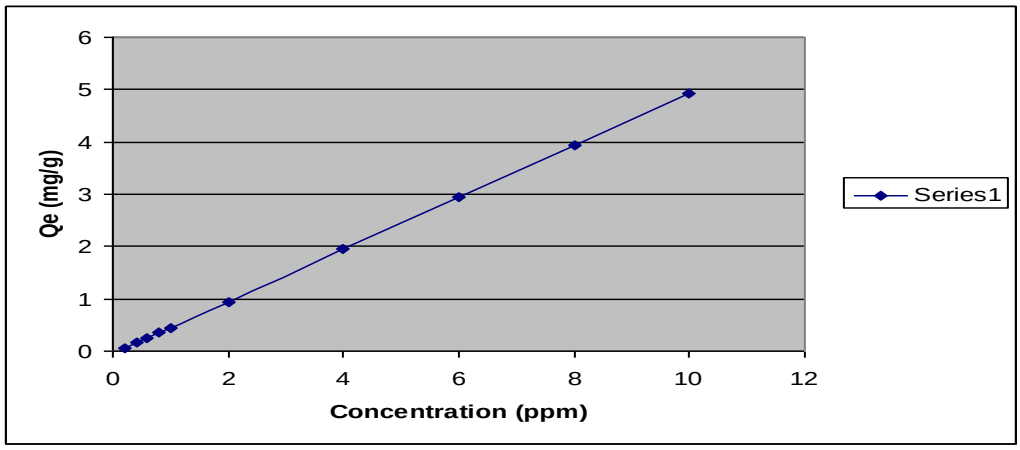


Fig (4.14): the effect of ionic strength on Hg^{+2} adsorption capacity by PAN at 0.2ppm

Same procedure was done with 1.0 M of $NaNO_3$ as following:

4.1.4.3 - with 10ml 1.0 M N_aNO_3

The results are shown in tables(4.15),(4.16) and Figure(4.16),(4.17).

Nu	Initial concentration (Ppm)	Equilibrium concentration (ppm)	Removal concentration (ppm)	% Removal
1	0.2	0.00848	0.19152	95.76
2	0.4	0.01072	0.38928	97.319
3	0.6	0.01201	0.58799	97.998
4	0.8	0.01272	0.78728	98.410
5	1.0	0.01499	0.98501	98.501
6	2.0	0.0173	1.9827	99.134
7	4.0	0.01894	3.98106	99.526
8	6.0	0.03291	5.96709	99.451
9	8.0	0.0328	7.9672	99.59
10	**10**	0.03612	9.96388	**99.638**

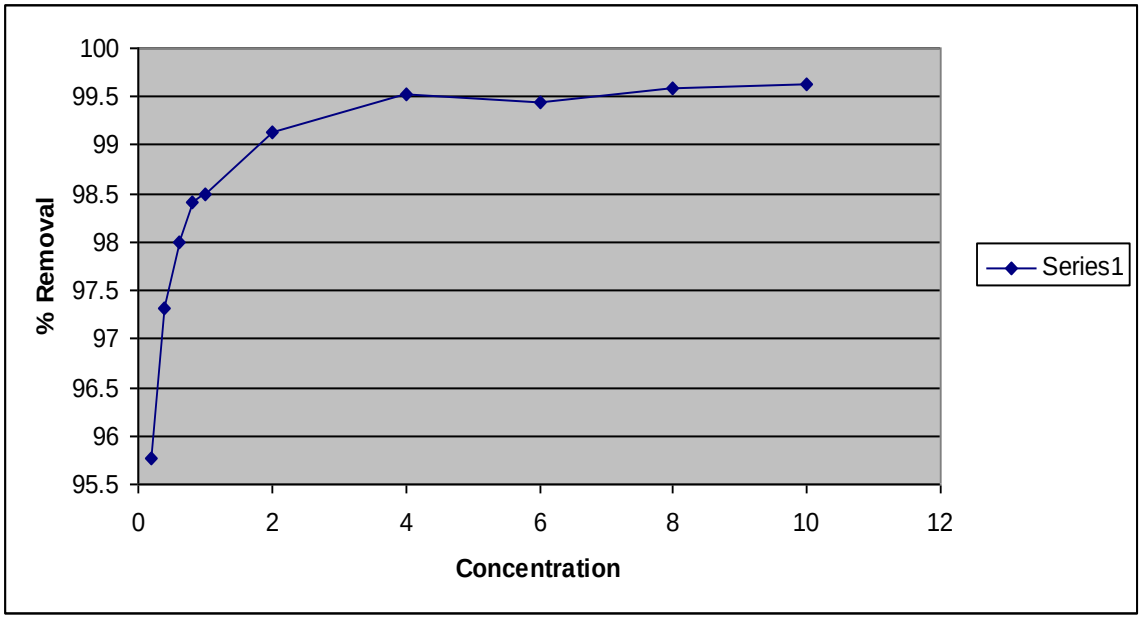


Table (4.16): The relation between Adsorption Capacity, and Ionic Strength at 1.0 M N_aNO_3

Initial Concentration Co ppm	Adsorption Capacity at Concentration (Qe) mg/g
0.2	0.0635
0.4	0.1605
0.6	0.2364
0.8	0.3451
1.0	0.4363
2.0	0.7222
4.0	1.9425
6.0	2.9545
8.0	3.9443
10.0	**4.9333**

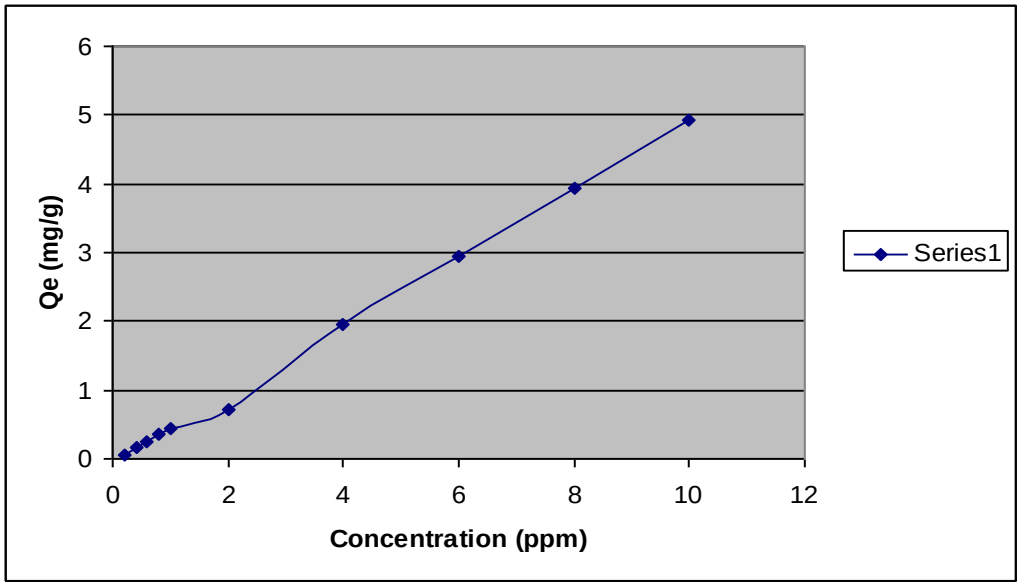


Fig (4.16): the effect of ionic strength on Hg^{+2} adsorption capacity by PAN surface at1.0ppm

4.2- Characterization of PAN and PAN/Hg^{-2}

4.2.1- Conductivity of PAN

The results are shown in tables(4.17) and(4.18).

Polymer	**Conductivity(Ω^{-1} cm^{-1})**
2MHCl	2.476×10^{-6}
1.8MHCl	2.794×10^{-6}
1.5MHCl	8.29×10^{-3}
$2MH_3PO_4$	7.98×10^{-6}
$1.8MH_3PO_4$	1.64×10^{-5}
$1.5MH_3PO_4$	1.89×10^{-5}

4.2.2-The conductivity of PNI/Hg^{+2}

Table (4.18): the conductivity of polyaniline (PAN)/Hg^{+2}

Polymer	**Medium (Oxidant matter)**	**Hg^{+2} Concentration(ppm)**	**Conductivity($\Omega^{-1}cm^{-1}$)**
2MHCl	0.03M $K_2Cr_2O_7$	0.4	6.49×10^{-6}
2MHCl	0.03M$K_2Cr_2O_7$	4.0	8.07×10^{-6}
1.8MHCl	0.03M$K_2Cr_2O_7$	0.4	9.70×10^{-6}
1.8MHCl	0.03M$K_2Cr_2O_7$	4.0	9.43×10^{-6}
1.5MHCl	0.03M$K_2Cr_2O_7$	0.4	9.28×10^{-6}
1.5MHCl	0.03M$K_2Cr_2O_7$	4.0	8.50×10^{-6}
2MH_3PO_4	0.03MKIO_3	0.4	4.46×10^{-6}
2MH_3PO_4	0.03MKIO_3	4.0	4.47×10^{-6}
1.8MH_3PO_4	0.03MKIO_3	0.4	9.23×10^{-6}
1.8MH_3PO_4	0.03MKIO_3	4.0	4.08×10^{-6}
1.5MH_3PO_4	0.03MKIO_3	0.4	8.90×10^{-6}
1.5MH_3PO_4	0.03MKIO_3	4.0	8.20×10^{-2}

From the table (4.17and 4.18) was found that:

1-2M for HCl, H_3PO_4 gives the best results conductivity, with PAN/H_3PO_4, the values were 2.476×10^{-6} $\Omega^{-1}Cm^{-1}$ for PAN/HCl, verses 7.98×10^{-6} Ω^{-1} $Cm^{-1}$for PAN/H_3PO_4

2-With 1.8M for both of acids the advantage was to PAN which prepared by H_3PO_4, the value was 1.64×10^{-5} while with HCl the value was 2.79×10^{-6} $\Omega^{-1}Cm^{-1}$

3-On another hand the 1.5M concentration for the both of acids explain that, the advantage conductivity was to PAN which prepared by the hydrochloric acid (HCl), and the value was 8.29×10^{-3} $\Omega^{-1}cm^{-1}$ while the conductivity of PAN which prepared by H_3PO_4 at the same concentration was 1.89×10^{-3} $\Omega^{-1}cm^{-1}$. So I was used the PAN which prepared by HCl in my work because the best results for conductivity was with the PAN prepared by 1.5M HCl.

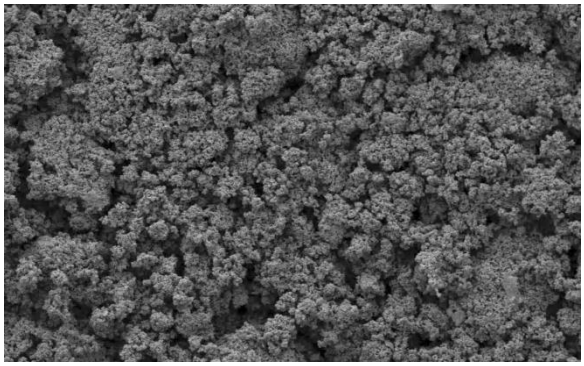
After adsorption, the advantage of the conductivity with both (2, 1.8)M concentration was to the PAN which prepared by HCl, and with 1.5M concentration the best conductivity was to PAN which prepared by HCl with low concentration as apparent in the tables (4.17, 4.18), while with the high concentration the advantage of conductivity was to PAN which prepared by H_3PO_4.

4.2.3-Scanning Electro Microscopic (SEM) of PAN and PAN/Hg^{+2}

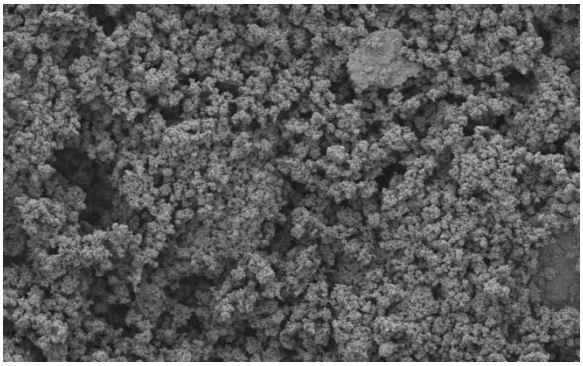
A jeal. SEM 100CX II Model Sanning Electron Microscopic (SEM) was utilized in analyzing the surface structures before and after adsorbed Hg^{+2} ions from aqueous solutions. The resulting micrographs are show before adsorption in figures (27A,27B, 27C,27 E) for PAN prepared by 1.5M HCl, 0.03M $K_2Cr_2O_7$, and 0.25M Aniline, (27B) PAN prepared by 1M H_2SO_4, 0.03M $(NH_4)_2S_2O_8$, 0.25M Aniline, (27C) PAN prepared by 1.5M H_3PO_4, 0.03M KIO_4, 0.25M Aniline, (27D) PAN prepared by 1M CH_3COOH, 0.03 $KMnO_4$, 0.25M Aniline.

The SEM micrograph for PAN/HCl powders has medium globular (rice grain) morphology similar to that previously reported for PAN Colloids. However the bulk powder rice grain features are fused together rather than being discrete particles. But the structure are different from PAN synthesized in CH_3COOH medium, the structure was fibrous and porous Also the sample of PAN – H_3PO_4 has the same morphological, structures of samples of PAN – HCl.

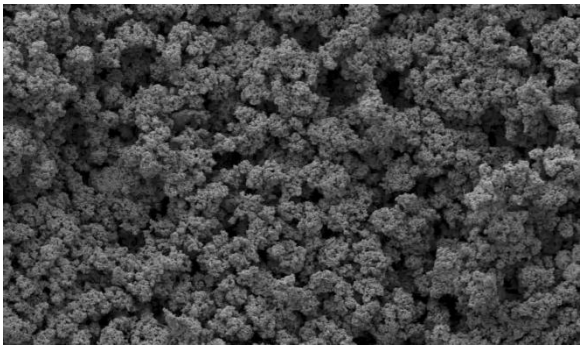
As the observations demonstrate different monomers may yield conductive polymers with different morphological structures even when the same conditions for synthesizing methods one used. The best morphological structure was with PAN synthesized in HCl medium [57]



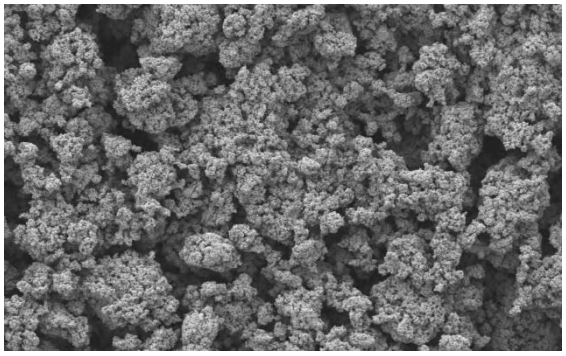
A_0.25M aniline 1.5M HCl 0.03M $K_2Cr_2O_7$



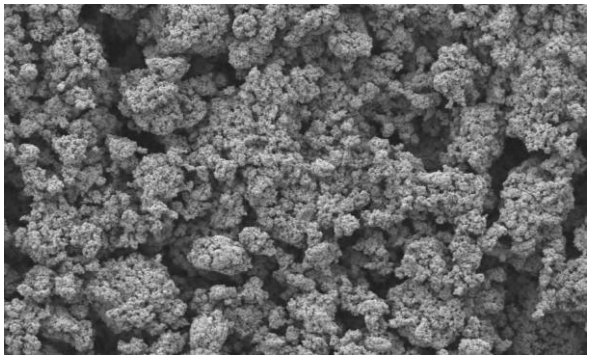
B_0.25M Aniline 1M H_2SO_4 0.03M $(NH_4)_2S_2O_8$



C_0.25M Aniline 1.5M H_3PO_4 0.03M KIO_3



D- 0.25M Aniline 1MCH_3COOH 0.03M $KMnO_4$



E- PAN/Hg^{+2}/1.5M HCl/0.03M $K_2Cr_2O_7$

Fig (4.17): SEM micrograph of PAN-HCl, and PAN-HCl/Hg^{+2}

4.2.4- XRD for PAN/HCl and PAN/HCl/Hg^{+2}

Powders X-ray diffraction observation were made using computer – controlled XRD system, RTNT 1800 Wide angle goniometer at an operating rate of 40 KN and 30 mA Cu Ka radiation λ = 1.54186 nm in the 2θ range of 2 – 80 degree, the step of scanning rate was 0.02 degree of a scan speed to deg/min.

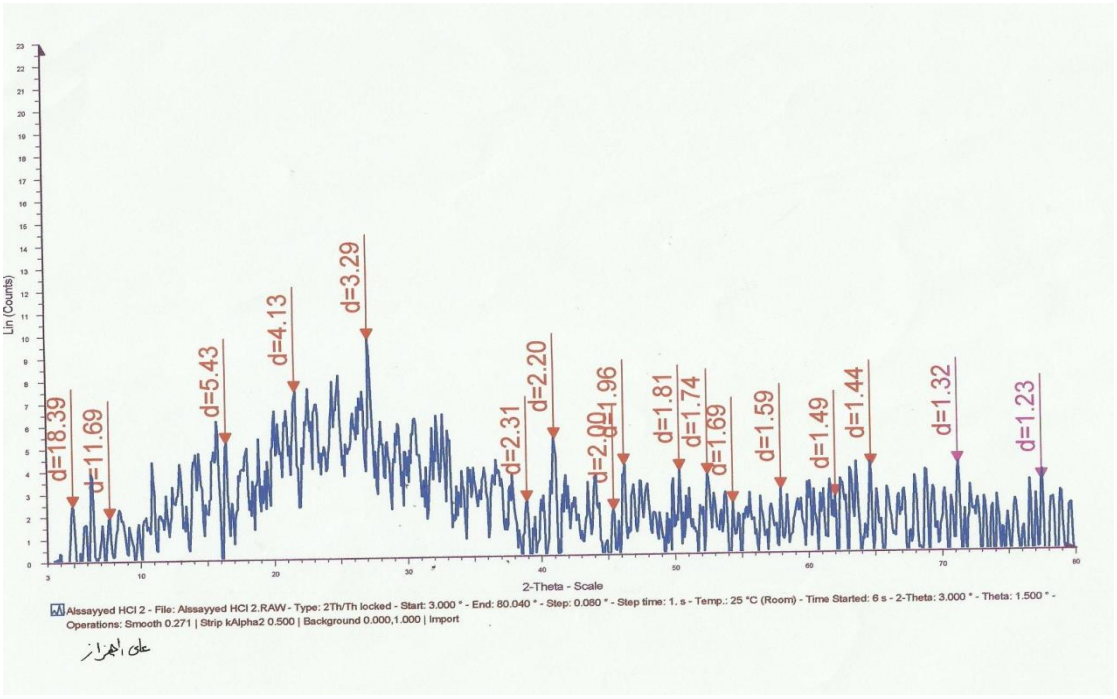
Figure (4.18), show the XRD patterns for PAN-HCl doped with HCl using starting materials (0.03M $K_2Cr_2O_7$, 0.25M Aniline, and 1.5M HCl) on magnetic stirrer, it's the better kind so it was used in the work.

Figure (4.19), show the XRD patterns for PAN-HCl doped with HCl using the same starting materials the oxidation material ($0.0KIO_3$) not on magnetic stirrer (without).

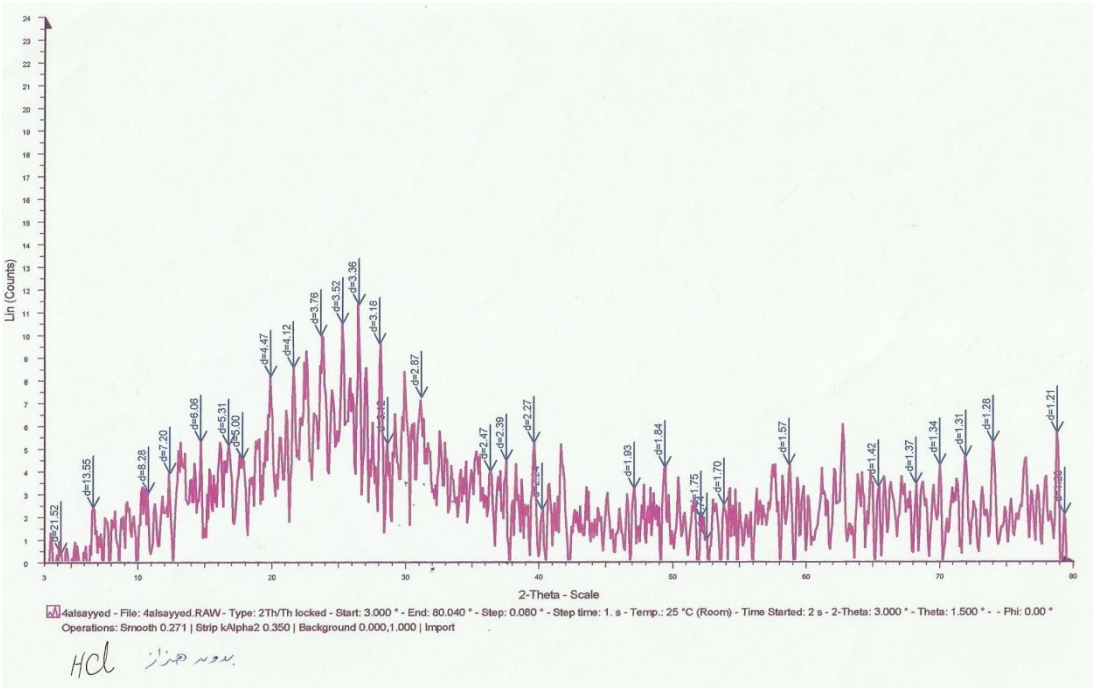
The XRD of PAN clearly suggest that the samples are amorphous in agreement with previous studies [57].

Figure (4.20) show the XRD for PAN after adsorption (100ppm)Hg(II) from aqueous solutions.

The values of peaks fig (4.18) were changed this indicate that the PAN adsorption Hg^{+2} from aqueous solutions. The peaks were at 1.21 and 18.69.

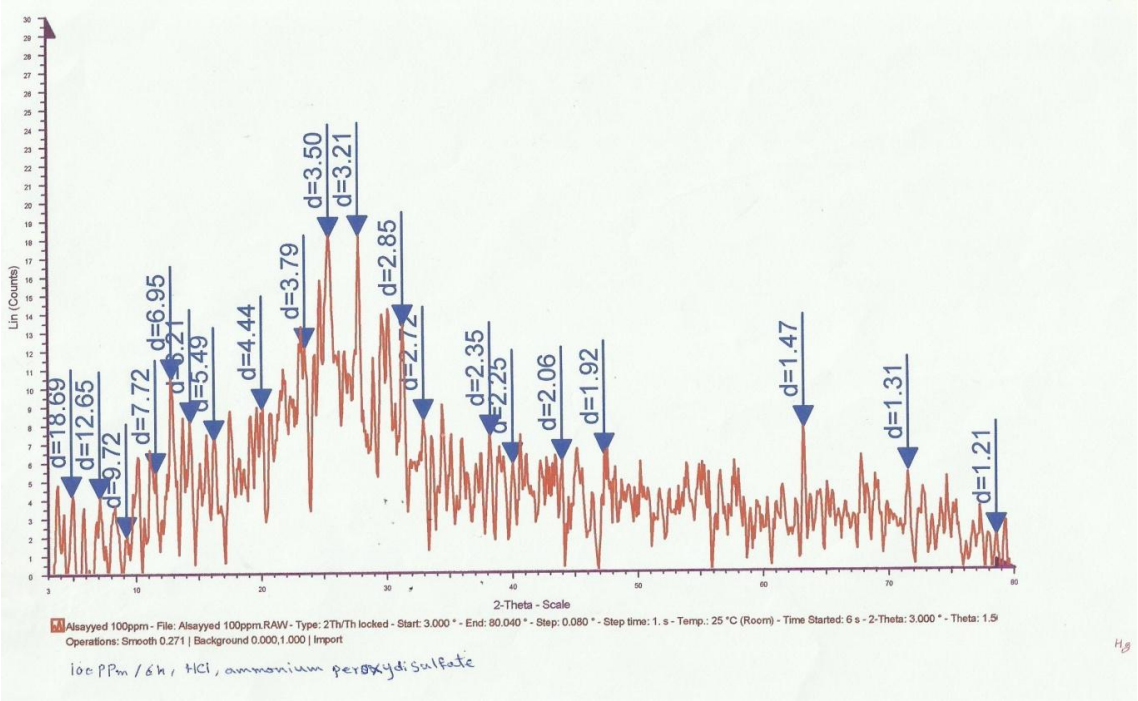


Fig(4.18): XRD for PAN prepared by 1.5M HCl, 0.03M $K_2Cr_2O_7$ on magnetic stirrer system



Fig(4.19): XRD for PAN prepared by 1.5M HCl, 0.03M KIO_3 without magnetic stirrer system

- XRD of PAN-HCl/Hg^{+2}/6hrs/Ph 4



Fig(4.20): XRD for PAN/HCl/Hg^{+2}

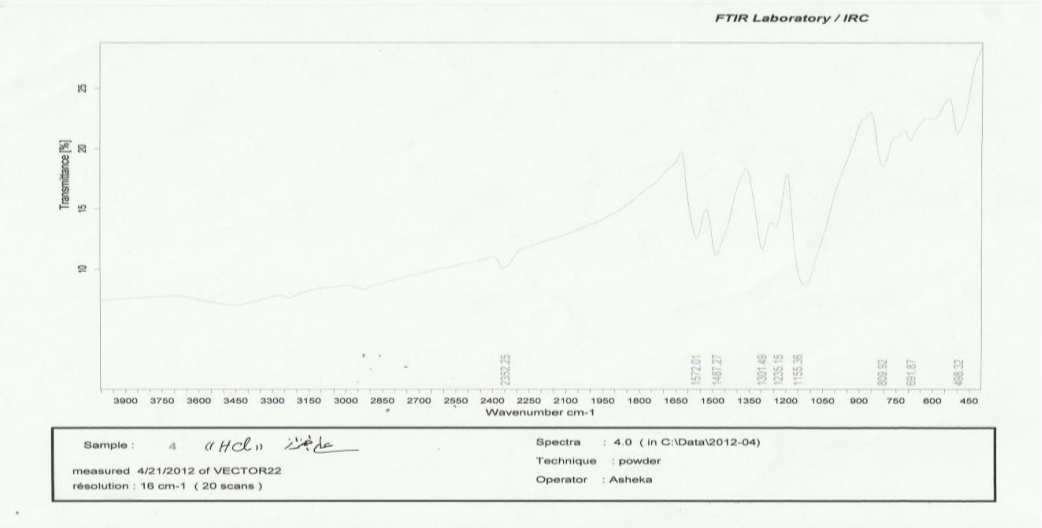
4.2.5-Fourier transform infrared Results (FTIR).

4.2.5.1- FTIR of PAN/HCl, and PAN/Hg^{+2}/HCl

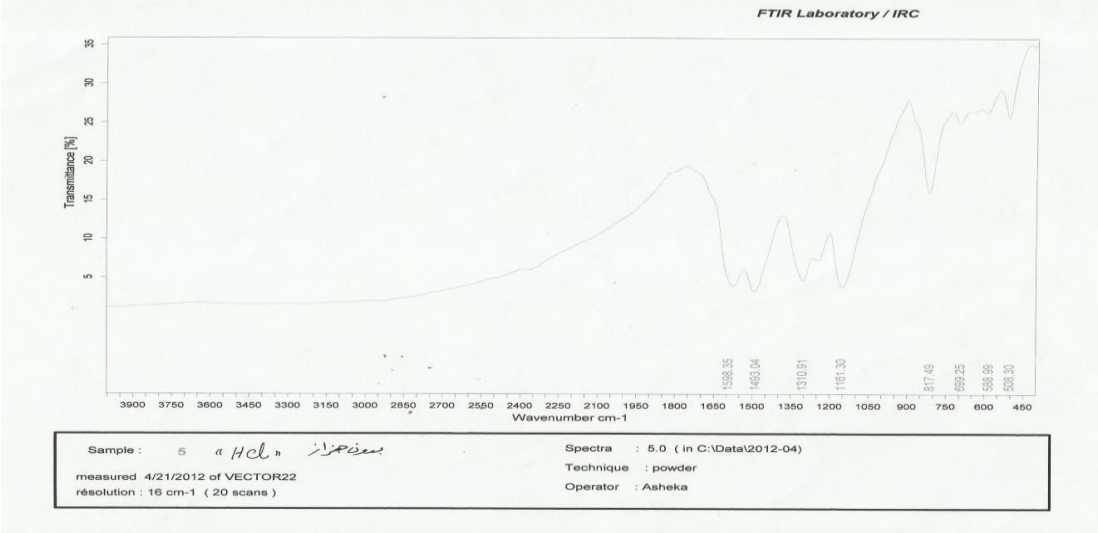
Figure (4.21) shows the FTIR spectra for PAN prepared by using starting materials (0.03M $K_2Cr_2O_7$, 1.5M HCl, and 0.25M Aniline) 0n magnetic stirrer. The kind of use in the work. Figure (4.22) shows the FTIR spectra for PAN prepared with same starting materials without magnetic stirrer.

Figure (4.23) shows the FTIR spectra after adsorption 100ppm (Hg^{+2}) ions from aqueous solutions. FTIR spectra of polyaniline has double peak belonging to $–NH_2$ at approximately 3422 cm^{-1} disappeared or turned into a

single in the polymer. This procures that the polymerization occurs through $-NH_2$ group the peaks also appears at 436.32, 2352 cm^{-1} before adsorption, and 500.70, 2352 cm^{-1} after adsorption also the peaks of FTIR was changed after adsorption Hg^{+2} ions from aqueous solutions.

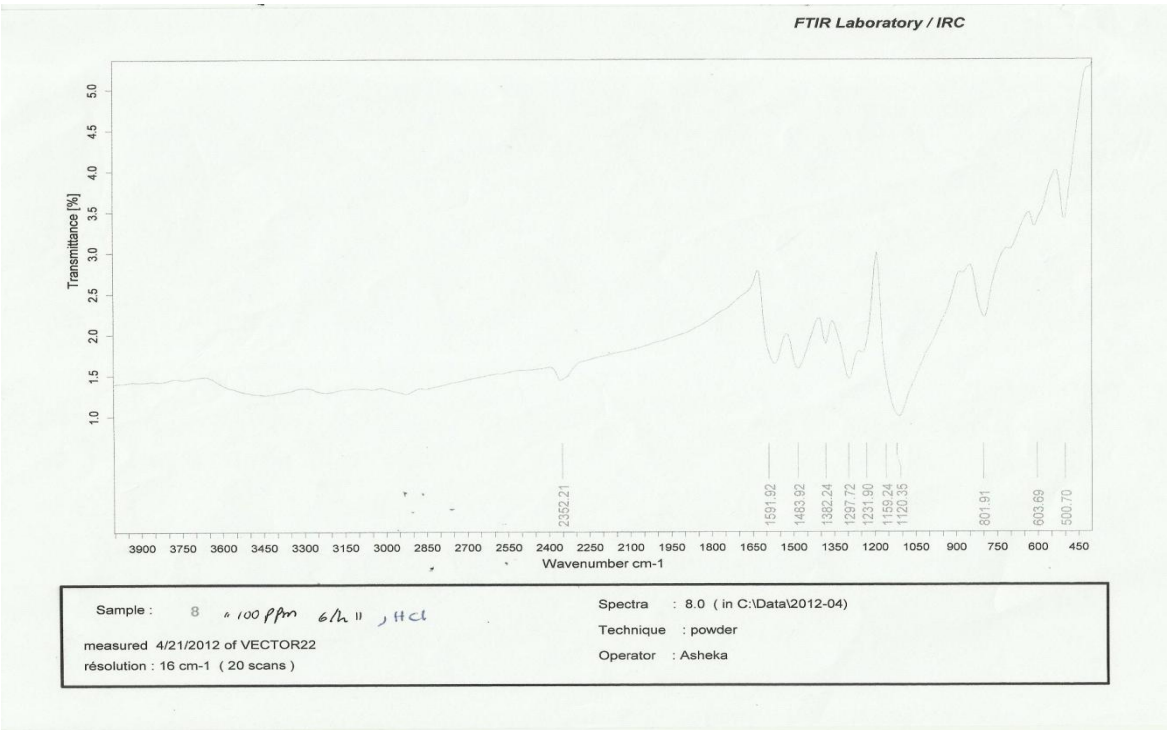


Fig(4.21): FTIR for PAN/HCl on magnetic stirrer system.



Fig(4.22): FTIR for PAN/HCl without magnetic stirrer system.

- FTIR of PAN-HCl/Hg^{+2}/6hrs/pH 4

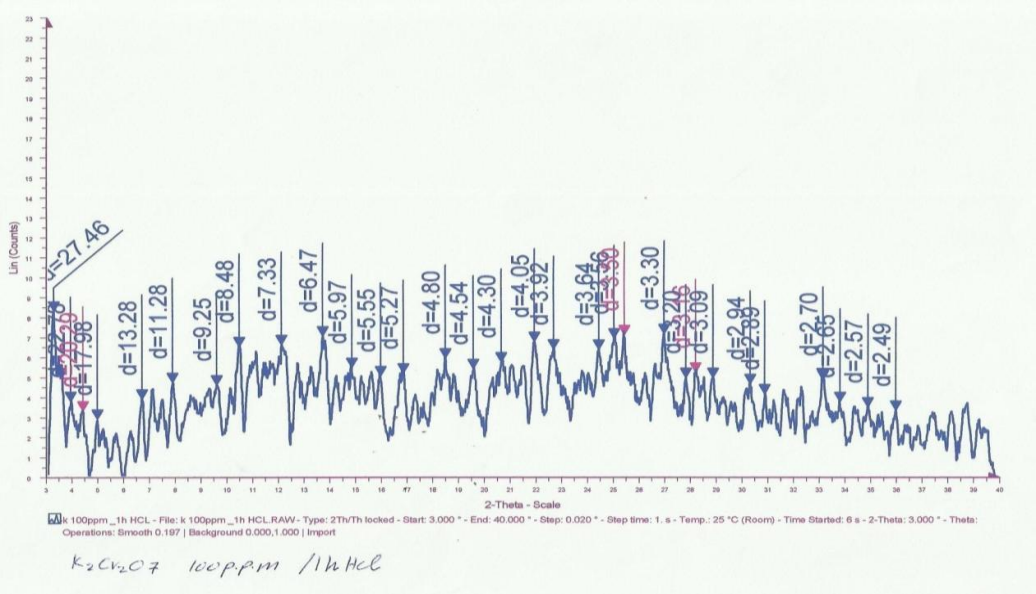


Fig(4.23): FTIR for PAN/HCl/Hg^{+2} with 100ppm concentration for 6hrs

4.2.6- XRD of Hg^{+2} adsorped Hg^{+2} on PAN surface of contact time experiment

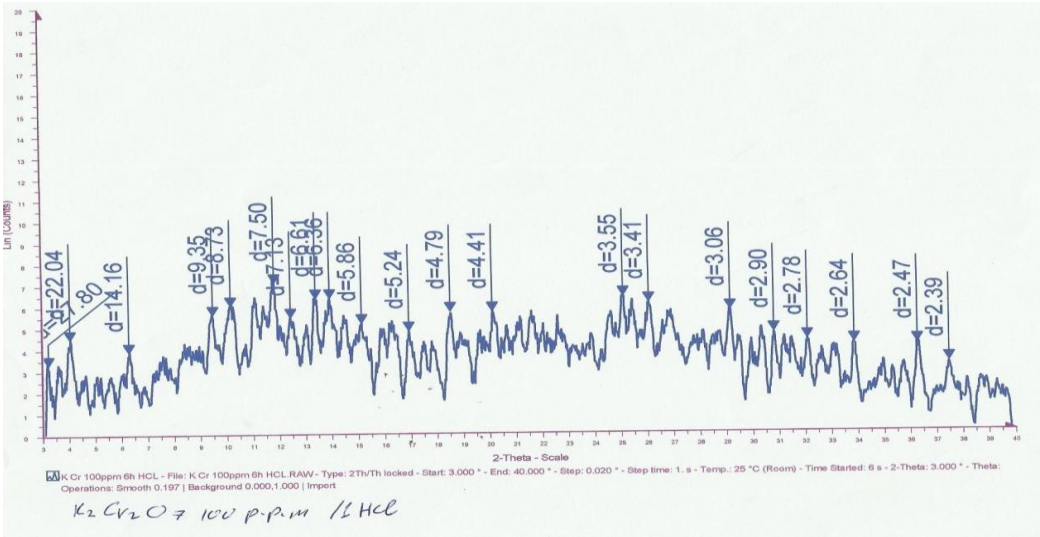
Figures (4.24), (4.25), and (4.26) shows the XRD for the PAN/Hg^{+2} through time experiment at different times (1, 6, and 24)hrs. The best XRD spectra was 6hrs (for adsorption Hg^{+2} ions) with 100ppm concentration of Hg^{+2}. The same procurer was repeated with 200ppm,) and again the best Hg^{+2} adsorption time was **6hrs** in figures (4.27), (4.28), and (4.29) with PAN prepared with another oxidation matter (KIO_3).

- XRD of PAN-HCl/Hg^{+2}/$K_2Cr_2O_7$/ 100ppm of $Hg(NO_3)_2$/ 1h/pH 4



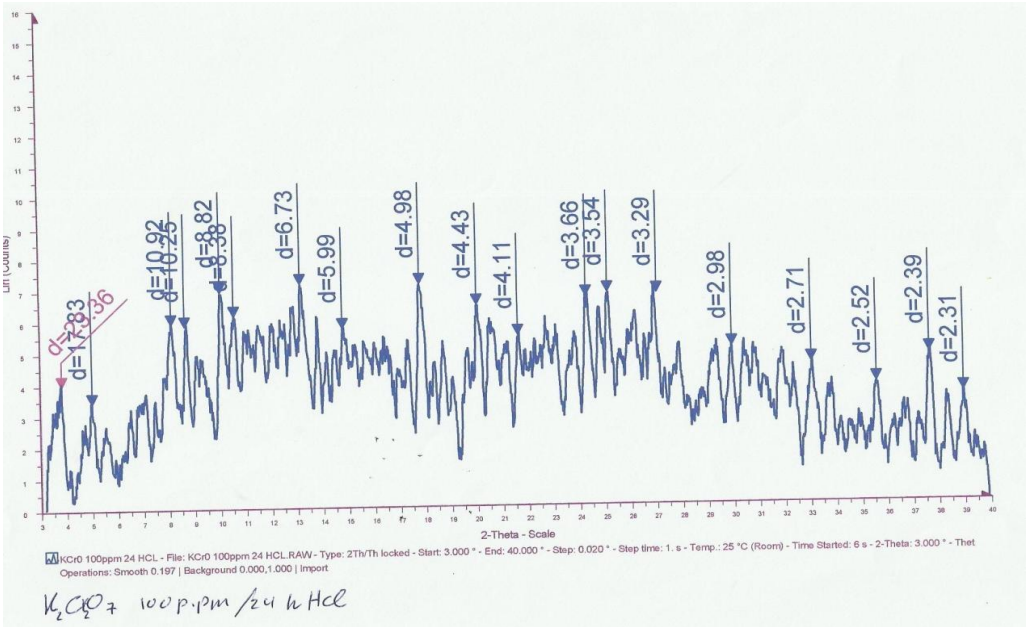
Fig(4.24): XRD for PAN/HCl/$K_2Cr_2O_7$/Hg^{+2} at 100ppm for 1hr

-XRD of PAN-HCl/Hg^{+2} /$K_2Cr_2O_7$/ 100ppm of $Hg(NO_3)_2$/ 6hrs/Ph 4



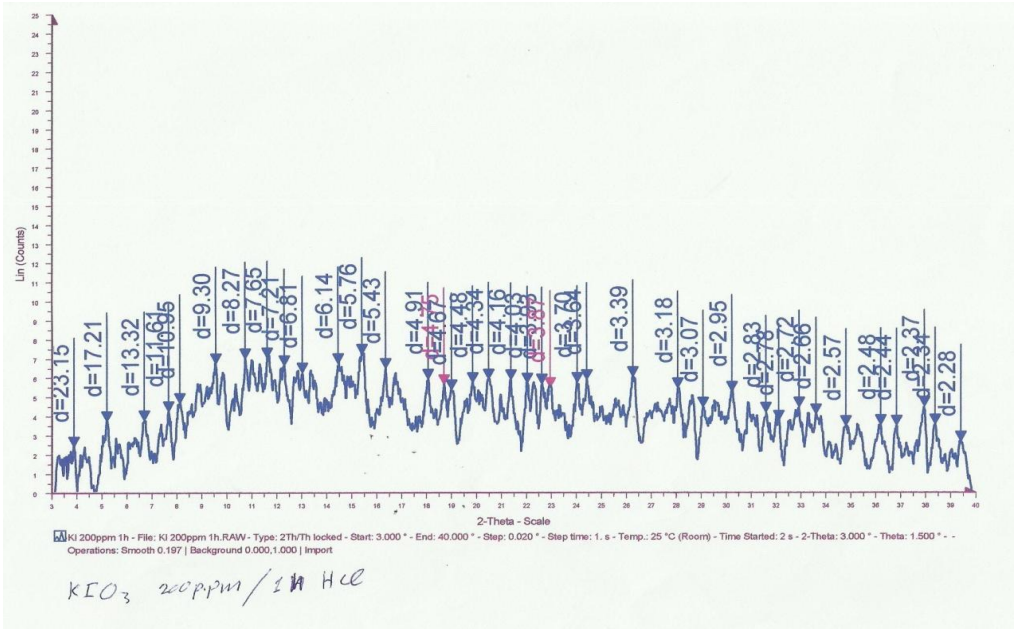
Fig(4.25): XRD for PAN/HCl/$K_2Cr_2O_7$/Hg^{+2} at 100ppm for 6hrs

- XRD of PAN-HCl/Hg^{+2} /$K_2Cr_2O_7$/ 100ppm of $Hg(NO_3)_2$/ 24hrs/pH 4



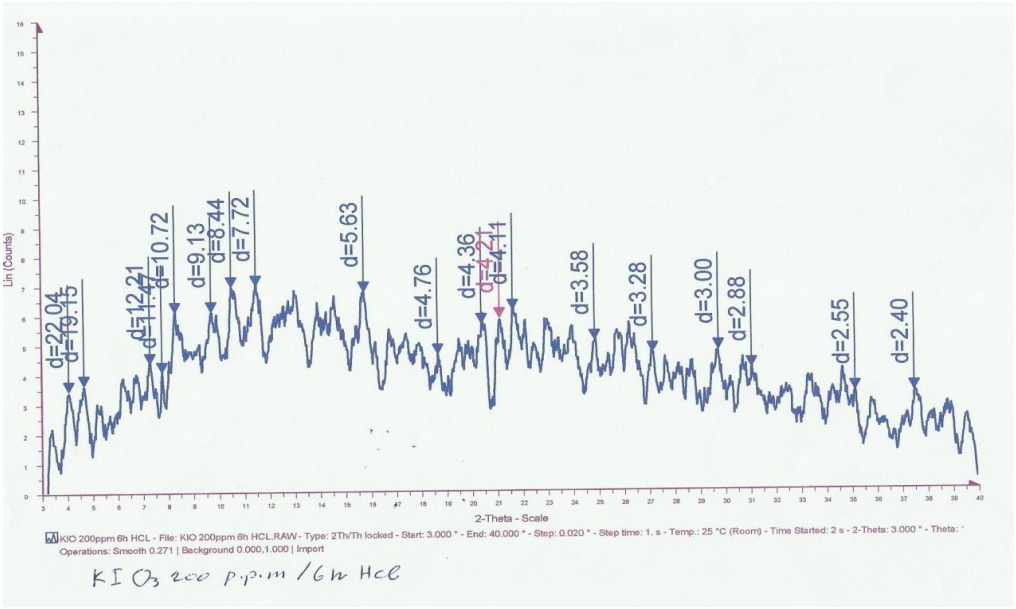
Fig(4.26): XRD for PAN/HCl/$K_2Cr_2O_7$/Hg^{+2} at 100ppm for 24hrs

- XRD of PAN-HCl/Hg^{+2} /KIO_3/ 200ppm of $Hg(NO_3)_2$/ 1h/PH 4



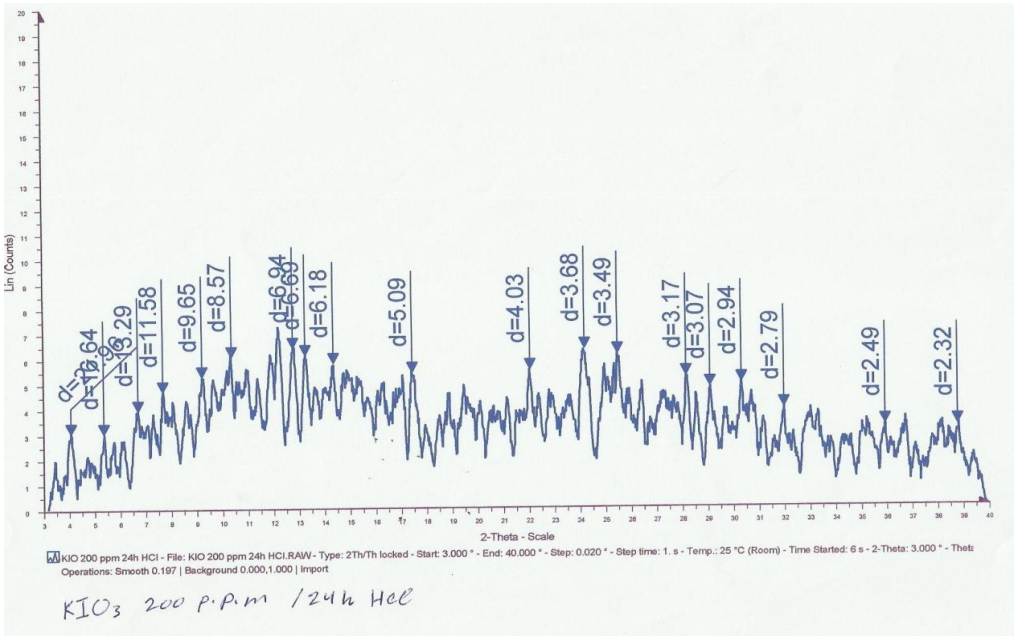
Fig(4.27): XRD for PAN/HCl/KIO_3/Hg^{+2} at 200ppm for 1hr

- XRD of PAN-HCl/Hg^{+2} /KIO_3/ 200ppm of $Hg(NO_3)_2$/ 6hrs/PH 4



Fig(4.28): XRD for PAN/HCl/KIO_3/Hg^{+2} at 200ppm for 6hrs

-XRD of PAN-HCl/Hg^{+2} /KIO_3/ 200ppm of $Hg(NO_3)_2$/ 24hrs/Ph 4

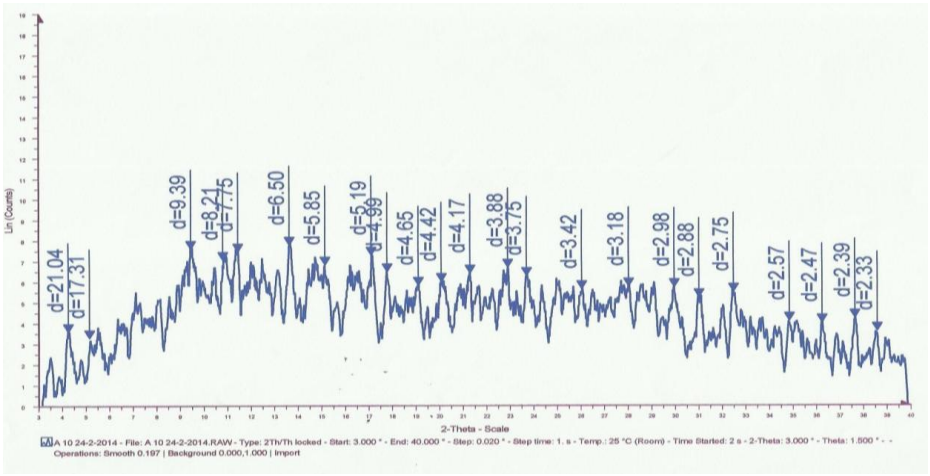


Fig(4.29): XRD for PAN/HCl/KIO_3/Hg^{+2} at 200ppm for 24hrs

4.2.7- XRD of Hg^{+2} adsorbed on PANI and the effect of in nicstruy

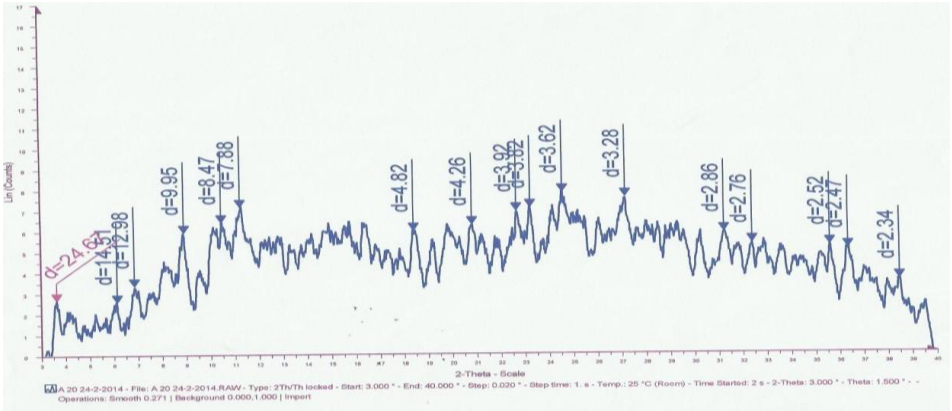
Figures (4.30), (4.31), and (4.32) shows the XRD patterns for PAN/Hg^{+2} at different ionic strength (0.02, 0.2, 1.00)M, and the concentration of Hg^{+2} was 10ppm. The ionic strength experiment explained that increase of ionic strength concentration due to decrease of Hg^{+2} adsorption on PAN surface.

- XRD of PAN-HCl/Hg^{+2} /$K_2Cr_2O_7$/ with 0.02 M $NaNO_3$/Ph 4



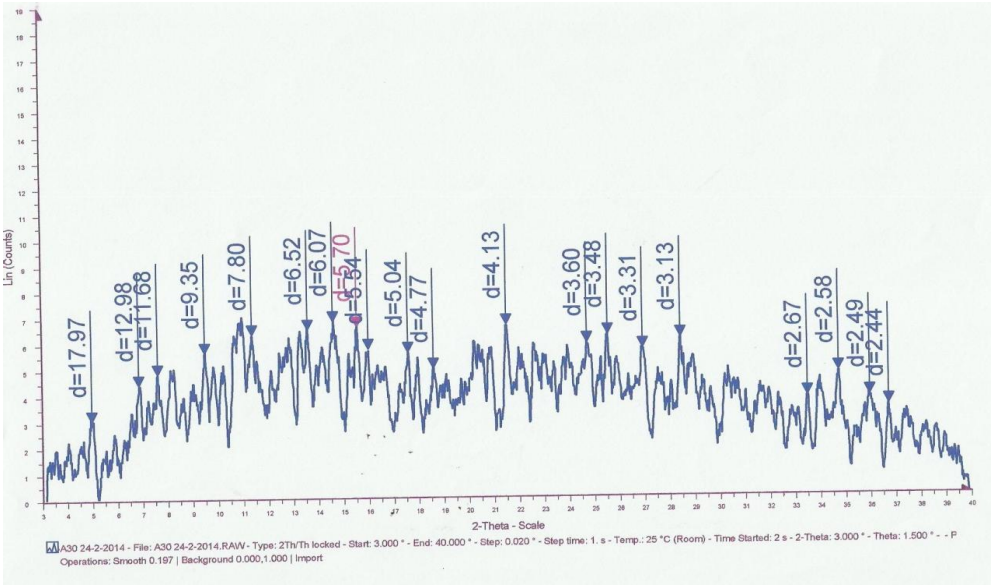
Fig(4.30): XRD for PAN/HCl/$K_2Cr_2O_7$/Hg^{+2}/0.02$NaNO_3$ for 6hrs

- XRD of PAN-HCl/Hg^{+2} /$K_2Cr_2O_7$/ with 0.2 M $NaNO_3$/pH 4



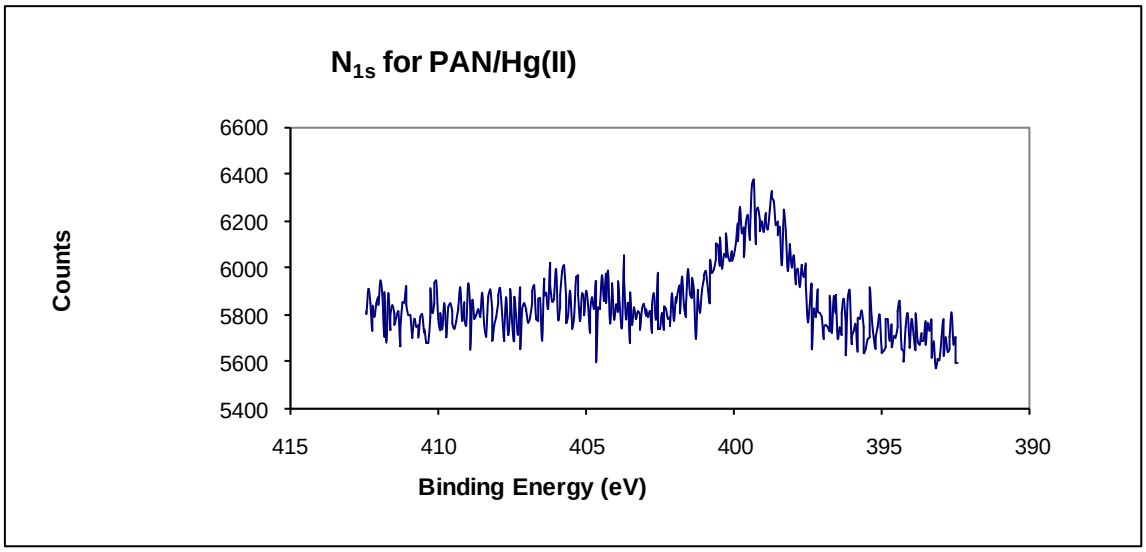
Fig(4.31): XRD for PAN/HCl/$K_2Cr_2O_7$/Hg^{+2}/0.2$NaNO_3$ for 6hrs

- XRD of PAN-HCl/Hg^{+2} /$K_2Cr_2O_7$/ with 1.0 M $NaNO_3$/pH 4



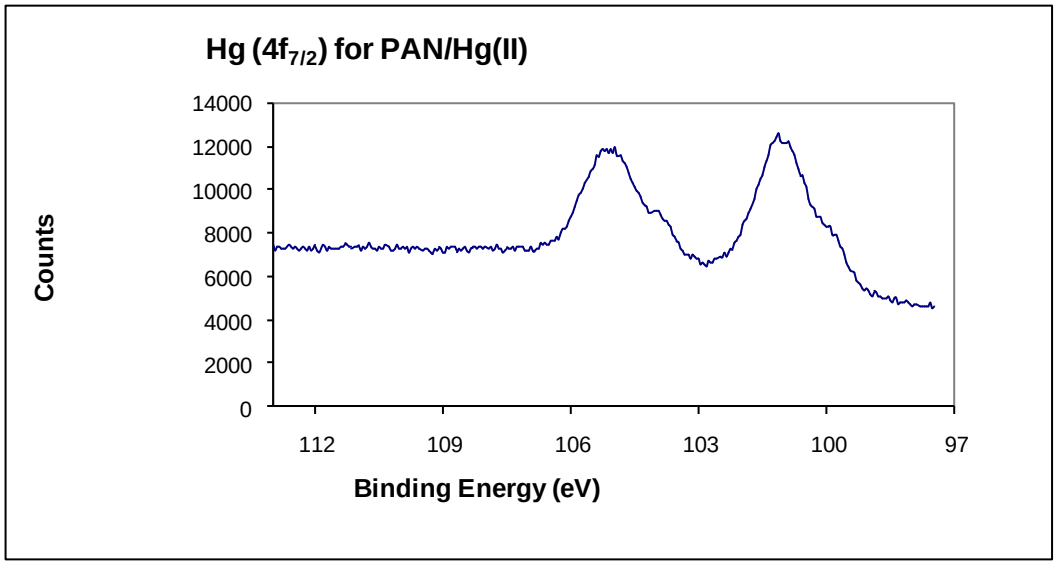
Fig(4.32): XRD for PAN/HCl/$K_2Cr_2O_7$/Hg^{+2}/1.0M$NaNO_3$ for

4.2.8-XPS For PAN and PAN/ Hg^{+2}



Fig(4.33):XPS pans of (PAN) after adsorption of Hg(II) ions

[adsorption time = 6hrs, pH = 4.00, t = 25 ^{0}C, C = 1ppm]



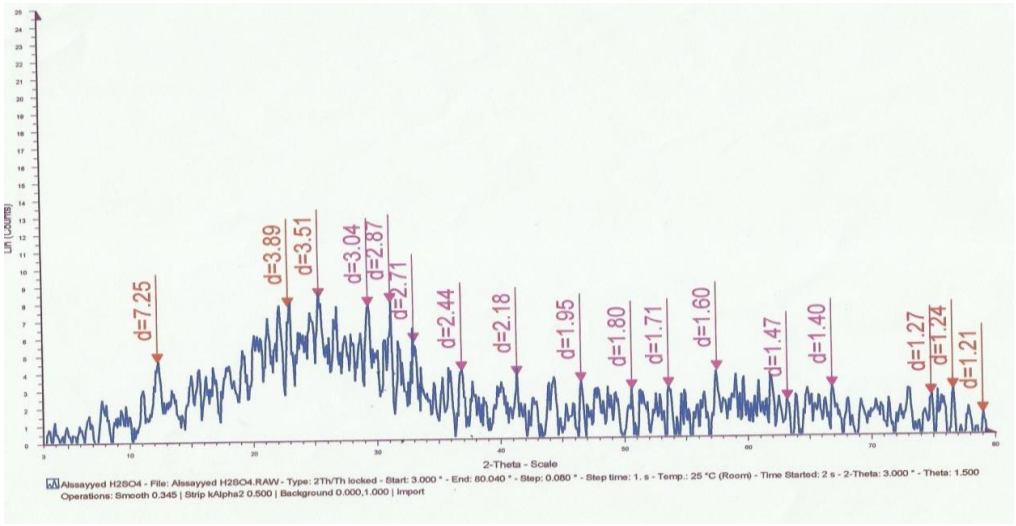
Fig(4.34) XPS pands of N-in (PAN) after adsorption of Hg(II) ions

[adsorption time = 6hrs, pH = 4, t = 25 ^{0}C, C = 1ppmof Hg(II)]

4.2.9- Characterization of PAN-H_2SO_4

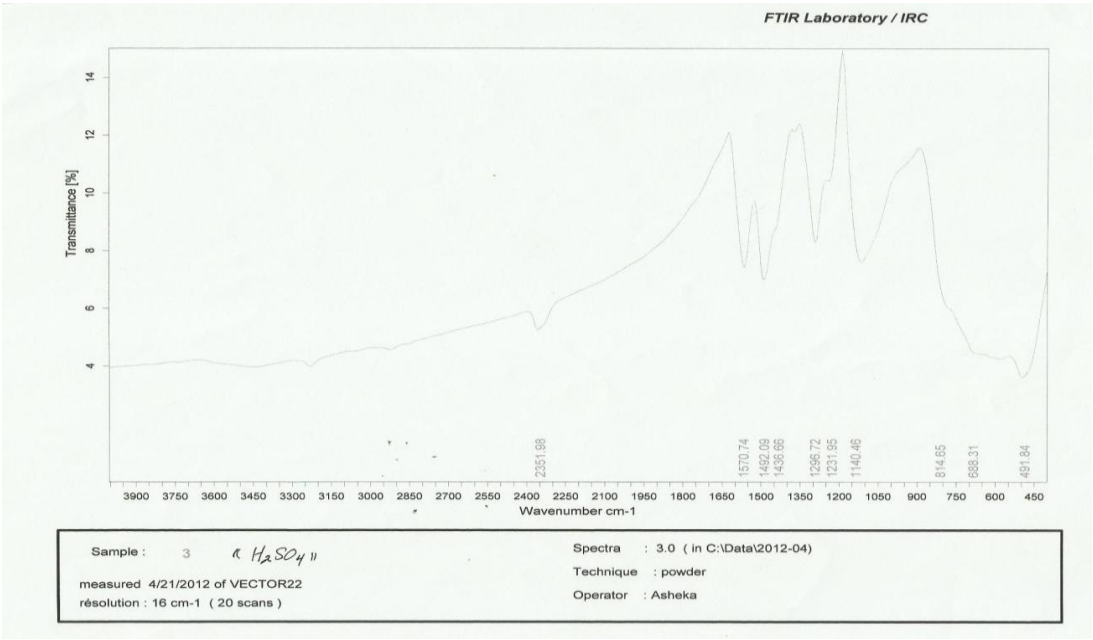
-XRD of PAN-H_2SO_4

Figures (4.35), and (4.36) shows the XRD, and FTIR for PAN prepared by 1M H_2SO_4, 0.03M $(NH_4)_2S_2O_8$, and 0.25M Aniline.



Fig(4.35): XRD for PAN/H_2SO_4/$(NH_4)_2S_20_8$

- FTIR of PAN-H_2SO4

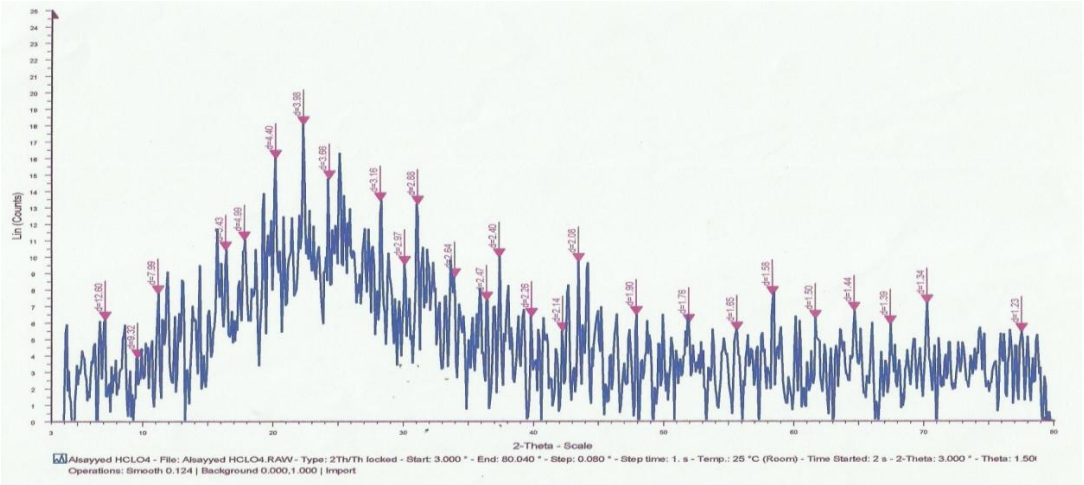


Fig(4.36): FTIR for PAN/H_2SO_4/$(NH_4)_2S_2O_8$

4.2.10- Characterization of PAN-H_3PO_4

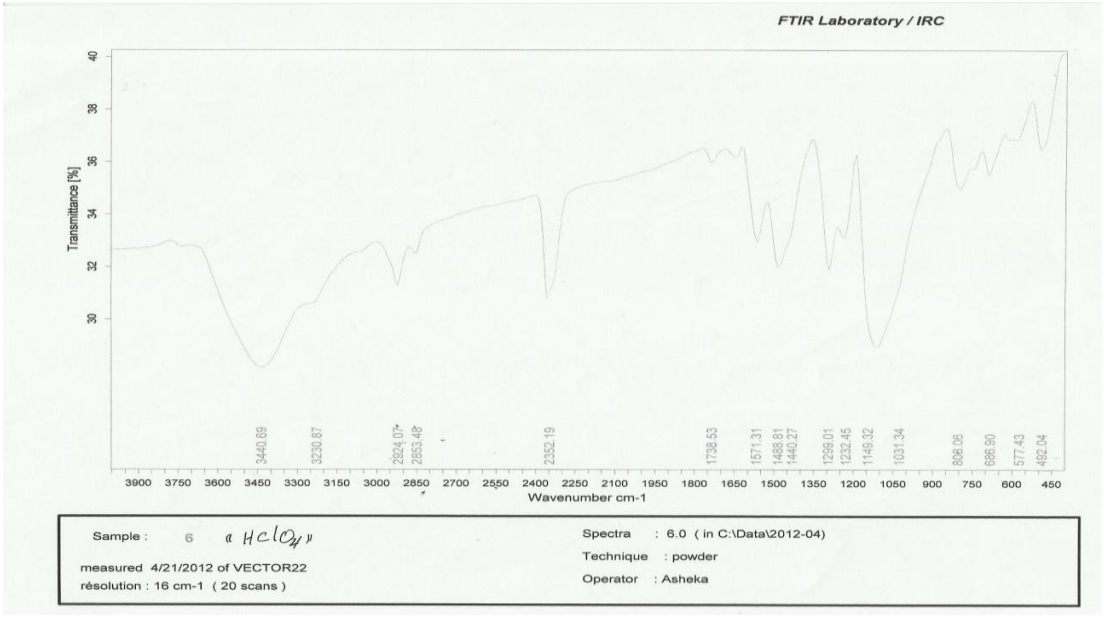
Figures (4.37), and (4.38) shows the FTIR spectra and XRD patterns for PAN prepared from 1.5M H_3PO_4, 0.03M KIO_3, and 0.24M Aniline

- XRD of PAN-H_3PO_4



Fig(4.37).- XRD for PAN/H_3PO_4/KIO_3

- FTIR of PAN-H_3PO_4

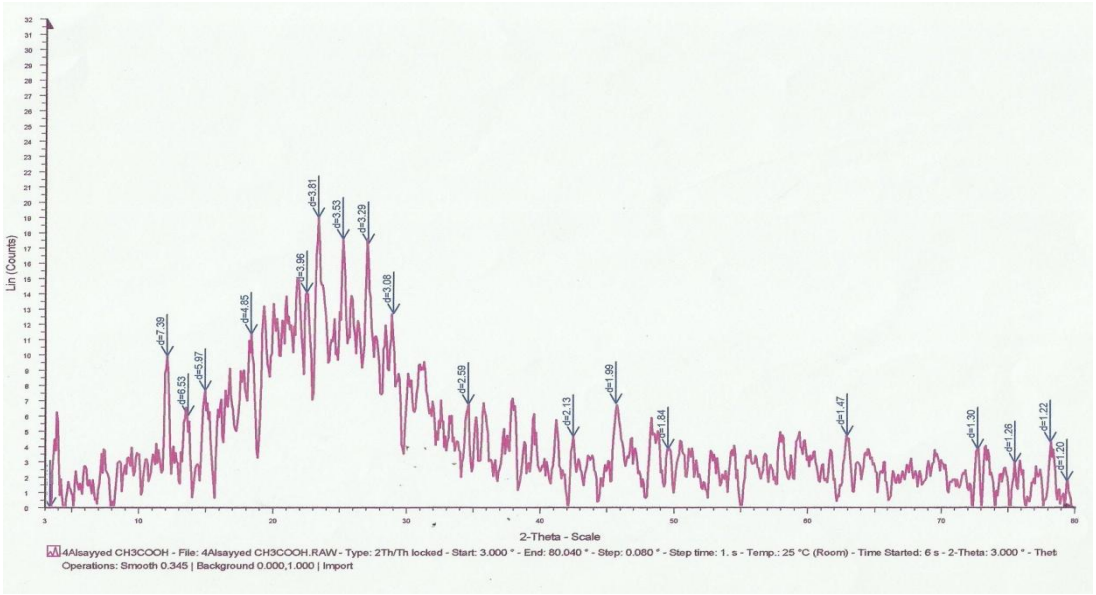


Fig(4.38): FTIR for PAN/H_3PO_4/KIO_3

4.2.11- Characterization of PAN-CH_3COOH

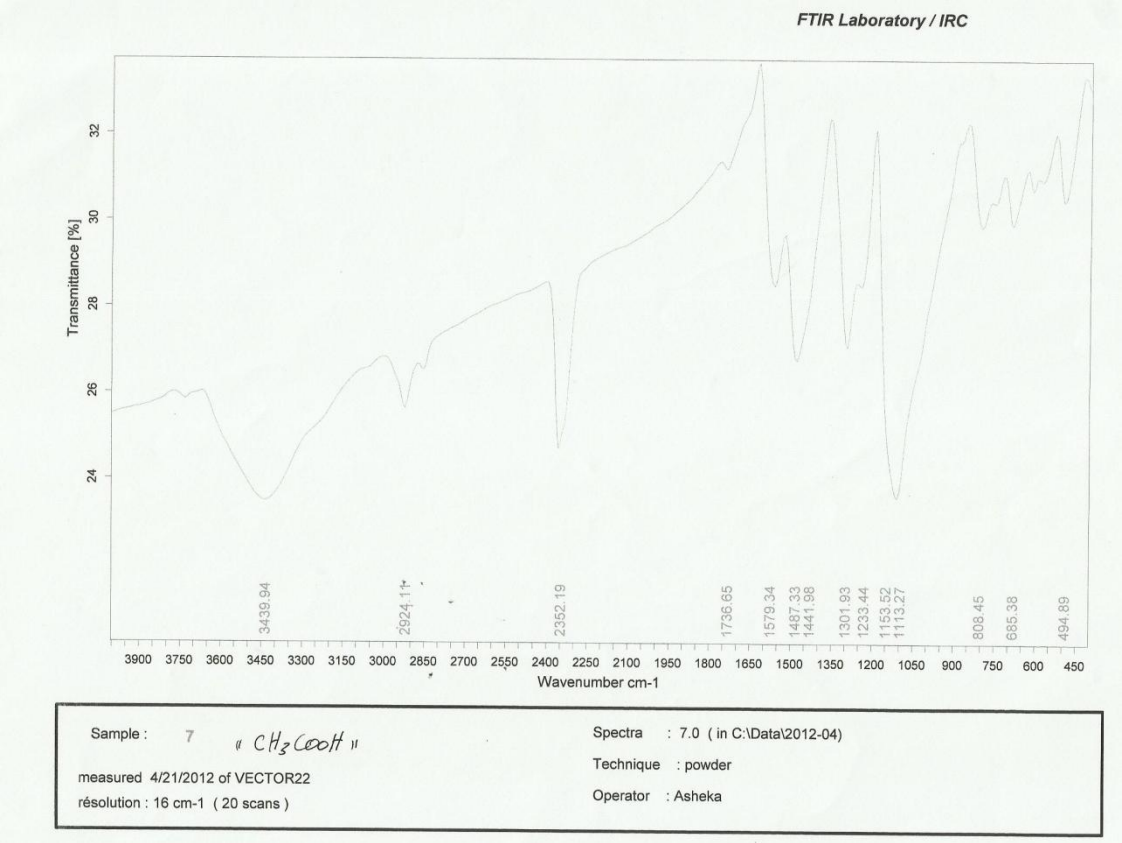
Figures (4.39), and (4.40) shows the XRD, FTIR spectra for PAN prepared from 1M CH_3COOH, 0.03 $KMnO_4$, and 0.25M Aniline.

- XRD of PAN-CH_3COOH



Fig(4.39): XRD for PAN/CH_3COOH/$KMnO_4$

- FTIR of PAN-CH_3COOH



Fig(4.40): XRD for PAN/CH_3COOH/$KMnO_4$

The results of XRD and FTTR of PAN and PAN-Hg(II) are shown in tables and(4.19) and(4.19).

Nu	Before	After	Conditions
	1.23-18.39		
1	**Time experiment for 100ppm of Hg^{+2}**	**2.49-27-46**	**1.5M HCl, 0.03M K_2Cr2O_7, 0.25M Aniline with 100ppm Hg^{+2}, 1hr**
2		**2.39-27.80**	**Same conditions with 6hrs time**
3		**2.31-23.36**	**Same conditions with 24hrs time**
4	**1.21-13-55 Time experiment for 200ppm of Hg^{+2}**	**2.28-27.15**	**1.5M HCl, 0.03M KIO_3, 0.25M Aniline with 200ppm Hg^{+2}, 1hr**
5		**2.40-22.04**	**Same condition with 6hrs**
6		**2.23-21.96**	**Same conditions with 24hrs**
7	**1.23-18.89 Ionic strength experiment of 10ppm of Hg^{+2}**	**2.33-21.04**	**1.5M HCl, 0.03M $K_2Cr_2O_7$, 0.25M Aniline, 0.02M of $NaNO_3$, 10ppm of Hg^{+2}**
8		**2.34-24.67**	**Same conditions with 0.2M $NaNO_3$.**
9		**2.44-17.97**	**Same conditions with 1.00M $NaNO_3$**

Table (4.20): the peaks values of FTIR for PAN, PAN/Hg^{+2} patterns

Nu	Before/Cm^{-1}	After/Cm^{-1}	Conditions
1	**498.32 - 2352.25**	**500.70 – 2352.21**	**PAN prepared by 1.5M HCl, 0.03M $K_2Cr_2O_7$, 0.25M Aniline on magnetic stirrer, 100ppm of Hg^{+2}, for 6hrs time.**
2	**508.30 - 1538.35**		**PAN prepared by 1.5M HCl, 0.03M, $K_2Cr_2O_7$, 0.25M Aniline, without magnetic stirrer.**
3	**491.34 – 2351.98**		**PAN prepared by 1M H_2SO_4, 0.03M $(NH_4)_2S_2O_8$, 0.25M Aniline, on magnetic stirrer.**
4	**492.04 – 3440.69**		**PAN prepared by 1.5 M H_3PO_4, 0.03M HIO_3, 0.25M Aniline, on magnetic stirrer.**
5	**494.39 – 3439.94**		**PAN prepared by 1M CH_3COOH, 0.03M $KMnO_4$, 0.25M Aniline, on magnetic stirre.**

RECOMENDATION

Conductive polymers play very important role in different kinds of life. I remanded for the following in future work

1-Working with nano conductive polymers in removal of heavy metals from waste water.

2-Working with green polymers in treatment of waste water.

3-Working with the (PAN) Composite materials.

4-Working with adsorption of mixture of metal ions on PAN – surface.

5-Working with other parameters on adsorption such as, interfering Ions, real water samples.

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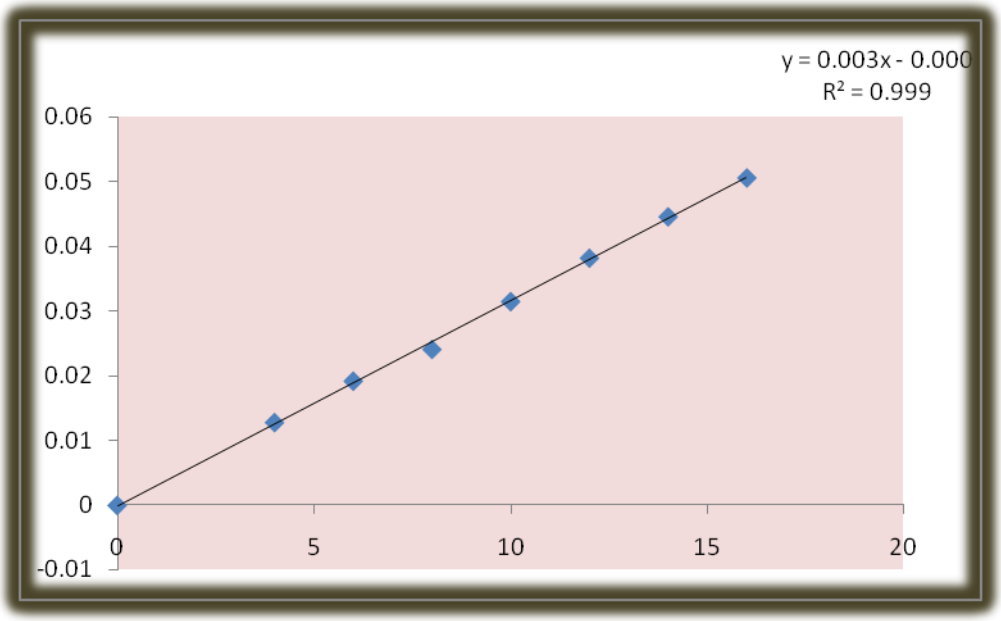
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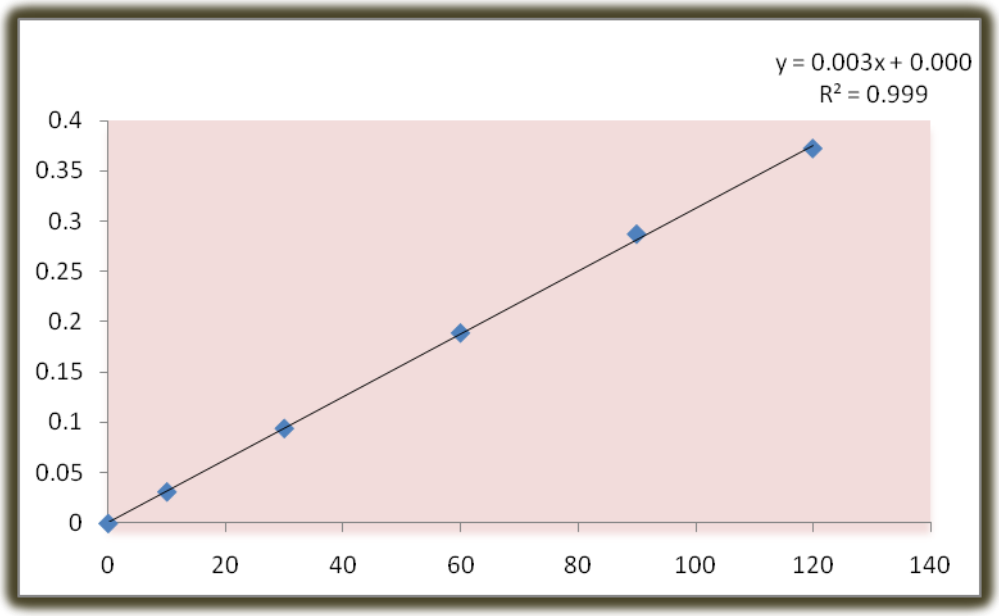
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57- Polyaniline and its Derivatives for Environmental Analysis.

APPENDEIXES



Standard calibration curve for Hg(II)


y = 0.003x + 0.000
R² = 0.999
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
20
40
60
80
100
120
140



Analytical chemistry lab

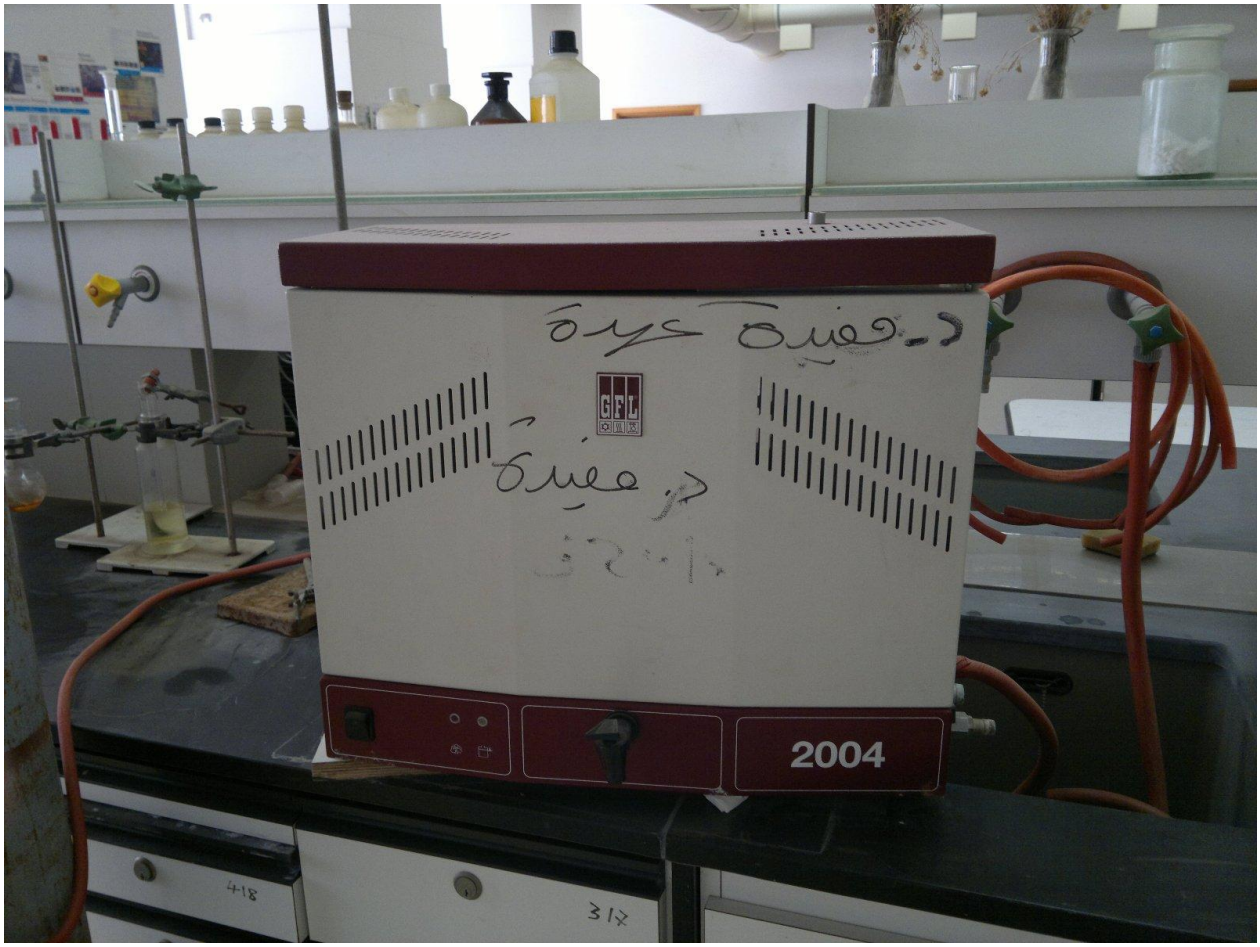


Chemical used





Glassware

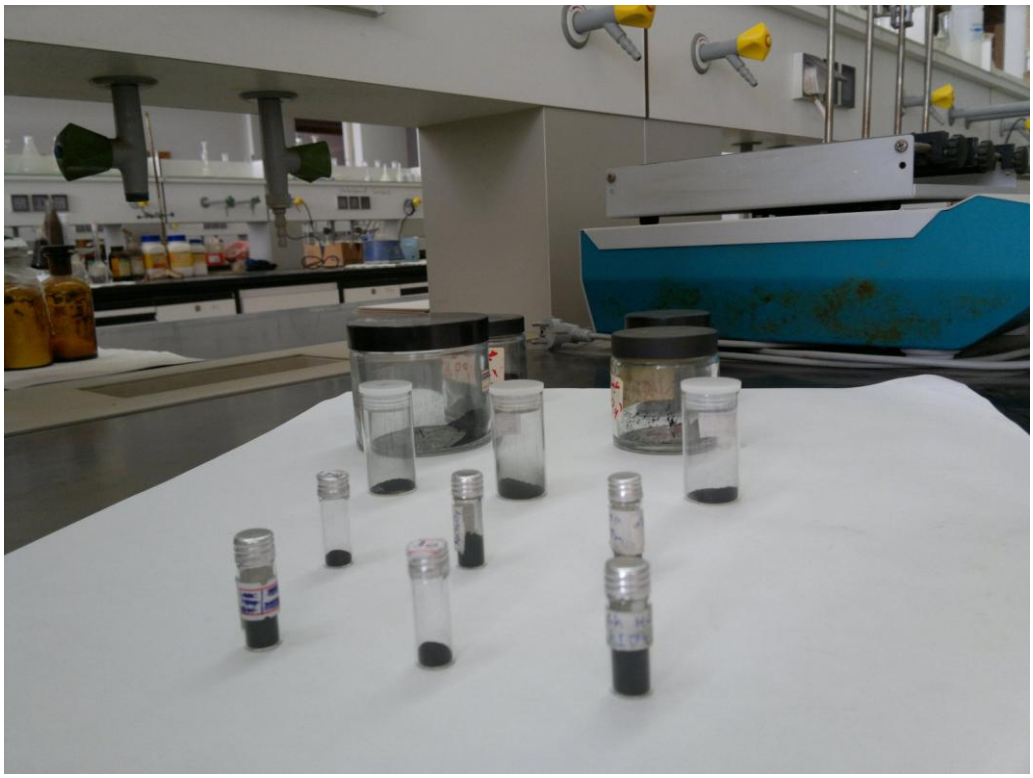



1000
800
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400
500
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300
200

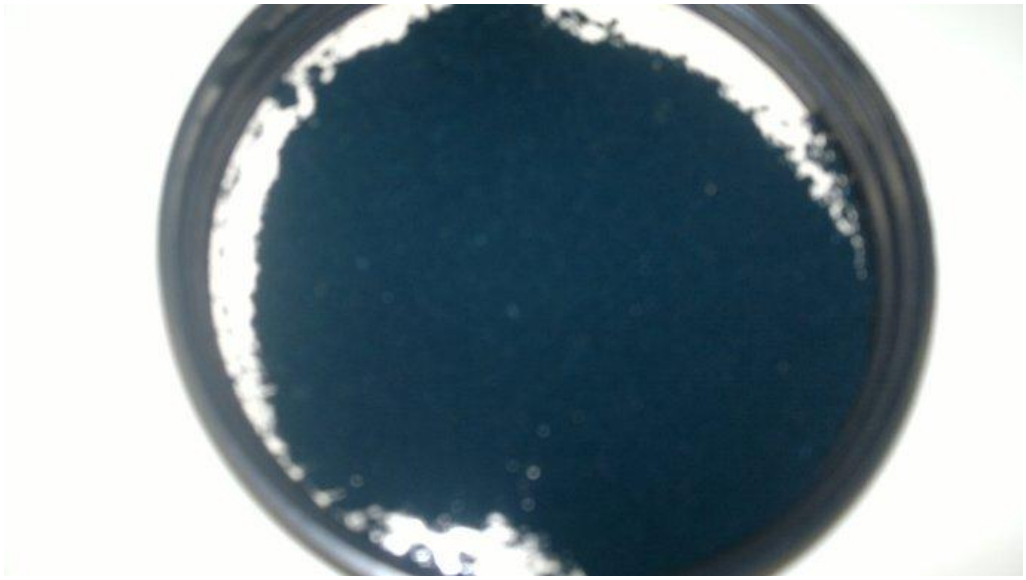


Preparation of Polymer (PAN)





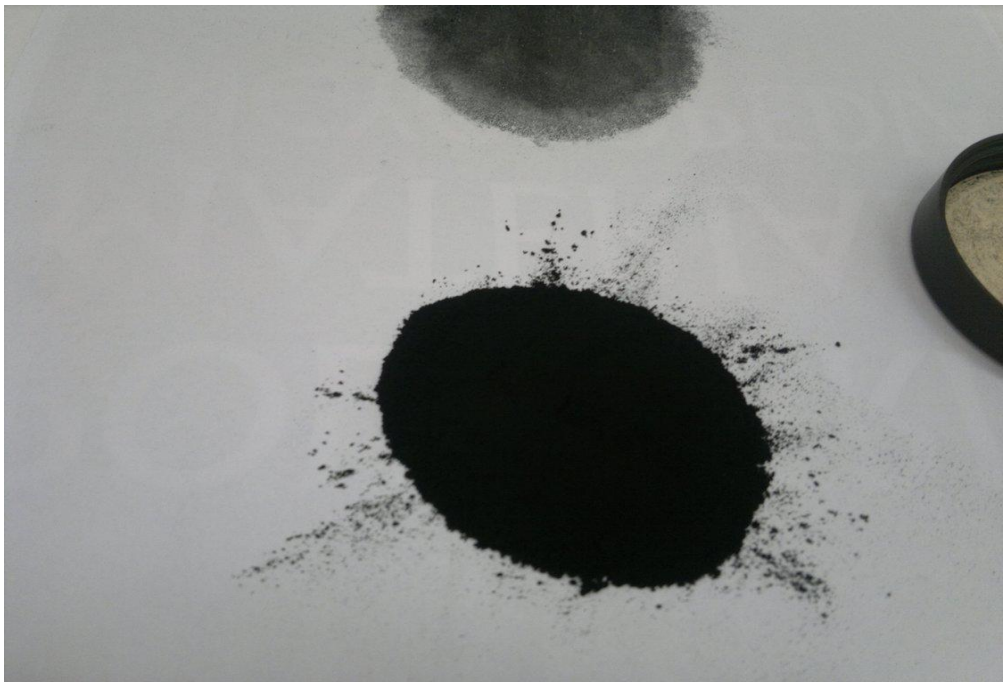
Samples after preparation



Emeraldine salte of PAN prepared by HCl



Emeraldine salt of PAN prepared by H_2SO_4



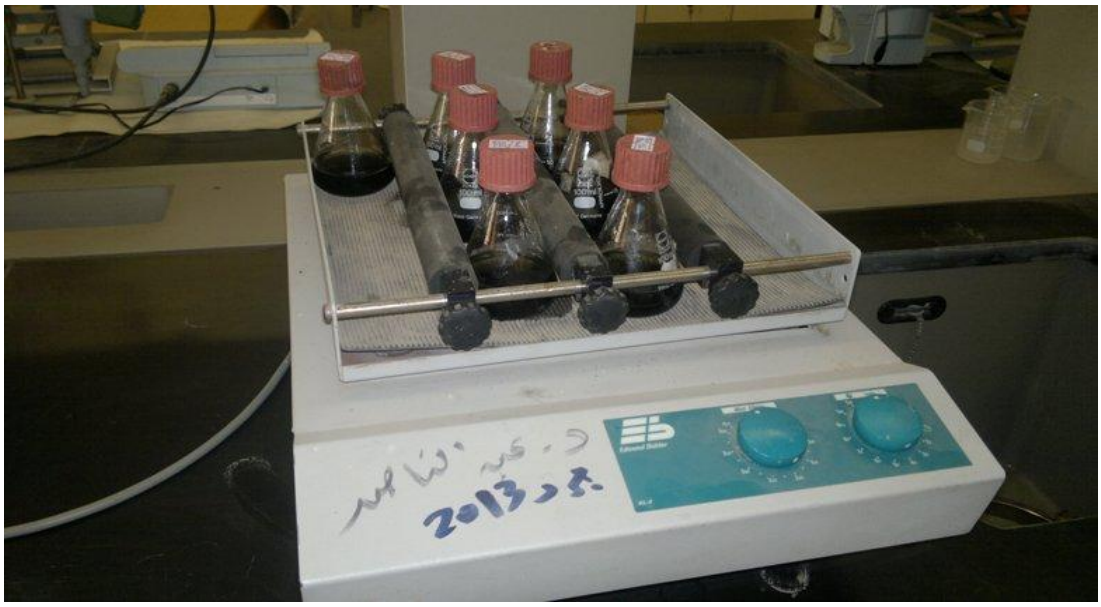
Emeraldine salt of (PAN) prepared by H_3PO_4



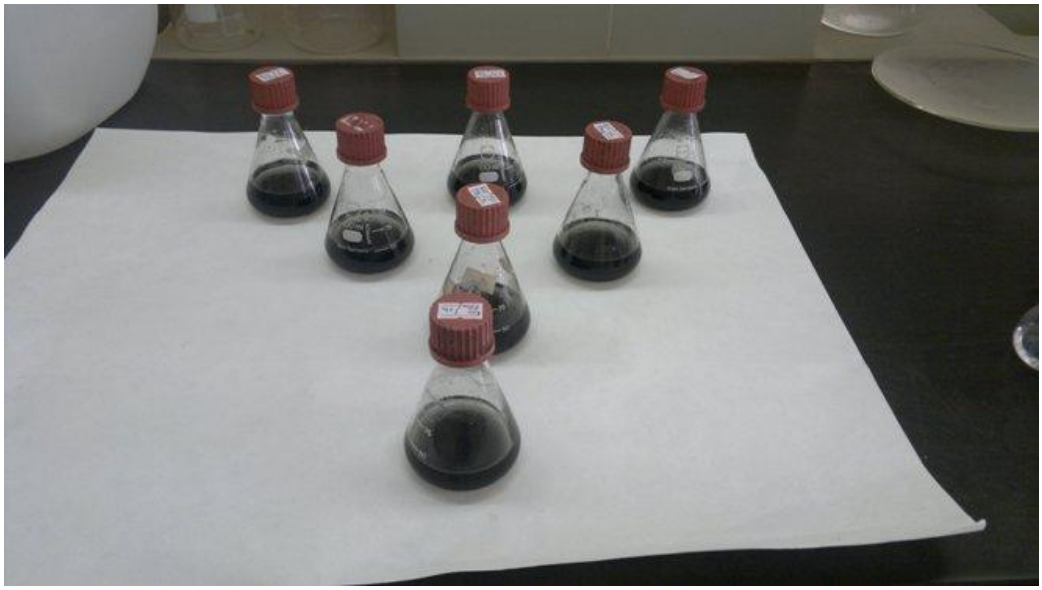
Emeraldine salt of (PAN) prepared by CH_3COOH



pH metter



Shakering machine



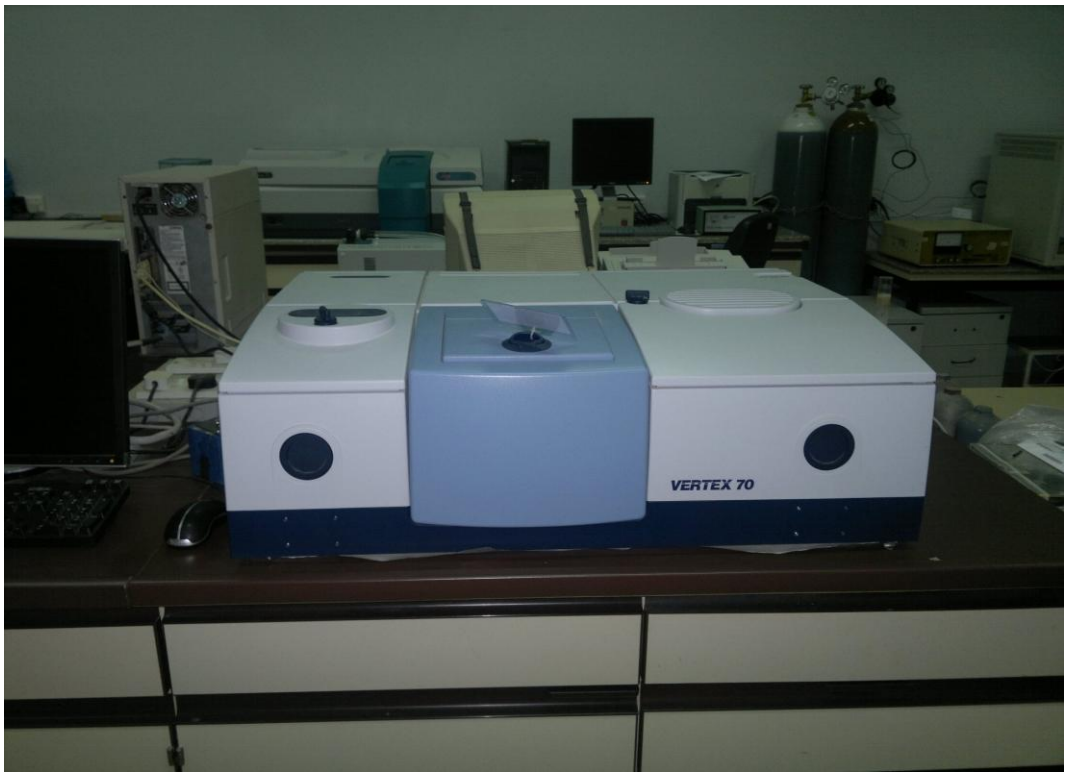
PAN with $Hg(NO_3)_2$ after adsorption



The amount of Hg^{+2} residual after adsorption.



SEM: AJeal. JEM 100CX II MODEL Germany



FTIR: Bruker S100



XRD: Pw-1800



Mercury Analyzer System Lab Analyzer – 254 Germany



Supervisor: Dr. Abd Elnasser Elturky



Submitted: Saied Ali Abou Farddah