

**ESTIMATION AND REMOVAL OF TOXIC METALS  
FROM INDUSTRIAL WASTE WATER  
BY POLYMER SUPPORTED SYSTEM**



by

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*Place: Karaikal*

*Date:*

## CONTENTS

CHAPTER	CONTENTS	PAGE NO
I	Introduction Objectives of the present work	1-24
II	Experimental, Results & Discussion	25-47
Appendix	References	48-52
	List of Publications	

## **I. INTRODUCTION**

### **1.1.ENVIRONMENTAL POLLUTION**

The environment consists of the atmosphere, the hydrosphere and the lithosphere in which life-sustaining resources of the earth are contained. The important components of environment which are identified are air, water and land with soil, minerals, plants and animals and climate. Environmental pollution has been defined as the unfavourable alteration of our surroundings, partly as an impact of increasing industrialization and related human activities. Several substances introduced by man to such an extent as to affect health of natural human system and the life in the environment as such[1]. The major source of pollution arises from man's activities. They include human, animal, industrial and agricultural wastes.

The spread of communicable diseases such as cholera, typhoid, dysenteries and other gastro-intestinal diseases due to human wastes contain pathogenic organisms. These wastes also contain putrescible materials which are responsible for obnoxious conditions and irreparable damage to the aesthetics of land and water environment. Industrial wastes contain a wide variety of organic chemicals and minerals including arsenic, cyanides, mercury, cadmium, carcinogens which are toxic to human, animal and plant life. Agricultural drainage carries dangerous pesticide residues and unused fertilizer ingredients. When the wastes are let out in the environment without adequate treatment they cause air, water and land pollution subsequently misbalancing the ecological cycle. In general terms, pollution causes degradation and/or damage to the natural functioning of the biosphere[2]. We are now aware that it is enormous task to make up within a few years for decades or rather centuries of environmental damage and degradation. Environmental pollution is not only linked with industrial growth but also with

the pressure of population on limited natural resources. Urbanization without town planning is a cause of land pollution.

Lack of fundamental civic amenities such as sanitation, water supply, housing in urban complex lead to the problem of waste disposal. The regular influx of population from rural areas to urban areas has added to this problem. Having polluted the land, we started also to pollute the last clean place on the globe, namely, seas and oceans on the assumption that the self purge abilities of the seas and oceans would somehow solve the problem. The oceanographer Jacques Cousteau warns us that the floor of the Mediterranean is littered with the debris and waste of modern technology. Ecologists assert that it is a dying sea. The cost of environmental pollution is high relative to socio-economic advantages of greater than before industrialization. Therefore, it is more than high time that the crisis of environmental pollution on an emergency basis have to be tackled.

## **1.2. WATER POLLUTION**

Water is one of the most important components in our environmental resources. Water pollution as a result of increasing industrialization and urbanization in the country is assuming a dangerous course. The reported work on water pollution is much more than on any categories of pollution. Water being such a good solvent is never found naturally in a complete pure state, e.g., rainwater contains dissolve  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{N}_2$  and other particulates from the atmosphere. The normal areas of water usage includes: recreation and aesthetics, public water supply, fish, other aquatic and wild life, agriculture and industry. Water is a probable carrier of pathogenic microorganisms which can endanger health and life[3]. They are responsible for infections of the intestinal tract causing typhoid fever, dysentery, cholera and polio, etc. These organisms are present in the faeces or urine of the infected people and are somehow

discharged into a water course from where the water is used for drinking and cooking purposes. The oil pollution is an almost unenviable consequence of dependence of a rapid growing population on an oil based technology. The sediments are soil and mineral particles washed from the land by storms and flood waters, from crop lands, unprotected forest soils, overgrazed pastures, strip mines, roads and bulldozed urban areas. Sediments fill stream channels and reservoirs, erode power turbines and pumping equipment, reduce the amount of sunlight availability to green aquatic plants, plug waterfilters and blanket fish nests, spawn, and food supplies thus reducing the fish and shellfish populations.

The inorganic pollutants (inorganic salts, mineral acids and finely divided metals or metal) is another category of water pollutants. The presence of these pollutants results in acidity and salinity of water and soil. Mine drainage and acidic rainfall are the two main sources of increased acidity in natural waters. The salts give rise to salinity. The toxic properties of numerous inorganics, particularly those of some heavy metals have been known for years.

The manufacture of synthetic organic compounds like fuels, plastics, fibres, detergents, elastomers, solvents, paints, pesticides, food additives and pharmaceuticals in the world has increased considerably. It is known that some detergents and pesticides are resistant even to the biochemical degradation by natural water bacteria and therefore persist in the marine environment for a longer period of time. Some are toxic to fish and other aquatic organisms when present even in very low concentrations[4].

### **1.3. HEAVY METAL POLLUTION**

Elements like H, C, N, O, Na, Mg, P, S, Cl, K, Ca constitute 99.9% of all living matter compare to all the elements present on the earth's crust,. In

addition 14 elements, viz., B, F, Si, V, Cr, Mn, Fe, Co, Cu, Sc, Mo, Sn and I are the essential trace elements. The rest of the elements are either not essential for growth and development of organisms or their purpose in the biological systems has not been established. Iron and aluminium which have extensive applications in industry and daily life, are also perhaps the major components of the earth's crust.

Fortunately the ecological consequences of the spreading of these two elements in our living environment have not so far posed any serious health problems. Some of the trace metals, like Hg, Pb, Cd, As, Cr, Zn, Cu, Mn, which are not necessary ones but when present in aquatic environment above certain levels are hazardous. Enhanced levels of heavy metals in the aquatic environment cause concern due to :

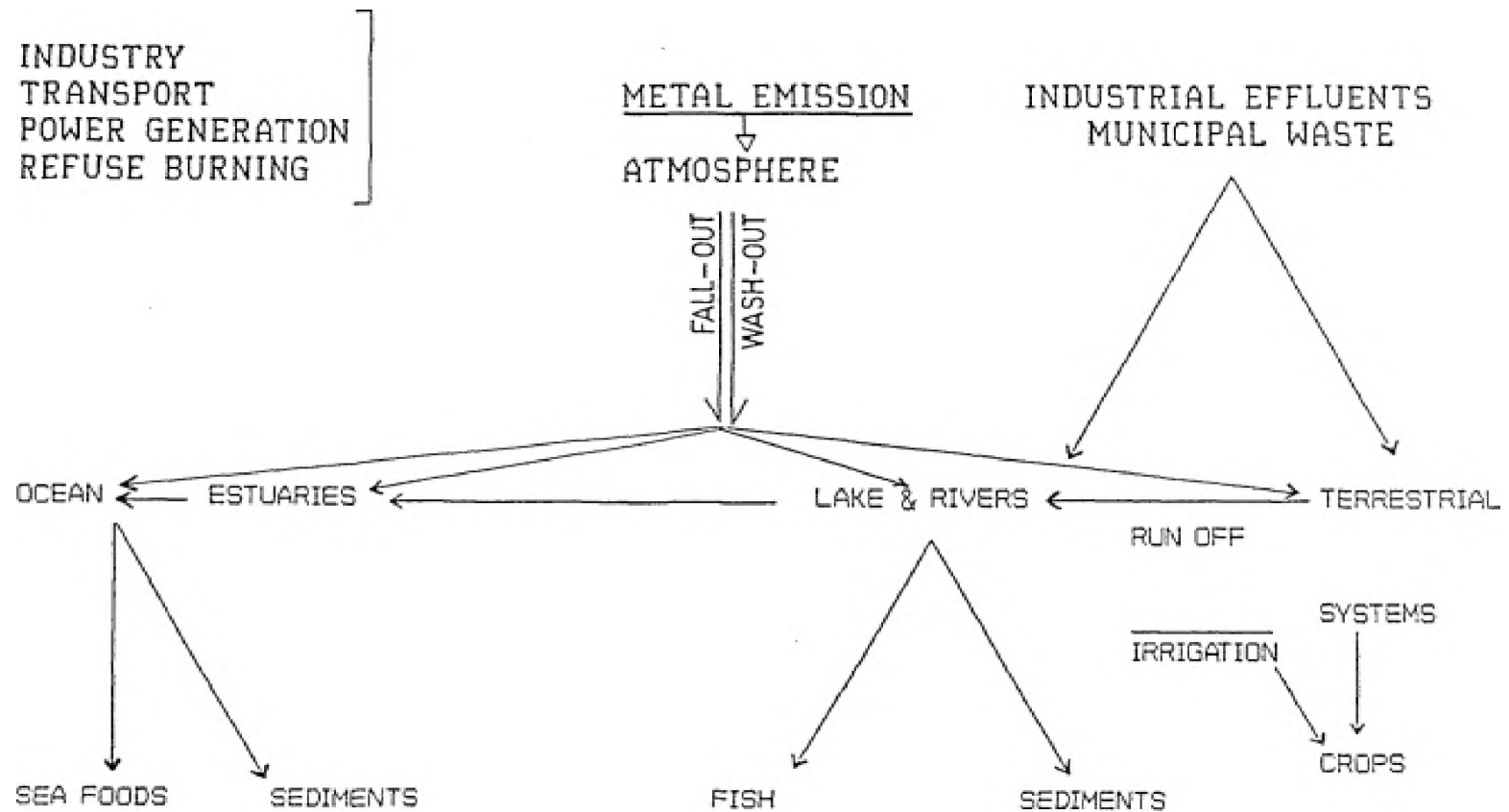
- (i) Opportunity of accumulation of these metals in human body and building-up with time to toxic levels.
- (ii) Chronic and sub-lethal belongings to organisms at low concentrations.
- (iii) Bio-concentration/ gathering and magnification by aquatic organisms.
- (iv) Persistence in the environment with potential for environmental transformation into more toxic compounds.
- (v) Promising intake through drinking water and aquatic food.
- (vi) High understanding of children for some of the heavy metals.
- (vii) Carcinogenic and teratogenic possibilities of some of the heavy metals and their compounds.
- (viii) Phyto-toxicity of heavy metals.
- (ix) Synergistic effect of heavy metals to organisms.

The accessible information on metal toxicity, as it relates to human beings is derived mostly from health surveys among workers occupied in mining and processing of these metals. The most toxic among the heavy metals known, in view of environmental degradation are Hg, Cd, Pb, Cr, Ni and As, which tend to accumulate in bodies of living organisms, persist and act as cumulative poison. A classic example of heavy metal enrichment of the aquatic environment is the clear of the catalyst methylated mercury chloride into Minamata Bay from a factory manufacturing plastics. The micro organism converted the sediment compound to monomethyl-mercury which led to an enrichment of this largely toxic compound in fish consumed by the local fisher-folk resulting in the well known Minamata disaster. Catastrophic episodes of metal poisoning such as cadmium poisoning causing itai-itai disease by the utilization of rice containing high levels of cadmium, lead poisoning in children who licked toys painted with lead based paints, chromium poisoning and arsenic poisoning in young children from the spending of dry milk powder to which arsenic-contaminated sodium phosphate had been added as stabilizer has dramatised the ill-effects of environmental contamination by toxic metals[5]. It is obvious that the exposure to toxic elements in the work and living environment leads to health risks. Therefore, the crucial problem is, to assess the safety margins from the available epidemiological data and from those generated by experimentation.

The problem into environment pollution by metal is, however universal and the situation in India may be measured very typical of the countries which are on the process of development. In general, it is possible to distinguish between different sources from which metal contamination of the environment originates: geological weathering, industrial dispensation of ores and metals, the use of metals and metal components, leakage of metals from garbage and solid squander dumps, and animal and human excretions which contain heavy metal.



Fig.1. Dispersion of metals in Environment



#### 1.4. PHYSICO-CHEMICAL STUDIES ON RIVER POLLUTION

The major problem to environmental resulting from water, air and soil pollution have been long known to mankind. However only during the last few decades have they come to be regarded as problems of considerable magnitude after the pollutants have accumulated to the point where they pose a serious threat to human life. This is a problem worthy of serious attention because rivers are the major source of fresh water supply. Intensive researches have been carried out on monitoring of rivers all over the globe since environmental awareness arose. Pollution studies on the water quality of twenty – six Nigerian rivers were undertaken [6] during the dry season periods of 1977-78. The samples were analysed for BOD, COD, pH, DO, ammonia, nitrate and phosphate. Seventeen of the rivers were found to be more or less unpolluted, six of them being of high quality and the remaining nine were found to be polluted naturally.

The environmental pollution monitoring of river Pandu at Kanpur was undertaken [7]. The variations in the chemical water quality were found to be due to the waste discharge and were also connected with organic and inorganic enrichment. Although most of the parameters studied conform to the standards, ammonical and organic nitrogen, sulfides and total solids exceeded the acceptable limits at four stations. The physico-chemical characteristics of Ganga river water in U.P. and Bihar in summer and winter was studied by Ajmal et al. [8]. They correlated the concentrations of chloride, sulfide and total solids with the variations of the volume of sewage and industrial waste discharged into the river. The river was found to be highly polluted at Kanpur, Allahabad (Sangam) and Varanasi; moderately at Fatehpur, Patna and Monghyr; and comparatively less \ at Narora and Kannauj. The large volumes of untreated tannery wastewater discharged into the Ganga river at Kanpur was

responsible for the increased water turbidity, COD, suspended solid and chromium concentrations [9].

The river, which is the only source of drinking water supply to the city poses an immediate hazard to public health. The water quality of Aona and Kuro rivers, Japan, studied [10] from April 1980 to March 1983 was found to be slightly polluted having pH 6.7-7.2, CI 5.5-6.7, BOD 0.9-1.2, COD 1.4-2.0, suspended solids 4-15, DO 1.5, total nitrogen 0.53-0.97 and total phosphorous 0.02 mg/l. The BOD, chloride concentration, pH and coliform count increased at downstream locations. The concentration of suspended solids and chloride was correlated with the flow rate which was influenced by rainfall. High coliform count, BOD, sodium and nitrogen content was found in the Godavari river, India, which is unsuitable for drinking [11]. The tap water in this area was also unfit for drinking purposes. It was concluded that tube well water in comparison to river and tap water was of better quality for drinking. A comparison of recent with previously collected biochemical data of the Wieprz river, Poland, was made [12].

The impact of sewage and industrial effluents on the physico-chemical characteristics and heavy metal content in the water, sediments, submerged plants and fish of the Hindon river and Kali Nadi have been studied [13]. Kali Nadi was found to be highly polluted by organic matter. Hindon river was grossly polluted along the urban and industrial belts. The water quality of both rivers was found improved where it merged with less polluted tributaries. The physico-chemical and biological studies on river Ganga, India, from Mirzapur to Ballia from 1984-86 was undertaken [14]. The water quality was found to be good at the point where it entered the city (U/S) and gets highly polluted at midstream as a result of sewage and industrial wastes flowing through drains into the river. The downstream water at Varanasi was found to be the most polluted, which was due to the discharge of sewage mixed with industrial

effluents through Rajghat nallah. The highest total coliform count was observed at midstream at each sampling site and downstream of Varanasi.

The quantitative estimation of the bacteriological indicators in Ganga river to assess the impact of human activities on sanitary quality of the river water was studied. It was observed that the control sites maintained quite satisfactory conditions in summer and winter months as the indicators density was within the permissible limits, whereas the experimental sites never fulfilled the desired limits, indicating the presence of hazardous conditions at these localities [15].

Principal component analysis of relations between physicochemical variables in a Mediterranean lagoon studied, showed that the mechanism within the lagoon affected the cycle of nutrient salt [16]. River Nandira, a tributary of Brahmani receives partially treated or untreated wastewater of Captive Power Plant, NALCO, Anugul; Fertilizer factory, FCI, Talcher and Talcher Thermal Power Plant [17]. Due to these industrial wastes, considerable change in colour, odour, pH and chemical characteristics (DO, BOD, COD) of the river water was observed. The planktons occurring in the unpolluted sites disappeared with a proportionate increase in the pollution load of Nandira.

A comparative study of the quality of potable waters from different sources at Bhagalpur, India, located on the south bank of the Ganges river which receives sewage and domestic wastewater discharges was carried out by Saha and Kumar [18]. The municipal surface water was found to be severely contaminated by rusted leaking pipelines and the groundwater was also contaminated by seepage from septic tanks, drains, and a deep sewage system. The contaminants from these sources have deteriorated the quality of potable water by increasing the turbidity (40 NTU),  $\text{NO}_3$  concentration (42.5 mg/l).

## 1.5 HEAVY METAL POLLUTION IN RIVERS

Metals are conservative elements which can neither be destroyed nor detoxified by modern technologies. The contamination of water by metal ions is increasingly felt from the last 10 to 20 years continuously. They occur naturally in aquatic environment. Release (both natural and man-induced) may be by air borne, liquid routes or as solid residues of manufacture which find their way into the aquatic system. The heavy metals are toxic at high concentration but some are highly toxic even at lower concentrations and are gladly concentrated by aquatic organisms and plants. They are generally water soluble, non-degradable, and vigorous oxidising agents. Due to these facts, many industrially developed countries have imposed regulatory on their release into the environment.

The concentration of metals viz., Zn 157.2-7424.2, Mn 230- 257.5, As 6-96, Hg 0.05-0.35, Cd 1-21, and Pb 69-1180.5 mg/l found in the Drau river water samples indicated that Zn and Pb values at some points along the river were critical as compared with the tolerance limit [19]. Slightly higher concentrations of heavy metals [20] in the Tyrrhenian river and Ionian sea were attributed to anthropogenic pollution from Silician coast, as well as to the metal inflow from Adriatic sea and air pollution from eruptions of Mt. Etna Volcano [21] concluded that these rivers were the main sources of metal pollution in coastal waters. The distribution of heavy metals (Fe, Mn, Zn, Cu, Pb, Cd, Ni, Ca, K, Mg, Co) in river water and sediments have been studied. It was found that the metal distribution in the rivers and lakes was controlled mainly by the organic matter.

Most of the heavy metals dissolved in river water combined with the soluble organic substances. Tada and Suzuki [22] found that the main factor controlling the adsorption of metals in bottom mud in urban rivers was organic matter, since the adsorbed metals decreased remarkably due to destruction of organic matter from the fine bottom mud. They used Freundlich adsorption isotherm for the study of adsorption of Cu, Zn, Cd and Pb. The effects of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Zn}^{2+}$  on the mycelia growth of three aquatic fungi and their ability to accumulate these heavy metals by adsorption to the surface of mycelium in vitro in the order of  $\text{Zn}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$  was reported. Bodies of poisoned shrimps contained  $\text{Cd}^{2+}$  ( 122.03 ug/g) showing that the metal can be transferred through a food chain involving freshwater fish and higher organisms [23].

The distribution of Pb, Zn, Cd, Cu, Cr, As, Se, Fe, Mn, V, Mo, U and Ra in water of Italian river were found to be relatively low i.e. within the permissible limits [24]. The accumulation of heavy metal viz., Cd, Cu, Cr and Pb in the Chao- Phraya river estuary was significant, which may have a long term impact on its aquatic environment [25]. A seasonal and spatial variations of heavy metals in the sediments and fish was also observed.

The heavy metal content in water and sediments of the Innersts Soese and Siber rivers, Germany, were determined and discussed in relation to wastewater discharge to the rivers. The relative standard deviation was found to be 7-5056 for most of the elements with higher values for Cr and As (130%) and Pb, Br, Ni, Hg and Cd ( 60 - 80 % ) in Elbe river [26]. The concentrations of heavy metals in the waters of Tiber river showed that the river caused significant pollution in the near shore as well as some in the offshore areas [27],

The water quality improved where it merged with less polluted tributaries. The monitoring of the Yamuna river water and the four major drains merging into the river to identify the sources of water pollution was carried out [28]. The dissolved material load of the river increased by 40% due to input from Delhi region through these drains. The metal concentration in the drains was found higher than those in the river. The heavy metal concentration at the entry point of the river were not in the detectable limits whereas at the exit point Cr, Fe, Mn, Ni and Pb concentration exceeded the WHO limits. Yoneda et al. [29] studied the contribution of domestic wastewater to heavy metal pollution and total organic carbon in sediments of the river in Nara City, Japan. The heavy metal concentration exhibited a log normal distribution at pollution free points. The heavy metal (Cd, Pb, Cr(VI), Cr, As, Ni) contents in acidic rivers in the Nagano prefecture were found below the water quality standards with the highest concentration of Fe 7.9 mg/l [30].

## **1.6. UNION TERRITORY OF PONDICHERY**

Pondicherry (U.T.) with four discontinuous regions enclaved in three southern States of India, namely Pondicherry and Karaikal regions nearing in Tamilnadu, Yanam region enclaved in Andhra Pradesh and Mahe region enclaved in Kerala (Fig.2-4). Pondicherry is the capital. The U. T. being an erstwhile French territory represents a unique blend of Indian and French cultures[31].

The Union Territory with two districts namely, Pondicherry and Karaikal consisting of 264 census villages, 129 revenue villages, 6 taluks (4 in Pondicherry, 2 in Karaikal) and 2 sub-taluks (Mahe & Yanam). For the reason of development administration the territory is divided into six blocks namely (i)

Ariankuppam block (ii) Oulgaret block (iii) Villianur block (iv) Kariakal block (v) Mahe block and (vi) Yanam block.



**Fig-2 Pondicherry Union Territory-Location**





The Municipal administration consist of of 5 municipalities namely Pondicherry, Oulgaret, Karaikal, Mahe and Yanam and 10 Commune Panchayats, namely (a) Villianur (b) Mannadipet (c) Ariankuppam (d) Bahour (d) Nettapakkam (e) Thirunallar (f) Neravy (g) Nedungadu (h) Kottucherry and (i) T.R. Pattinam.

As per 2001 census, the population of the U.T. is 9,74,345, totally 0.09% of India's total population. With a geographical area of just 480 sq. km., the U.T. accounts for 0.000154 % of that of India. The population density is 2029, one of the highest in India. The sex ratio is 1001. Geologically, Pondicherry, Karaikal and Yanam regions are more or less flat. The terrain of Mahe is little undulating. Two small main rivers Sankarabarani and Penniar pass through Pondicherry region. In Karaikal Arasalar and Thirumalairayan rivers are the most important ones. Distributaries of Cauvery River also pass through Karaikal. In Yanam Gouthami (a tributary of Godavari) is the important river. In Mahe a small river by name Mahe. Though the U.T. is very small, it has made rapid strides in industrial expansion in view of the industrial friendly policies of the successive Governments.

The U.T. might realize a fairly decent industrial growth despite the lack of natural resource base. Tax sops, easy availability of power, very good infrastructure and connectivity and ready availability of skilled manpower contributed for this.

### **1.7. THIRUMALAIRAYAN RIVERS & INDUSTRIAL ZONE.**

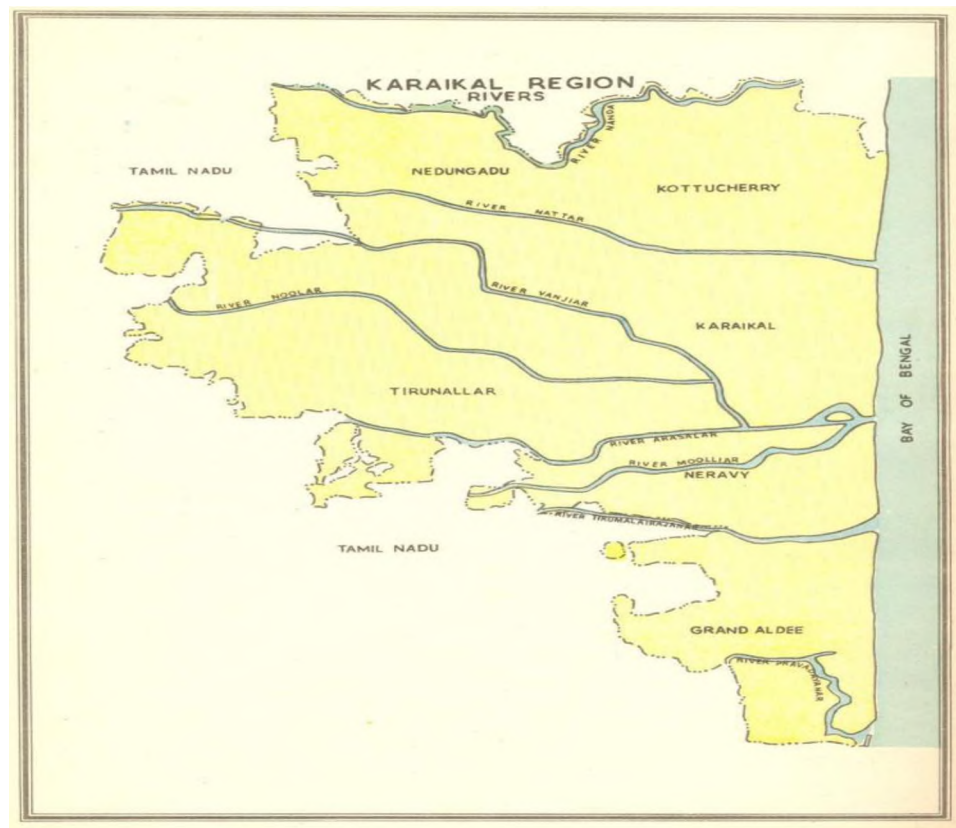
The fluvial concentrations of trace metals increased in water and decreased in sediments in the Periyar river, India, during summer due to solubilization and concentration by evaporation. The levels of Fe and Mn increased tenfold in water and sediments in the industrial zone. The river

meandering was found responsible for the large scale deposition of suspended solids in the industrial zone during the monsoon period. The levels of metals (Cu, Co, In, Pb, Mn, Li, Na, K and Ca) in the bottom sediments were found to be much higher than those in the water of Nainital Lake [32]. A comparative study of trace elements with earlier data over a period of time at various sites on Ganga river was carried out [33].

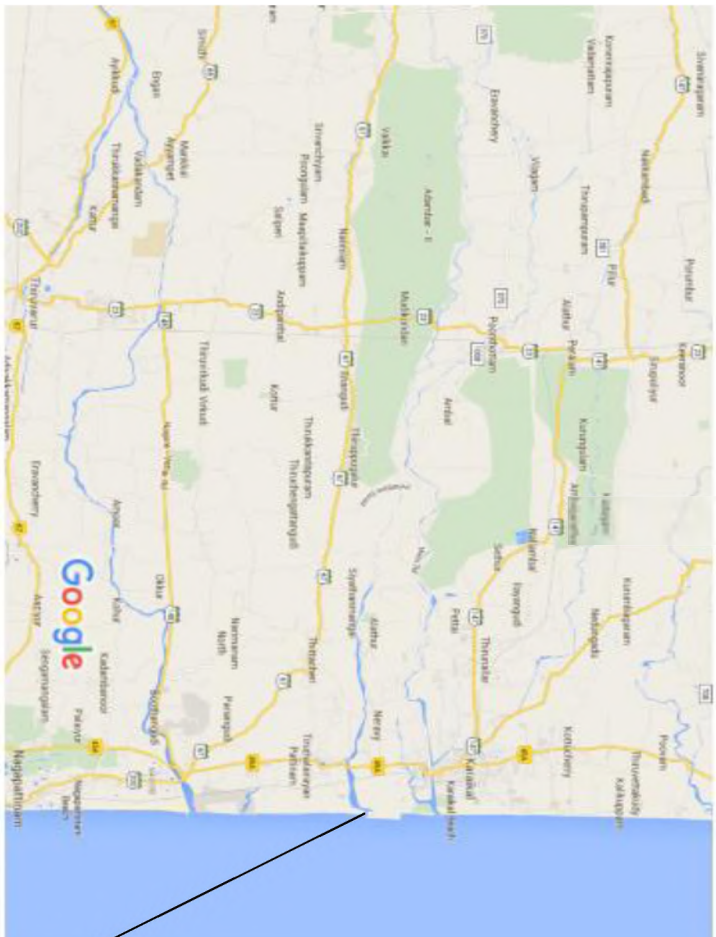
The metals Pb, Zn, Cd, Co, Cu, Cr, Ni, Fe and Mn were determined by atomic absorption spectrophotometer in water and sediments of the lower reaches of Weser river, Germany [34]. It was observed that these metals were concentrated in the river water from industrial effluents and emitted before being absorbed by the sediments. The concentration of Hg, Pb, Cd, Cr and Cu in sediments collected from the Besos and Leobregat rivers was found to be influenced by Barcelona Harbour and discharges from the Zona Franca Collector [35]. The average rainfall is 1200 mm in Karaikal regions. Sometimes Karaikal experiences drought situation with the annual rainfall less than 75% of the normal. Pondicherry and Karaikal regions get most of the rainfall (nearly 70 %) from the North-East monsoon (Fig.4.a-b). The major list of industries around Thirumalairayan rivers

1. Karaikal Port
2. Kothari Sugars & Chemicals Ltd., Karaikal.
3. Kothari Petro Chemical Ltd., Nagore Salai, Karaikal.
4. Chemplast Sanmar Pvt Ltd., Polagam, Karaikal.
5. Elango Steel Ltd., Polagam, Karaikal.
6. Kannappan Steel Ltd., Nagore Salai Vanjure, Karaikal.
7. Rengaraj Steel Ltd., Nagore Salai Vanjure, Karaikal.
8. MMS Steel Ltd., Nagore Salai Vanjure, Karaikal.
9. Motorola Steel Ltd., Nagore Salai Vanjure, Karaikal.
10. PSP Steel Ltd., Keezhavanjure, Karaikal.

11. Padma Balaji Steel Ltd., Keezhavanjore, Karaikal.
12. Midas Rubberf Ltd., Nagore Salai Vanjore, Karaikal.
13. Kiran Pandy Chemicals Ltd., Nagore Salai Vanjore, Karaikal.
14. Praveen Chemicals Ltd., (Power Soap), Keezhavanjore, Karaikal.
15. Vani Soap Company, Nagore Salai Vanjore, Karaikal.
16. Vasantha Carnite Ltd., Nagore Salai Vanjore, Karaikal.
17. AVM Battery Ltd., Mudalimedu, Polagam Karaikal.
18. Mahalakshmi Garments, Nagore Salai Vanjore, Karaikal.
19. VPS Polythine Ltd., Keezhavanjore. Karaikal.
20. Lakshmi Polythine Ltd., Medalimedu, Karaikal.
21. Jothi Chloride Ltd., Polagam, Karaikal.
22. Commando Soap Company, Polagam, Karaikal.
23. Raja Oil Mill, Nagore Salai Vanjore, Karaikal.
24. Varahini chems nagore salai, karaikal.



**Fig-4.1 Karaikal region – Rivers**



Thirumalairayan River  
(Analytic area)

Fig.4.2 Karaikal region – Rivers maps

## 1.8. IRON (Fe) SOURCES AND TOXICITY:

Major constituents of the lithosphere is Iron, approximately 5 %. It is routinely detected in municipal waste sewage, particularly in cities where iron and steel are manufactured. Iron readily complexes with sulphates in the residue of many surface waters.

The primary concern about the presence of iron in drinking water is its abhorrent taste. The taste of iron in drinking water can be easily detected even at low concentrations of about 1.8 mg/L [36]. Iron has broad industrial applications. Anthropogenically, entry of iron into the environment is mainly through effluents of industries like ink, paint and pharmaceutical products, mining industries, ore processing, electroplating industries, zinc and steel processing plants. The presence of Fe(II) in water leads to the growth of iron bacteria which in turn leads to undesirable colour, taste and odour to water. Abundant growth of iron bacteria in water leads to a slimy condition.

So the water becomes unfit for domestic and industrial purposes. The recommended iron content in stream water is 0.3 mg/L [37], at higher concentrations it causes vomiting [38]. Presence of iron in water makes the water dirty, another causing staining of plumbing fixtures and laundry. Moreover, iron precipitates in the gills of fishes, which is deleterious to them [39].

Iron is essential for human health and necessary for proper functioning of the biological system. Deficiency of iron causes anemia. However, excess of iron is toxic to human beings. Excessive iron intake leads to haemochromatosis



resulting in tissue damage due to iron accumulation [40]. Initial symptoms of iron toxicity on human are vomiting, diarrhea and damage to the intestine.

### **1.9. MANGANESE (Mn) SOURCES AND TOXICITY:**

Mn has been determined in at least 869 of the 1,699 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities. Manganese is ubiquitous in the environment, and human exposure arises from both natural and anthropogenic activities[41]. It occurs naturally in more than 100 minerals with background levels in soil collection from 40 to 900 mg/kg, with an estimated mean background concentration of 330 mg/kg. Manganese is released to the environment from various industrial emissions, fossil fuel combustion, and erosion of manganese-containing soils. Mn may also be identified to the environment through the use of MMT as a gasoline additive. Thus, all humans are exposed to manganese, which is a normal component of the human body. Background levels of manganese in the atmosphere vary extensively depending on the proximity of point sources, such as ferroalloy production facilities, coke ovens, and power plants.

The general population is exposed to manganese primarily through food intake. The World Health Organization estimates that adults usages between 0.7 and 10.9 mg of manganese per day in the diet, with higher intakes for vegetarians who may consume a larger proportion of manganese-rich nuts, grains, and legumes in their diet as compared to non-vegetarians in the general population (WHO 2004b)[42].

Estimated releases of 103,53 pounds ie,46 metric tons, of manganese to water from 1,929 domestic built-up and processing facilities in 2009, accounted for about 0.1% of the estimated total environmental releases from facilities.

Estimated releases of 5,741,194 pounds (2,604 metric tons) of manganese compounds to water from 1,656 domestic MANGANESE 393.

Manganese in water may undergo oxidation at high pH and is also subject to microbial activity. Mn(II) was oxidized during the summer months, but this was inhibited by a microbial poison, representing that the oxidation was mediated by bacteria. The microbial metabolism of manganese is presumed to be a function of pH, temperature, and other factors, but no data were located on this.

Mining and processing industries in Friends Stand United nations have provided many economic and societal benefits, they also have caused important environmental effects, including acid mine drainage (AMD) in some areas and contamination of groundwater, surface water, and soils. The quantity and implication of AMD and metal contamination of water and soils are affected by complex biochemical responses in the disturbed ore bodies and associated mine waste materials (43-45). Microbes in soils and water facilitate to oxidize the sulfide minerals and catalyze acid- and dissolved metalgenerating reactions. However, in Mn deposits, AMD generation is often not the most important problem.

#### **1.10.POLYMER SCIENCE:**

Polymer science has emerged as active authority of materials science. This field impinges on areas of commodity, engineering and speciality polymers thereby stimulating interest all over the globe in utilizing newer domains. One such branch that has emerged is polymer metal complexes containing an organic polymer containing co-ordinating sites, complexed with metals[46]. This is of relatively current origin and an interdisciplinary approach



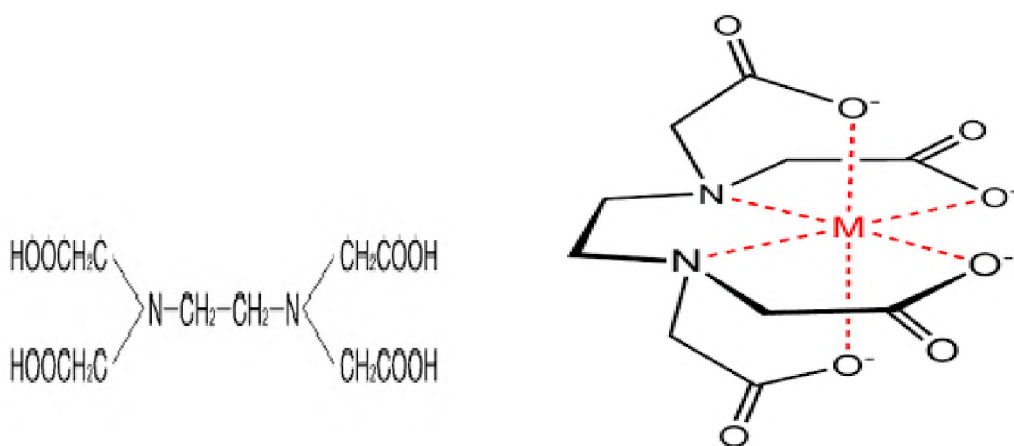
taking into its fold areas viz; chemistry, metallurgy, environmental and material sciences. A co-ordination compound may be defined as a compound with a central metal atom or ion to which are attached to ions or molecules or neutral molecules whose number usually exceeds the number corresponding to the oxidation number or valency of the central atom or ion. The groups that are hop to the central metal atom or ion in a symmetrically oriented fashion through coordinate or co-ordinate covalent bond are called ligands. For a long time, the co-ordination compounds were measured as a rare and special class but subsequently have become flexible.

Coordination polymers are comparatively low weight and posses high thermal stability [47]. Polymeric metal complexes have a assortment of geometries that are not available in organic polymers; some combine the properties of anisotropy with photo responsive behaviour that give ascend to applications in areas such as optical storage, optical switching, diffractive optical elements, non-linear optical devices, liquid crystal displays (LCD's) etc. Coordination polymers have provided humankind since before recorded history. The tanning of leather and generation of selected colored pigments depend on the coordination of metal ions. A number of biological agents, as well as humans, owe their survival to coordination polymers have unknown and/or irregular structures. The explore on synthesis and applications of coordination polymers have become a popular field since the past 20 years because of the excellent characters, such as molecular recognition, microelectronics, nonlinear optics, 6 porous materials [48].

#### **1.10.a.Polymer-Ethylenediaminetetraacetic Acid (EDTA)**

In recent years metal complexes with functionalized polycarboxylic acid ligands viz. ethylenetriaminetetraacetic acid (EDTA) (Fig. 6) have attracted attention of inorganic and bioinorganic chemists [49-51]. The ligating characteristics of these flexible functionalized polycarboxylic acid ligands

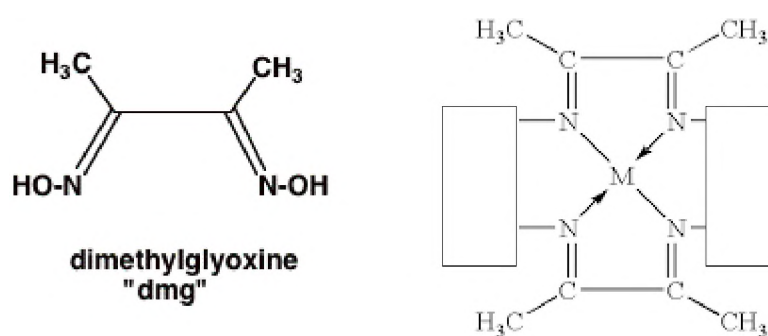
constitute of polydentate [N,O,O] or [O,O,O] chelators resulting in metal complexes differing in coordination numbers, structure and 3-D architectures. The carboxylate moiety may adopt a range of different coordination modes whether it coordinated by metal ion as anionic  $(\text{COO})^-$  or neutral unionized  $(\text{COOH})$ . Polymer with EDTA ligand as best for metal removal from waste water.



**Fig:6 Structure of EDTA & complex**

#### 1.10.b. Polymer-Dimethylglyoxime (DMG)

Dimethylglyoxime (DMG) has been used as a ligand in these ion-imprinting polymerisation reactions. DMG has been used for the identification and determination of nickel using colourimetric and gravimetric techniques [52] designed a Pd(II)-DMG for the careful uptake of palladium ions from dilute aqueous solutions. The total time needed to prepare the polymer was more than 2 days. Therefore, new methods are needed to reduce this period of time if DMG-based ion-imprinted polymers are to be successfully used as SPE sorbents. Dimethylglyoxime (DMG) is used to extract metals from solution also containing other ions. Polymer with DMG ligand (Fig.7) as suitable material for removal of waste metals present in polluted water.



**Fig:7 Structure of DMG & complex**

### 1.11. OBJECTIVES OF THE PRESENT WORK

The survey of literature shows that intensive researches have been carried out on the monitoring of rivers all over the globe but little or no work has been done so far on Indian rivers with special reference to heavy metal pollution of this stretch of the river.

The work described in this thesis consists of the following objects:

- Chemical identification, characteristics of heavy metals in Thirumalairayan rivers.
- Preparation of polymers compounds for absorption of metals.
- Characterisation of polymer-metal complexes.
- Metal absorption by polymer compounds in Thirumalairayan rivers.

## CHAPTER – II

### EXPERIMENTAL, RESULTS & DISCUSSION

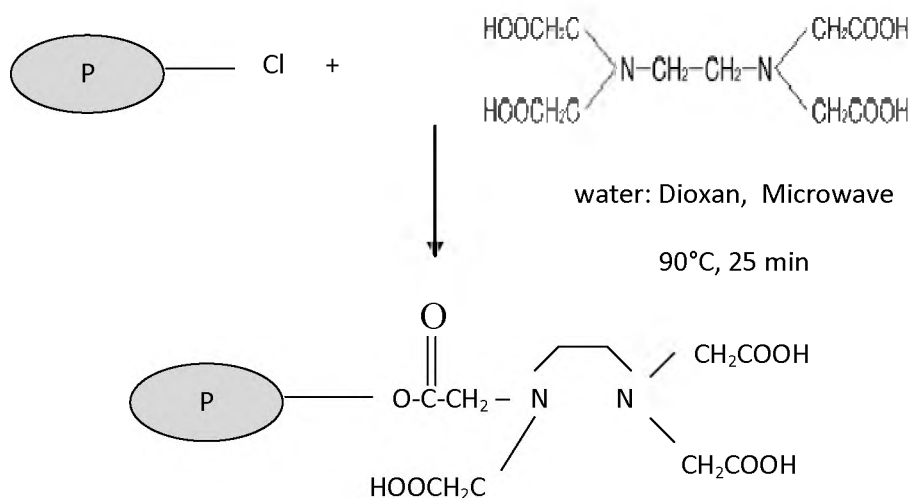
#### 2.1. Purification of chemicals

All the solvents methanol, acetone, DMF, DMSO, were purified by standard methods [53-54]. Ethylenediaminetetraacetic acid (EDTA) and dimethylglyoxime (DMG) the analar grade samples supplied by Merck were used as such. Polystyrene resin (Anion exchange resin) were supplied by Ion exchange (India) Ltd.

#### 2.2. ADSORBENTS

##### 2.2.a. Preparation of polymer-anchored Ethylenediamine-Tetraaceticacid (EDTA)

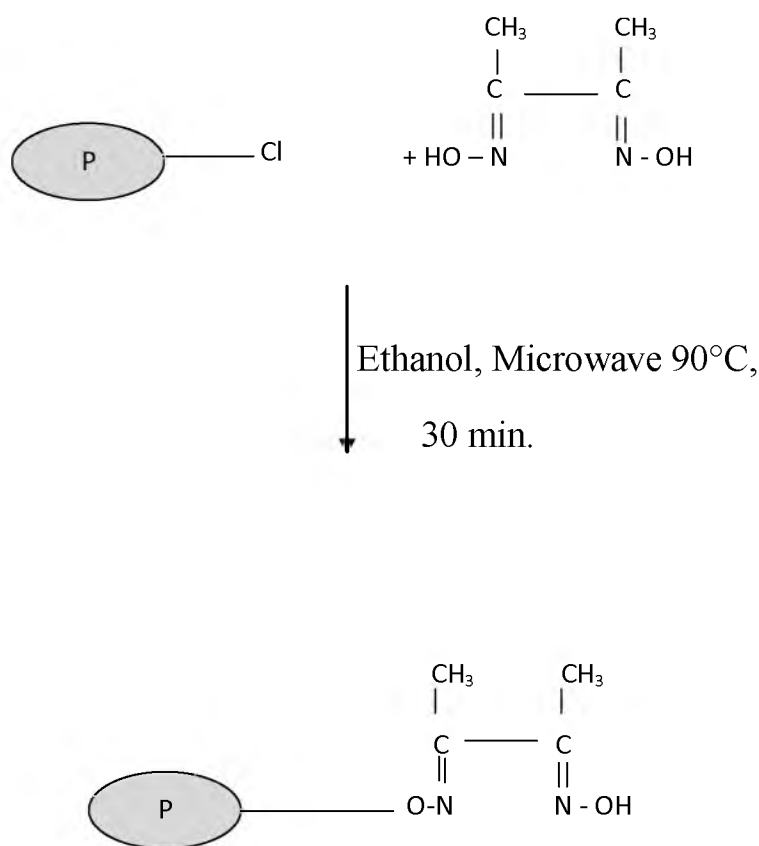
Ethylenediaminetetraacetic acid (EDTA) was anchored to Polystyrene N-IP treating by excess of ethylenediaminetetraacetic acid in 1:1 mixture of water and dioxane in the microwave oven at 90°C for 25 min. The resin **Polymer-EDTA [AD1]** was washed with aqueous dioxane, deionized water and dried at 70°C [55] (Scheme-1).



**Scheme 1: Polymer-EDTA [AD1]**

### 2.2.b. Preparation of Polymer anchored Dimethylglyoxime

Dimethylglyoxime was anchored to polystyrene N-IP resin by refluxing with excess of dimethylglyoxime in absolute ethanol treated in the microwave oven at 90°C for 30 min. The resin **Polymer-DMG [AD2]** was filtered and washed with water and absolute ethanol for numerous times and dried under vacuum (Scheme-2).

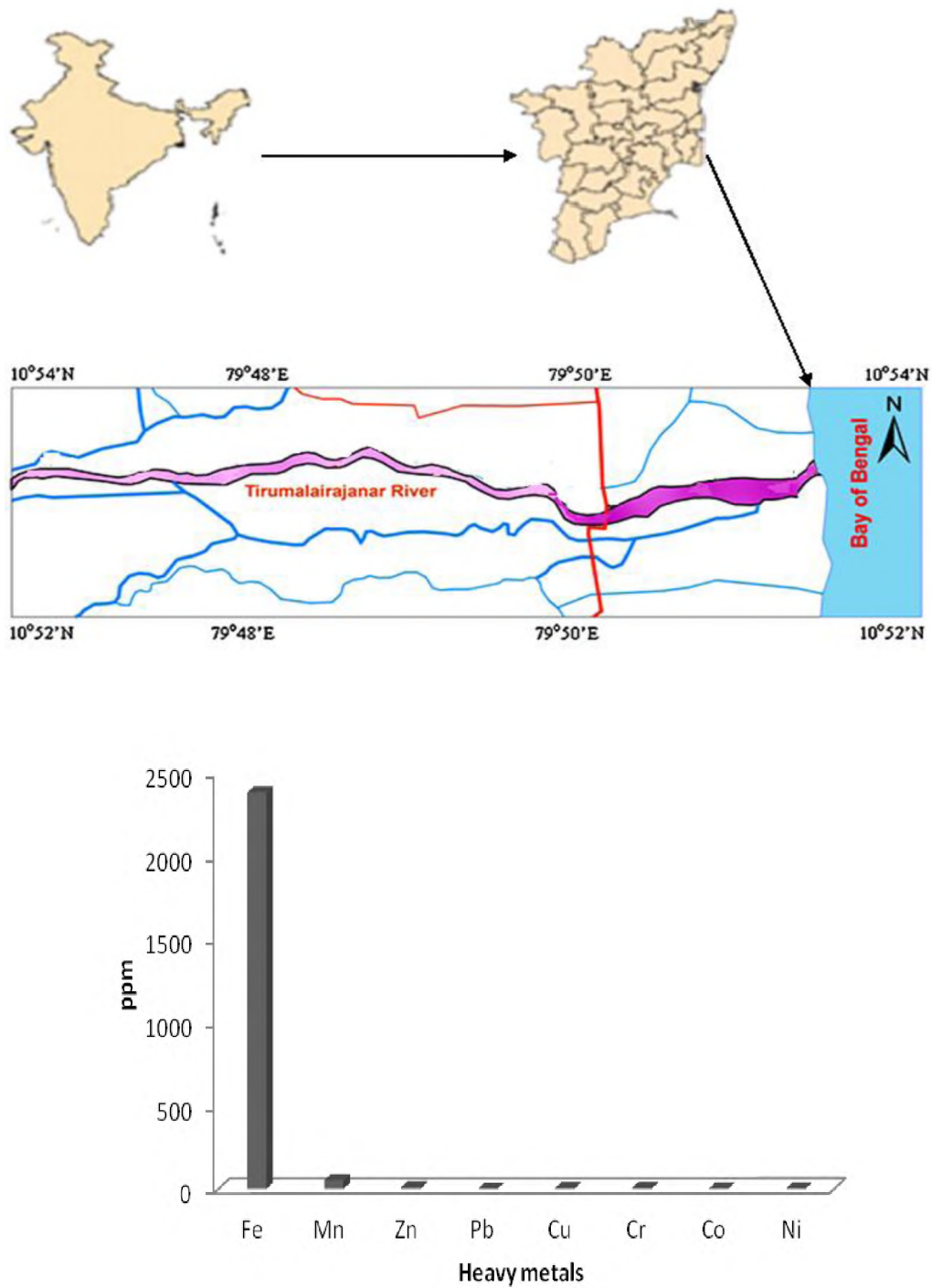


**Scheme:2 Polymer-DMG [AD2]**

### 2.3. Estimation of metal content in Thirumalairajanar River:

Estimation of metal contents in the thirumalairajanar was made with HITACHI instruments, Inc, U-2001 spectrophotometer according to standard procedure [56]. The amount of the metal ion in river water estimated by spectrophotometric method. The concentration was estimated by comparing the

absorbance with that of a standard curve [57]. From experimental data analysis (Figure:1&2) show Thirumalairajanar river with more pollutant of Fe and Mn (58-59).



**Fig:2 concentration of heavy metals in study area**

## 2.4. INSTRUMENTAL MEASUREMENTS

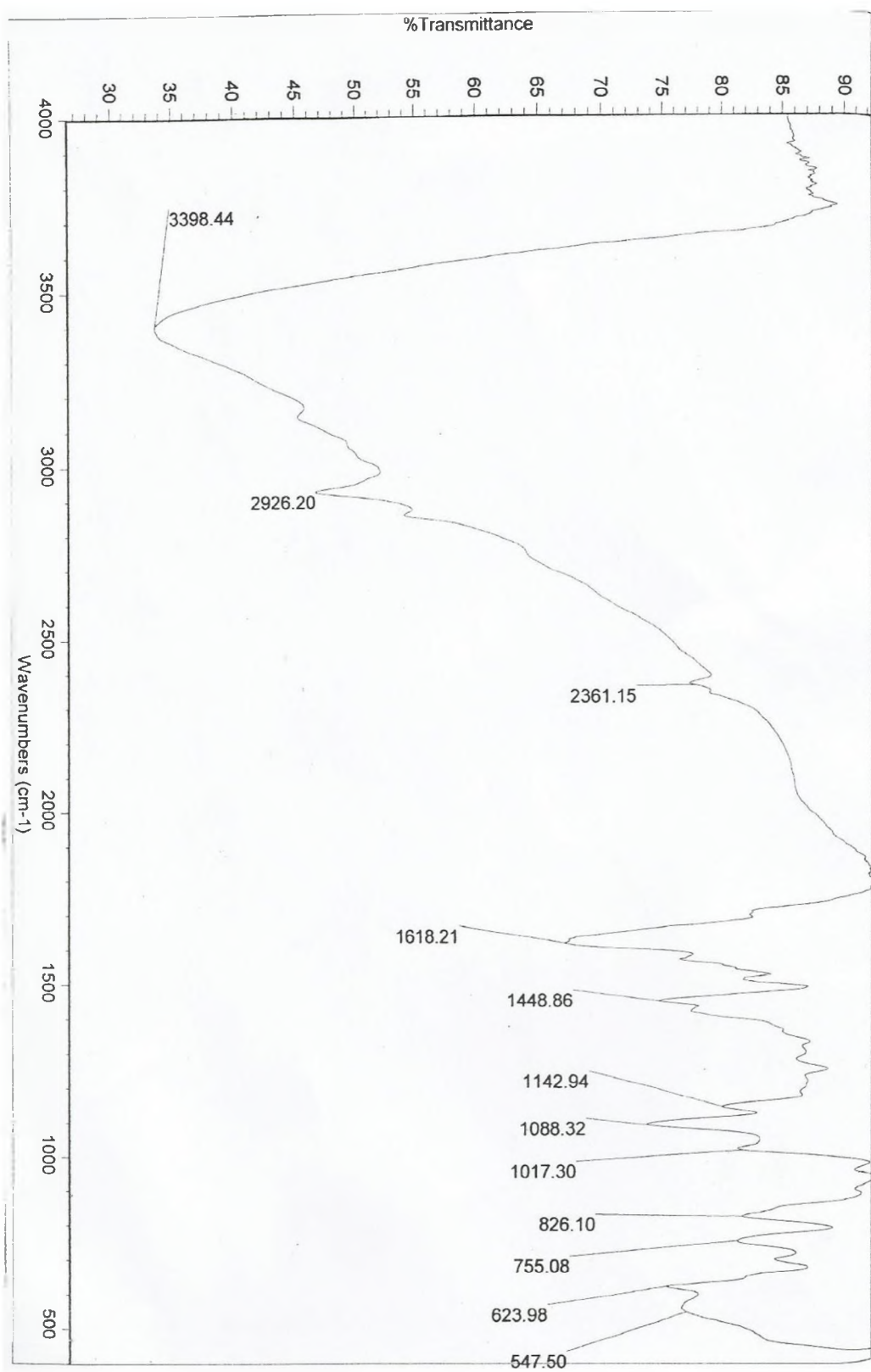
### a) Infrared spectrophotometer

ABB Boomen MB-104 spectrophotometer was used for recording the IR spectra of the compounds with potassium bromide disc of the compound. The percentage transmission was recorded against wave number.

The sample were ground to a fine powder and mixed with KBr and then ground again to mix thoroughly. The KBr sample mixture was then pressed into a thin disc. IR spectrum of Polymer and adsorbents show in **Fig.3.a-c**.

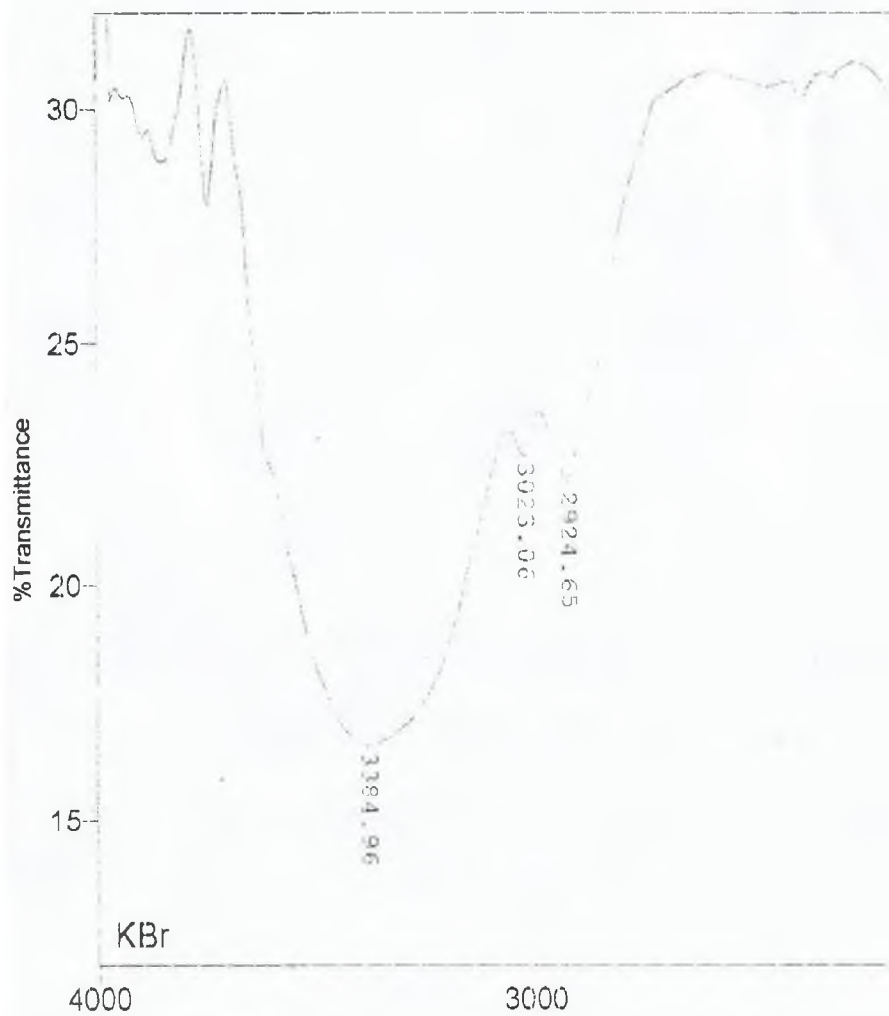
### b. SEM

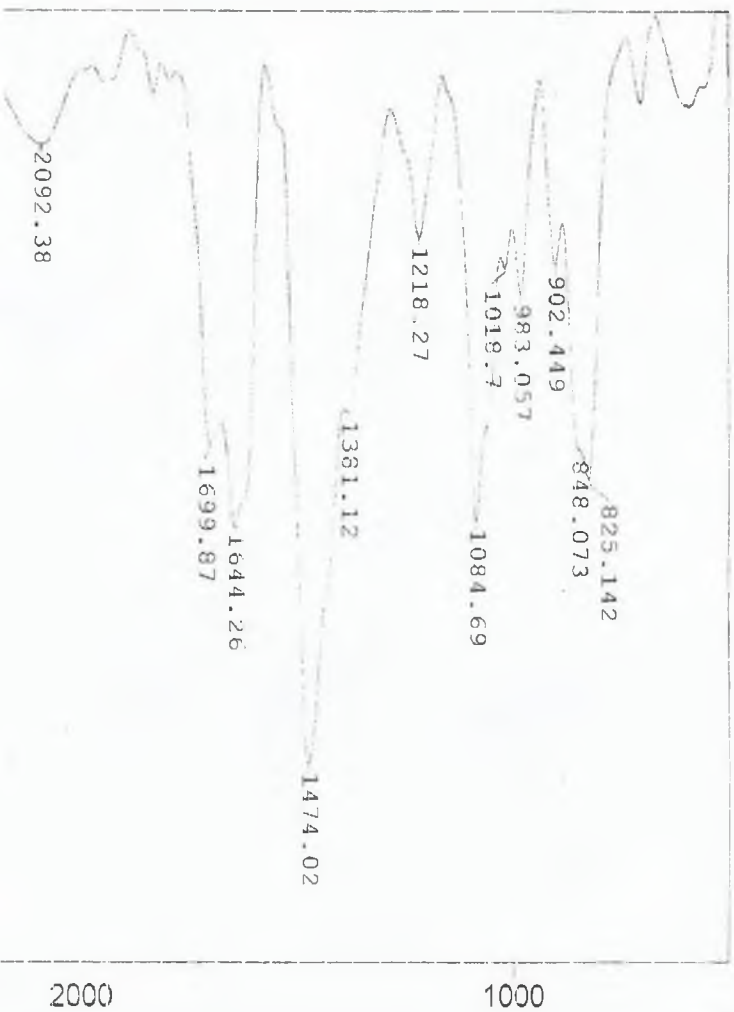
The morphological characteristics of the polymer and the adsorbents were recorded on Jeol 5610 scanning electron microscope. The surface morphology of adsorbents were examined using Scanning Electron Microscopy (SEM), before and after adsorption, and the corresponding SEM micrographs were obtained **Fig.4.a-e**.

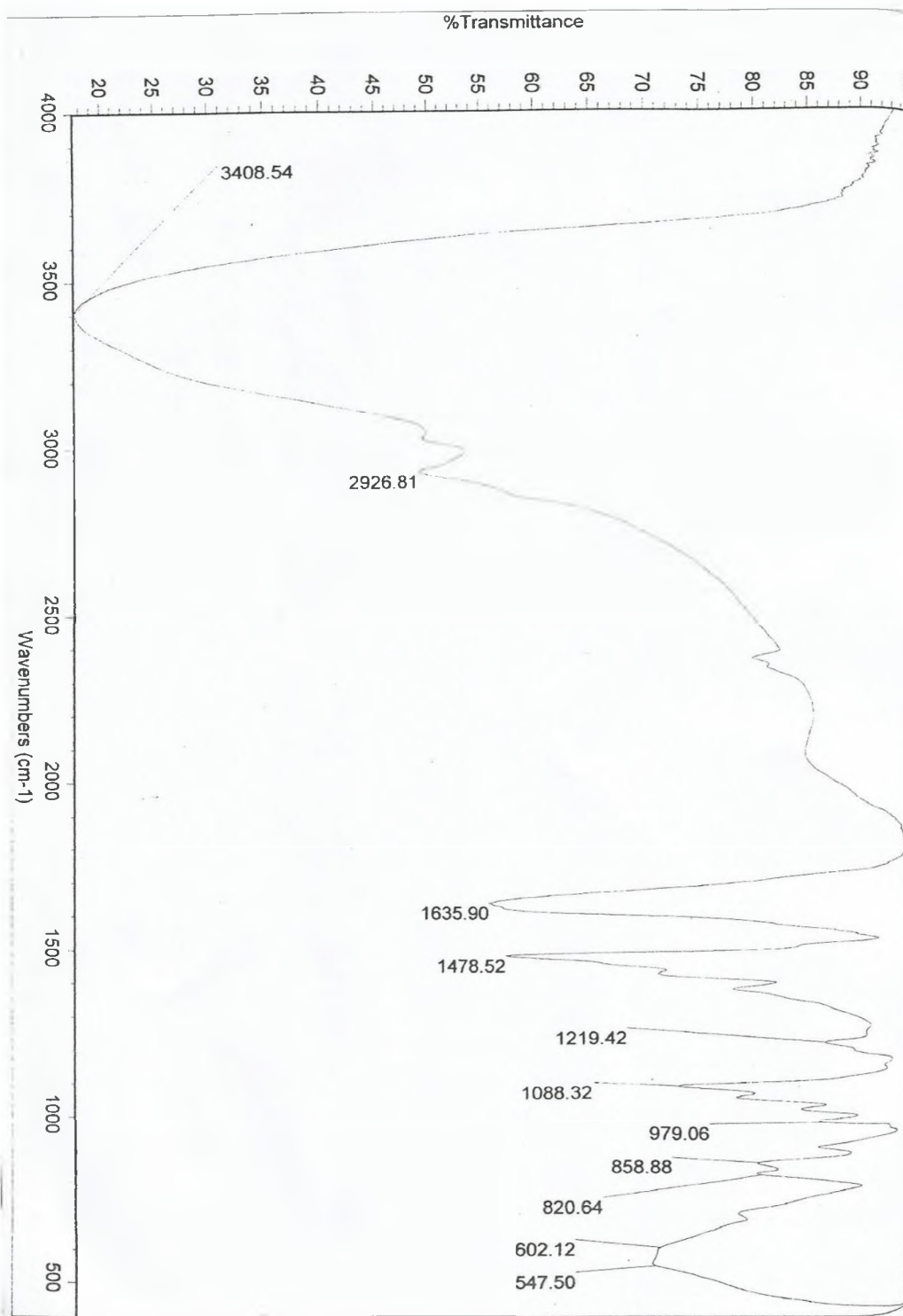


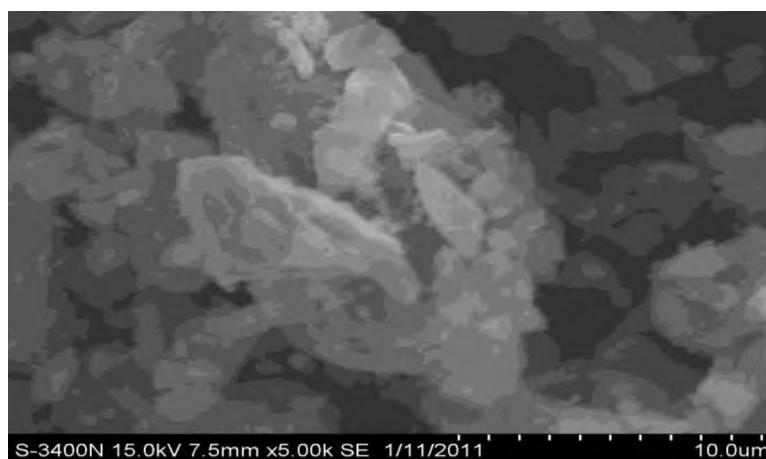
67



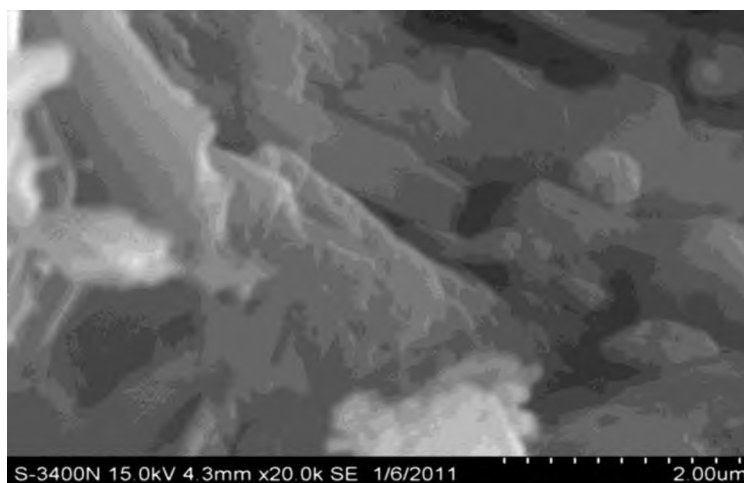




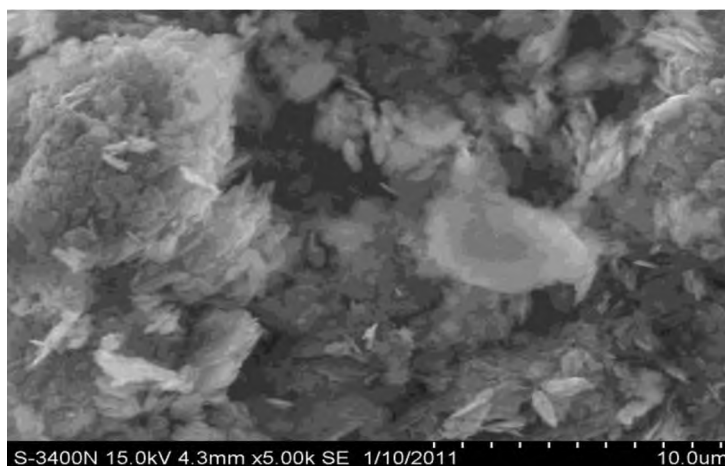




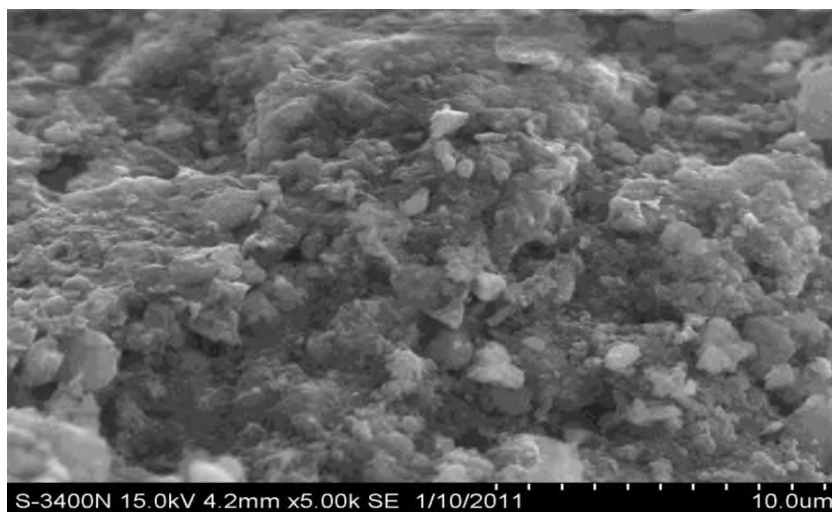
**Fig.4.a: SEM micrograph of Polymer**



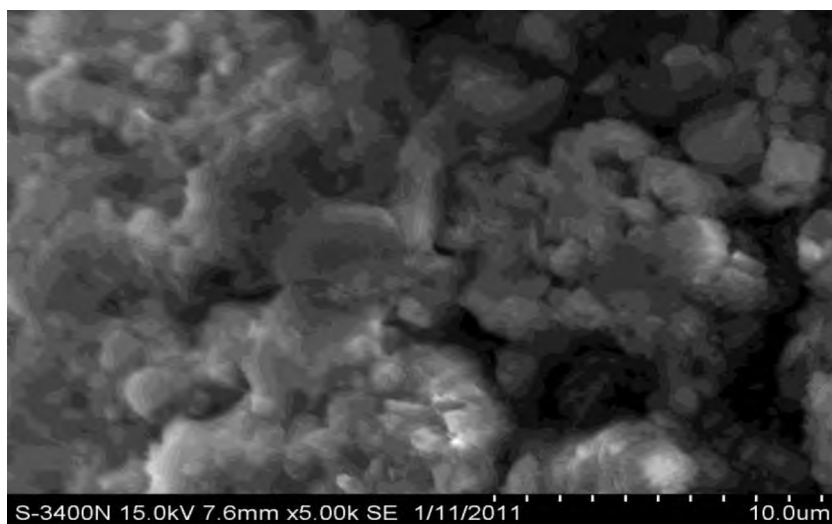
**Fig.4.b: SEM micrograph of Polymer-EDTA (AD1)**



**Fig.4.c: SEM micrograph of Polymer-EDTA (AD1) with Fe**



**Fig.4.d: SEM micrograph of Polymer-DMG (AD2)**



**Fig.4.e: SEM micrograph of Polymer-DMG (AD2) with Mn**

## **2.5. PREPARATION OF STOCK SOLUTIONS**

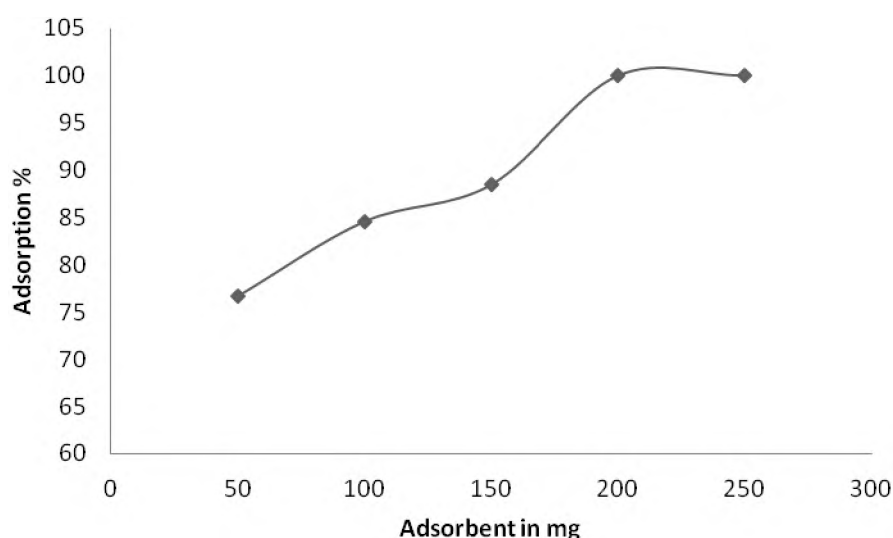
Stock solutions (1000 mg/L) of Fe(III), and Mn(II) were prepared by dissolving the required amount of the respective salt in one liter of doubly distilled water.  $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  with 9.644 mg/L and  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  with 3.958 mg/L.

## 2.6. METAL ADSORPTION STUDIES

### 2.6.a. Fe(II) Adsorption by Polymer-EDTA Adsorbent:1 [AD1]

#### i) Effect of adsorbent dosage

The effect of the mass of the adsorbent in the adsorption of Fe (II) ions was studied at the pH 5.0 and at (30<sup>0</sup>C). 50 ml of a solution of Fe (II) ions with an initial concentration of 50 mg/L was mixed with 50.0 mg of the adsorbent(AD1) and the mixture was shaken for 60 minutes. After centrifugation, the amount of Fe (II) ions in the supernatant was estimated quantitatively. From this the percentage of lead adsorbed on the adsorbent was deduced. This procedure was repeated with different concentration which is shown in the Figure 5.1.a

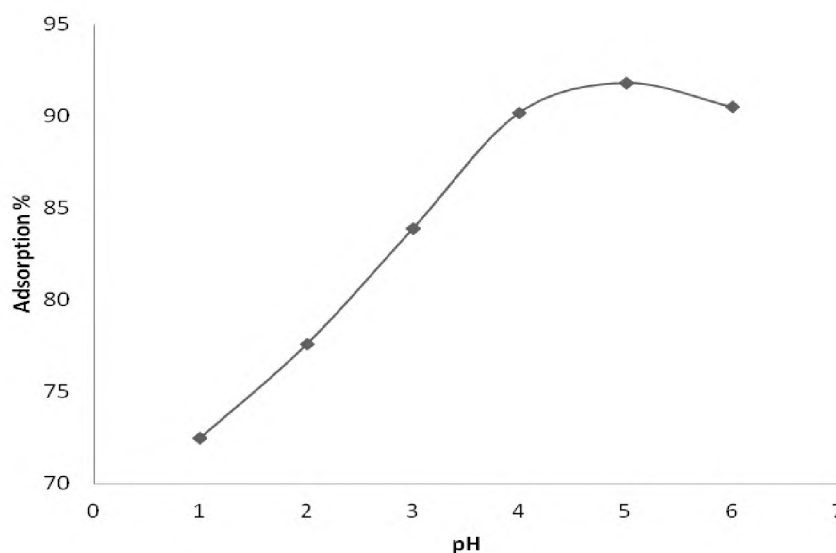


**Fig;5.1.a. Effect of adsorbent on removal of Iron using AD1**

#### ii) Effect of pH

The experiments were carried out at different pH values. There was a change in the percentage adsorption of Fe (II), this is shown in Figure 5.1.b. This indicates the strong force of interaction between the Fe (II) ions and the

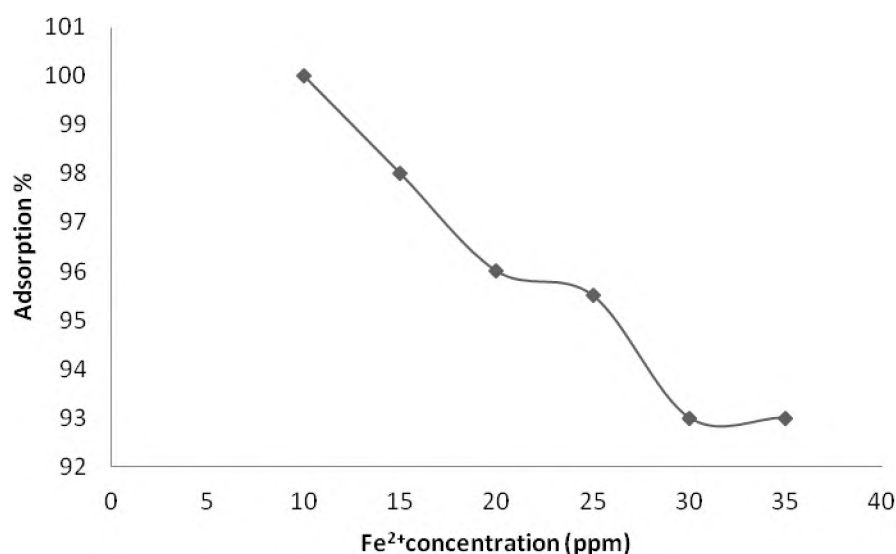
adsorbent(AD1). The adsorption is maximum (91.8%) at pH 5.0. Consequently adsorption decreases.



**Fig;5.1.b. Effect of pH on removal of Iron using AD1**

### **iii) Effect of initial concentration**

The experimental results of adsorption (200mg) of Fe (II) ions on adsorbent (AD1) at various initial concentrations of metal ions are shown in Figure 5.1.c. Adsorption is maximum when the initial concentration of Fe (II) ions were 10 mg/L. As the concentration increases, all the adsorption sites are being filled up and there remains unabsorbed metal ions, hence the decrease in percentage adsorption



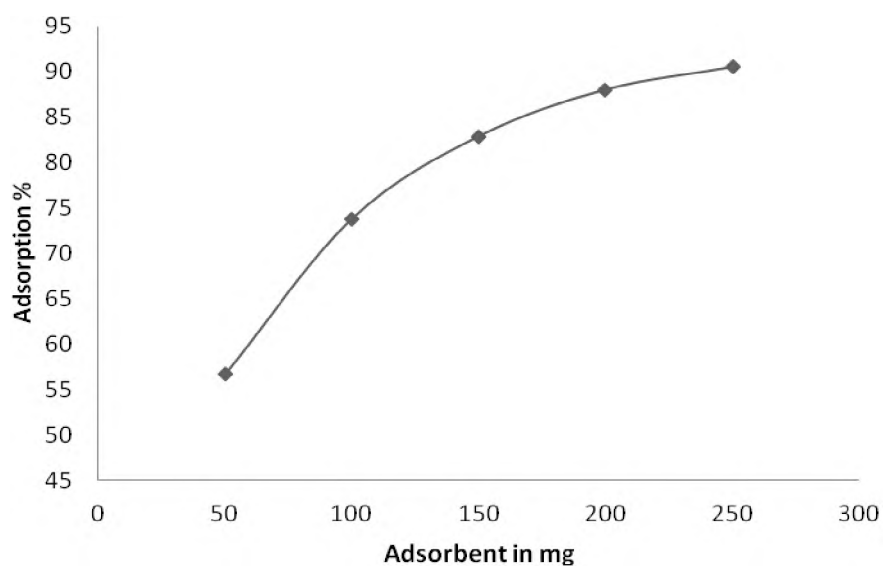
**Fig;5.1.c. Effect of initial concentration adsorption of Iron on AD1**

## **2.6.b. Mn(II) Adsorption by Polymer-EDTA Adsorbent:1 [AD1]**

### **i) Effect of adsorbent dosage**

The effect of the mass of the adsorbent in the adsorption of Mn(II) was studied at the optimum pH of 6.5 and at room temperature (30<sup>0</sup>C). 50 ml of a solution of Mn(II) with an initial concentration of 25 mg/L was mixed with 50.0 mg of the adsorbent(AD1) and the mixture was shaken for 90 minutes. After centrifugation, the amount of Mn(II) in the supernatant was estimated quantitatively. This process was repeated with different concentration which is shown in the figure 5.2.a

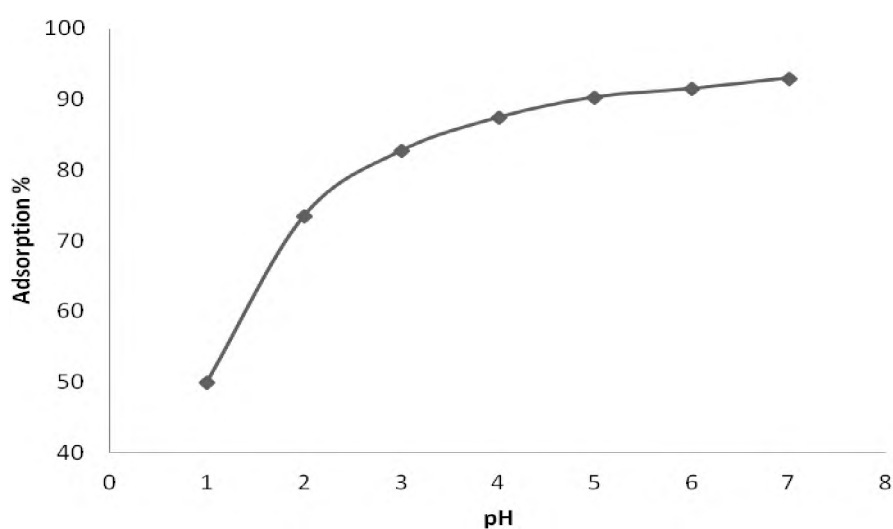




**Fig;5.2.a. Effect of adsorbent on removal of Manganese using AD1**

## ii) Effect of pH

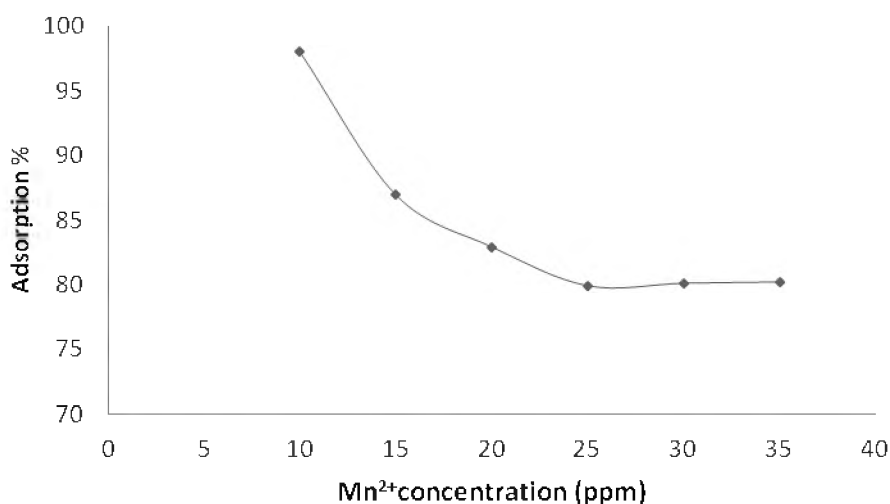
Percentage adsorption were carried out at different pH values. There was a change in the adsorption of Mn(II) on adsorbent(AD1), the entire pH range of 1.0 to 7.0. This is shown in Figure 5.2.b



**Fig;5.2.b. Effect of pH on removal of Manganese using AD1**

### iii) Effect of initial concentration

The adsorption of Mn (II) ions at various initial concentrations on adsorbent(AD1) (200mg) are shown in Figure 5.2.c. Adsorption is maximum when the initial concentration were 10 mg/L. As the concentration increases, all the adsorption sites are being filled up and there remains unabsorbed metal ions, hence the decrease in percentage adsorption. 98% adsorption occurs when the initial concentration was 10 mg/L, adsorbent(AD1) appears to be very effective adsorbent in removing even traces of the metal ion.



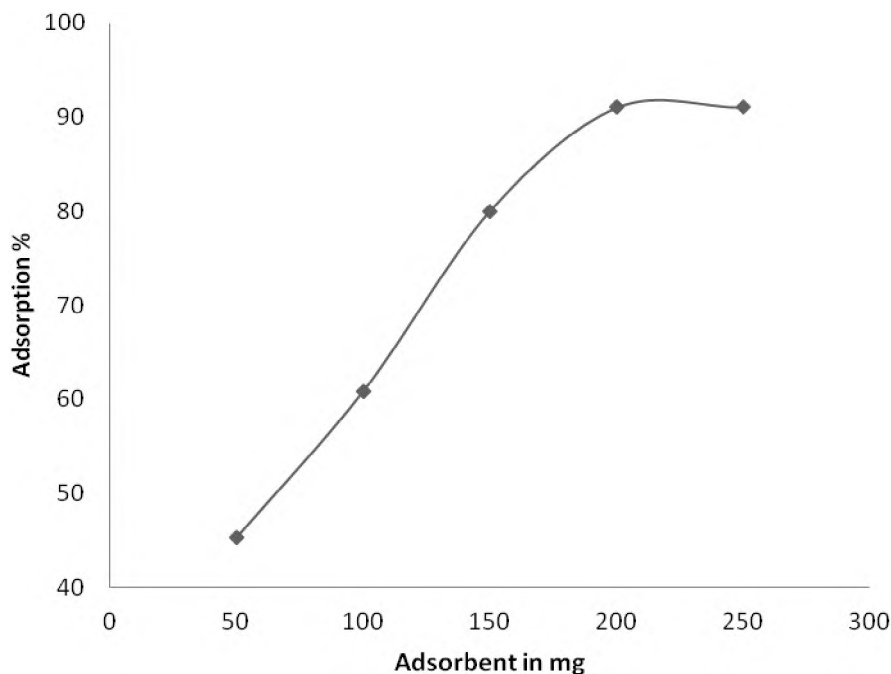
**Fig;5.2.c. Effect of initial concentration adsorption of Manganese on AD1**

### 2.6.c. Fe(II) Adsorption by Polymer-DMG Adsorbent:2 [AD2]

#### i) Effect of adsorbent dosage

Adsorption of Fe (II) was studied with different mass of the adsorbent(AD2) in the at the optimum pH of 6.5 and at room temperature (30°C). 50 ml of a solution of Fe (II) with an initial concentration of 25 mg/L was mixed with 50.0 mg of the adsorbent and the mixture was shaken for 80

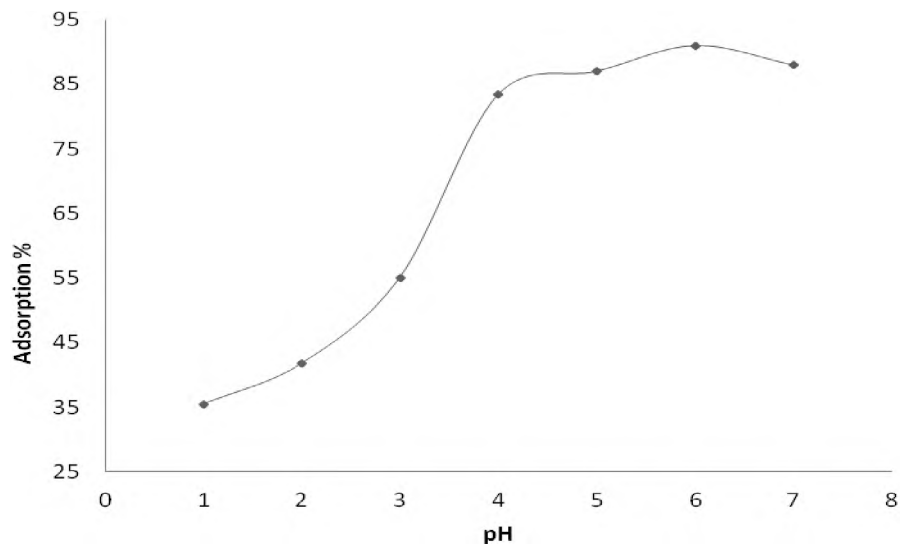
minutes. This procedure was repeated with 100, 150, 200 and 250 mg of the adsorbent(AD2) shown in the Figure 5.3.a.



**Fig;5.3.a. Effect of adsorbent on removal of Iron using AD2**

## ii) Effect of pH

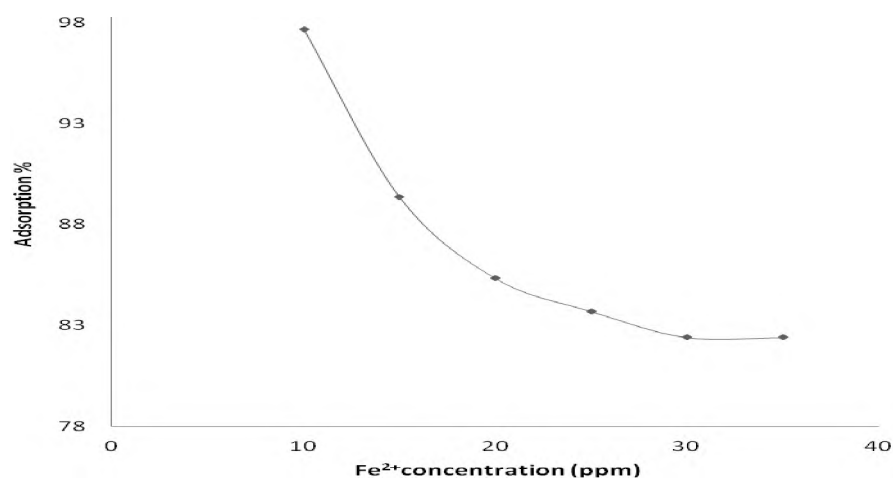
The percentage adsorption of Fe (II) on adsorbent(AD2) experimentally measured with pH range of 1.0 to 7.0. This indicates the strong force of interaction between Fe (II) and adsorbent(AD2). The adsorption is maximum (89.39%) at pH 6.5. The adsorption of the metal ion on the adsorbent(AD2) powder may involve coordination reaction mechanism Figure 5.3.b.



**Fig;5.3.b. Effect of pH on removal of Iron using AD2**

### iii) Effect of initial concentration

The experimental results of adsorption of Fe (II) ions on adsorbent(AD2) at various initial concentrations are shown in Figure 5.3.c. Adsorption is maximum (97.68 %) when the initial concentration of metal were 10 mg/L.

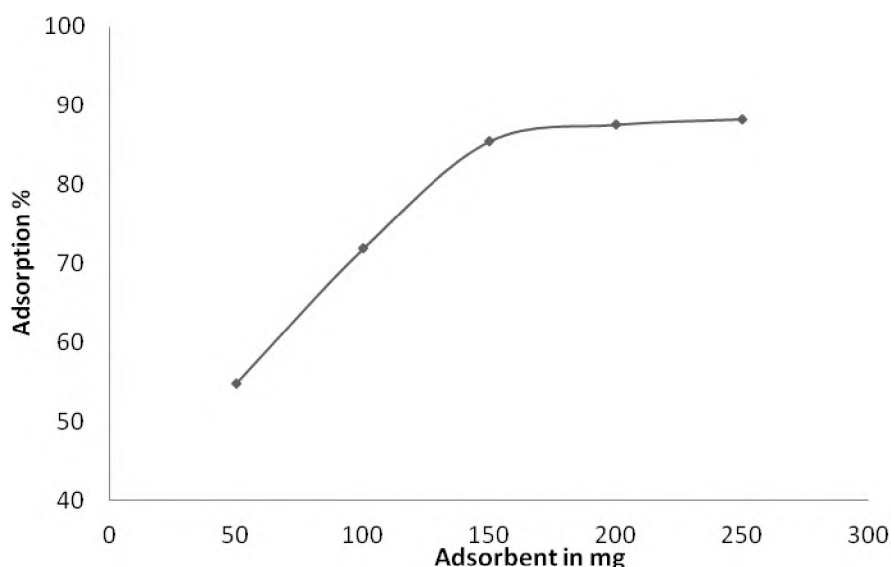


**Fig;5.3.c. Effect of initial concentration adsorption of Iron on AD2**

#### 2.6.d. Mn(II) Adsorption by Polymer-DMG Adsorbent:2 [AD2]

##### i) Effect of adsorbent dosage

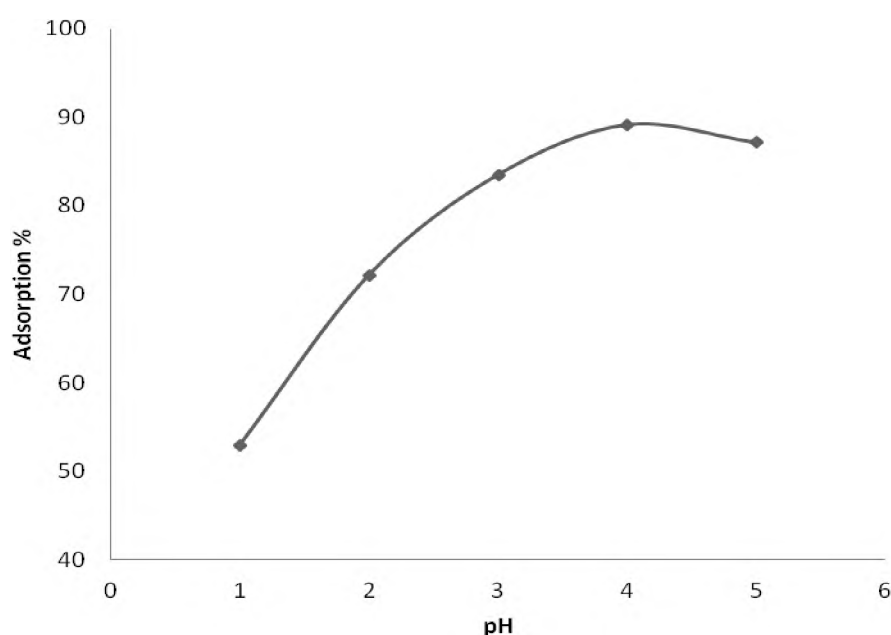
The absorption of manganese was studied at the optimum pH of 4.0 and at room temperature. 50 ml of a solution of manganese with an initial concentration of 25 mg/L was mixed with 50.0 mg of the adsorbent(AD2) and the mixture was shaken for 120 minutes. After centrifugation, the amount of manganese in the supernatant was estimated quantitatively. From this the percentage of manganese adsorbed on the adsorbent was deduced Figure 5.4.a.



**Fig;5.4.a. Effect of adsorbent on removal of Manganese using AD2**

## ii) Effect of pH

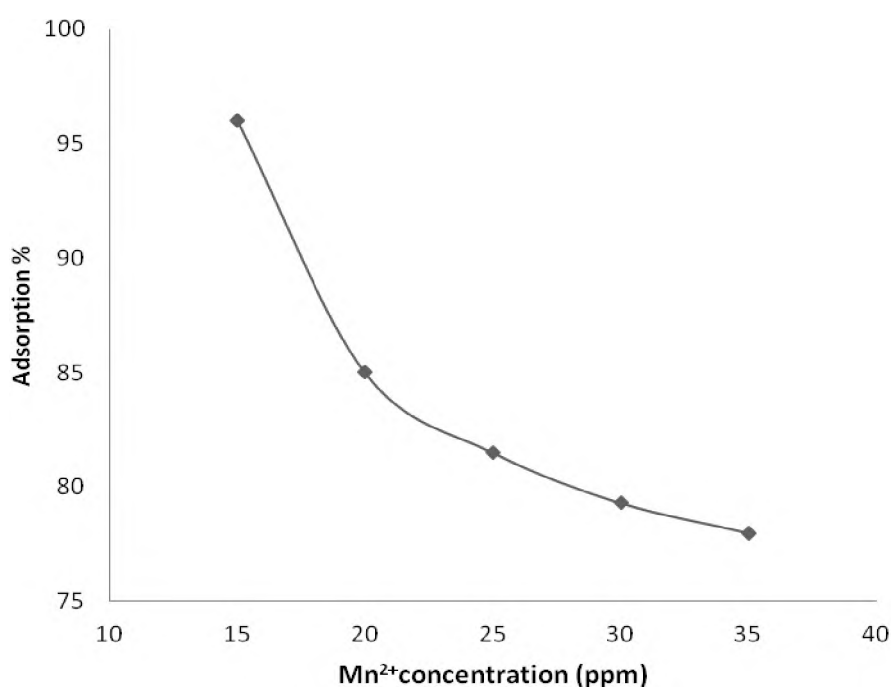
Percentage adsorption of manganese on adsorbent(AD2) carried out at different pH values of 1.0 to 5.0. This is shown in figure 5.4.b. The adsorption is maximum (86.96%) at pH 4.0



**Fig;5.4.b. Effect of pH on removal of Manganese using AD2**

## iii) Effect of initial concentration

The adsorption of manganese on adsorbent(AD2) at various initial concentrations are shown in Figure 5.4.c. Adsorption is maximum when the initial concentration of manganese were 15 mg/L. As the concentration increases, all the adsorption sites are being filled up and there remains unabsorbed metal ions, hence the decrease in percentage adsorption.



**Fig;5.4.c. Effect of initial concentration Manganese on AD2**

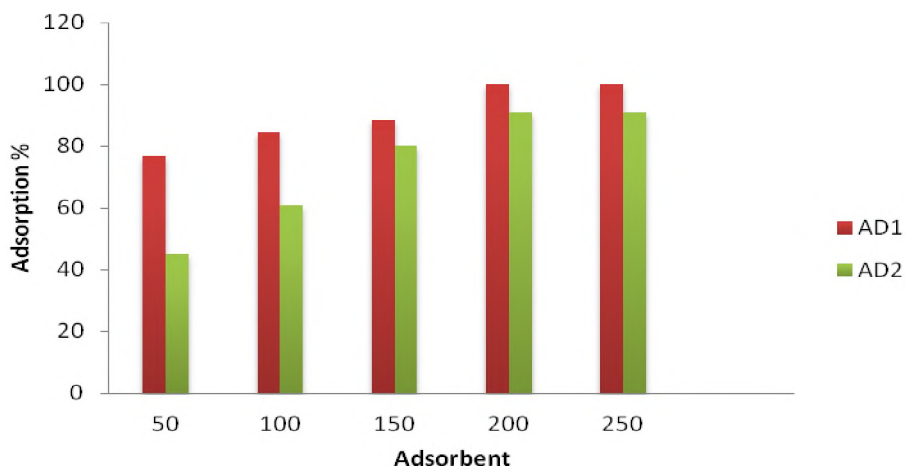
## SUMMARY AND CONCLUSION

Adsorption of metal ions  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  were studied through batch mode, making use of different variables like adsorbent dosage, pH of the medium, initial concentration of adsorbent.

### 2.7. Adsorption of Iron( $\text{Fe}^{2+}$ ) by Adsorbent1 (AD1) and Adsorbent2 (AD2)

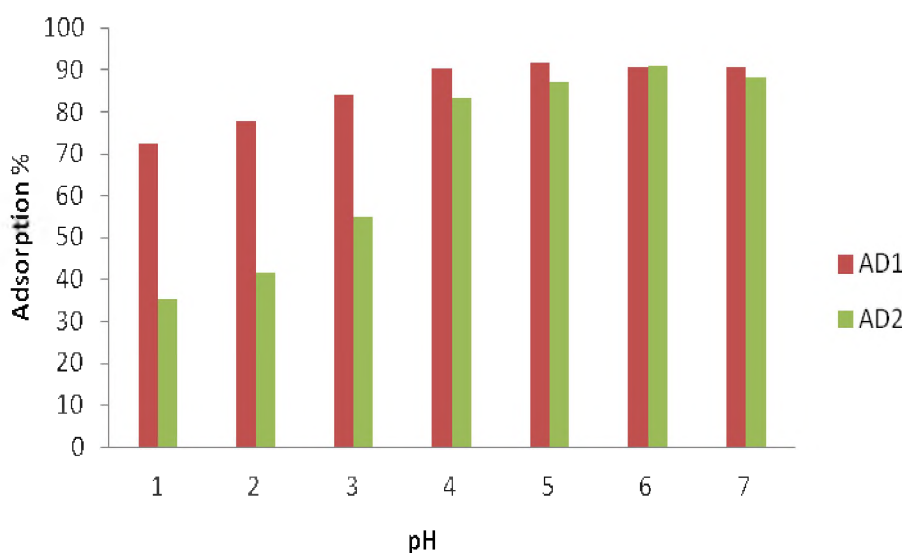
Adsorption was found to increase with increase in adsorbent dosage, probably, due to increase in adsorption sites. Adsorption experiments, with at the optimum pH, with 2.5 mg metal ion, showed that adsorbents recorded maximum adsorption (100%) when the dosage was 200 mg for

adsorbent (AD1), 91% when the dosage was 200 mg for adsorbent(AD2) to Iron (Fig.6.1.a). The adsorption ability decreased in the order, AD1>AD2



**Fig:6.1.a. Effect of adsorbent on removal of Iron using AD1&AD2**

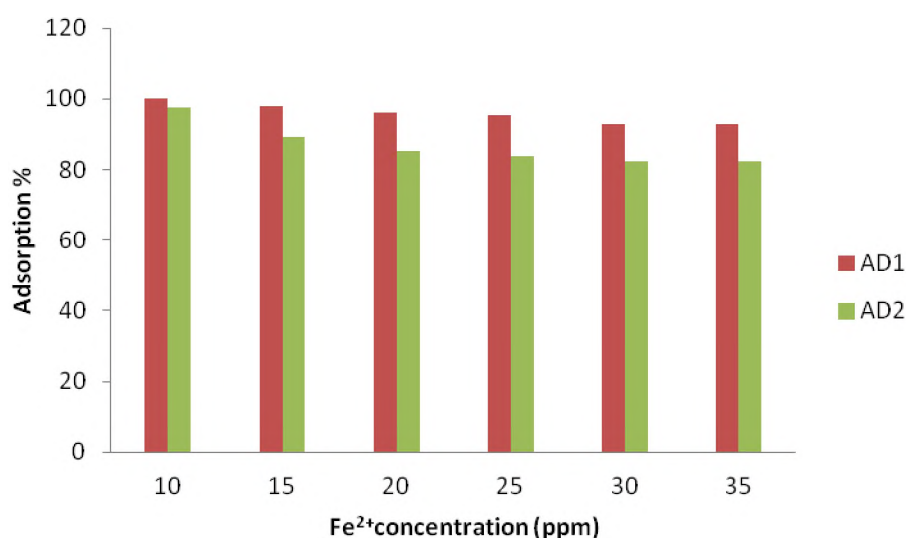
Adsorption was found to be maximum at an optimum pH, which depends on the metal ion involved. Iron show maximum adsorption at lower pH, 91.8% for AD1 at pH:5, 91.0% for AD2 at pH:6 (Fig.6.1.b).



**Fig:6.1.b. Effect of pH on removal of Iron using AD1&AD2**



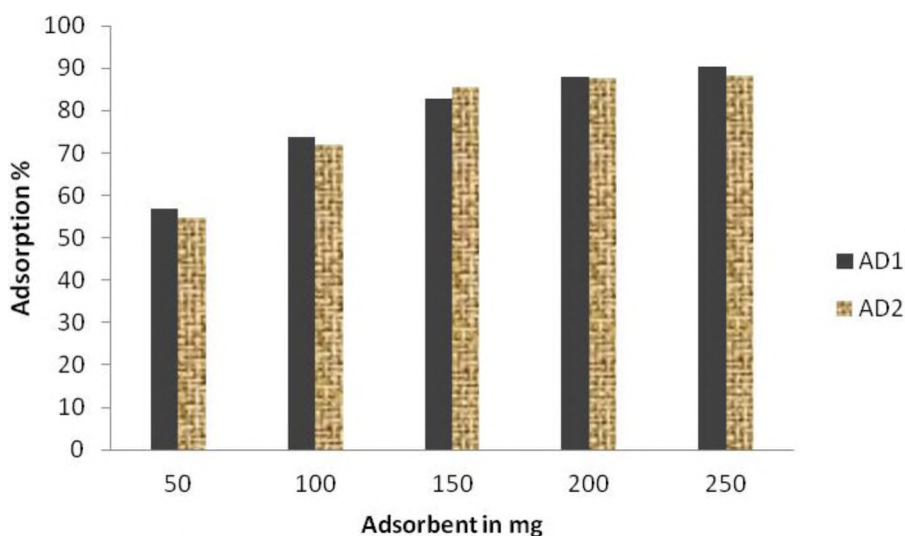
For Iron(Fe), initial concentration was varied from 10 mg/L to 35 mg/L. In general, decreasing of adsorption, when increase in initial concentration of metal. The metal showed 100% adsorption for AD1 and 97.68% for AD2 (Fig.6.1.c)



**Fig; 6.1.c. Effect of initial concentration adsorption of Iron on AD1&AD2**

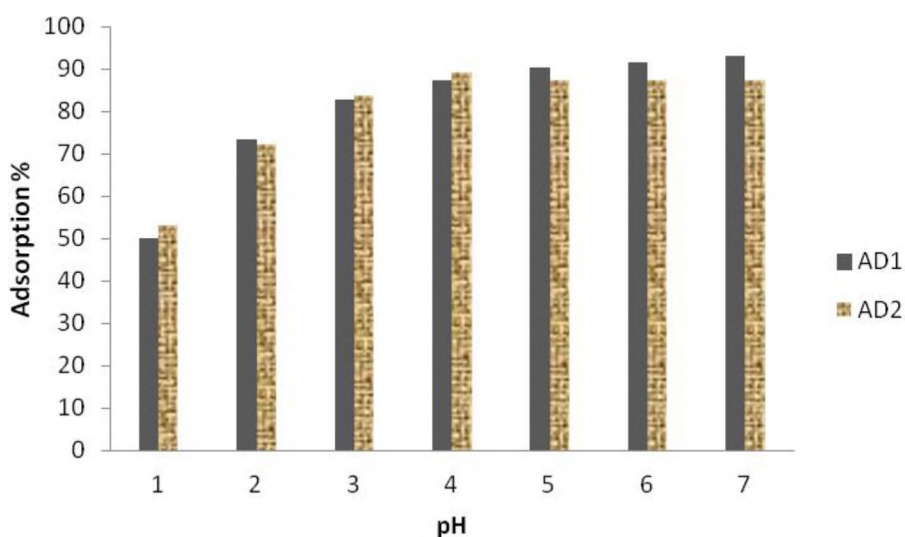
## **2.8. Adsorption of Manganese (Mn<sup>2+</sup>) by Adsorbent1 (AD1) and Adsorbent2 (AD2)**

The adsorption increase with increase in adsorbent dosage. Adsorption experiments, with at the optimum pH, with 25 mg metal ion, showed that adsorbents recorded maximum adsorption (90.5%) when the dosage was 250 mg for adsorbent(AD1), 88.31% when the dosage was 250 mg for adsorbent(AD2) to Manganesh (Fig.6.2.a). The adsorption ability decreased in the order, AD1>AD2



**Fig; 6.2.a. Effect of adsorbent on removal of Manganese using AD1&AD2**

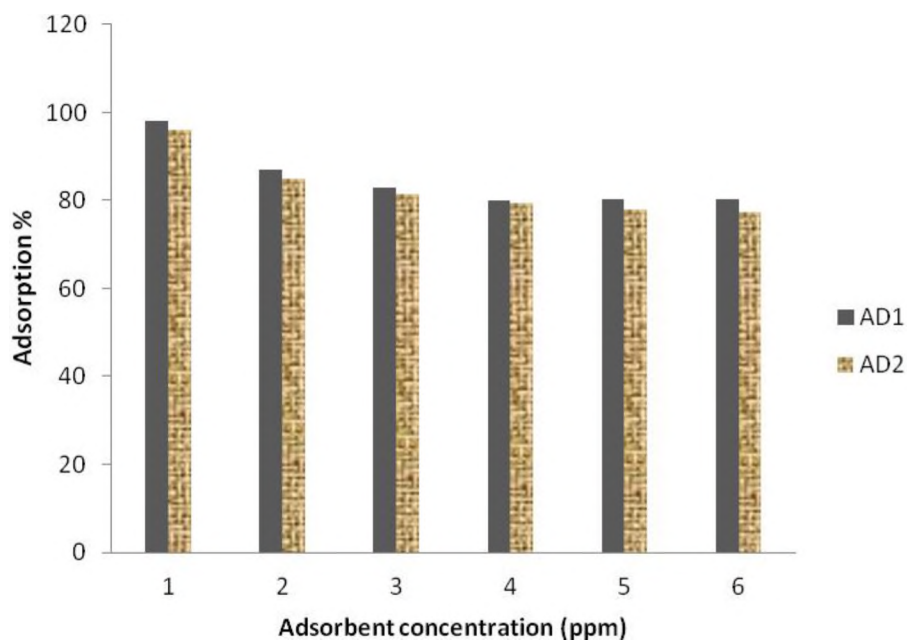
Adsorption was found to be maximum at an optimum pH, which depends on the metal ion involved. Manganese adsorption maximum at lower pH, 93.0% for AD1 at pH:7, 89.2% for AD2 at pH:4 (Fig.6.2.b).



**Fig; 6.2.b. Effect of pH on removal of Manganese using AD1&AD2**

For Manganese (Mn), initial concentration was varied from 10 mg/L to 35 mg/L. In general, decreasing of adsorption, when increase in initial

concentration of metal. The metal showed 98% adsorption for AD1 and 96% for AD2 (Fig.6.2.c)



**Fig; 6.2.c. Effect of initial concentration Manganese on AD1&AD2**

Fe(II) and Mn(II) adsorbed onto Polymer-EDTA [AD1] and Polymer-DMG [AD2]. The results showed that remove cationic heavy metal species from river waste in order **Polymer-EDTA [AD1] > Polymer-DMG [AD2]**

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