SYNTHESIS AND STUDIES ON POLYANILINE AS AN EFFECTIVE ADSORBENT FOR THE REMOVAL OF HEAVY METALS FROM WASTEWATER

A DISSERTATION

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I **Devvrat Tiwari**, 2K17/PTE/02, student of M.Tech Polymer Technology hereby declare that the project dissertation titled "**SYNTHESIS AND STUDIES ON POLYANILINE AS AN EFFECTIVE ADSORBENT FOR THE REMOVAL OF HEAVY METALS FROM WASTEWATER"** submitted by me to the Department of Applied Chemistry, Delhi Technological University, Delhi in the partial fulfillment of the requirement for the award of the degree of Master of Technology, is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any degree, Diploma Associate-ship, Fellowship or other similar title or recognition.

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CERTIFICATE

I hereby certify that the project dissertation titled "**SYNTHESIS AND STUDIES ON POLYANILINE AS AN EFFECTIVE ADSORBENT FOR THE REMOVAL OF HEAVY METALS FROM WASTEWATER"**, submitted by **Devvrat Tiwari** (Roll No.: 2K17/PTE/02), Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Technology, is a record of the project work carried out by him under my supervision. To the best of my knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

Place: Delhi **Dr. Raminder Kaur**

Date: **SUPERVISOR**

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ABSTRACT

Due to rapid industrialization and urbanization, huge amount of waste is being discarded from both households as well as industries which is hazardous to our surroundings. The dumping of the waste directly, which consists of toxic metals and other hazardous substances is of great concern as it may cause land and water pollution. The treatment of the wastewater prior discarding it may reduce the land and water pollution significantly. In this project, the polyaniline has been synthesized and further utilizes as an adsorbent for the removal of heavy metals from wastewater. The emphasis has been given mainly on the removal of Cr and Hg ions. The adsorption study has been conducted for the removal of Cr and Hg ions from their aqueous solution. UV-Visible Spectroscopy was used to find out the concentration of the heavy metal ions prior and post to adsorption. Atomic Absorption Spectroscopy (AAS) confirmed the presence of Hg and Cr ions. Percentage adsorption varied from 60.1% to 97.40%. Polyaniline was found to be the effective adsorbant, with low cost and ease in synthesis. Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD) and Transmission Electron Microscope (TEM) confirmed the nano-structure of the synthesized polyamine.

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CHAPTER 1.
INTRODUCTION AND LITERATURE REVIEW

1.1 Introduction

The accelerated industrialization and urbanization, the release of harmful pollutants in the environment has increased significantly. These very varied contaminants are a significant problem both for the surroundings and living organisms. The pollutants include the organic and inorganic compounds that are released directly into the environment and poses many health hazards. Though organic pollutants do not pose a severe threat to the environment, being somewhat degradable, but, it is the inorganic pollutants like the heavy metal ions, are non-degradable and end up as harmful waste being toxic to many life forms. Many industries like the storage batteries industries, metal plating, mining operations, radiator manufacturing industry, etc., release a large amount of aqueous waste which contain a high degree of heavy metal ions [2]. Heavy metals are atomic weight components from 63.5 to 200.6 and with elevated specific gravity i.e. 5.0. The heavy metals are non biodegradable and, unlike organic contaminants, appear to collect in living organisms. These may have toxic and lethal health impacts on humans and other organisms, depending upon their extent of exposure.In the face of increasingly stringent legislation and environmental concern, today, heavy metals are global key pollutants and become one of the most serious economic problems. To safeguard individuals and the environment these poisonous discharge from the effluent must be treated and removed.

Chromium is a damaging metal that can trigger serious wellness issues from easy burning of the skin to cancer of the lungs. It is present in two stable statements oxidation states Cr(lll) and Cr(Vl). The Cr(Vl) state is more hazardous and dangerous for health due to its carcinogenic properties. It can enter the food chain and can alter the human physiology. In the similar manner, mercury (Hg) is extremely toxic and may trigger lung and kidney function deficiency, chest pain and dyspnea.

1.2 Methods used for the extraction 0f Heavy Metals

Pollution from toxi metals has become one of today's most severe environmental issues. Because of their recalcitrance and persistence in the setting, heavy metal treatment is of particular concern. For heavy metal removal from wastewater, a broad variety of treatment techniques such as chemical precipitation, coagulation- flocculation, flotation, ion exchange and membrane filtration have been created to fulfill the increasingly stringent environmental regulations. In their study, Fenglian Fu, Qi Wang, et al. [4], reviewed and evaluated the current methods used to treat heavy metal wastewater. The major treatment methods used in the industries for heavy metal removal are categorized into following classes:

1.2.1 Chemical Precipitation

Chemical precipitation is efficient and by far the most commonly used method for the removal of heavy metal ions [5], because operation is comparatively straightforward and cheap. Chemicals respond with heavy metal ions in precipitation procedures to form insoluble precipitates. Sedimentation or filtration can separate the precipitates from the water. Then the treated water is decanted and discharged or reused properly. The procedures of standard chemical precipitation include precipitation of hydroxide and precipitation of sulfide.

1.2.2 Ion Exchange

Ion exchange methods have been commonly used to remove heavy metals from sewage because of their significant benefits, such as high treatment capability, high effectiveness in removal and fast kinetics [6]. Ion-exchange resin, either synthetic or natural strong resin, has the capacity to exchange its cations with the wastewater metals. Synthetic resins are commonly preferred among the materials used in processes of ion exchange, as they are effective in almost removing 95 % heavy metals from the solution [7]. Strongly acidic resins with sulfonic acid groups (-SO_3H) and low acid resins with carboxylic acid groups (-COOH) are the most prevalent cation exchangers. Hydrogen ions can serve as exchangeable ions with metal cations in the resin's sulfonic group or carboxylic group. As the solution containing heavy metalpasses through the cations column, metal ions are exchanged for the hydrogen ions on the resin with the following ion-exchange process:

$$nR\text{-}SO_3H + M^{n+} \rightarrow (R\text{-}SO_3^-)_n M^{n+} + nH^+$$

$$nR\text{-}COOH + Mn+ \rightarrow (R\text{-}COO^-)_n M^{n+} + nH^+$$

Some factors such as pH, temperature, original metal concentration and contact time affect the absorption of heavy metal particles by ion-exchange resins [8]. In addition to synthetic resins, owing to their low price and elevated abundance, natural zeolites, naturally occurring silicate minerals, were commonly used to remove heavy metal from aqueous solutions. Many scientists have shown that zeolites have excellent cation exchange capabilities for heavy metal ions under various experimental circumstances [9,10]. Clinoptilolite is one of the most commonly researched natural zeolites owing to its selectivity for heavy metals that has gained comprehensive attention.

1.2.3 Membrane filtration

For elevated effectiveness, simple operation and room saving, membrane filtration techniques with distinct kinds of membranes demonstrate excellent potential for heavy metal extraction. Ultrafiltration, inverse osmosis, nanofiltration and electrodialysis are the membrane processes used to extract metals from wastewater.

1.2.4 Coagulation and flocculation

Also used for removing heavy metal from wastewaters is coagulation and flocculation followed by sedimentation and filtration. Coagulation is the colloid destabilization by neutralizing the forces that keep colloids apart. Many coagulants are commonly used in conventional wastewater treatment procedures such as aluminum, ferrous sulfate and ferric chloride, leading in the efficient removal of wastewater particulates and impurities by charging particle neutralization and enmeshing impurities on the precipitated amorphous metal. El Samrani et al. (2008) explored heavy metal removal through coagulation of combined sewer overflow with two commercial coagulants, a ferric chloride solution and a polyaluminum chloride (PAC) solution. They discovered outstanding heavy metal elimination around optimum levels of coagulant was accomplished within a limited range of coagulant.

In an another study, the cluster of sodium xanthogenate was grafted into polyethyleneimine to efficiently extract both soluble heavy metal and insoluble materials by coagulation [12]. At lower pH, it can coagulate the colloidal substances with negative charges, but if the water sample pH is greater, the removal of turbidity will decrease and the removal of Ni^{2+} will increase.

Flocculation is the activity of plastics creating links between flocks and binding objects into large agglomerates or clumps. Once suspended ions are flocculated into larger droplets, they can usually be removed or separated by filtration, squeezing or floating. Many types of flocculants, such as PAC, polyferric acid (PFS) and polyacrylamide (PAM), were commonly used in wastewater treatment today, but it's almost impossible for these present flocculants to remove heavy metal from wastewater very well. A fresh type of flocculant is the macromolecule heavy metal flocculants. By responding chitosan with mercaptoacetic acid, Chang et al., 2009 [13], prepared a heavy metal macromolecule flocculant mercaptoacetyl chitosan. They disclosed that it could not only extract turbidity from this new flocculant, but also extract heavy metals from wastewater. Coagulation-flocculation generally cannot fully treat heavy metal sewage . Therefore, other treatment methods must be accompanied by coagulation-flocculation. Plattes et al., 2007 [14], used procedures of precipitation, coagulation and flocculation to remove tungsten from industrial wastewater using ferric chloride.Tungsten extraction in acidic circumstances ($pH < 6$) was discovered to be most effective (98-99%). In a laboratory semi-flow scheme, Bojic et al., 2009[15] used micro-alloy aluminum alloy to handle model heavy metal sewage as a natural reduction-coagulation technique. The residual metal concentrations were at qualified levels after only 20 minutes of treatment.

1.2.5 Flotation

The flotation process has now discovered comprehensive use in the processing of wastewater. Using bubble attachment, flotation was used to distinguish toxic metal from a liquid phase, originating in mineral processing. The primary flotation procedures for removing metal ions from the solution are dissolved air flotation (DAF), ion flotation and precipitation flotation.

The purpose of DAF is to enable micro-bubbles of air to be connected to suspended objects in water, to create agglomerates with a reduced density than water, to cause flocks to grow through water and to collect as sludge on the bottom. A promising technique for removing heavy metal ions from wastewater has been shown for ion flotation. The ion flotation process is based on the distribution of ionic metal species in hydrophobic wastewater using surfactants and subsequent removal by air bubbles of these hydrophobic species [16]. Yuan et al., 2008 [17] explored the ability of ion flotation with a plant-derived biosurfactant tea saponin to remove cadmium, lead and copper from dilute aqueous solution. Up to 89.95 percent, 81.13 percent and 71.17 percent, respectively, can be reached when the ratio of collector to metal was 3:1. The precipitate flotation process is another flotation method option based on precipitate formation and later removal by attachment to air bubbles. The precipitation may continue through the creation of metal hydroxide or as a salt with a particular anion (sulfide, carbonate, etc.) depending on the concentration of the metal solution. The removal of Cr(III) was investigated at the laboratory scale by precipitate flotation from dilute aqueous solutions using SDS as anionic collector and ethanol as a frother. The findings showed a peak removal of 96.2 percent at pH approximately 8.0.

1.2.6 Electrochemical Treatment

The electro-chemical techniques require placing metal ions on the surface of the cathode and in the elementa1 meta1 state can retrieve metals. The electrochemical waste-water techniques require comparatively big investment in capital and costly supply of electricity, so they have not been commonly used. However, electrochemical techniques have recovered their significance globally over the previous two decades with the strict environmental regulations on sewage discharge [18]. Electrocoagulation (EC) includes in situ coagulant generation by electrically dissolving the aluminum or the iron ions from aluminum or iron electrodes (Chen, 2004). Metal ion formation takes place at the anode, releasing the cathode hydrogen gas. Hydrogen gas can assist the objects floating out of the water (Chen, 2004). Heidmann and Calmano (2008) investigated the performance of an aluminum electrode EC system in order to remove Zn^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+} and $Cr_20_7^{2-}$. The initial concentrations from 50 mg / L to 5000 mg / L Ni, Zn, Cu and silver does not influence the rate of production, whereas higher initial concentrations triggered higher levels of Chromium, Zinc, Copper, Nickel and Silver ions to be hydrolyzed and co-precipitated as hydroxides. It had been suggested that Cr(VI) be lowered first in cathode to Cr(III) before it was precipitated as hydroxide. EC has also been used by Nanseu-Njiki et al., 2009 [20], to evaluate the treatment of synthetic solutions containing concentration $2*10^{-5}$ M Hg^{2+}. The effectiveness of removal was higher than 99.9 percent when the distance between the electrodes was 3 cm, the current density varying from 2.5 Adm^{-2} to 3.125 Adm^{-2} and the pH of 3 to 7 of Hg^{2+} alternatives.Ölmez, 2009 [32] researched EC's efficiency in removing hexavalent chromium with a elevated 1470 mg/L Cr(VI) concentration. The optimum requirements for 100% Cr(VI) suppression were created as 7.4 A applied electrical current, concentration of 33.6 mM electrolyte (NaCl) and implementation time of 70 min. In addition, EC was used to extract Mn^{2+}, As(V), Mn^{2+}, and Ni^{2+}, etc.

1.2.7 Adsorption

The adsorption process is now recognized as a cost-effective and effective method for heavy metal sewage treatment. Adsorption is a system in which physical power or chemical bonding attracts the formed adsorbate molecules to the adsorbent layer. The adsorption of the metal ion as a pollutant is based on factors such as contact time, temperature, pH, particle size and surface area. Attachment of ionic and molecular species with distinct functional groups depends on the complexity of the adsorbent and adsorbent molecules relationship. It may be electrostatic interactions at the adsorbent layer between opposite charged sites or owing to weak van der waals pressures it may be physiosorption. Or it may be chemisorption, requiring powerful adsorbent interaction, or easy adsorbent molecule connection at a specific location on the adsorbent surface. The technique of adsorption offers stability in layout and implementation and in many cases produces high-quality processed effluent. In addition, since adsorption is sometimes reversible, adsorbents can be regenerated by a suitable desorption technique. The adsorption method appears to be quite efficient when the adsorbent is not so expensive and does not involve any previous treatment.

1.3 Comparison of Different Treatment Processes of Heavy Metal Removal

Although it is possible to use all heavy metal sewage treatment methods to extract heavy metals, they have their own benefits and constraints. The chemical precipitation process has traditionally carried out the extraction of heavy metals from aqueous solutions for its simplicity method and low cost of capital. Chemical precipitation, however, is generally tailored to process elevated concentration wastewater that contains heavy metal ions and is useless if the concentration of metal ions is small. The chemical precipitation is not cost-effective and can produce large amounts of waste that can be handled with great difficulty. The Ion exchange process for removing heavy metal from wastewater has been commonly used. However, when exhausted, ion-exchange resins need to be regenerated by chemical reagents and regeneration can trigger severe secondary pollution. It is expensive, especially when treating large amounts of heavy metal-containing wastewater in low concentration, so they can not be used on a large scale. Membrane filtration technique can extract heavy metal particles from elevated efficiency, but its problems such as high price, method difficulty, membrane fouling, and low-permeate flux have limited its use in heavy metal extraction. The sludge produced has outstanding floating and dewatering characteristics using high metal wastewater treatment technique for coagulation-flocculation. But this method involves chemical consumption and increased sludge quantity production, flotation offers several advantages over more conventional methods such as high metal selectivity, elevated extraction efficiency, elevated overflow levels, small containment times, small operating costs and more concentrated manufacturing of sludge, but the drawbacks are elevated original cost of capital, high cost of maintenance and operation. Treatment methods for electrochemical heavy metal sewage are considered fast and well-controlled, requiring fewer chemicals, providing excellent returns for decrease and producing less sludge. However, electrochemical techniques involving elevated original investment in capital and costly supply of electricity restrict its growth.

1.4 Adsorption as an Effective Treatment Technique

Adsorption is a quick, cheap and efficient technique for removing contaminants from aquatic settings through physicochemical interactions among these techniques. Studies have shown that adsorption is a highly effective technique for the removal of heavy metal ions from wastewater containing heavy metal from low concentration. Many low cost adsorbents have been developed and tested by the researchers to remove heavy metal ions. The adsorption effectiveness, however, relies on the adsorbent type. Biosorption of heavy metals from aqueous solutions is a fairly fresh method that has proved very promising for wastewater removal of heavy metal.

Activated carbon have been widely used as an adsorbent for the same, but due to its high cost, researches are now intended towards some cost effective materials. Different sorbent types such as activated carbon, silica, plant-based biosorbents, clay minerals, chelating materials and chitosan / natural zeolites were used to remove heavy metal ions from waste and sewage. But all of these products have certain disadvantages, such as operational processes and elevated treatment expenses, and residual metal sludge disposal.

Some researchers, studied the adsorption behavior of some low-cost adsorbents, such as peanut husk charcoal, fly ash and natural zeolite, with respect to Cu2+ and Zn2 + ions, in order to consider their application to the purification of wastewater for metal finishing.Parameters such as pH, contact time, and original concentration of metal were researched using the batch technique. The pH of the metal ion solutions was influenced by the various adsorbents used to absorb metal ions between pH 4 and pH 11.In the case of peanut husk charcoal and natural zeolite, the optimal pH for copper and zinc removal was 6, and in the case of flyash it was 8. The adsorption of Cu(II) and Zn(II) ions on peanut husk charcoal and fly ash needed an equilibrium time of 2 h, and the adsorption of Cu(II) and Zn(II) ions on natural zeolite needed an equilibrium time of 3 h.Adsorption parameters were determined using both Langmuir and Freundlich isotherms, but the experimental information were better adapted to the equation of Langmuir than to the equation of Freundlich. The findings showed that peanut husk charcoal, fly ash and natural zeolite all have the ability to remove cationic heavy metal species from industrial sewage in the order of fly ash < peanut husk charcoal < natural zeolite.

1.5 Polyaniline:

Polyaniline (PANI) is a semi-flexible rod polymer conductive fiber. Although the compound itself was found over 150 years earlier, the intense interest of the scientific community has been caught by polyaniline only since the mid 1980s. This concern is related to elevated electrical conductivity being rediscovered. Polyaniline has many appealing handling characteristics among the class of conductive materials and organic semiconductors. Polyaniline is one of the most researched binding materials of the last 50 years due to its wealthy content. Polymerized from the cheap aniline monomer, polyaniline can be discovered in one of three idealized oxidation states:

- Leucoemeraldine – white/clear & colorless $(C_6H_4NH)_n$
- Emeraldine – green for the emeraldine salt, blue for the emeraldine base $([C_6H_4NH]_2[C_6H_4N]_2)_n$
- Nigraniline – blue/violet $(C_6H_4N)_n$

Polyaniline has been recently reported to be a potentially useful material for rechargeable batteries, electrochemical actuators, organic electroluminescent devices, electro chromic devices, photoresist for lithography, sensor, control of electromagnetic radiation, separation of gases, corrosion inhibition of metals and as a semi conductor in photochemical assemblies. The polyaniline powder can be retrieved after polymerization can be rendered dispersible and thus helpful for practical apps using unique polymerization processes and surfactant dopants. Bulk synthesis of polyaniline nanofibers has resulted in a extremely scalable and widely relevant polyaniline type which has been widely investigated since its discovery in 2002.

1.5.1 Polyaniline in Metal Ion Removal

Polyaniline is discovered to be capable of removing damaging dyes and metal ions from the manufacturing effluent in latest literature research. Polyaniline's textured features such as surface area, pore amount and median pore diameter (in the event of porous composites) are the main factors that determine adsorption ability. Polyaniline can be synthesized using simple chemical method or by interfacial polymerization. But polyaniline nanofibers made from interfacial polymerization, owing to their inferior characteristics relative to standard polyaniline mass, have received much publicity. In addition, polyaniline's adsorption surface sites (> NH) may also play a significant part in the adsorption cycle as they are generally extremely reactive. The polyaniline surface carbonaceous skeleton and surface groups may also be regarded amphoteric where they may be protonated (positive charged) or deprotonated (negative charged) depending on sample pH. In addition, it is also possible to add other chelating groups such as sulfur, oxygen and/or phosphorus along with nitrogen, which can provide fresh chemical adsorption sites. The aim in this chapter is to provide information on the adsorption features of polyaniline-based nanocomposites and their implementation for the removal of metal ions. A Schematic diagram illustrating the chemical structure, synthesis, reversible acid / base doping / doping and redox PANI chemistry as shown in Figure 1.1.

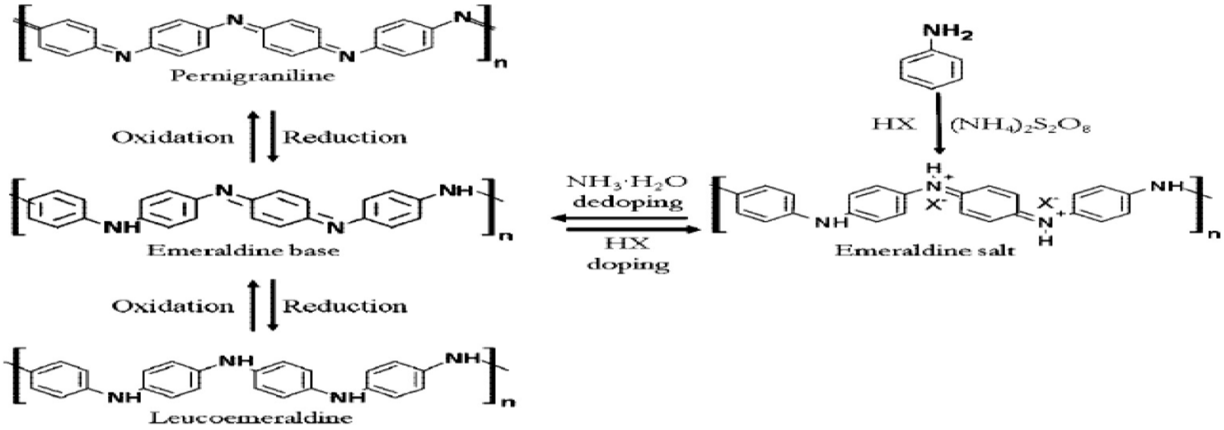

Figure 1.1: The above reaction shows the chemical structure, synthesis, reversible acid/base doping/dedoping of polyaniline.

A composite of PANI/GAC was synthesised by chemical oxidative polymerisation and was further used efficiently for the extraction of Cu (II) from the industrial effluent. Also, polyaniline and humic acid (PANI/HA) composite was reported to be used for the removal of Hg (II) and Cr (VI) ions from the effluent. Polyaniline and polystyrene were used to form a composite to separate out the Hg (II) ions from industrial wastewater. It had been found that removal of these harmful metallic ions from the wastewater increased with rise in concentration and temperature of solution under test. Nanocomposite of polyaniline with rice husk ash (RHA) was reviewed as a good adsorbent for the removal of Hg (II) from its aqueous solution. In an another study, polyaniline/rice husk (RH) nanostructured composite was prepared by chemical oxidative polymerization and further used to eliminate the Zn from wastewater. This composite was found to be a potential adsorbent for the Zn 4removal. The capacities of the different forms of polyaniline to adsorb Hg were found to have followed the given order i.e.: polyaniline (treated by alkali) > polyaniline sulphate > polyaniline hydrochloride. Different metal ions in their individual or mixture forms were used to study the removal capacity of these synthesised adsorbents and following order of competition between the metal ions was observed: Zinc(II), < Copper(II), < Cadmium(II), < Mercury(II), <Lead(II). This order is quite similar to that of the order of the respectively

their atomic radius, atomic weight and electronegativity of these metal ions. In addition, natural products such as jute fibers were used as a substrate to synthesise polyaniline and used it to investigate the absorptive removal of hexavalent chromium Cr (VI) from its aqueous solution in batch experiments. In addition, Cr (VI) can be separated from the wastewater by using composites of polyaniline with maize bran, wheat bran and rice bran [26]. Removal of the chromium from the effluent was also carried out by using polyaniline and its composites. The adsorption capacities of these synthesised composites were also compared with some other adsorbents such as amberjet, anthracite and purolite-302. PANI/PVA composite was found to be a potential adsorbent for chromium removal. An effective removal of hexavalent chromium was observed by this composite of polyaniline and polyvinyl alcohol (PANI/PAV), consisted of aniline (0.2 mol/L) and PVA (2% w/v), generated by in situ polymerisation [27]. But the removal percentage is lower in case of PANI/anthracite composite in comparison to PANI [30]. A colorimetric determination of the adsorption was carried out in a study, in which chemically synthesised sawdust- polyaniline nanocomposite was used to clear away the Cr (VI) from the environment. It has been found that, all the examined composites reportedly achieved more than 80% adsorption during the first 30 minutes and the rate of adsorption depended upon the time [27]. Adsorption of Cd (II) ion by polyaniline/saw dust (PANI/S.D) and polyaniline/rice husk (PANI/R.H) was also reported in the literature. Results showed that these composites are suitable for the eviction of Cd (II) ions from the effluent [31]. According to a research, it is possible to expel the harmful Hg (II) ion from the industrial waste by using chemically synthesised polyaniline (PANI). The preferential adsorption method used during this research was batch experiment and the adsorbent was found to be efficient for the removal of Hg (II) ions [32]. Treatment of Cr (VI) polluted water was efficiently carried out by using sulphuric acid doped PANI as an adsorbent [29]. Nanocomposite of polyaniline and rice husk (PANI-RH) was employed for the treatment of industrial effluent containing lead and cadmium ions. The reported results clearly indicated the higher adsorption capacity of the adsorbent for Pb (II) ions as compare to the Cd (II) ions [31]. In another study, a nanocomposite of polyaniline and humic acid (PANI/HA) was prepared and used for the separation of the Cr (VI) ions from the industrial effluent. Major role of humic acid (HA) in this composite was reported to stabilize the PANI by preventing its agglomeration [22]. Metal ion contamination of water and its removal by nanocomposites based on polyaniline is as shown in Figure 1.2. Work carried out by the different researchers on the polyaniline as adsorbent for metal ion is as given in Table 1.

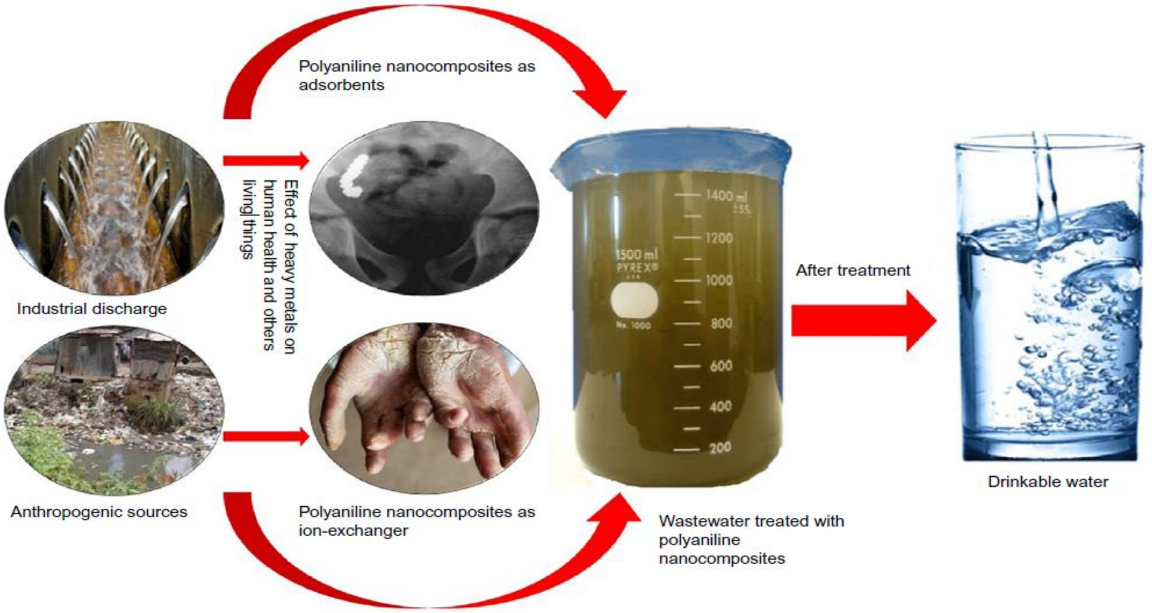

Figure 1.2: Metal ion contamination of water and its removal by nanocomposites based on polyaniline.

Table 1: Work performed for metal ions by various researchers on polyaniline as adsorbent.

Adsorbent	**Metal Ion Studied**	**Adsorption Capacity (q_m)**	**Reference**
Polyaniline/coconut shell–activated carbon (PANI/GAC) composite	Cu(II)	38.97mg/g	[21]

Polyaniline/Humic acid composite	Hg(II) Cr(VI)	671mg/g -Hg(II) 150mg/g- Cr(VI)	[22]
Polyaniline/ Polystyrene composite	Hg(II)	0.671 mol/g × 10^6	[23]
Polyaniline (PANI)/ Rice husk nanocomposite	Zn(II)	24.3mg/g	[24]
Polyaniline synthesized on jute fiber	Cr(VI)	62.8mg/g	[25]
PANI/Wheat bran	Cr(VI)	33.44mg/g	[26]
Polyaniline/Polyvinyl alcohol (PANI/PVA) composite	Cr(VI)	111.23mg/0.1g	[27]
PANI/ Saw dust PANI/ Rice husk	Cd (II)	PANI/ S.D-4.739mg/g PANI/R.H-5.128mg/g	[28]
Sulphuric acid doped PANI	Cr(VI)	95.79mg/g	[29]

1.6 0bjective of the Project

The aim of this project is:

"SYNTHESIS AND STUDY ON POLYANILINE AS AN EFFECTIVE ADSORBENT FOR THE REMOVAL OF HEAVY METALS FROM WASTEWATER."

To achieve this aim, some sub-objectives of the study has been set as follows:

1. Synthesis of polyaniline nanofibers by interfacial polymerization.
2. Characterization of polyaniline nanofibersusing FTIR, XRD, TEM etc.
3. Adsorption studies of Cr and Hg ions from their aqueous solution onto polyaniline.
4. Atomic Absorption Spectroscopy (AAS) confirmed the presence of Cr and Hg ions.

CHAPTER 2.
MATERIALS AND METHODS

2.1 Materials

2.1.1 Raw materials/Chemicals

In the present study, following raw materials/chemicals are employed:

1) Aniline
2) Toulene
3) Ammonium per sulphate (APS)
4) Hydrochloric Acid (HCl)
5) Mercuric Chloride
6) Potassium dichromate
7) Distilled Water

2.1.2 Specification and Sources of Raw Materials/Chemicals

Specification and sources of raw materials/chemicals used in the studies are shown in Table 2.1.

Table 2.1 Specifications and Sources of Raw Materials/Chemicals

Sr. No.	Chemicals	Source	Specification
1	Aniline	Thomas Baker (Chemicals) Private Limited	Laboratory Reagent Grade
2	Toulene	High Purity Chemicals Pvt. Ltd.	Analytical Reagent Grade
3	Ammonium per sulphate (APS)	Central Drug House Private Ltd.	Industrial and Laboratory Reagent Grade
4	Hydrochloric Acid (HCl)	Central Drug House Private Ltd.	Industrial and Laboratory Reagent Grade
5	Mercuric Chloride	LOBA Chemie Pvt. Ltd.	Laboratory Grade
6	Potassium dichromate	Central Drug House Pvt. Ltd.	Laboratory Grade

2.1.3 Purification of Raw materials/Chemicals

The consistency and accuracy in the results highly depends on the quality and purity of reactants employed. The percentage purity of the chemicals used during experimental work is given in Table 2.2. The chemicals that were received were usedas it is, without doing any further treatment.

Table 2.2. Percentage Purity of the Chemicals

Sr. No.	Chemicals	Percentage Purity

1	Aniline	98.5%
2	Toulene	99.5 %
3	Ammonium per sulphate (APS)	98%
4	Hydrochloric Acid (HCl)	37% AR
5	Mercuric Chloride	99.5%
6	Potassium dichromate	99.5 %

2.2 Methodology

The systematic methodology highlighting how the progress of proposed work towards achieving desired objectives was proceeded, involves the following steps:

- Synthesis of polyaniline (PANI) nanofibers by interfacial polymerization.
- Characterization of polyaniline nanofibers was carried out (FTIR, XRD, TEM).
- Preparation of Hg ion and Cr ion solutions.
- Adsorptive study of Hg ion and Cr ion on synthesized PANI by U-V Visible Spectrophotometry.
- Atomic Absorption Spectroscopy (AAS) to confirm the presence of Cr and Hg ions.

2.2.1 Procedure

2.2.1.1 Synthesis of Polyaniline Nanofibers

Chemicals Used

1. Aniline - 2 g
2. Toulene – 20ml
3. Ammonium per sulphate – 5 g
4. 1M HCl – 20 ml

Apparatus Used

1. Beaker
2. Burette
3. Stirrer
4. Glass Funnel
5. Whatman Filter Paper

Procedure Followed :

1. 2 ml of aniline was taken in a beaker.
2. 20 ml of toluene was added to it.
3. The mixture was stirred with the help of the magnetic stirrer for 5 minutes to prepare organic phase. Label the solution as, Solution 1. (Figure 2.1)
4. A mixture of 5g of ammonium per sulphate (APS) and 20 ml of 1M HCl was prepared (Aqueous Phase) and taken in a burette.Label the solution as, Solution 2.
5. Solution 2 was added drop by drop from the burette to the Solution 1for a span of 1 hours (Figure 2.2).
6. The reaction mixture was kept for next 24 hours for the completion of the reaction.
7. After 24 hours, the polyaniline (PANI) nanofibers formed, were filtered using whatman filter paper (Figure 2.3) and washed repeatedly.
8. The PANI thus obtained was dried in oven (80-100 ^{o}C) to get fine powder.

Figure 2.1: Preparation of Organic Phase i.e. Solution 1.

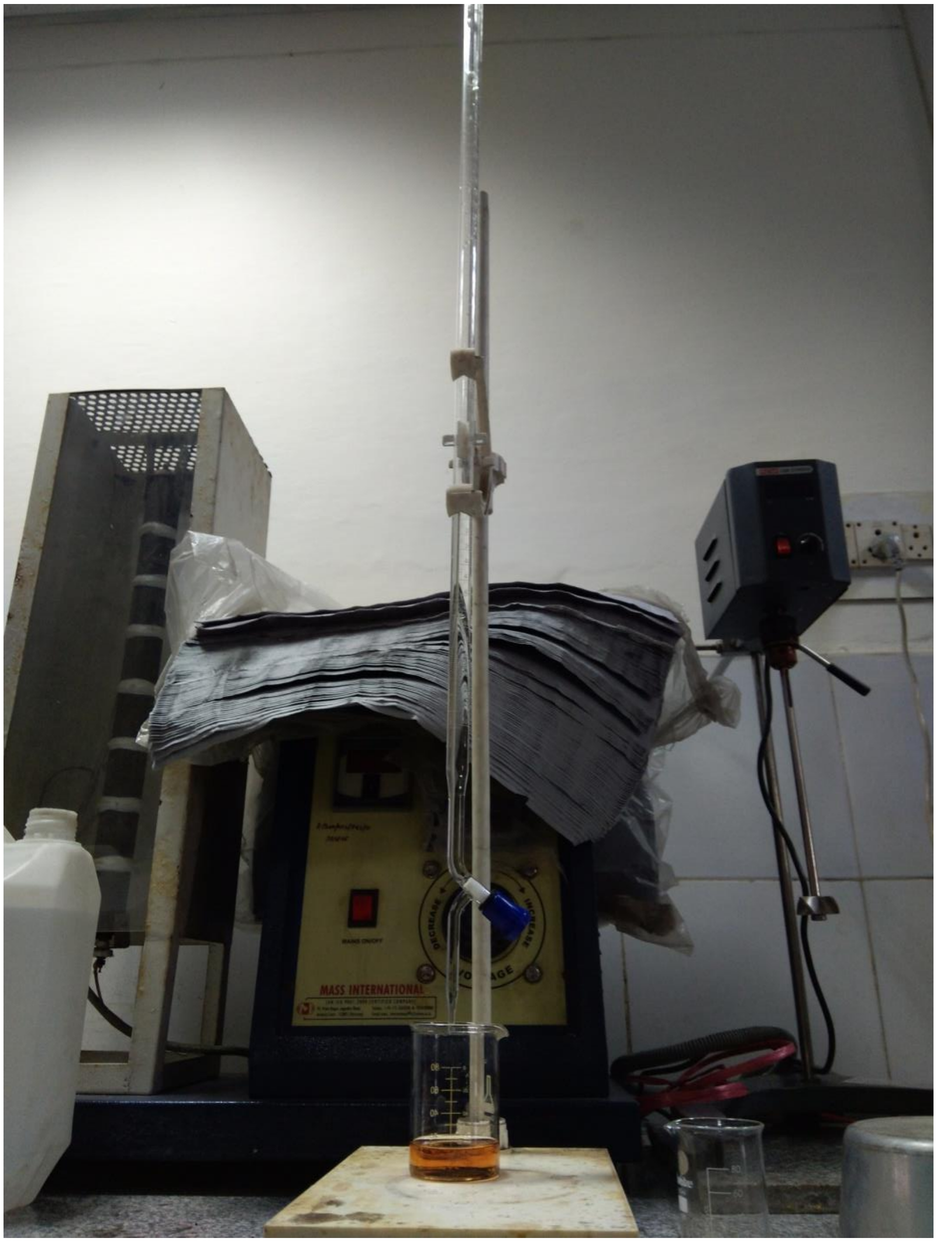

Figure 2.2: Set-up for the preparation of polyaniline nanofibers.

Figure 2.3 Filtered Polyaniline

2.2.1.2 Preparation of metal ions solutions

Solution containing Cr(VI) ions

The solution of potassium dichromate of 100 ppm was prepared separately in distilled water. From this stock solution, different concentrations of Cr (VI) had been prepared by dilution of specific volume of the stock solution. All batch experiments had been carried out by mixing 20 ml of certain concentration of Cr (VI) with 50 mg of polyaniline powder grinded in mortar pastel in a shaker incubator for about 45 minutes.

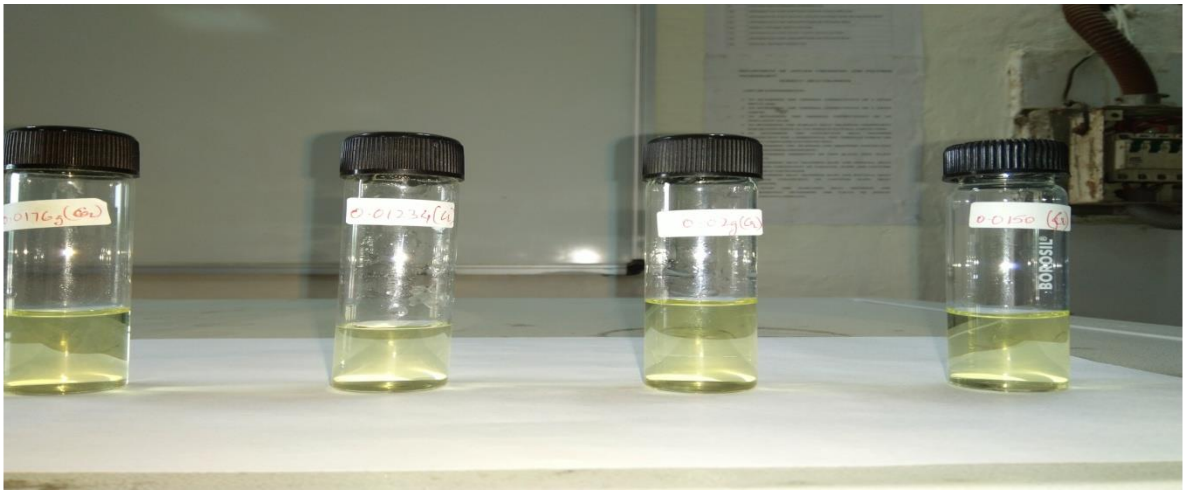

Figure 2.4: Samples of different concentrations of Cr(VI) ions.

Solution containing Hg ions :

Similarly a stock solution of mercuric chloride of 100 ppm was prepared separately in distilled water. From this stock solution, different concentrations of mercuric chloride had been synthesized by dilution of specifc volume of the stock solution. All batch experiments had been carried on by mixing 20ml of specific concentration of mercuric chloride with 50mg of polyaniline powder prepared in mortar pastel in a shaker incubator for about 45 minutes.

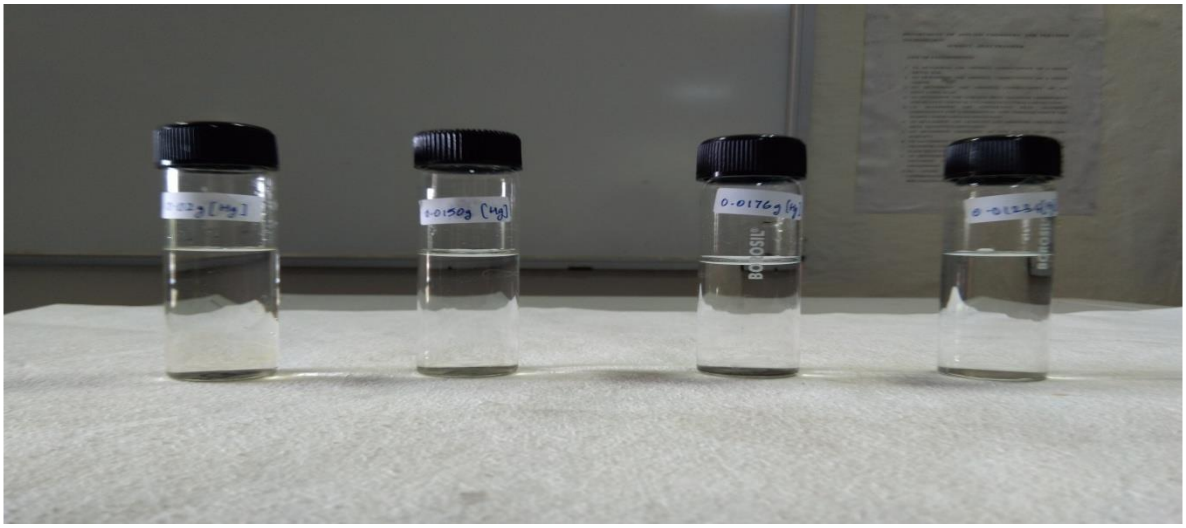

Figure 2.5: Samples of different concentration of Hg.

2.2.1.3 Adsorption Studies

After the preparation of samples, the adsorption process was carried out by mixing 50mg of polyaniline powder in a shaker incubator at room temperature. After almost 45 minutes, the shaker incubator was turned off and the samples were taken out and filtered again.

Figure 2.6: The adsorbed samples of different concentration Cr (VI) ions.

After almost 45 minutes, the shaker incubator was turned off and the samples were taken out and filtered again.

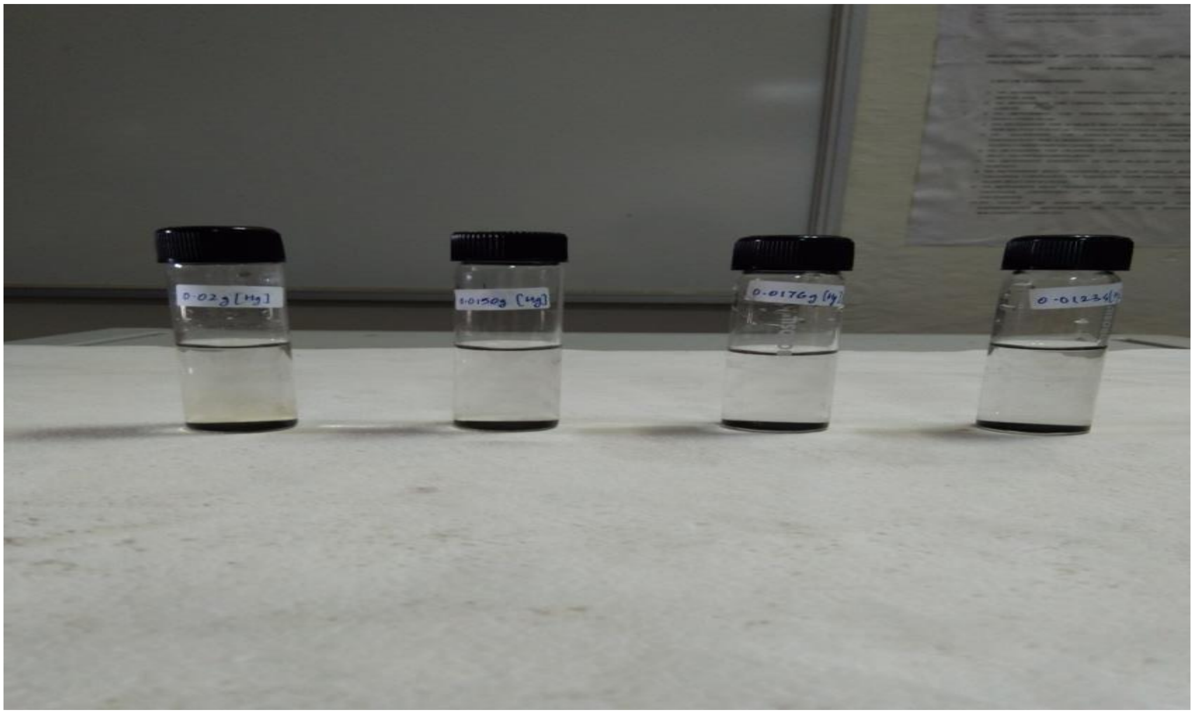

Figure 2.7 The adsorbed samples of Hg.

2.2.2 Characterization

2.2.1.4 Infrared Spectroscopy

The infrared spectroscopy is very important method for characterizing the polymers. One of the great advantages of infrared spectroscopy is that virtually any sample in any state can be examined. Fourier transforms infrared radiation (FITR) spectrometer calculates the transmission percentage of infrared. Here FT-IR spectrophotometer Nicolet 380 (shown in fig.2.8) had been used to procure IR spectra of synthesized sample. For FTIR analysis, the sample, prepared polyaniline nanofibers were first dried in oven and collected in powder form. A small amount of potassium bromide (KBr) was segregated with salt sample in attempt to create pellet and after that blend stirring was performed. This pellet was analyzed using FTIR by maintaining the pellet in the possession of the sample holder.

Figure 2.8: Nicolet 380 FT-IR Spectrometer

2.2.2.2 X-RayDiffraction

Wide angle X-ray diffraction or WAXD is a method commonly used to determine polymers' crystalline microstructure. This method relates specifically to the assessment of dispersed Bragg peaks at wide angles, which (by Bragg's Law) means that they are created by structures of sub-nanometer size. Diffraction pattern obtained tells researchers t0 determine phase c0mp0siti0n and hence, this technique can also be used for determination of percentage crystallinity of a sample. According to this technique, the sample will be tested at a wide angle X-Ray goniometer and the scattering strength will be measured as a function of the 2Ө angle.

Figure 2.9: An X-Ray Diffractometer

2.2.2.3 Transmission Electron Microscope (TEM) :

TEM typically use high energy electron beams transmitted through very thin sample in order to analyze the micro structure of materials. Electrons are accelerated at several hundred kV, resulting in wavelengths much smaller than that of light and are focused with electromagnetic lenses for imaging. Images of samples generated are recorded on digital camera. Collected images provide detailed information about the size, shape and morphological detail of materials.

Figure 2.10: A Transmission Electron Microscope

2.2.2.4 Atomic Absorption Spectroscopy:

Atomic Absorption Spectrophotometer analyzes the concentration of elements in a liquid sample on the basis of energy absorbed by light wavelengths (190 nm to 900 nm). To atomize the sample, it involves a fire burner, a monochromator, and a photon detector.
Thus atomic absorption spectroscopy (AAS) confirms the presence of Cr(VI) ions and Hg ions in the solution.

Figure 2.11: Atomic Absorption Spectrometer

CHAPTER 3.
RESULTS AND DISCUSSION

3.1 FTIR Analysis

The formation of polyaniline was confirmed by the FTIR. FTIR spectrum of polyaniline nanofibers prepared by interfacial polymerization is as shown in Fig. 3.1.

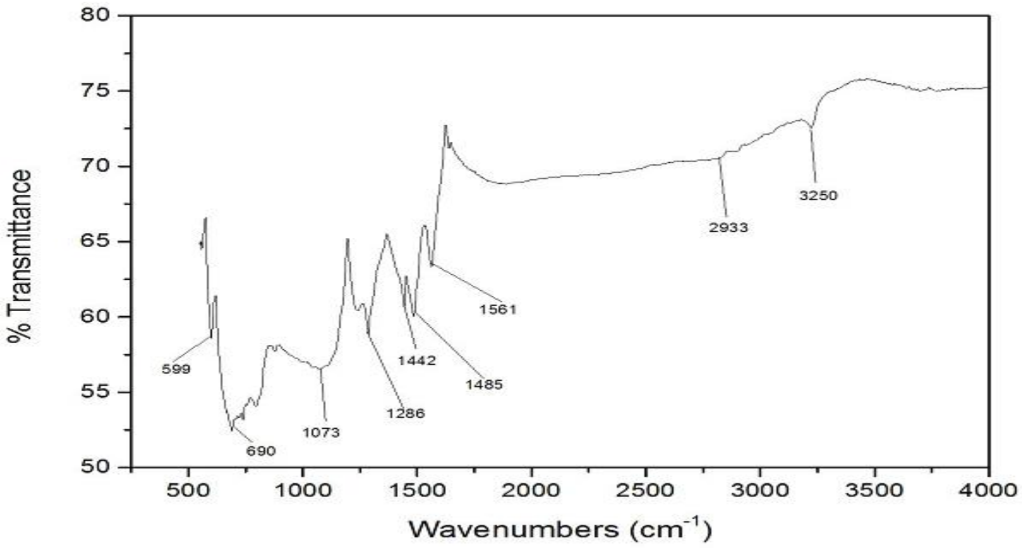

Figure 3.1: FTIR spectrum of polyaniline nanofibers prepared by interfacial polymerization

As evident, the Figure 3.1 demonstrates the primary distinctive polyaniline (emeraldine saline) FTIR spectrum peaks. The peak at 3450 cm^{-1} represents the structure's N-H stretch. Due to the asymmetric stretching mode of C-H aromatic bond, the absorption band at 2923 cm-1. The sample's quinoid composition is ascribed to peak at 1560 cm^{-1}. The maximum at 1296 cm^{-1} confirms the C-N stretching of secondary amines. The C-H bending vibration is the result of the absorption band found at 1105 cm^{-1}. The C= N stretching in organic compounds is ascribed to the absorption maximum at 1466 cm-1. The absorption band is attributable to 1,4 di-substituted benzene at 799 cm-1.The similar peaks was obtained by other researchers (Tariq S. Najim, Ali J. Salim, 2014)[33] in their research paper. Table 3.1 shows the different peaks and their range, as observed by FTIR.

Table 3.1: Different peaks observed by FTIR Analysis

Range cm-1	**Observation**
3450	N-H stretching
2924	CH asymmetric stretching
1560	Quinoid Structure
1296	C-N Stretching of secondary amines
1105	C-H Bending vibration
1466	C=N stretching
1170	1,4-disubstituted benzene

3.2 X-Ray Diffraction Studies :

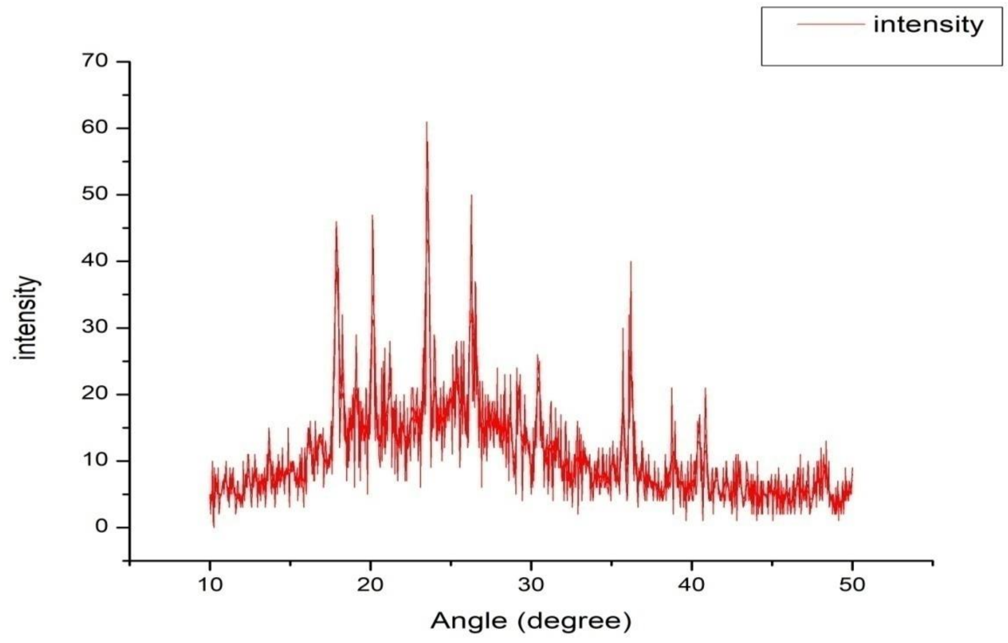

Figure 3.2: XRD of polyaniline nanofiber.

The findings of X-ray diffraction verified the development of polyaniline nanofiber, two distinctive peaks in the XRD structure of PANI nanofiber around 2ϴ=20º and 2ϴ=25º. The similar XRD pattern was obtained by other scholars (Tariq S. Najim, Ali J. Salim, 2014)[33].

3.3 Transmission Electron Microscopy (TEM) :

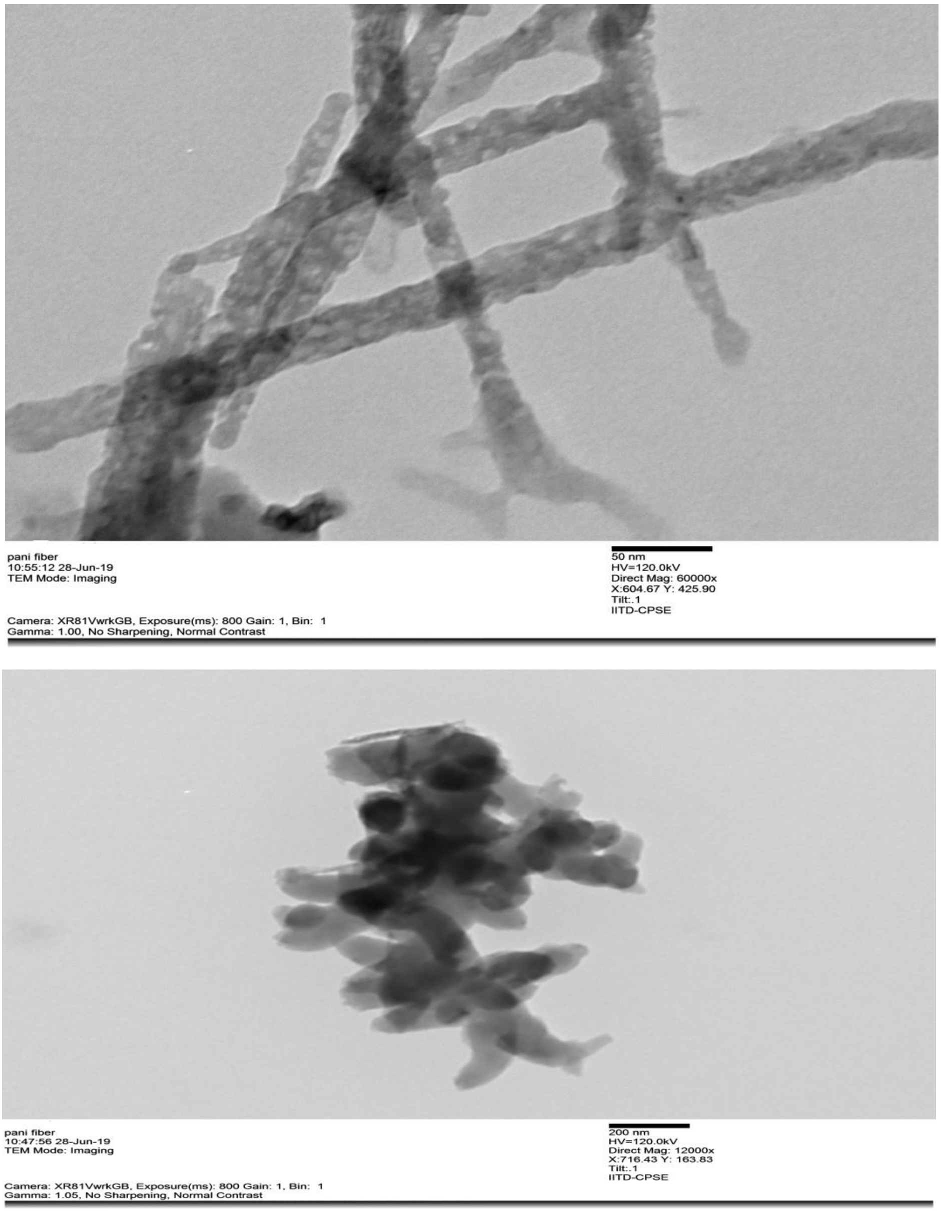

Figure 3.3: TEM images showing the formation of polyaniline nanofibers.

As the TEM reveals that synthesized polyaniline exhibit fibrillar morphology (Figure 3.3). The formed polyaniline nanofibers have average diameter of 21.4 nm and having a size distribution of 15.7 nm to 40 nm. Hence, the polyaniline nanofibers were successfully formed.

4.4 Adsorption Studies

Adsorption Studies of Cr (VI) Ion

UV-Visible Spectroscopy of the pure aqueous solution containing Cr ions helped in plotting the following calibration curve as shown in Figure 3.4.

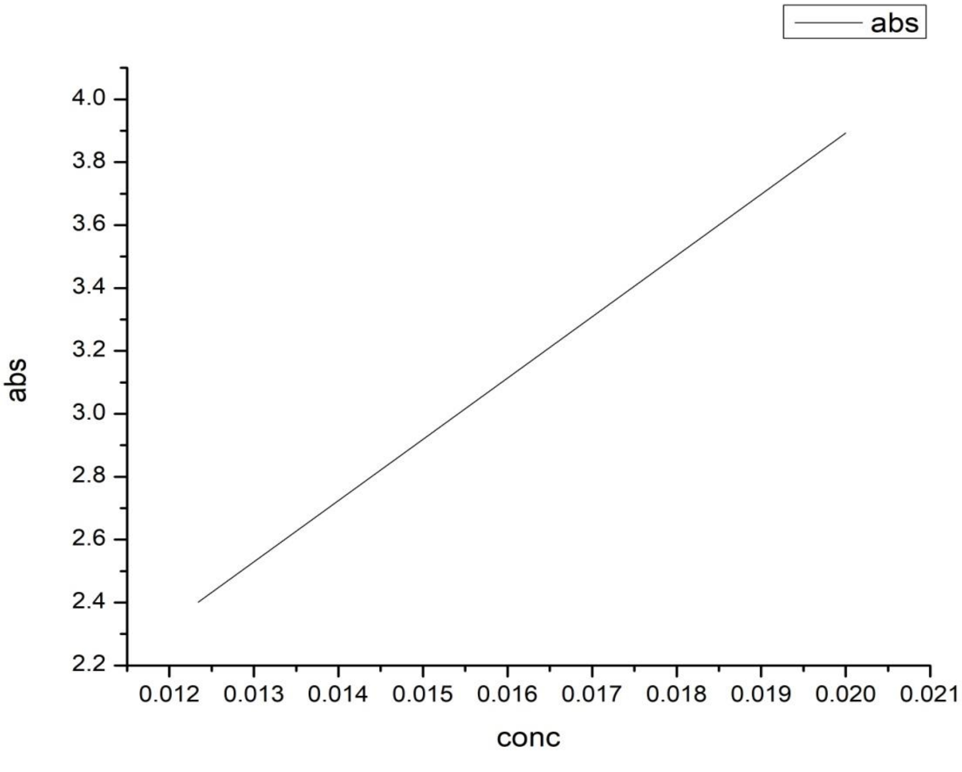

Fig. 3.4: Ca1ibration Curve giving relationship between Conc. of Cr ion and absorption observed by UV-Visible Spectrophotometer

Table 3.2: Absorbance at different concentrations (Cr).

Conc.(g/l) Of Cr.	**Absorbance**
0.01234	2.40158
0.01500	2.91926
0.01760	3.42526
0.02001	3.89235

Percentage adsorption or adsorption capacity was obtained by the following formula :

$$\text{Adsorption Capacity} = [(C_o - C_e)/ C_o] * 100$$

Where,

C_o= initial concentration

C_e= final concentration

Again UV-Visible spectroscopy was used to determine the final concentration after adsorption.Hence, a final graph was plotted between final concentration of the Cr ion remaining vs percentage adsorption as shown in Figure 3.5.

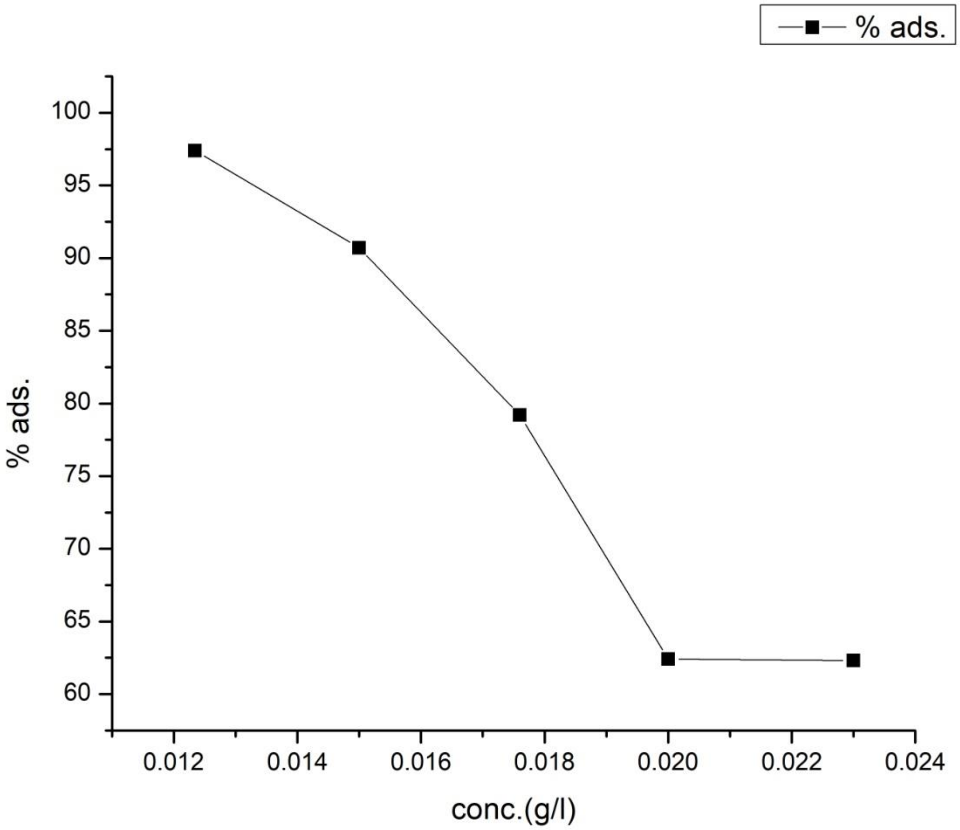

Figure 3.5: Final concentration of the Cr ion remaining after adsorption vs percentage adsorption.

Table 3.3: Adsorption Capacity at different concentrations (Cr).

Conc.(g/l)	**% Adsorption**
0.01234	97.40
0.01500	90.71
0.01760	79.20
0.02000	62.40

From the graph, it can be concluded that as the concentration was increased, adsorption capacity was gradually reduced and at a certain concentration it became constant.

Adsorption Studies of Hg Ion

UV-Visible Spectroscopy of the pure aqueous solution containing Hg ions helped in plotting the following calibration curve (Figure 3.6).

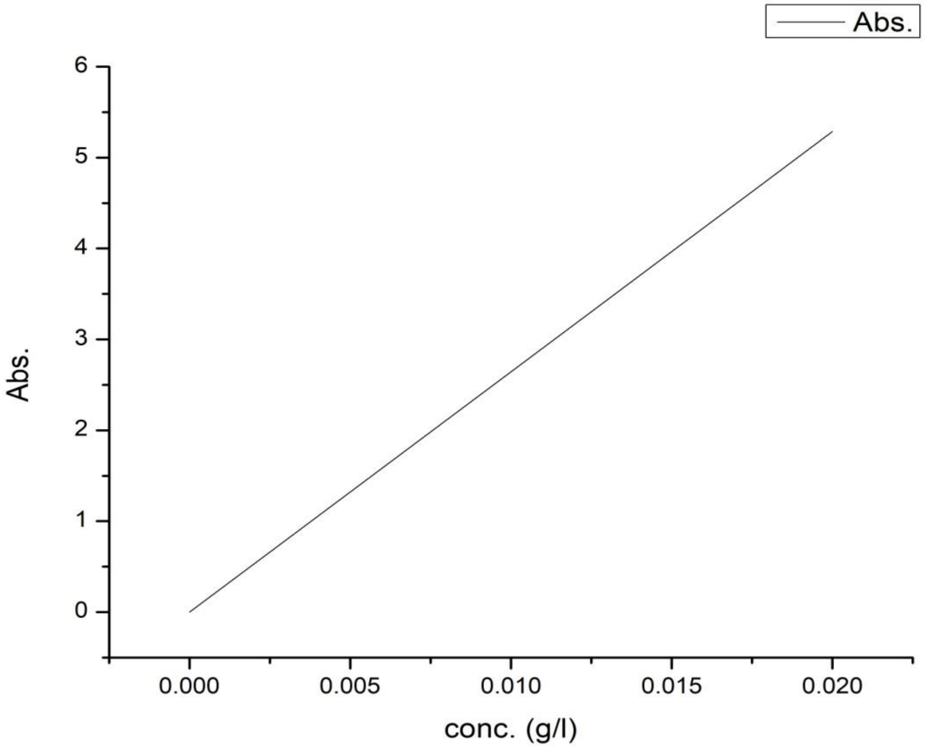

Fig.3.6: Ca1ibration Curve giving relationship between Conc. of Hg ion and absorption observed by UV-Visible Spectrophotometer

Table 3.4: Absorbance at different concentrations of Hg

Conc.(g/l) Of Hg.	**Absorbance**
0.01234	2.2693
0.01500	2.7508
0.01760	3.2276
0.02001	3.6677

Percentage adsorption or adsorption capacity was obtained by the following formula :

$$\text{Adsorption Capacity} = [(C_o - C_e)/ C_o]* 100$$

Where,

C_o= initial concentration

C_e= final concentration

Again UV-Visible spectroscopy was used to determine the final concentration after adsorption.Hence, a final graph was plotted which tells how much adsorption was done at different concentrations (Figure 3.7). The Table 3.5 showing the adsorption capacity at different concentrations is as follows :

Table 3.5: Adsorption Capacity at different concentrations (Hg)

Conc.(g/l)	**% Adsorption**
0.01234	91.76
0.01500	80.30
0.01760	50.20
0.02000	40.95

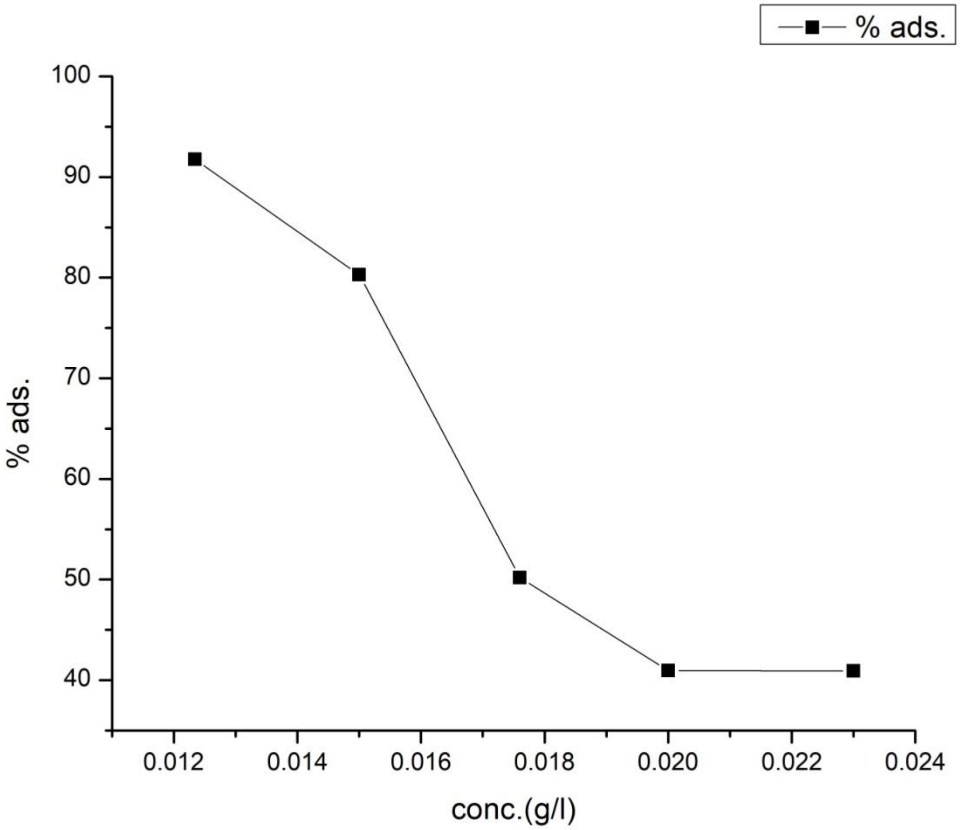

Figure 3.7: Final concentration of the Hg ion remaining after adsorption vs percentage adsorption

From the graph, it can be concluded that as the concentration was increased, adsorption capacity was gradually reduced and at a certain concentration it became constant.

Effect of contact time on the adsorption of Cr(Vl) ions :

The impact of interaction moment by adsorbent polyaniline on the extraction effectiveness of Cr ions was researched. The adsorption frequency of metal ions was quite fast; metal extraction was 88.91% for the Cr ions in the first 20 minutes, using polyaniline. Therefore, after every 10 minutes interval, the adsorption process was studied and it was found that after 90 minutes, 92.92% of Cr ions were removed. Hence, from the graph it can be said that after almost 90 minutes, equilibrium was reached as on afterwards no more adsorption was done. This can be confirmed with the results obtained by Sharma et.al. [34]. The graph is as follows :

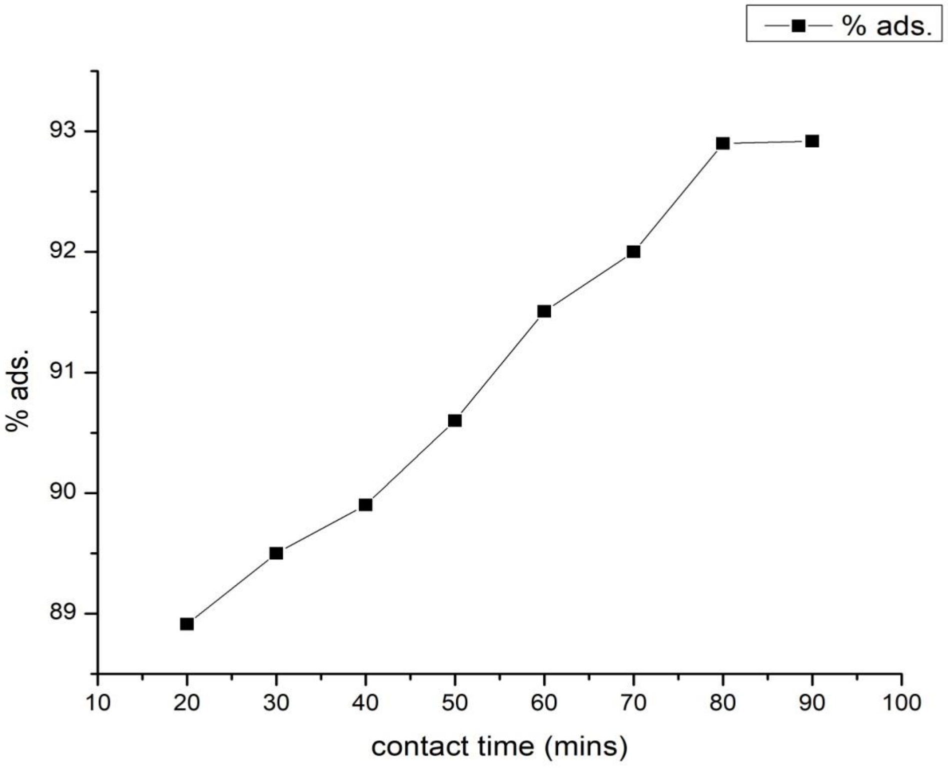

Fig.3.8 : Contact time Vs Percentage adsorption graph of Cr ions.

Table 3.6 : Percentage adsorption of Cr ion at different contact time

CONTACT TIME (IN MINUTES)	% ADSORPTION
20	88.91
30	89.50
40	89.90
50	90.60
60	91.51
70	92.00
80	92.90
90	92.92

Effect of contact time on the adsorption of Hg ions :

The effect of contact time on the removal efficiency of Hg ions by the adsorbant polyaniline was studied. The adsorption frequency of metal ions was quite fast; metal extraction was 85.30% for the Hg ions in the first 20 minutes, using polyaniline. Therefore, after every 10 minutes interval, the adsorption process was studied and it was found that after 90 minutes, 88.0% of Hg ions were removed. Hence, from the graph it can be said that after almost 90 minutes, equilibrium was reached as on afterwards no more adsorption was done. This can be confirmed with the results obtained by R. Ansari et.al. [35]. The graph is as follows :

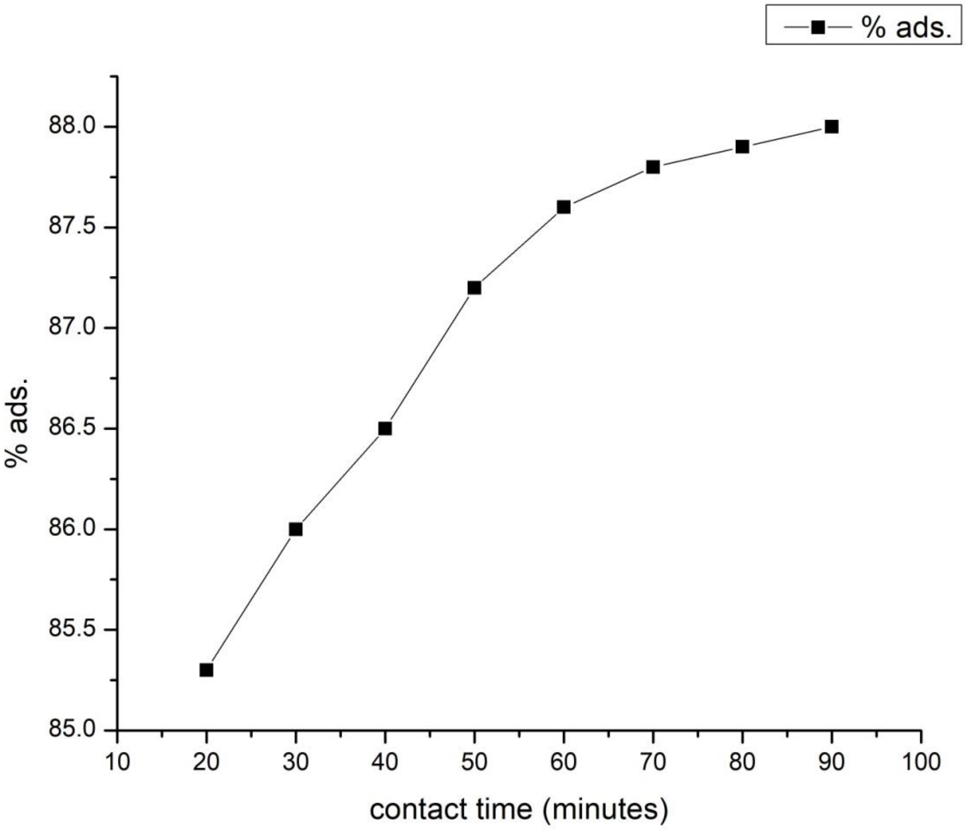

Fig.3.9 : Contact time Vs Percentage adsorption graph of Hg ion.

Table 3.7 : Percentage adsorption of Hg ion at different contact time.

CONTACT TIME (IN MINUTES)	% ADSORPTION
20	85.3
30	86.0
40	86.5
50	87.2
60	87.6
70	87.8
80	87.9
90	88.0

Effect of sorbent dosage on adsorption of chromium ion by Polyaniline:

In this experiment, various adsorbent weights (Polyaniline) (0.03-0.07 g) have been handled with alternatives of 20 mL chromium ion with a steady level of 100 ppm. As shown by our results (fig.3.10), the percentage of sorbent dosage increases to 0.60 g.

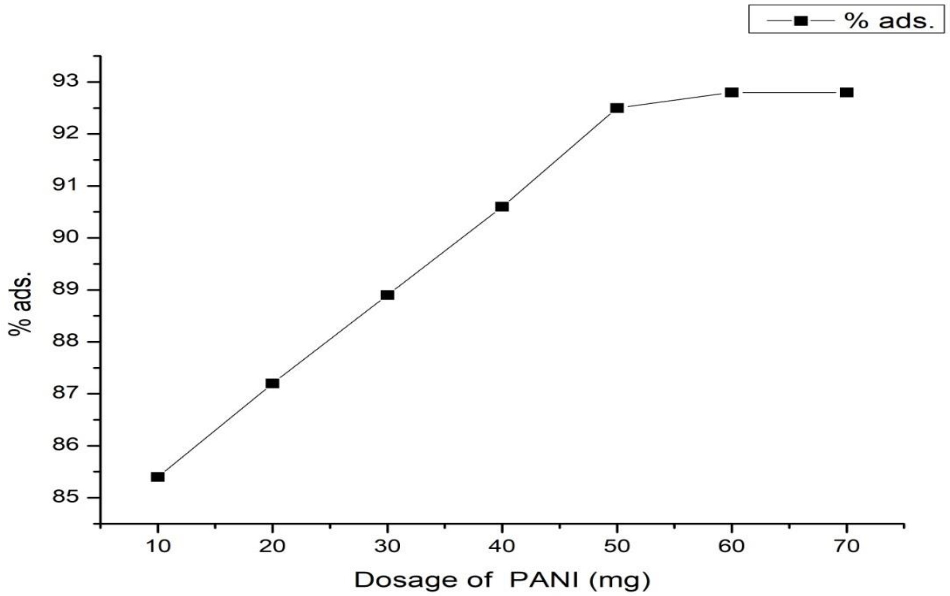

Fig.3.10: Different dosages of polyaniline (PANI) Vs Percentage adsorption graph of Cr ions.

Table 3.8 : Percentage Adsorption of Cr ion at different dosages of polyaniline.

DOSAGE OF POLYANILINE (in mg)	% ADSORPTION
10	85.4
20	87.2
30	88.9
40	90.6
50	92.5
60	92.8
70	92.8

Effect of sorbent dosage on adsorption of mercuric ion by Polyaniline:

In this experiment, various adsorbent weights (Polyaniline) (0.03-0.07 g) have been handled with alternatives of 20 mL mercuric ion with a steady level of 100 ppm. As shown by our results (fig.3.11), the percentage of sorbent dosage increases to 0.60 g.

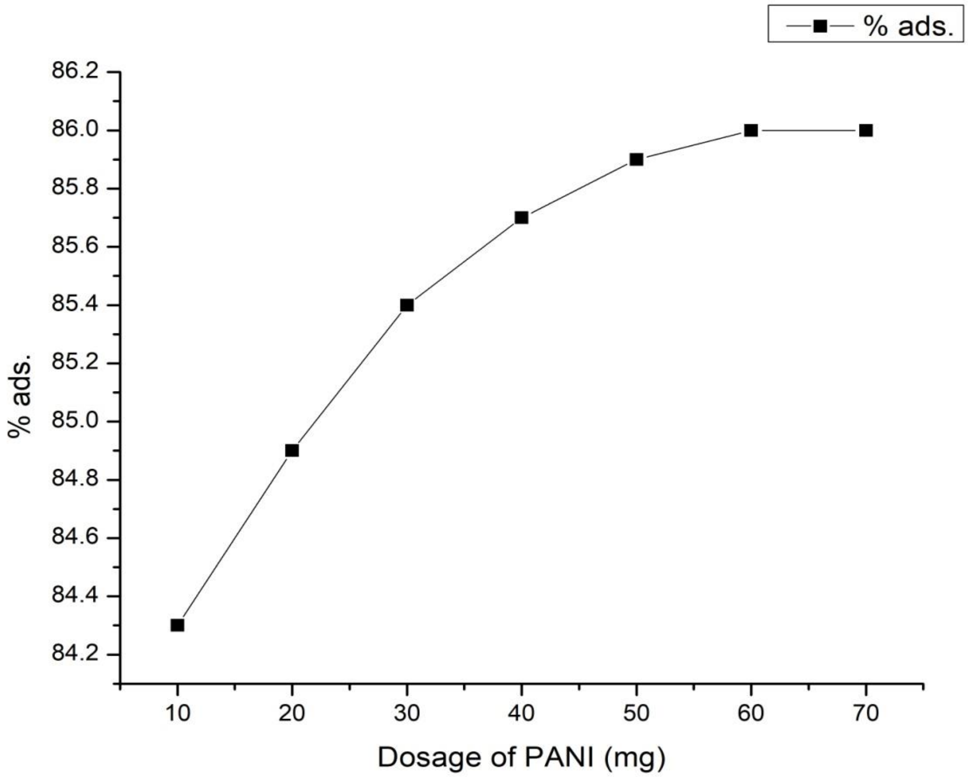

Fig.3.11: Different dosages of polyaniline (PANI) Vs Percentage adsorption graph of Hg ions.

Table 3.9 : Percentage Adsorption of Hg ion at different dosages of polyaniline.

DOSAGE OF POLYANILINE (in mg)	% ADSORPTION
10	84.3
20	84.9
30	85.4
40	85.7
50	85.9
60	86.0
70	86.0

3.5 Atomic Absorption Spectroscopy (AAS) Analysis :

Atomic Absorption Spectroscopy (AAS) confirmed the presence of Chromium ion in the aqueous solution.

Table 3.10 : AAS Analysis Report

Sample Name	Absorbance	% Transmittance	Concentration (in ppm)
Standard 1	0.000	99.9	0.00
Standard 2	0.003	99.3	1.00
Standard 3	0.006	98.6	2.00
Standard 4	0.008	98.3	3.00
Standard 5	0.011	97.4	4.00
Test Sample	0.066	98.5	2.148

Instrument Used : ECIL Atomic Absorption Spectroscopy

Element : Chromium (Cr)

Wavelength : 359.3 nm

Mode of Analysis : Linear

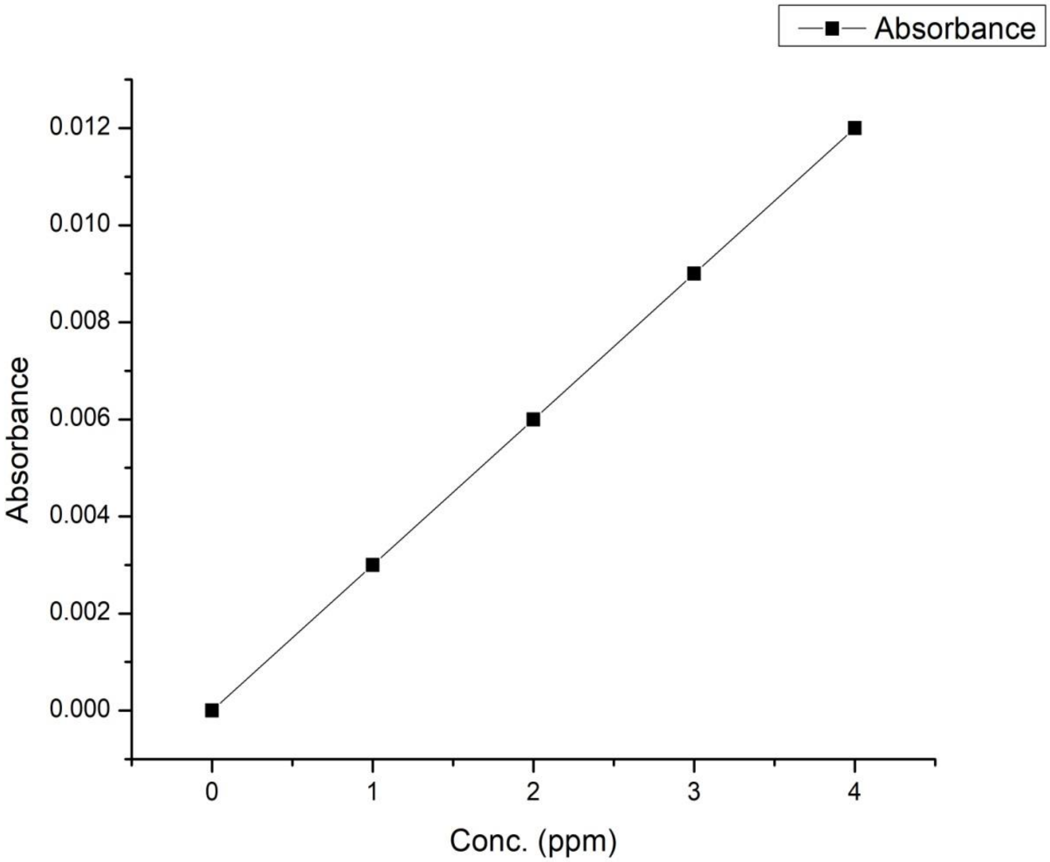

Fig.3.12 : AAS Linear Graph of Cr ion.

3.6 Atomic Absorption Spectroscopy (AAS) Analysis :

Atomic Absorption Spectroscopy (AAS) confirmed the presence of Mercuric ion in the aqueous solution.

Table 3.11 : AAS Analysis Report

Sample Name	Absorbance	% Transmittance	Concentration (in ppm)
Standard 1	0.000	99.9	0.00
Standard 2	0.040	96.3	1.00
Standard 3	0.120	90.1	3.00
Standard 4	0.240	86.4	6.00
Standard 5	0.360	78.2	9.00
Test Sample	0.280	87.8	6.60

Instrument Used : ECIL Atomic Absorption Spectroscopy

Element : Mercury (Hg)

Wavelength : 253.7 nm

Mode of Analysis : Linear

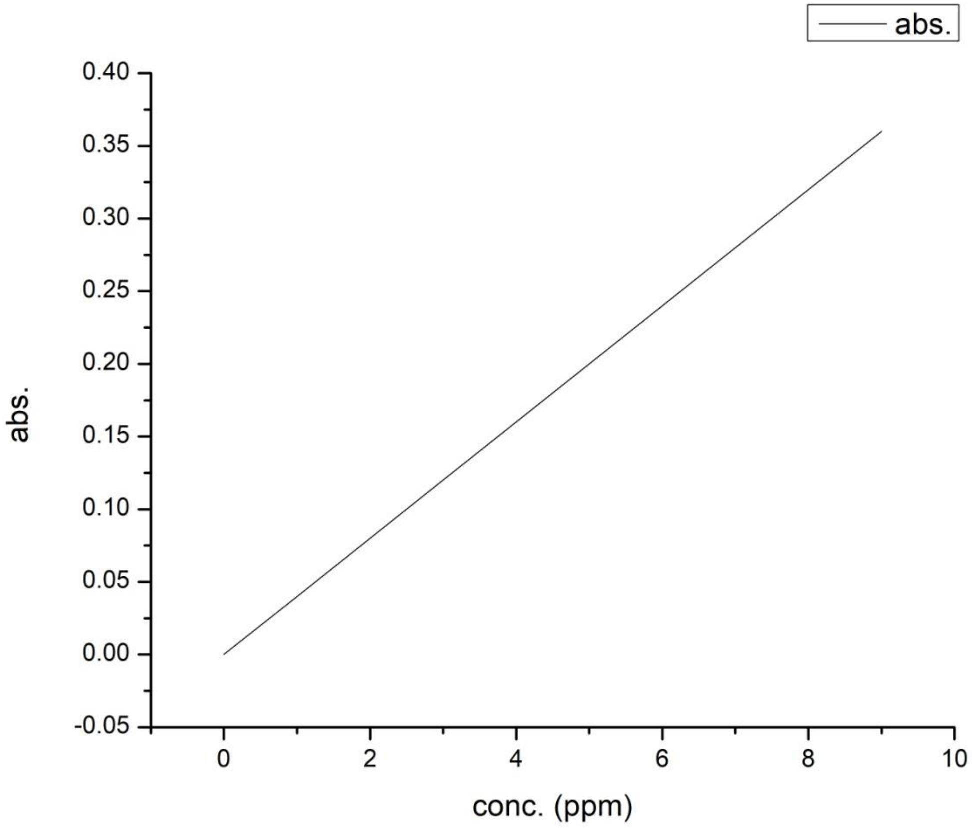

Fig.3.13 : AAS Linear Graph of Hg ion.

CHAPTER 4.
CONCLUSION

Rapid population growth and industrial activity intensification have led in a drastic rise in the amount of effluents released out into the atmosphere. These very diverse contaminants are a major environmental and public health problem. As a result, a global effort is being made to develop sound systems for efficient removal of contaminants from both water and air. Polyaniline can be easily synthesized chemically by interfacial polymerization. These results obtained had shown that polyaniline had potential to remove chromium and mercury from its aqueous solution. Adsorption is considered one of the most effective techniques for water treatment due to the flexibility and simplicity of layout, small cost, convenience of procedure and insensitivity to toxic pollutants. The adsorption process or metal absorption by the newly synthesized polyaniline appears to occur mostly through complex formation reaction or chelating in polymer (Polyaniline) between metal ion and amine groups. The existence of the chelating locations on the material gives electron pairs to metals and makes the chelates of metal. Polyaniline nanofibers' exceptional features makes them favourable products in applications of environmental pollutant remediation. Polyaniline occurs in deprotonated form under neutral circumstances, making the free -N groups accessible for metal chelating. The finding in this project is very essential to extract toxic metal ions from the point of perspective of water and waste water treatments.

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